NITROGEN CONTAINING DERIVATIVES OF DIACETYL AND THEIR USE AS LIGANDS

JOSEPH A. BOLGER

Ph.D. **1992**

To my Parents, Seán and Eileen.

This thesis has not previously been submitted as an exercise for a degree at this or at any other university. Except where otherwise indicated, this work has been carried out by the author alone.

Joseph A. Bolger

Joseph Bolger

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LIST OF ABBREVIATIONS

δ	Chemical Shift
λ	Wavelength
υ	Stretching frequency
aph	N-acetylpyridinehydrazone
apph	N-acetylpyridinephenylhydrazone
BTEAC	Benzyltriethylammoniumchloride
bipy	2,2'-bipyridyl
Bu	Butyl
COSY	Correlated Spectroscopy
CV	Cyclic Voltammogram
ddba	Diacetyldi(benzilazine)
ddh	Diacetyldihydrazone
ddmh	Diacetyldi(di-N,N-methylhydrazone)
ddmph	Diacetyldi(N-methyl,N-phenylhydrazone)
ddoth	Diacetyldi(ortho-tolylhydrazone)
ddph	Diacetyldi(phenylhydrazone)
Diacetyl	2,3-butanedione
DMF	Dimethylformamide
EPR (or epr)	Electron Paramagnetic Resonance
ESR (or esr)	Electron Spin Resonance
Et	Ethyl group
h.	Hours
IR	Infrared
HPLC	High Performance Liquid Chromatography
L, LL	Ligand
LC	Ligand Centred
M	Metal
MC	Metal Centred
Me	Methyl
min.	Minutes
MLCT	Metal to Ligand Charge Transfer
mol	mole
NHE	Normal Hydrogen Electrode
NMR	Nuclear Magnetic Resonance
NOE	Nuclear Overhauser Effect

PDA	Photodiode Array
Pet. Ether	Petroleum Ether
Ph	Phenyl
R, R', R"	Alkyl or Aryl group
RR	Resonance Raman
Rt	Retention Time
S	Solvent
SCE	Saturated Calomel Electrode
TEAP	Tetraethylammoniumperchlorate
TLC	Thin Layer Chromatography
UV/Vis.	Ultra Violet / Visible
X	Halogen

ABSTRACT

The main objective of this thesis is to synthesise and examine the chelating properties of substituted dihydrazones of diacetyl, $CH_3C(O)C(O)CH_3$. The synthesis, structures, spectroscopic and electrochemical properties of the substituted dihydrazones and their metal complexes are described.

Chapter I provides a general introduction to the chemistry of substituted dihydrazones and describes the advantages of their use as coordinating ligands over more commonly studied ligands such as 2,2'-bipyridine (bipy). A review of previously reported metal complexes of substituted dihydrazones of diacetyl and their applications is described.

The synthesis and characterisation of a series of substituted mono- and di-hydrazones of diacetyl including the preparation of some novel asymmetric dihydrazones are described in chapter II. The development of a new synthetic route for the preparation of azine oligomers of discrete sizes, $H_2N\text{-}[\text{-}N{=}C(CH_3)\text{-}C(CH_3){=}N\text{-}]_n\text{-}NH_2$ (for n = 1 to 5), where n is the number of repeat units, has been developed. A HPLC method is used to assign the number of repeat units of the oligomers.

In chapter III, an introduction to the properties of $[Ru(bipy)_3]Cl_2$ is given. $[Ru(bipy)_3]Cl_2$ has the disadvantage of being photolabile which has led to considerable interest in a search for a complex which has more suitable properties. Dihydrazone and dihydrazone derivatives of diacetyl have been bound to $[Ru(bipy)_2Cl_2]$ to give complexes $[Ru(bipy)_2(LL)](PF_6)_2$, (where LL = diacetyldi(phenylhydrazone), diacetyldi(methylphenylhydrazone), diacetyldi-(o-tolylhydrazone), diacetyldi(dimethylhydrazone), diacetyldihydrazone, diacetyldi(benzilazine)).

Some of the complexes were found to be photostable whereas other complexes decompose when irradiated by white light. Two features of interest of the complexes investigated include lack of emission and unusual highfield aromatic proton shifts in the ^1H NMR spectra. Electrochemical analysis indicates that the hydrazone ligands are stronger π-acceptors than bipy. Excitation of the complexes is located on the hydrazone ligands and it is thought that these ligands do not emit. The highfield aromatic proton resonances are caused by the phenyl rings being positioned directly over the bipyridyl groups resulting in deshielding.

To examine the contribution of the hydrazone ligands to the lack of emission, complexes of the type $[Ru(bipy)_2(LL)](PF_6)_2$, (LL = 2-acetylpyridine-phenylhydrazone, 2-acetylpyridinehydrazone), were prepared. The ligands LL are effectively a "half" bipy, half "hydrazone ligand" having both a hydrazone group and a pyridine ring. Both complexes display emission but are not photostable, indicating that it is possible to have an emitting complex containing a hydrazone ligand.

Variable temperature ^1H NMR analysis of the complexes was carried out. With the aid of single crystal X-ray diffraction study of the complex $[Ru(bipy)_2(ddph)](PF_6)_2$, various rotational isomeric structures arising from rotation about the N-N bond of the hydrazone ligand within the complexes in solution at various temperatures were proposed.

The polyazine oligomers which contain a repeating diimine unit, in the presence of high metal concentrations, were found to coordinate transition metals including zinc(II) to form stable metal complexes, described in chapter IV. To assist in the elucidation of the structures of transition metal polyazine complexes, the X-ray crystal structure of $[Zn(ddh)Cl_2]$, (ddh = diacetyldihydrazone) was obtained. Using the crystal structure of $[Zn(ddh)Cl_2]$ together with the shape of N-H stretching frequency bands in the infrared spectra of the complexes, coordination modes for the polyazine ligands around the metal centres are proposed.

In dilute metal containing solutions, an unusual coupling reaction of the dihydrazone oligomers occurs, catalysed by various transition metals. The reaction most likely involves the coordination of two polyazine molecules around the metal, which orientates the terminal amino groups close enough together to react, resulting in disproportionation of the azine oligomers. Endcapping the dihydrazone oligomers with a phenyl group as in $PhHN\text{-}[\text{-}N{=}C(CH_3)\text{-}C(CH_3){=}N\text{-}]_n\text{-}NHPh$ for (n = 1 to 4), produces a more stable oligomer, which also bind to metals.

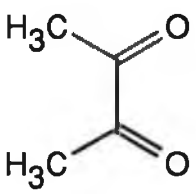
CHAPTER I

METAL COMPLEXES OF SUBSTITUTED DIHYDRAZONES OF DIACETYL

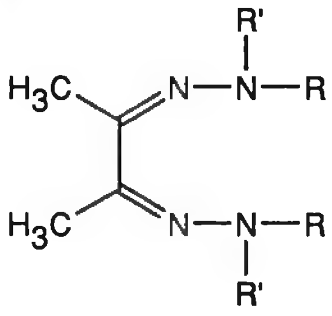
1.1 INTRODUCTION

The main aim that we initially set out to achieve was to undertake a thorough investigation of the chelation properties and characterisation of a series of compounds which may be described as substituted hydrazones of diacetyl. The compounds under investigation belong to a class of compounds derived from the reaction between hydrazine or hydrazine derivatives with diacetyl (2,3-butanedione) **(1)**. Although these compounds have been known since the last century, particularly in the area of the identification of sugars, the research to date on the use of substituted dihydrazones of diacetyl as ligands is scattered and in general unrelated.

Diacetyldihydrazone derivatives **(2)** were first reported by Klingermann[1] and Pechmann[2]. They are widely used in organic synthesis particularly in the area of oxidation of 1,2-dihydrazones[3,4,5] and osazones[6,7].



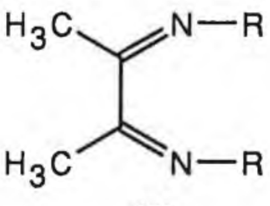
(1)



R' = H ,CH_3
R = H, Alkyl, Aryl

(2)

Relatively less well investigated but increasingly of interest is the use of diacetyldihydrazone derivatives as complexing ligands. Diacetyldihydrazones **(2)** contain a basic diimine functional group suitable for chelation, and belong to the diazabutadiene **(3)** class of ligands. The coordination chemistry of 2,2'-bipyridine (bipy) **(4)** has been, by far, more extensively investigated than the related diazabutadiene ligand system. This is especially true for ruthenium, since research interests have focused on the potential applications of rutheniumtris(bipyridyl) ions in the photochemical water-splitting reaction, by Dressick *et al.*[8] and Grätzel[9].



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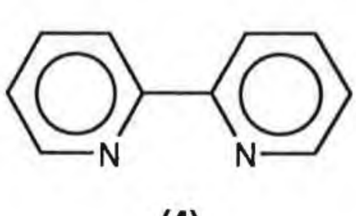


(4)

It has only recently become clear that the diazadienes, (which includes the diacetyldihydrazone derivatives), show a much wider range of coordination modes and reaction types,[10,11] than 2,2'-bipyridine. Other advantages that can be ascribed to the diazadiene system are;

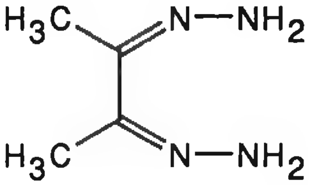
(i) simple synthesis from inexpensive starting materials;

(ii) broad variability of substituents;

(iii) simple theoretical description of the small -N=C-C=N- system[12,13,14];

(iv) enhanced solubilities compared to many analogous 2,2'-bipyridyl complexes[15].

Diacetyldihydrazone derivatives also possess the added advantages of being particularly stable. However in the case of the simplest of this class, diacetyldihydrazone **(5)** contains two terminal amino groups which have the potential to polymerise or to bind to other molecules containing carbonyl groups via a condensation reaction.



(5) (ddh)

At the outset, we hoped to prepare a series of substituted hydrazones of diacetyl, both mono- and di- substituted, and to achieve complete control over the chemistry of their synthetic routes. To examine the chelation properties of the hydrazones of diacetyl, we intended to prepare rutheniumbis(bipyridyl) derivatives of the substituted dihydrazones of diacetyl. There are a number of advantages accompanying the use of the rutheniumbis(bipyridyl) moiety, including the fact that the rutheniumbis(bipyridyl) moiety has four of its six coordination sites already occupied which would reduce the number of possible products and ruthenium(II) is also diamagnetic which facilitates characterisation of products by NMR spectroscopy.

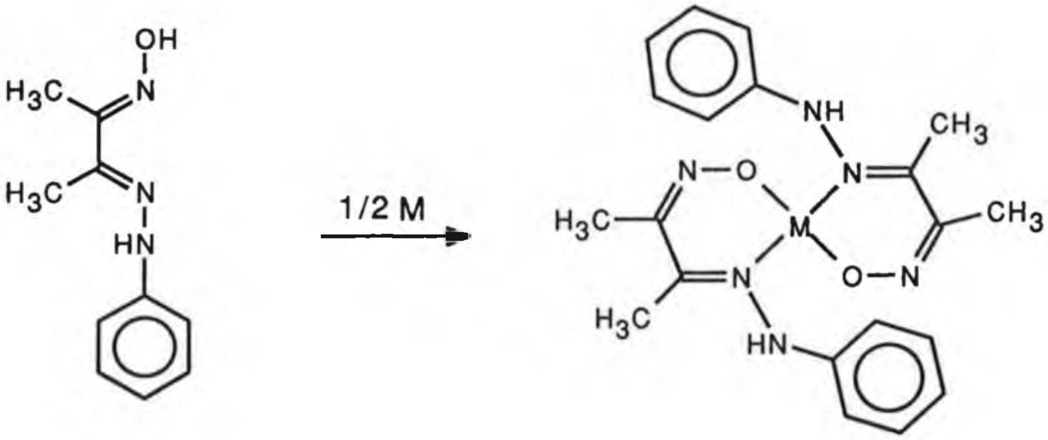
We also hoped to examine the possibility of preparing some multinuclear metal complexes of hydrazone derivatives of diacetyl. Reacting diacetyldihydrazone **(5)** with a dicarbonyl compound has the potential of producing oligomers or polymers with a diimine -[-N=C-C=N-]$_n$- repeat unit. From these polymers, it was hoped that multinuclear metal complexes could be formed. Complexes of this nature would be potentially useful in a variety of areas such as, conducting polymers, metal extraction from waste solvents, electrochemistry, spectrophotometric analyses, *etc*.

On examining the literature, it was found that quite a number of substituted hydrazones of diacetyl have been complexed to a variety of metals. The majority of the research to date concentrated on the transition metal complexes. To date, no ruthenium complexes of dihydrazones of diacetyl have been reported.

The following sections in this chapter, provide a summary of the metal complexes of substituted hydrazones of diacetyl. In general, the reported complexes are divided into groups based on the type of substituted hydrazone.

1.2 COMPLEXES OF DIACETYLARYLHYDRAZONES

The earliest report in the literature of the ability of hydrazones to act as chelates to form metal complexes was carried out by Walter Ciusa in 1936[16]. He described the preparation of copper(II) and nickel(II) complexes, **(7)** and **(8)** of the ligand diacetylmonoximemonophenylhydrazone **(6)** according to scheme [1.1].



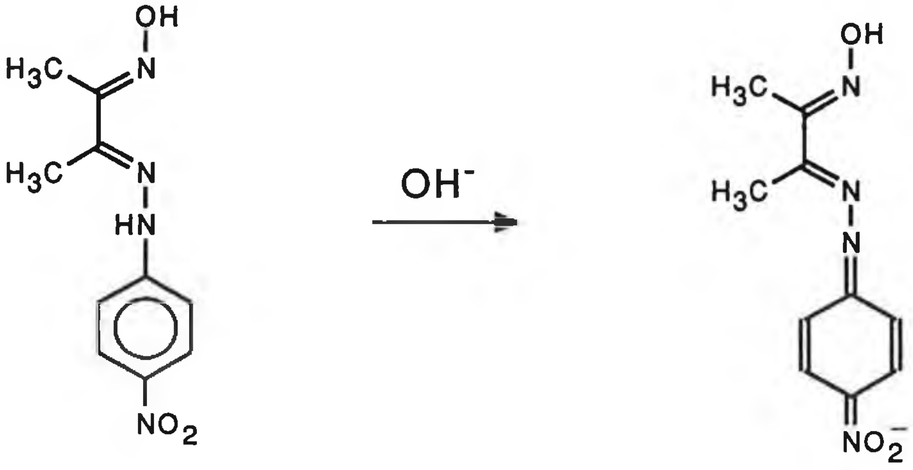
(6)

(7) M = Cu(II)
(8) M = Ni(II)

Scheme [1.1]

The main technique for the characterisation of the complexes was by C,H,N and Ni elemental analysis.

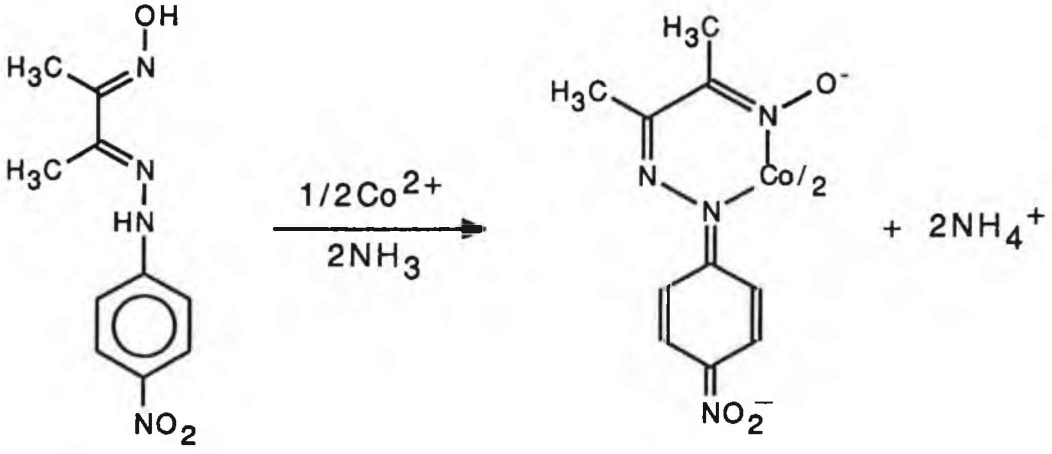
One of the first groups to develop an application for a hydrazone of diacetyl was Feigl and Goldstein in 1956[17]. They proposed the use of the p-nitrophenylhydrazone of diacetylmonoxime **(9)** as a specific reagent for cobalt, a violet-coloured complex being formed, according to scheme [1.2]. Diacetylmonoximemono(p-nitrophenylhydrazone), a monobasic acid by virtue of the oxime group, is soluble in alkali hydroxide, the quinoidal anion **(10)** having a deep violet colour.



(9) (10)

Scheme [1.2]

The rearrangement in scheme [1.2] occurs to not more than a slight extent with dilute ammonium hydroxide, which provides too low of a concentration of the hydroxyl ions forming a faint yellow colour in solution. Investigation of the analytical behaviour of the p-nitrophenylhydrazone of diacetylmonoxime **(9)** demonstrated that on the addition of an ethanol solution of this compound to ammonical solutions of ions (palladium(II), silver(I), copper(II), nickel(II) and cobalt(II)), only cobalt ions react in a characteristic fashion. A violet colour was obtained, the intensity relating to the cobalt(II) content of the system, thus the reaction of the p-nitrophenylhydrazone with cobalt was specific. The proposed reaction has been given in scheme [1.3].

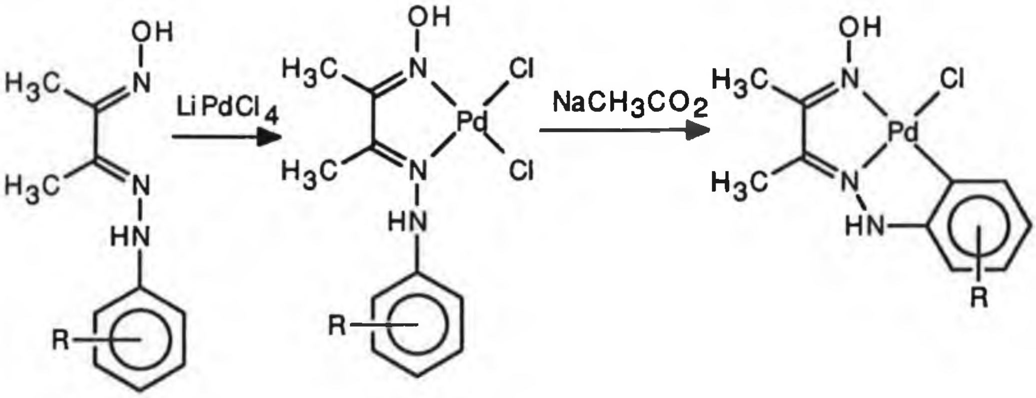


(9) (11)

Scheme [1.3]

Hsi-Hua *et al.*[18] using this principle, measured microgram quantities of cobalt colorimetrically, stating that the method was simple, rapid, reproducible and obeyed Beer's Law . The formation of the violet complex and its resistance to alkali cyanides made possible a new and rather sensitive test for cobalt, which could also serve as the basis of a colorimetric procedure for the determination of this metal. Pearson and Seim[19] refined this phenomenon and put it into practice, using ion exchange separation, and found the method to be five times more sensitive than atomic absorption spectroscopy.

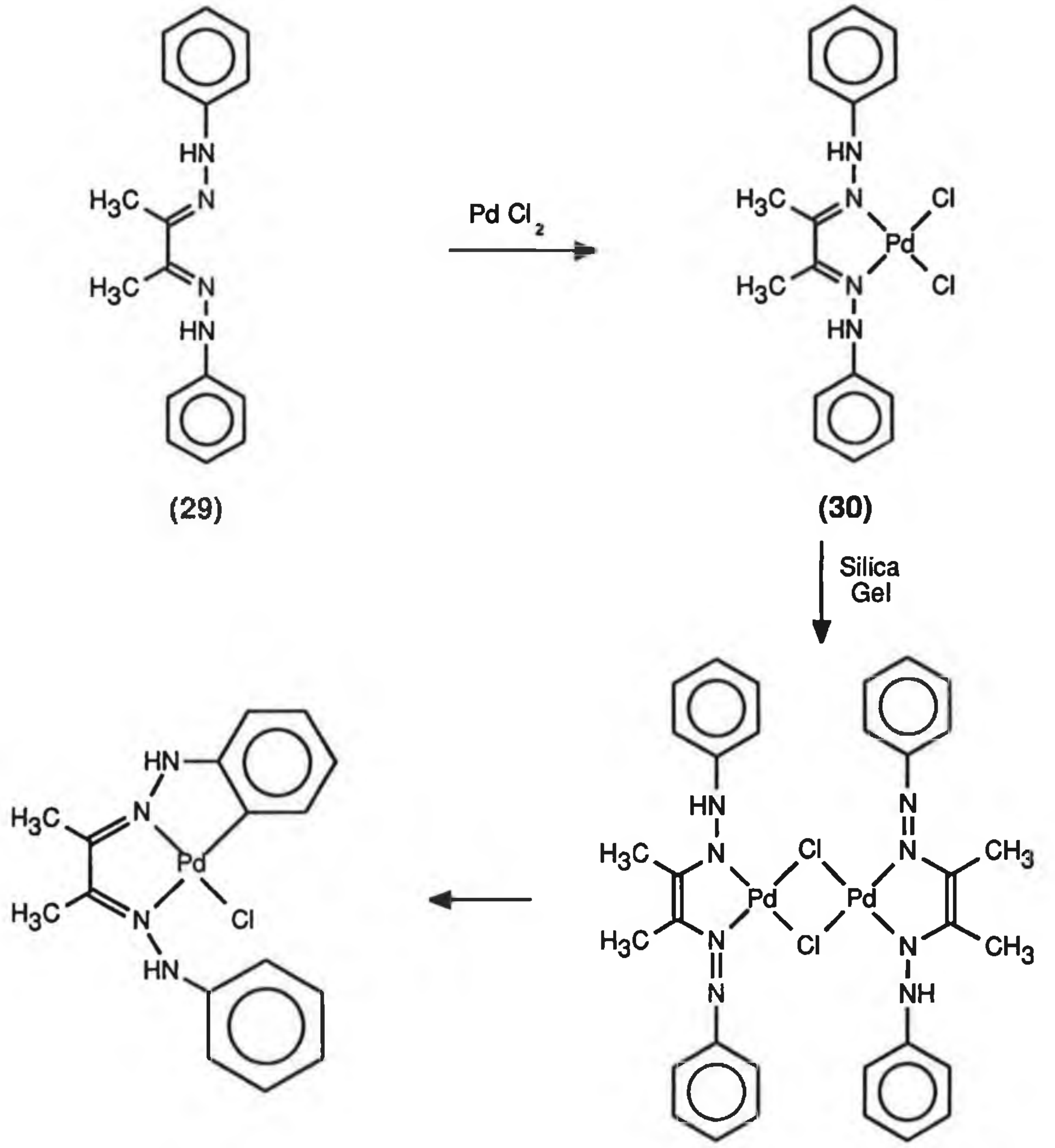
Nonoyama[20,21] prepared and characterised a series of palladium(II) complexes of diacetylmonoximearylhydrazones. The hydrazoximes **(6)**, **(12)** - **(16)** react with lithiumtetrachloropalladate in methanol to form complexes **(17)** - **(22)** which can be reacted further with sodium acetate to form the palladium complexes **(23)** - **(28)** with hydrogen chloride, according to scheme [1.4].



(6)	**R = H**	**(17)**	**R = H**	**(23)**	**R = H**
(12)	**R = o-methyl**	**(18)**	**R = o-methyl**	**(24)**	**R = o-methyl**
(13)	**R = m-methyl**	**(19)**	**R = m-methyl**	**(25)**	**R = m-methyl**
(14)	**R = p-methyl**	**(20)**	**R = p-methyl**	**(26)**	**R = p-methyl**
(15)	**R = p-chloro**	**(21)**	**R = p-chloro**	**(27)**	**R = p-chloro**
(16)	**R = p-nitro**	**(22)**	**R = p-nitro**	**(28)**	**R = p-nitro**

Scheme [1.4]

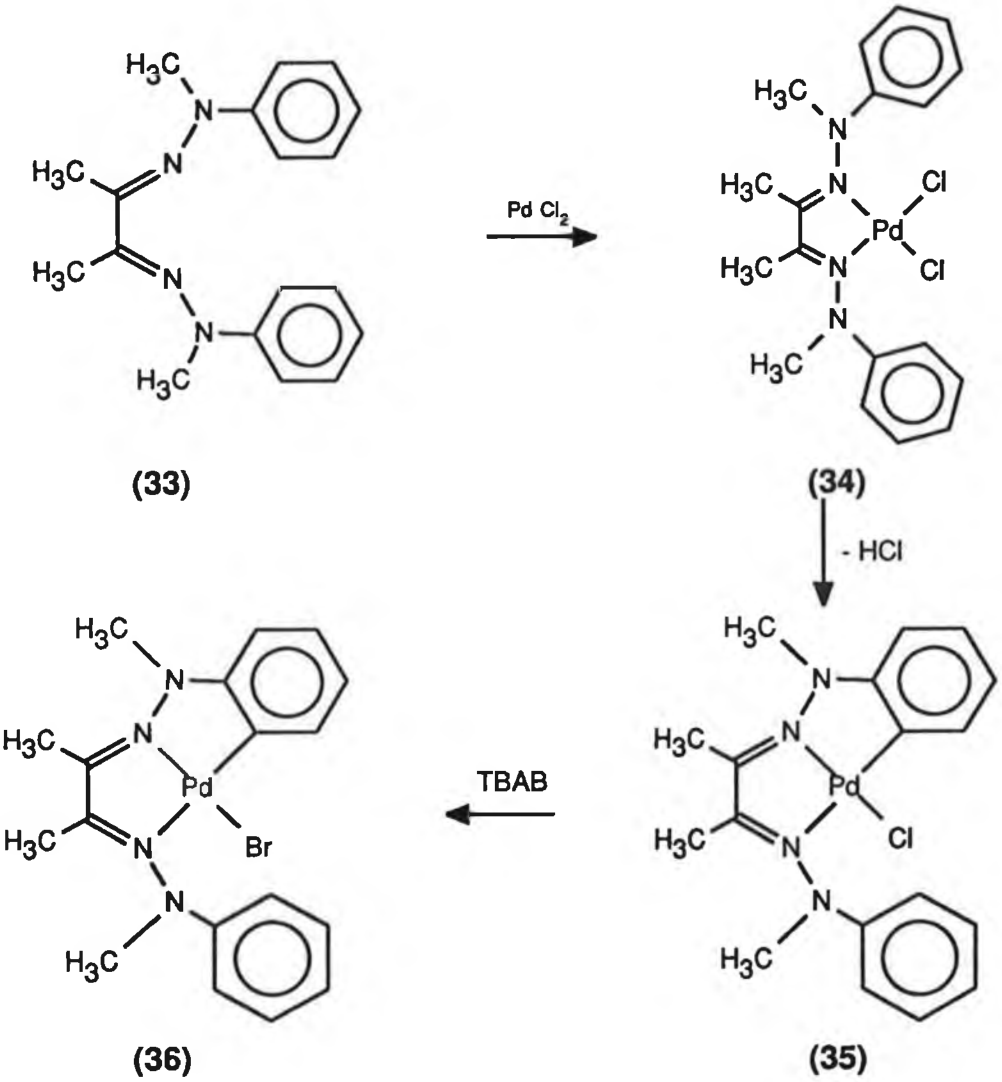
Diacetyldi(phenylhydrazone) **(29)** was prepared by reacting diacetyl with a two molar equivalent of phenylhydrazine[22]. Subsequently, the diacetyldiphenylhydrazonepalladium complex **(30)**, was prepared by Cattalini *et al.*[23,24] and was found to lose HCl on treatment with silica gel, or triethylamine, forming a green species **(31)**, a complex with two bridging chlorines. This may subsequently undergo ortho-metallation of the phenyl ring to yield **(32)**, according to scheme [1.5].



(29) (30) (31) (32)

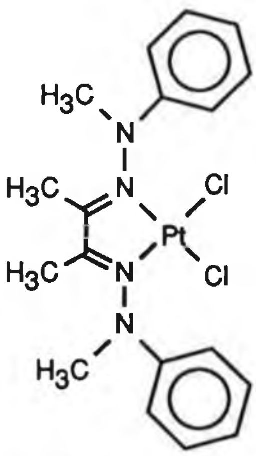
Scheme [1.5]

Further experiments revealed that the palladium complex **(34)** of the ligand diacetyldi(N-methyl,N-phenylhydrazone) **(33)**, which does not contain NH groups, also undergoes HCl elimination to form **(35)**[25,26,27,28]. Treatment of complex **(35)** with tetrabutylammoniumbromide (TBAB) produces the bromide complex **(36)**, according to Scheme [1.6]. Caglioti *et al.*[29] reported the crystal structure of the diacetyldi(N-methyl,N-phenylhydrazone)palladium complex **(36)** obtained from the corresponding ligand **(33)**.



Scheme [1.6]

The platinum analogue complexes **(37)** and **(38)** of the palladium complexes **(34)** and **(35)**, have been reported by Cattalini *et al.*[30].



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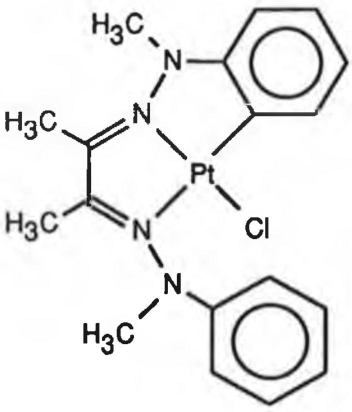
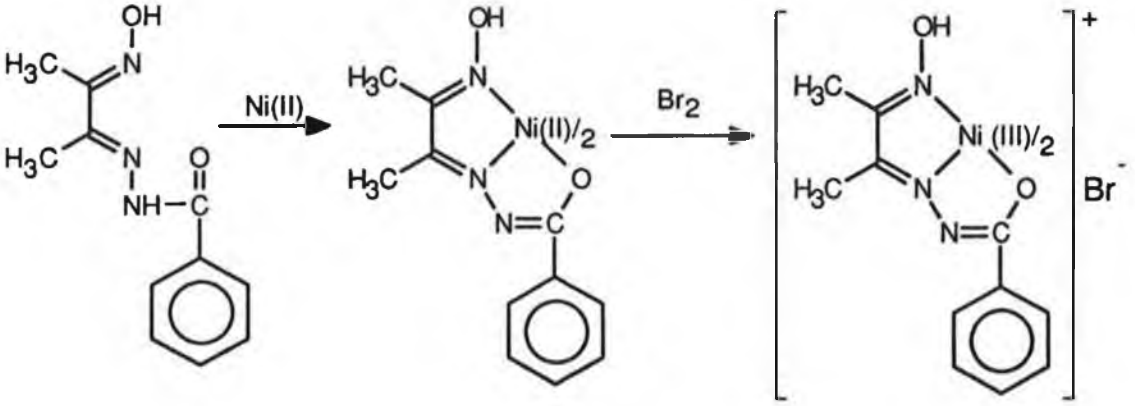


(38)

1.3 COMPLEXES OF DIACETYLDI(BENZOYLHYDRAZONES)

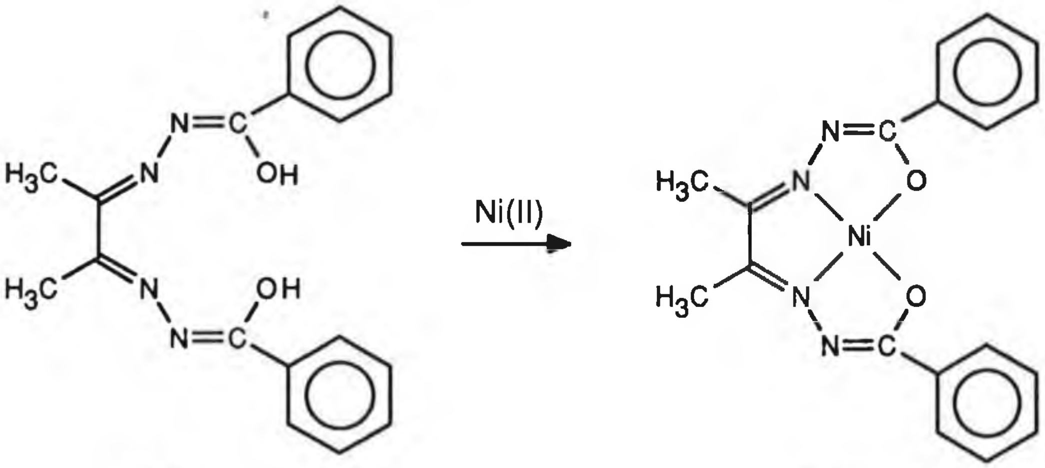
Edelman in 1950[31] described the preparation of new complexes of trivalent nickel, using the ligand diacetylmonoximemonobenzoylhydrazone **(39)**. Treating the Ni(II) complex **(40)** with bromine in carbontetrachloride solution produces a stable trivalent nickel(III) bromide chelate derivative **(41)**, according to scheme [1.7]. The report suggests that coordination with the oxime group may be a stabilizing factor for the higher valency states of nickel.



(39) **(40)** **(41)**

Scheme [1.7]

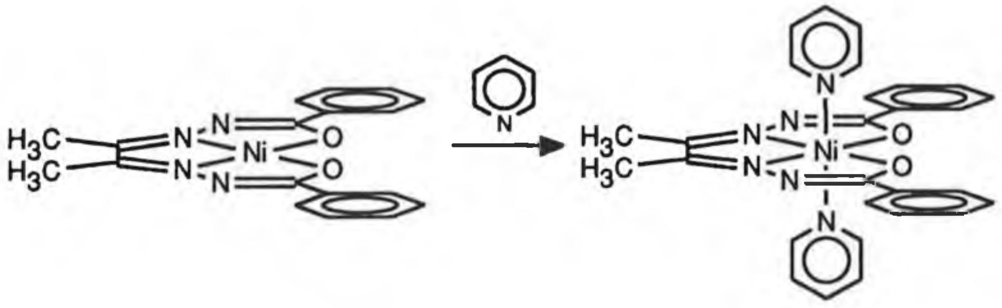
Following in Edelmans footsteps, Sacconi[32] reported the preparation of the nickel complex **(43)** of the enolic form of diacetyldi(benzoylhydrazone) **(42)**, according to scheme [1.8].



(42) **(43)**

Scheme [1.8]

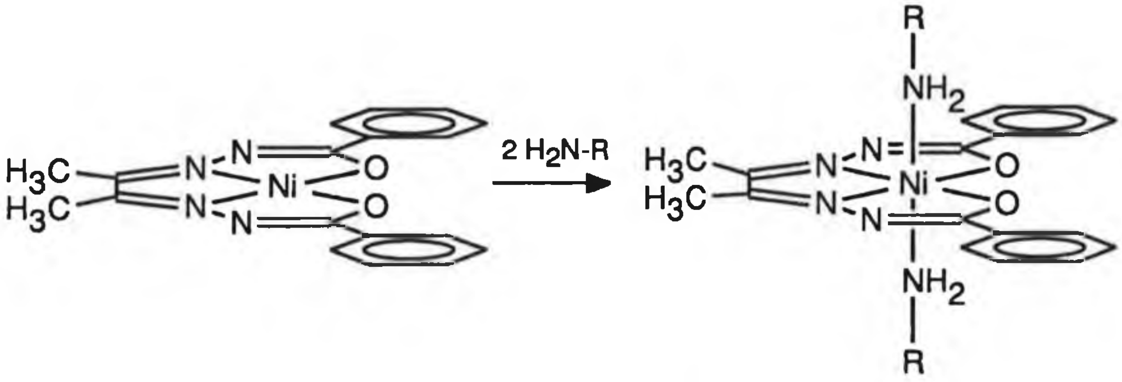
Further research by Sacconi *et al.* in 1958[33] indicated that the complex **(43)** is planar with dsp^2 hybridization, and with various nitrogen bases forms an addition compound containing two molecules of base. Diacetyldi(benzoylhydrazone)nickel(II), **(43)** gives green diamagnetic solutions in "non-coordinating" solvents, e.g. chloroform and benzene. In donor solvents, e.g. pyridine, the solutions are yellow-brown and paramagnetic, which can be attributed to the formation of an octahedral complex **(44)** according to scheme [1.9].



(43) **(44)**

Scheme [1.9]

Sacconi *et al.*(34,35,36) reported on the thermodynamics of the equilibria between the complex diacetyldi(benzoylhydrazone)nickel(II) **(43)** with primary alkylamines (R-NH_2) in benzene, according to scheme [1.10].

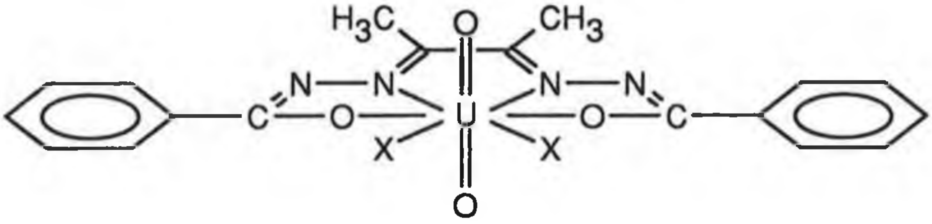


(43)

(45) **R = CH_3**
(47) **R = C_2H_5**
(49) **R = n-propyl**
(51) **R = i-propyl**
(53) **R = n-butyl**
(55) **R = i-butyl**
(57) **R = s-butyl**
(59) **R = t-butyl**
(46) **R = n-amyl**
(48) **R = i-amyl**
(50) **R = n-hexyl**
(52) **R = n-heptyl**
(54) **R = n-octyl**
(56) **R = n-nonyl**
(58) **R = n-decyl**

Scheme [1.10]

As part of a programme of exploring the coordination behaviour of multidentate mixed N-O donors towards oxometal cations, Ghosh and Maiti[37] reported the synthesis and characterisation of the octa-coordinated dioxouranium(VI) complexes of diacetyldi(benzoylhydrazone), **(60) - (65)**.

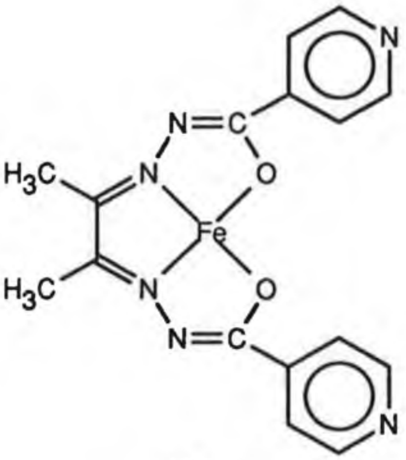


(60) $X = Cl^-$ **(61)** $X = Br^-$ **(62)** $X = NO_3^-$

(63) $X = NCS^-$ **(64)** $X = ClO_4^-$ **(65)** $X = OAc^-$

Colours of the dioxouranium(VI) complexes vary from yellow to reddish brown. All the complexes are diamagnetic indicating the presence of d^0 systems.

Farbenfabriken and Bayer in 1956[38] patented a process for producing a series of metal complexes of hydrazide-hydrazones. Included was the iron complex of di(isonicotinic acid hydrazide-hydrazone) of diacetyl **(66)** and the metal complexes of the isonicotinic acid hydrazide-hydrazone of diacetylmonoxime, **(67) - (72)**.



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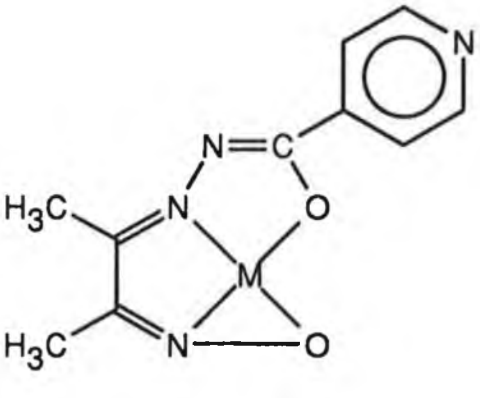


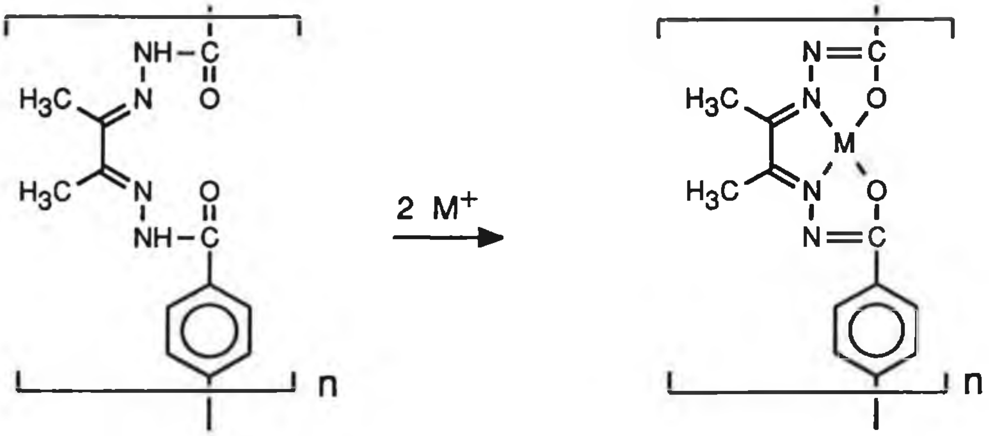
(67) M = Fe(II) **(68)** M = Co(II)

(69) M = Zn(II) **(70)** M = Mn(II)

(71) M = V(II) **(72)** M= Ni(II)

These types of heterocyclic carboxylic acid hydrazide-hydrazone complexes have been found to be of therapeutic significance and, in particular isonicotinic acid derivatives have been found to be effective for combating tuberculosis in humans and animals[38].

Archer and coworkers in 1985[39] prepared poly(terephthaloylbutane-2,3-dihydrazone) **(73)**, by reacting diacetyldihydrazone **(5)** with terephthaloylchloride. Zinc(II), nickel(II), copper(II), cadmium(II) and lead(II) derivatives **(74) - (78)** of this polymer were prepared from the aqueous ammonia solution of the metal salts. 100% saturation for metal ion per polymer unit was obtained for Zn(II), Ni(II) and Pb(II), 75% saturation for Cd(II) and 55% loading for Cu(II), scheme [1.11].

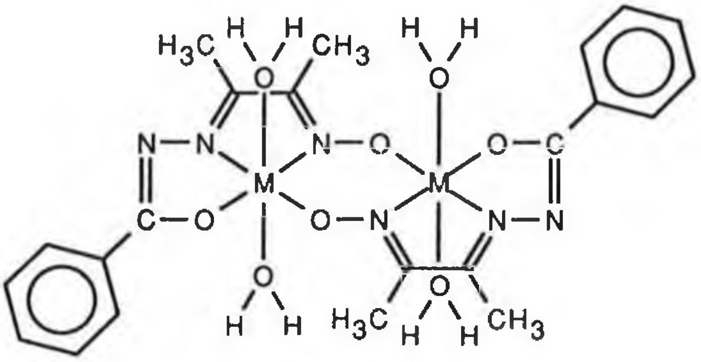


(73)

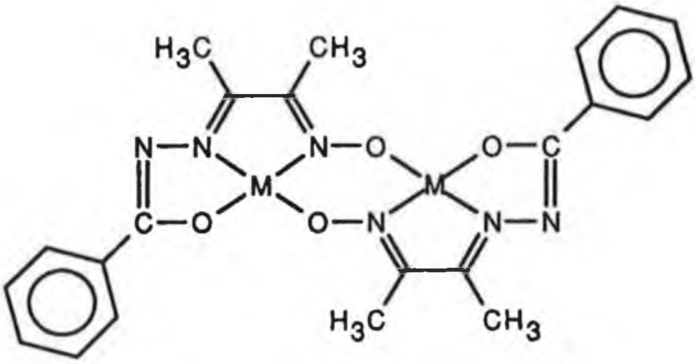
(74) M=Zn(II) **(75) M=Ni(II)**
(76) M=Cu(II) **(77) M=Cd(II)**
(78) M=Pb(II)

Scheme [1.11]

Some binuclear metal complexes of diacetylmonoximemonobenzoylhydrazone **(39)** of the type **(79) - (84)** have been described by Satpathy *et al.*[40]. The complexes were prepared and characterised on the basis of elemental analyses and some physical methods.



(79) M = Co(II)
(80) M = Ni(II)
(81) M = Cu(II)

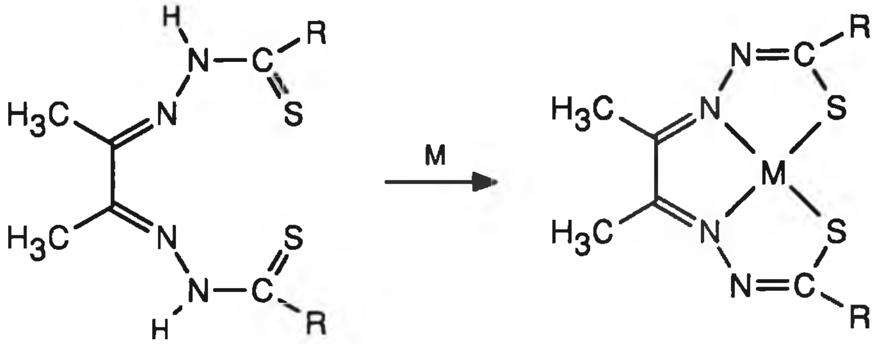


(82) M = VO(II)
(83) M = Zn(II)
(84) M = Cd(II)

An octahedral geometry has been proposed for the metal (II) ions, except around Zn(II) and Cd(II) for which a tetrahedral geometry has been postulated based on the spectral, magnetic properties and thermal studies of the complexes.

1.4 COMPLEXES OF DIACETYLDI(THIOBENZOYLHYDRAZONE)

A related class of compounds to the diacetyldi(benzoylhydrazone) complexes, is the diacetyldi(thiobenzoylhydrazone) complexes, where the oxygen of the previous class is replaced by a sulphur. Complexes of the ligand diacetyldi(thiobenzoylhydrazone), **(85)** were prepared, **(86)** - **(93)** by Bahr and Schleitzer in 1955(41), according to scheme [1.12].



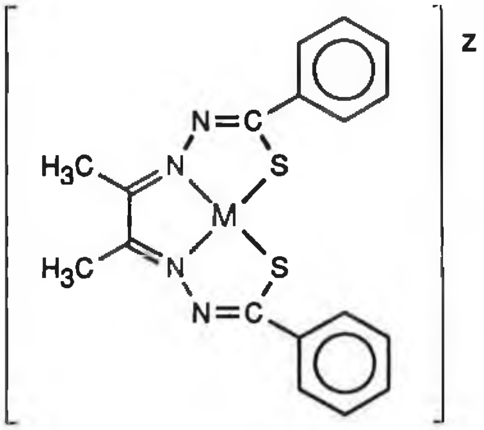
(85)

(86) M = Cu(II) R = C_6H_5
(87) M = Cu(II) R = SCH_3
(88) M = Cu(II) R = NH_2
(89) M = Ni(II) R = C_6H_5
(90) M = Ni(II) R = SCH_3
(91) M = Ni(II) R = NH_2
(92) M = Pt(II) R = SCH_3
(93) M = Pt(II) R = NH_2
(94) M = Pd(II) R = NH_2

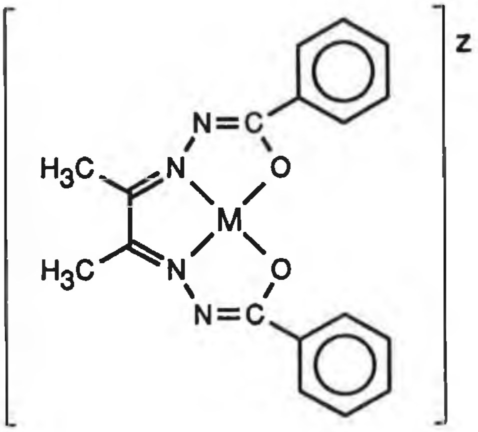
Scheme [1.12]

A method by Bahr and coworkers(42,43) was described for the spectrophotometric determination of copper using diacetyldi(thiobenzoylhydrazone), which forms a stable violet complex **(86)**, soluble in chloroform. The method was independent of metals such as Ag(I), Zn(II), Cd(II), Al(III), Pb(II), Sn(II), Cr(III), Mn(II), Fe(III) and Co(II).

In an attempt to understand the chemical behaviour of electrochemical one-electron reductions of the di-chelate complexes, Balch *et al.* in 1967(44), prepared complexes of the types **(95)** - **(97)** and **(98)** - **(99)**, from the ligands diacetyldi(thiobenzoylhydrazone) **(85)** and diacetyldi(benzoylhydrazone) **(42)** respectively.



(95) M = Ni(II)
(96) M = Zn(II)
(97) M = Cd(II)



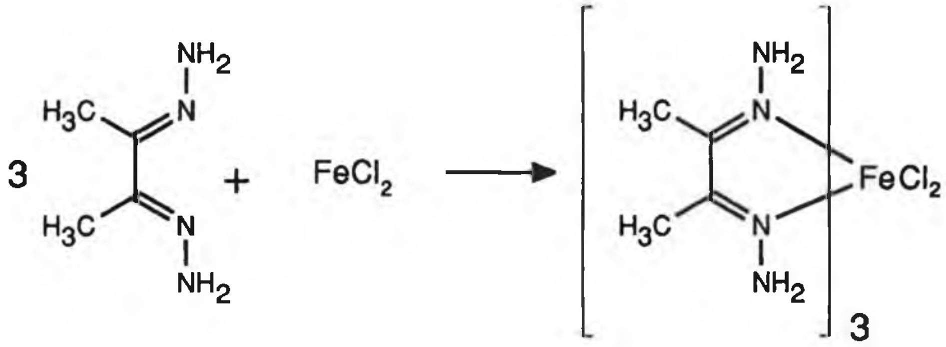
(98) M = Ni(II)
(99) M = Zn(II)

The nickel(II), zinc(II) and cadium(II) complexes are electrochemically reducible in non aqueous media to z = -1 and z = -2 species.

1.5 COMPLEXES OF DIACETYLDIHYDRAZONE

Busch and Bailar in 1956(45), in an attempt to discover the exact nature of the interaction between an α-diimine and an iron(II) chromophore, prepared a series of iron(II) complexes which included the iron(II) complex **(100)** of the ligand diacetyldihydrazone **(5)**. Their results support the earlier work by Krumholtz(46), suggesting that the unusual stability and characteristic colour reaction involved in the linking of an iron(II) atom to the α-diimine structure, are a result of the π-bonding between the conjugated ligand and the unhybridised d-electron pairs of the iron atom.

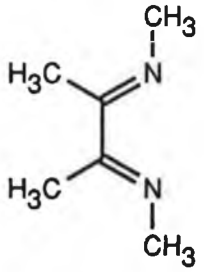
Addition of diacetyldihydrazone **(5)** to iron(II)dichloridetetrahydrate, in a 2:1 molar ratio in hot absolute ethanol, yielded rust coloured crystals of tri(diacetyldihydrazone)Iron(II), **(100)**, according to scheme [1.13].



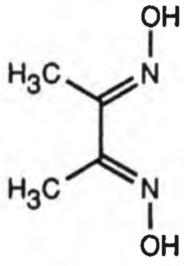
(5) **(100)**

Scheme [1.13]

The composition of the complex cation, with three molecules of ligand coordinated to each metal ion, indicated that this donor molecule, diacetyldihydrazone **(5)**, more closely resembles diacetyldi(methylimine) **(101)** than dimethylglyoxime **(102)**, in its complexation reaction with iron(II).

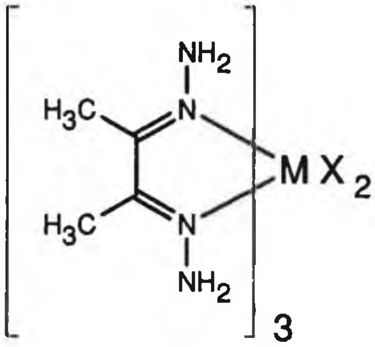


(101)



(102)

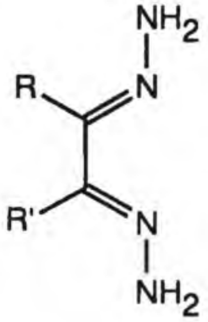
Busch and coworkers[47,48,49] report complexes of the ligand diacetyldihydrazone **(5)** with iron(II), cobalt(II) and nickel(II), **(103) - (107)**. The complexes were found to have a metal to ligand ratio of 1:3, and were isolated for each of the three metals. Also, complexes having a metal to ligand ratio of 1:2 were isolated for cobalt(II) and nickel(II). The colours, solubilities, magnetic moments and chemical properties indicated that the diacetyldihydrazone complexes were closely related to the well known complexes of α-diimines and the aromatic heterocyclic diamines such as 2,2'-bipyridine **(4)**.



(103) $[Fe(ddh)_3]I_2$
(104) $[Co(ddh)_2]Cl_2$
(105) $[Co(ddh)_3]I_2$
(106) $[Ni(ddh)_2]Cl_2$
(107) $[Ni(ddh)_3]Cl_2$

Tri(diacetyldihydrazone)iron(II) **(103)** is diamagnetic whereas the corresponding 3:1 cobalt(II) **(105)** and nickel(II) **(107)** complexes are paramagnetic. The 2:1 complexes of cobalt(II) **(104)** and nickel(II) **(106)** were also highly paramagnetic, indicating three and two unpaired electrons, respectively.

The similarity of diacetyldihydrazone **(5)** to the α-diimines and the aromatic heterocyclic amines was found to be more striking in the case of nickel(II). The cobalt(II) complexes also bear resemblances to those of 2,2'-bipyridine. In an infrared analysis of these compounds, Busch *et al.*[50,51,52], suggest that on the basis of decreasing interaction between the metal atom and ligand groups, the complexes can be placed in the order $[Fe(ddh)_3]I_2$ **(103)** > $[Ni(ddh)_3]Cl_2$ **(107)** > $[Ni(ddh)_2]Cl_2$ **(106)** > $[Co(ddh)_3]I_2$ **(105)** > $[Co(ddh)_2]Cl_2$ **(104)**. The iron(II) complex **(103)**, which was clearly of the robust type, most likely involves metal-ligand π-bonding. Strouffer *et al.*[53,54,55] carried out an investigation of inter-ligand steric hindrance in α-dihydrazone complexes of cobalt(II), iron(II) and nickel(II), $[M(L)_3]X_2$. It was found that there was a decreasing order of repulsion (in the complexes) in the order of diacetyldihydrazone **(5)** > benzildihydrazone **(108)** > pyruvaldihydrazone **(109)** > glyoxaldihydrazone **(110)**.



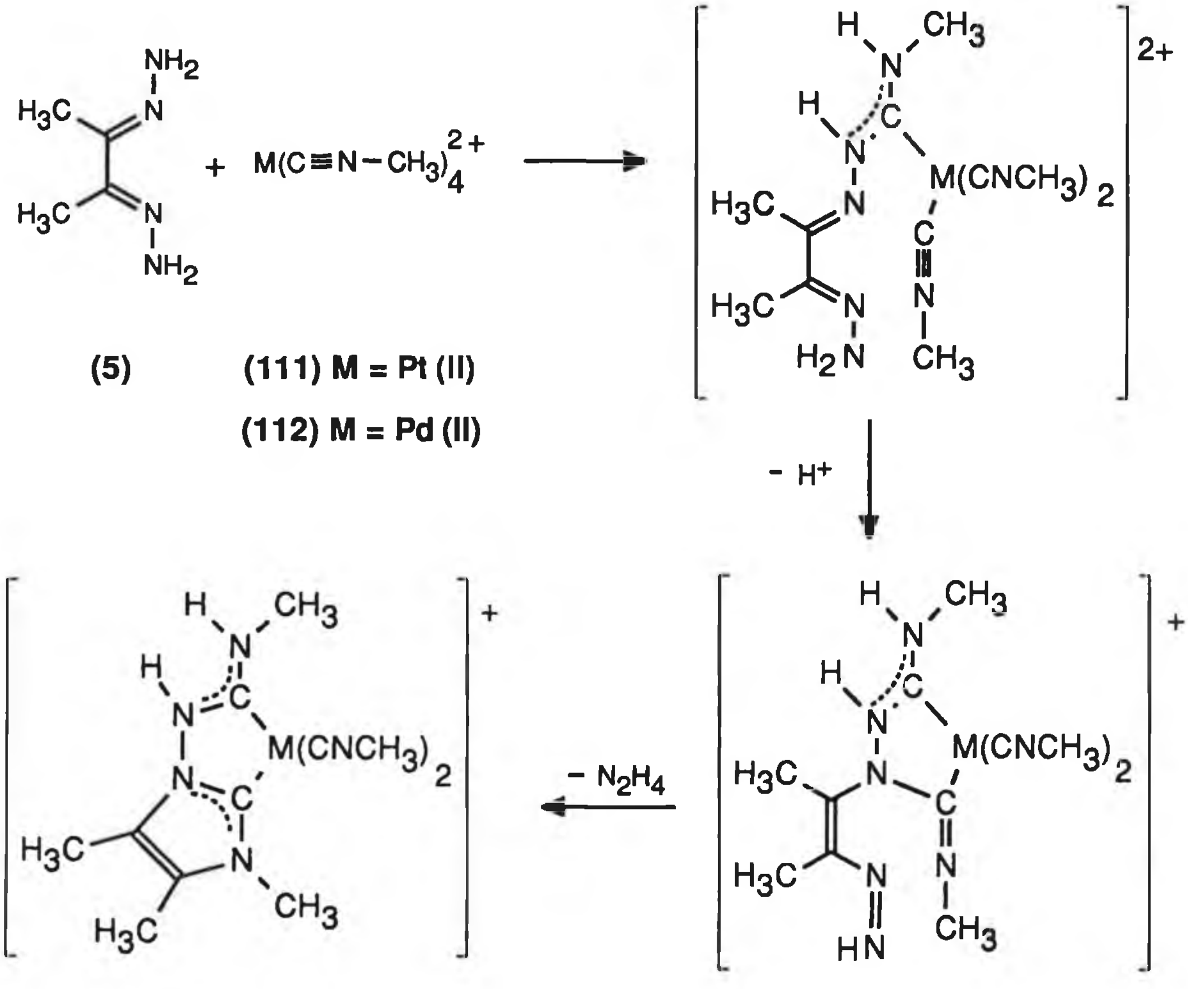
(5) R = R' = CH_3

(108) R = R' = C_6H_5

(109) R = CH_3 ; R' = H

(110) R = R' = H

The reaction of diacetyldihydrazone **(5)** with $[M(CNCH_3)_4]^{2+}$, **(111)** M = Pt(II), **(112)** M = Pd(II) unexpectedly leads to the formation of **(113)** and **(114)**[56]. In this one reaction an imidazole ring has been created, with the suggested mechanism illustrated by scheme [1.14].



(5) **(111) M = Pt (II)**

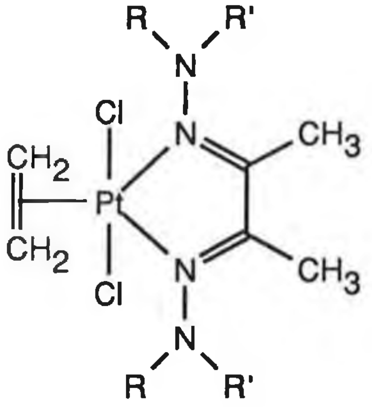
(112) M = Pd (II)

(113) M = Pt(II)

(114) M = Pd(II)

Scheme [1.14]

Natile *et al.*[25,27] reported the first authenticated case of the isolation of a five-coordinate platinum(II) olefin intermediate produced from the reaction between K[$PtCl_3(C_2H_4)$] and diacetyldihydrazone derivatives at 0°C, to yield complexes **(115) - (118)**.



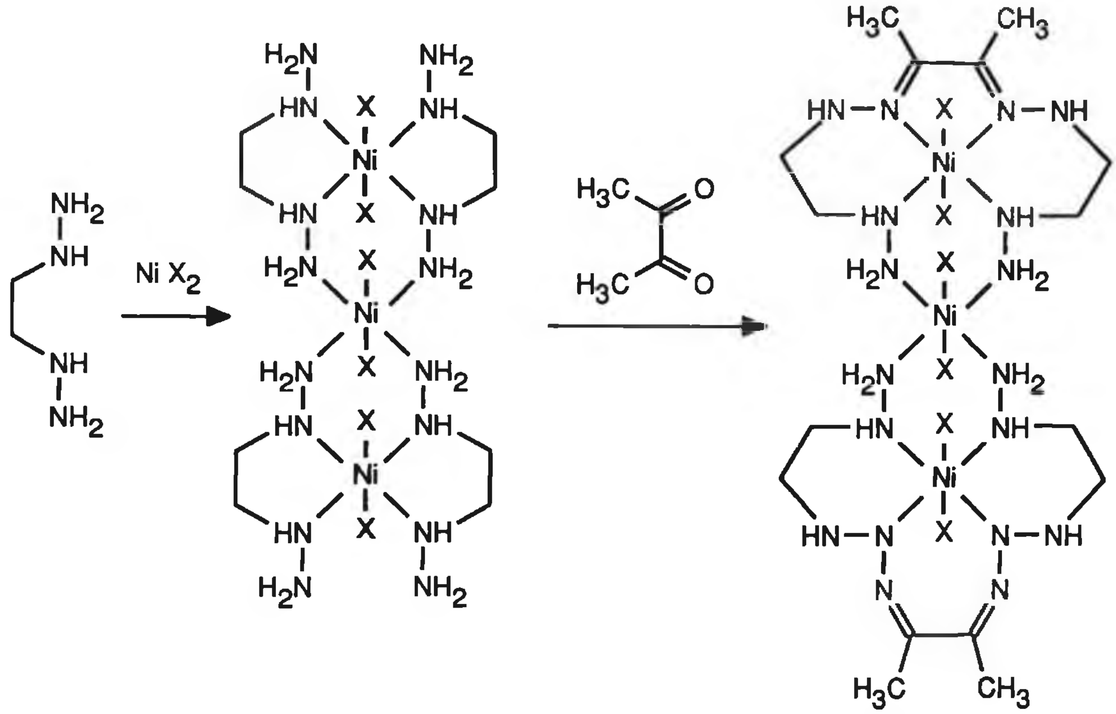
(115) **R = H** **R = Ph**

(116) **R = CH_3** **R = Ph**

(117) **R = CH_3** **R = H**

(118) **R = CH_3** **R = CH_3**

Kubokura and coworkers in 1978[57] prepared and characterised nickel(II) polymer complexes of N,N'-ethylenedihydrazine, **(119)** and **(120)**. The condensation products of these complexes with diacetyl resulted in the discrete complexes **(121)** and **(122)**, scheme [1.15].

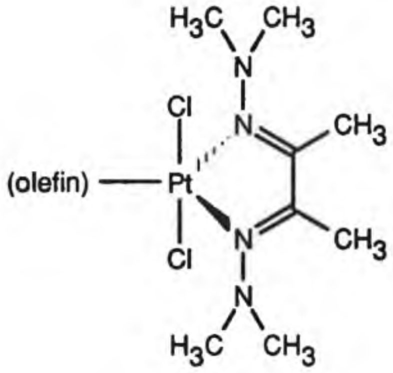


(119) **X = Cl**
(120) **X = Br**

(121) **X = Cl**
(122) **X = Br**

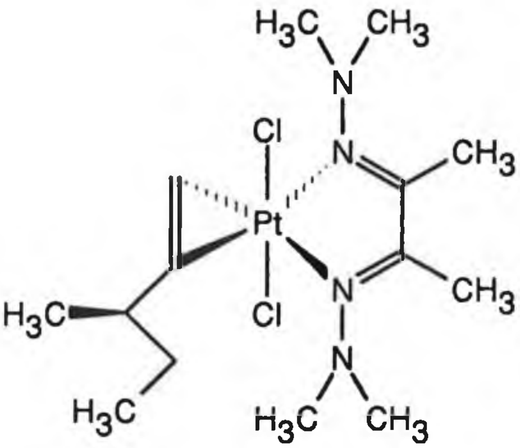
Scheme [1.15]

The investigation of penta-coordinated Pt(II) complexes of the type $[PtCl_2(diacetyldi(di\text{-}N\text{-}methylhydrazone))(olefin)]$ where the olefins are fumarodinitrile **(123)**, acrylonitrile **(124)**, acrolein **(125)**, methylacrylate **(126)** and (E)-2-butene **(127)** was carried out by De Renzi *et al.*{58,59,60}.



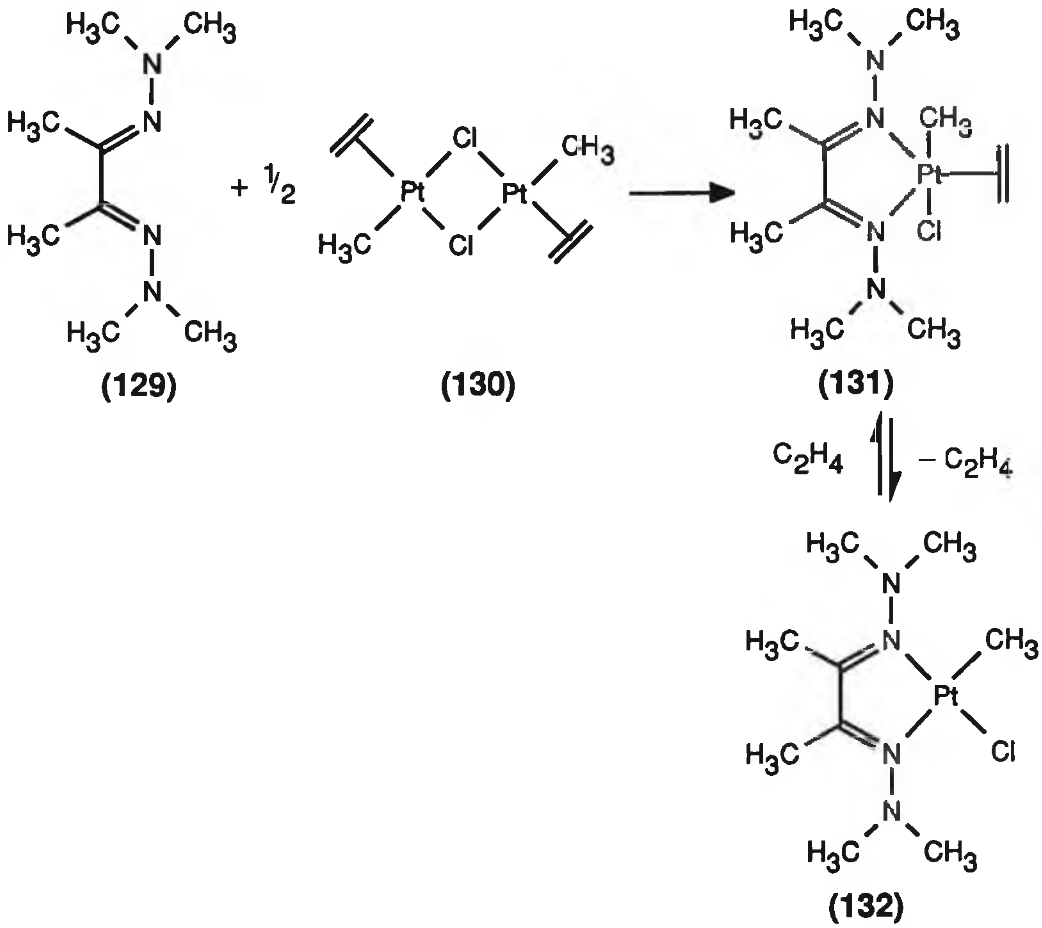
	olefin
(123)	**E-$CNCH{=}CHCN$**
(124)	**$CH_2{=}CHCN$**
(125)	**$CH_2{=}CHCHO$**
(126)	**$CH_2{=}CHCOOCH_3$**
(127)	**E-$CH_3CH{=}CHCH_3$**

In an effort to find platinum complexes as models for Ziegler-Natta catalytic sites with stereoselective polymerisation catalytic properties, Panunzi *et al.*{61,62,63} prepared $[Pt(diacetyldimethylhydrazone)(SMP)Cl_2]$, [(SMP) = (+)-(s)-3-methyl-1-pentene] **(128)**.



(128)

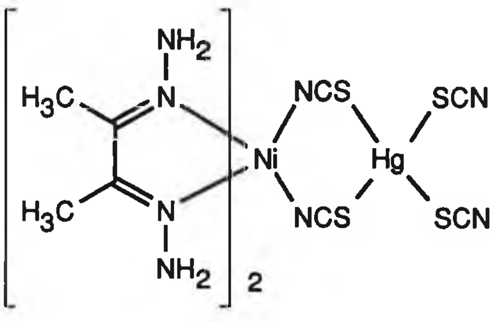
Albano and coworkers{64,65,66,67} reported five coordinated olefin complexes of platinum(II) containing σ-bonded carbon ligands, formed by the addition of **(129)** to $PtCl(\eta^2\text{-}C_2H_4)CH_3$ **(130)**, according to scheme [1.16].



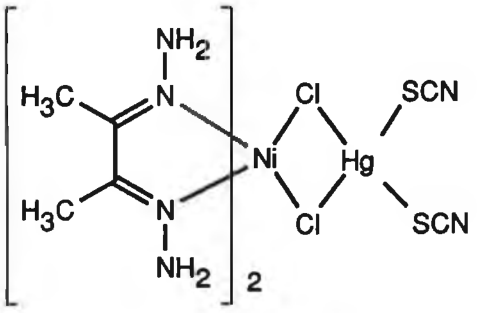
Scheme [1.16]

Complex **(131)** can lose ethylene reversibly, giving the corresponding four coordinate complex **(132)**.

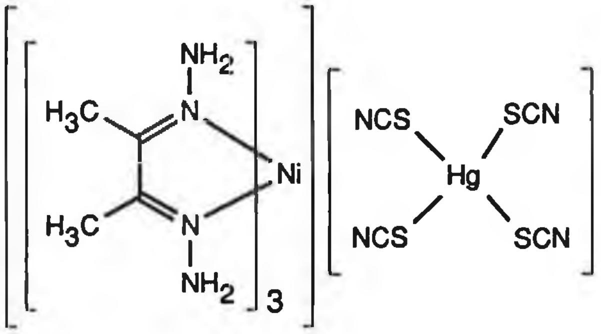
In a study of the formation of complexes derived from NiHg(SCN)$_4$ with chelating N,N-donor ligands, Tigeras and Santos in 1984$^{(68)}$ reported diacetyldihydrazone **(5)** complexes of Ni(II)/Hg(II) bimetallic tetrathiocyanates, **(133)**, **(134)** and **(135)**.



(133)

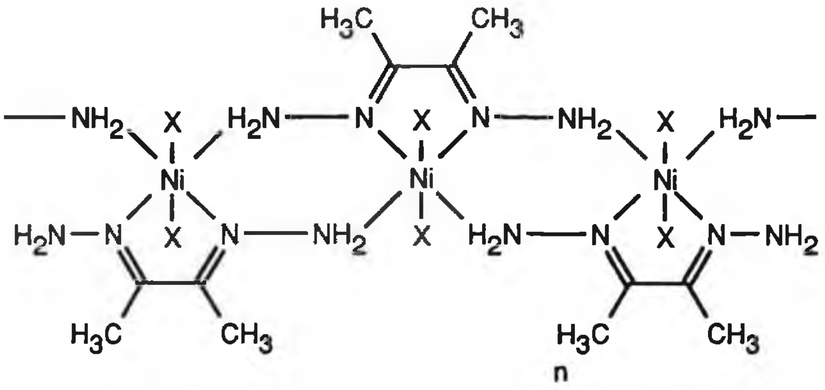


(134)



(135)

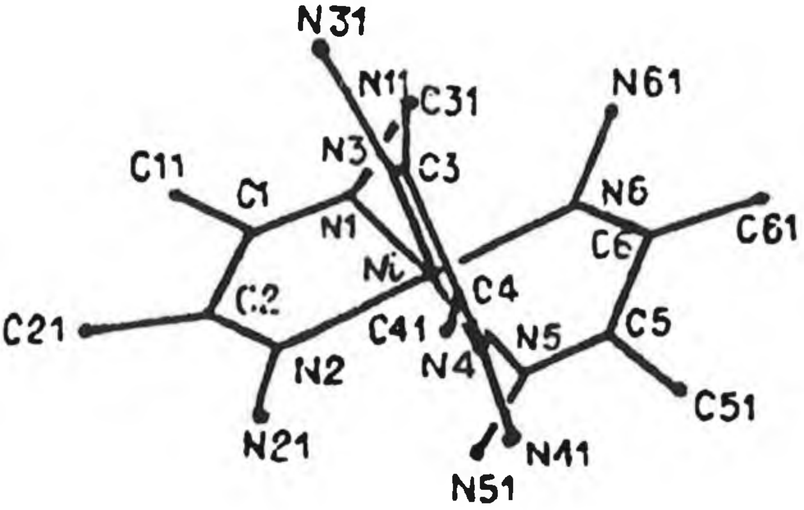
Sharma *et al.*[69] described the preparation, properties and characterisation of complexes of cobalt(II) and nickel(II) with diacetyldihydrazone **(5)** of the type **(136)** - **(141)** where the nitrogen of the amino groups as well as the nitrogen atoms of the azomethine linkage participate in coordination.



(136) M = Co(II) X = Cl$^-$ **(137) M = Ni(II) X = Cl$^-$**
(138) M = Co(II) X = Br$^-$ **(139) M = Ni(II) X = Br$^-$**
(140) M = Co(II) X = I$^-$ **(141) M = Ni(II) X = I$^-$**

In a study of the use of hydrazones for the spectrofluorometric determination of technetium(VII), diacetyldihydrazone **(5)** was investigated. Grases and March[70] mixed diacetyldihydrazone **(5)** with pertechnetate in the presence of a reducing agent, tin(II)chloride in acid medium. On heating on a steam bath, different colours are obtained, varying from yellow to mauve-red, depending on the diacetyldihydrazone **(5)** to technetium ratio. However interference for this method by other metals was high.

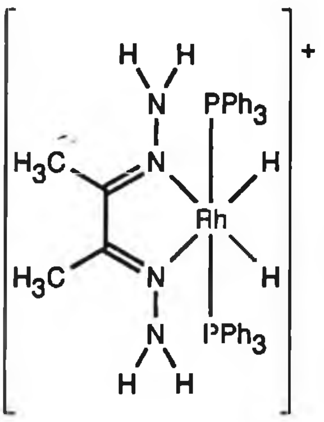
A more recent characterisation of diacetyldihydrazone complexes of cobalt(II), copper(II), nickel(II) and iron(II) has been carried out by Gonzalez Garmendi and coworkers[71,72]. Characterisation included chemical analysis, conductance measurements, electronic, infrared, EPR spectral studies, and magnetic susceptibility. A mononuclear octahedral configuration was proposed for all complexes studied. The crystal structure of nickel(II)tri(diacetyldihydrazone)dichloride **(142)** has been reported by Pomahehko(73).



(142)

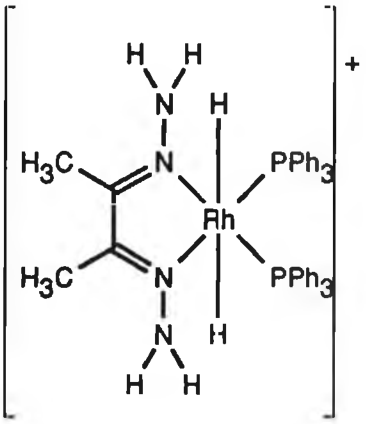
Figure [1.1] **Crystal Structure of Nickel(II)tri(diacetyldihydrazone)dichloride**

The synthesis and characterisation of some new cationic hydride complexes of rhodium(III) **(143)** - **(145)** is described by Iglesias and Del Pino(74,75).



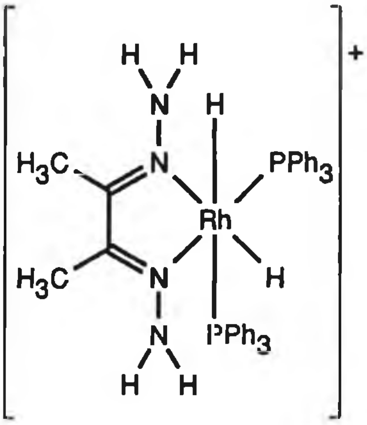
trans-cis

(143)



cis-trans

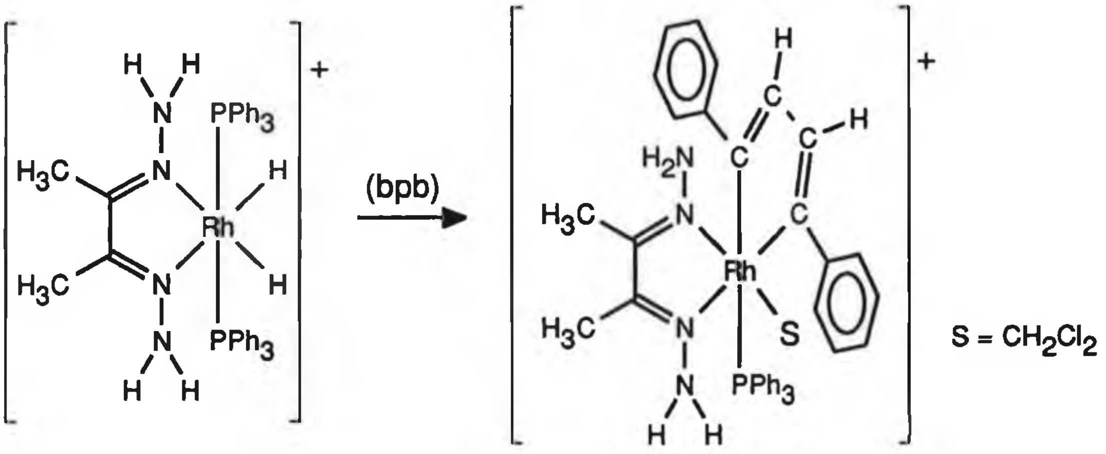
(144)



cis-cis

(145)

The rhodium cis-dihydride complex **(143)** reacts readily at room temperature with excess 1,4-diphenyl-1,3-butadiene (bpb) in dichloromethane with the evolution of hydrogen to give **(146)** according to scheme [1.17].

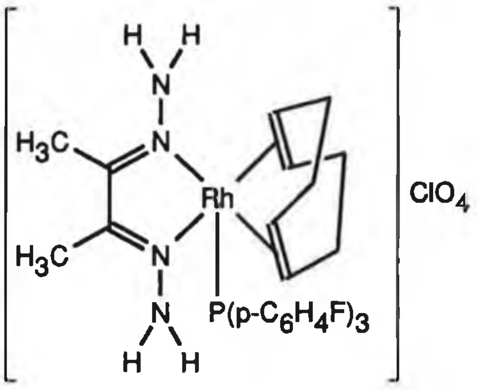


(143) (146)

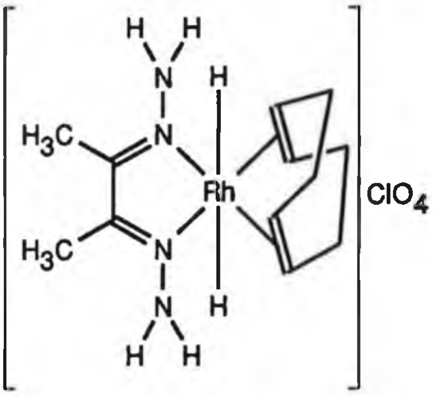
S = CH_2Cl_2

Scheme [1.17]

The rhodium complexes **(147)** and **(148)** are discussed by Iglesias and Del Pino[76,77]. Their synthesis and activity as precursors in olefin hydrogenation processes has been studied.



(147)

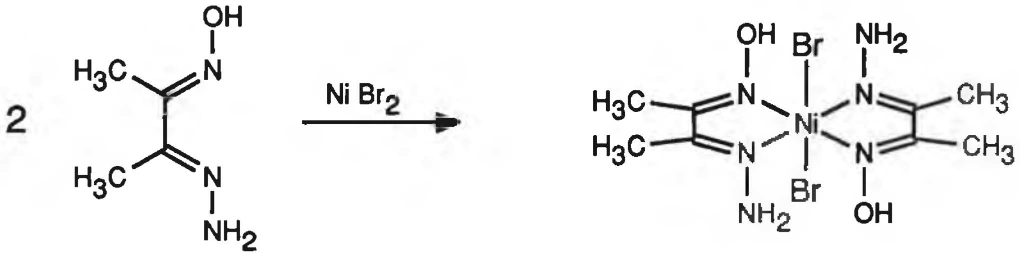


(148)

Compound **(147)**, pentacoordinated without a hydride ligand shows a hydride in both IR and NMR spectra indicating the presence of a solvated hydride species in solution after reaction with molecular hydrogen. Catalyst **(148)**, a dihydride hexacoordinate complex, analysed after the hydrogenation process, appears unaltered.

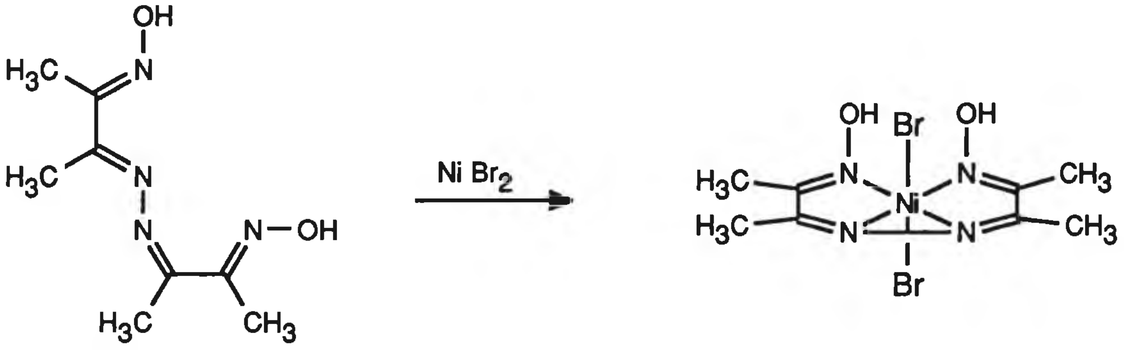
1.6 SYNTHESIS OF COMPLEXES OF DIACETYLMONOXIMEHYDRAZONE

The ligand diacetylmonoximemonohydrazone **(149)** was prepared by the addition of diacetylmonoxime to hydrazine[78]. The nickel complexes **(153)** - **(156)** of the ligands diacetylmonoximehydrazone **(149)**, diacetylmonoximeazine **(150)** and diacetylmonoxime(alkyl)azines **(151)** and **(152)** respectively, were reported by Ablov and Proskina[79], schemes [1.18] - [1.20].



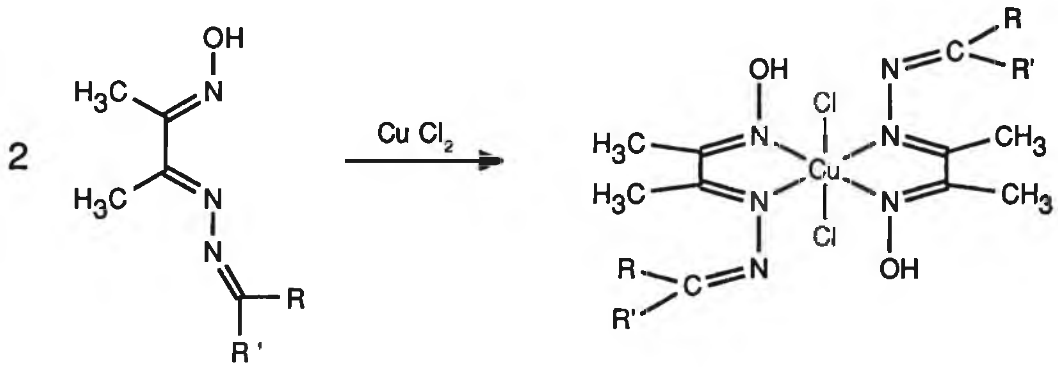
(149) **(153)**

Scheme [1.18]



(150) **(154)**

Scheme [1.19]



(151) $\mathbf{R = R' = CH_3}$

(152) $\mathbf{R = CH_3 \quad R' = C_2H_5}$

(155) $\mathbf{R = R' = CH_3}$

(156) $\mathbf{R = CH_3 \quad R' = C_2H_5}$

Scheme [1.20]

The complexes **(153)** - **(156)** are particularly interesting, due to the fact that the oxime groups remain protonated and do not get involved in chelation.

The nickeldichloride complex **(157)** of the ligand **(149)**, with a metal to ligand ratio of 1:2 was later reported by Ablov *et al.*(80,81). The crystal structure of diacetylmonoximehydrazone-nickel(II)dichloride **(157)**, was reported by Bremard *et al.*(82), and is illustrated in figure [1.2].

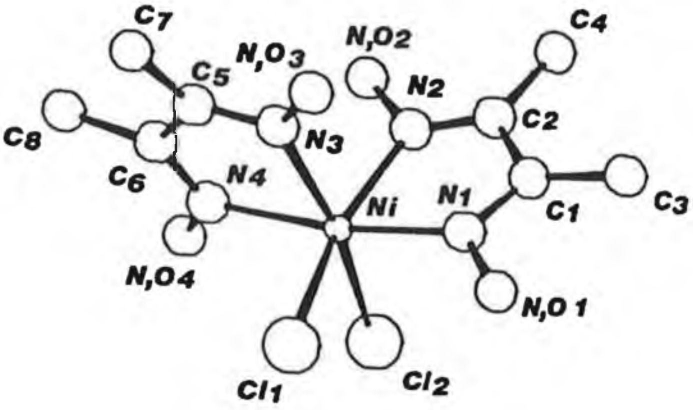
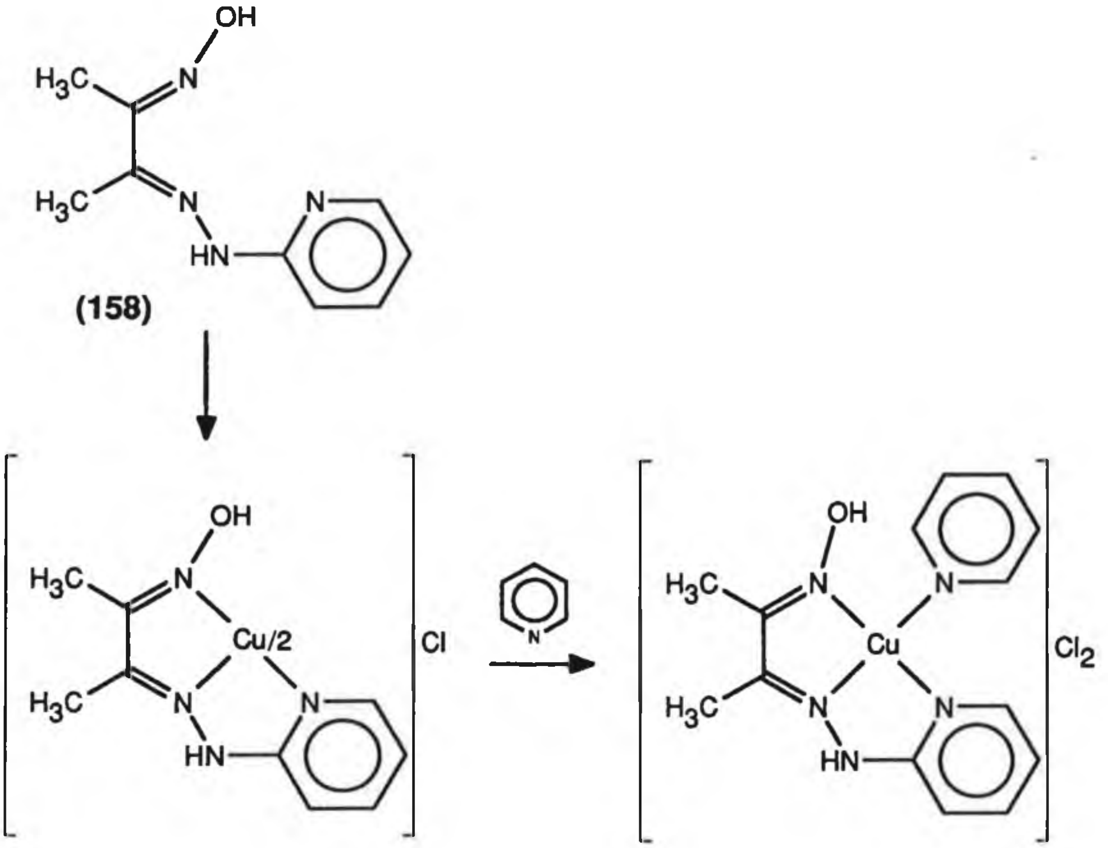


Figure [1.2] Crystal Structure of diacetyloximehydrazonenickel(II)dichloride (157)

1.7 COMPLEXES OF DIACETYL(α-PYRIDYLHYDRAZONE)

Lions and Martin[83] reported the reaction between diacetylmonoxime **(149)** and α-pyridylhydrazine at 100°C to yield diacetyloximeα–pyridylhydrazone **(158)**. The ligand **(158)**, reacts with copper(II)chloride in ethanol to give bright green solid diacetyloxime(α-pyridylhydrazone)copper(II)chloride **(159)**, which coordinates further with pyridine to give complex **(160)**, according to scheme [1.21].



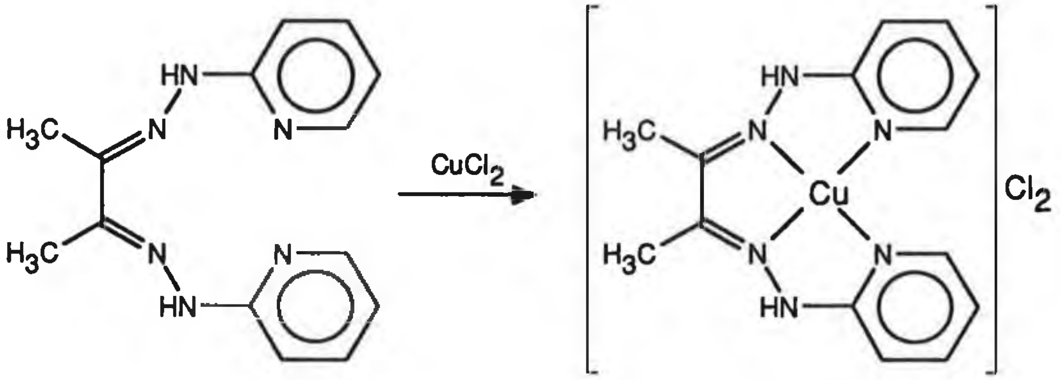
(158)

(159)

(160)

Scheme [1.21]

Diacetyl on reaction with a two molar equivalent of α-pyridylhydrazine readily yields the substituted hyrazone **(161)**. Diacetyldi(α-pyridylhydrazone) **(161)** in ethanol solution reacts with copper(II)chloride to give the brown crystalline diacetyldi(α-pyridylhydrazone)copper(II)chloride **(162)**, according to scheme [1.22].

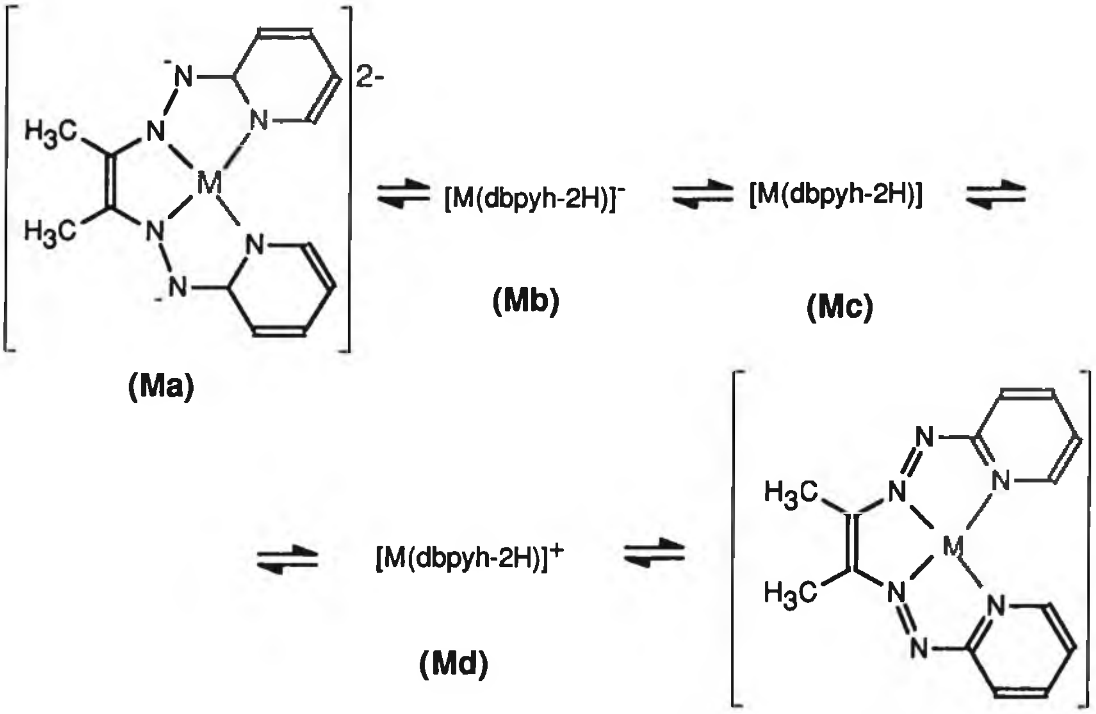


(161) (dbpyh) **(162)**

Scheme [1.22]

Chiswell and Lions[84] reported the diacetyldi(α-pyridylhydrazone) complexes of metals such as copper(II), nickel(II), zinc(II) and palladium(II) **(162)** - **(165)**.

Holm *et al.*[85,86] presented evidence that the copper(II), nickel(II), zinc(II) and palladium(II) complexes of diacetyldi(α-pyridylhydrazone) **(162)** - **(165)**, form the first member of a five-membered electron transfer series, scheme [1.23].



(Ma) **(Mb)** **(Mc)** **(Md)** **(Me)**

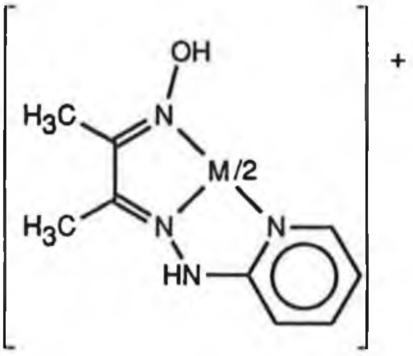
(162a) M = Cu(II)
(163a) M = Ni(II)
(164a) M = Zn(II)
(165a) M = Pd(II)

(162e) M = Cu(II)
(163e) M = Ni(II)
(164e) M = Zn(II)
(165e) M = Pd(II)

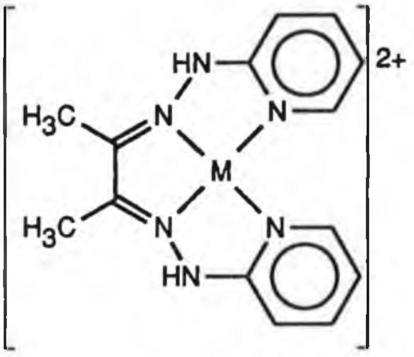
Scheme [1.23]

In DMF [Pd(dbpyh)-2H]^0 **(165c)** shows two one electron oxidations and reductions, shown to be reversible by cyclic voltammetry. The crystal and molecular structure of the neutral nickel complex [Ni(dbpyh)-2H]^0 **(163c)** has been reported by Olcott and Holm[87].

Rose in 1975[88], in association with Henkel Products patented the use of diacetyl(α-pyridylhydrazone) complexes **(163)** and **(166)** - **(168)** as hair dyes.



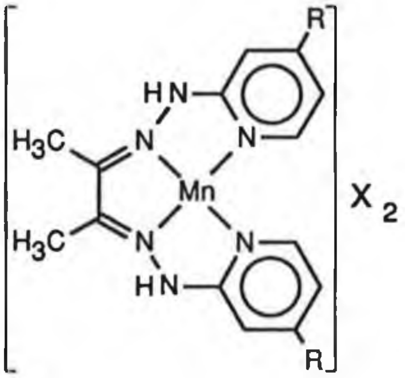
(166) M = Ni(II)
(167) M = Co(II)



(163) M = Ni(II)
(168) M = Co(II)

Hair was dyed different colours, varying from light green shades to red shades, with the dyes diacetylmonoxime(α-pyridyl)hydrazone complexes **(166)** and **(167)**. Diacetyldi(α-pyridylhydrazone) complexes **(163)** and **(168)** gave green brown-green shades of hair.

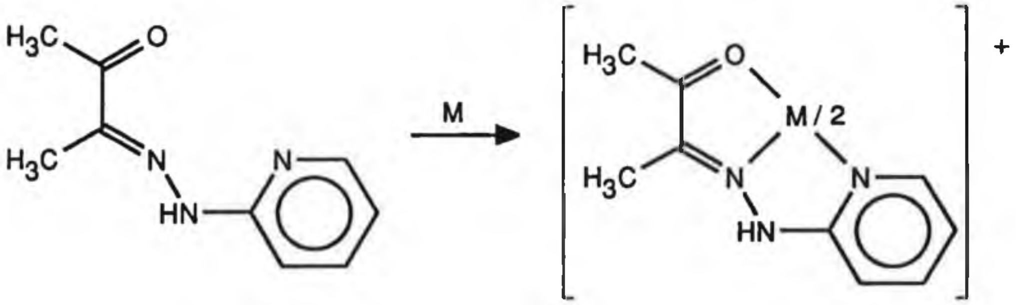
The preparation and properties of manganese(II) complexes of diacetyldi(α-pyridylhydrazones) **(169)** - **(173)** are described by Chiswell[89,90].



(169) R = H X = Br
(170) R = H X = ClO_4
(171) R = Cl X = Cl
(172) R = Br X = Cl
(173) R = CH_3 X = ClO_4

The spectrophotometric determination of cobalt(II) with diacetylmono-α-pyridylhydrazone **(174)** is described by Asuero *et al.*[91,92]. Advantages of this new reagent include, high solubility of both reagent **(174)** and complex **(175)** in aqueous media, negligible absorption of ligand at the λ_{max} and selectivity. The method has been applied to the determination of cobalt in nitrates.

A variation of this method, can also be used for the spectrophotometric determination of zinc[93,94,95]. Concentrations as low as 40 ppb of zinc(II) can be measured as the complex **(176)**, according to scheme [1.24]. The method is highly selective and is regarded as an acceptable reagent for the determination of zinc in potable waters.



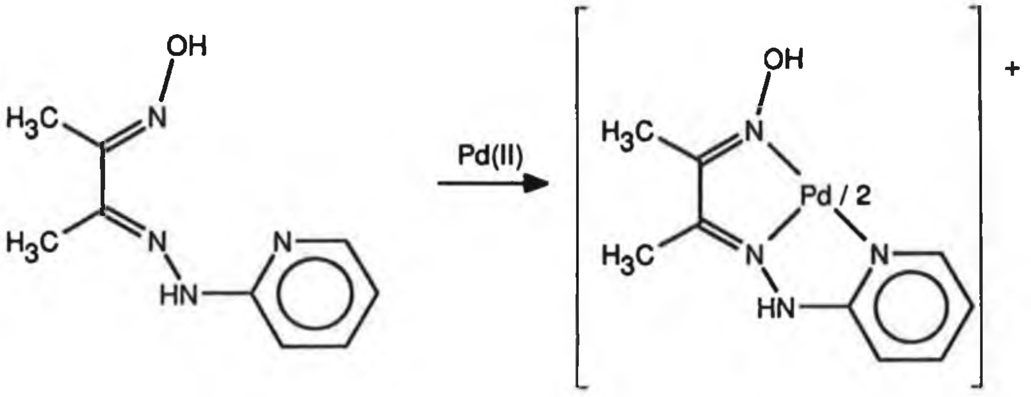
(174)

(175) M = Co(II)
(176) M = Zn(II)

Scheme [1.24]

Diacetylmonoxime(α-pyridyl)hydrazone **(158)** has also been used for the determination of cobalt by Asuero and coworkers in 1982[96]. Ligand **(158)** reacts with cobalt to form a yellow complex **(167)** under suitable conditions and allows quantitative determination of cobalt by measuring the absorbance at 430 nm. This method was found to be rapid, precise, selective and easy to use and has been applied to the determination of cobalt in synthetic mixtures, aluminium-molybdenum-nickel-cobalt catalysts, alloys and salts.

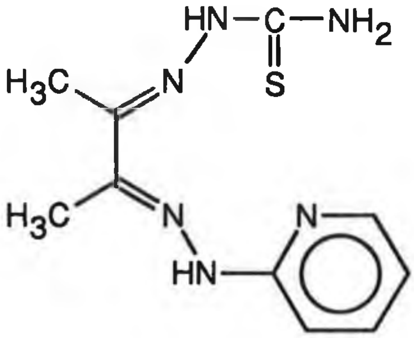
Further work by Asuero *et al.*[97,98] indicated that diacetylmonoxime-(α-pyridyl)hydrazone **(158)** can also be used for the spectrophotometric determination of palladium. The method relies upon the extraction of the palladium(II)diacetylmonoxime(α-pyridyl)hydrazone complex **(177)**, forming a purple-reddish complex, according to scheme [1.25].



(158) **(177)**

Scheme [1.25]

Pino and coworkers in 1985[99] examined the use of the asymmetric hydrazone diacetylmonothiosemicarbazone(α-pyridyl)hydrazone (dtpyh) **(178)**, as a spectrophotometric analytical reagent.

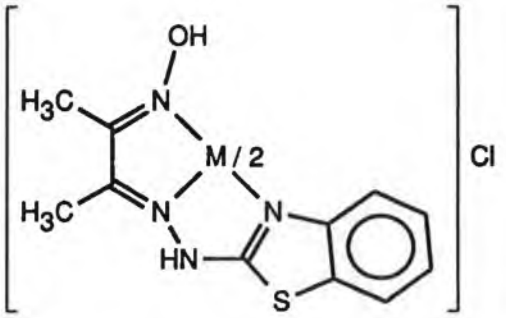


(178) (dtpyh)

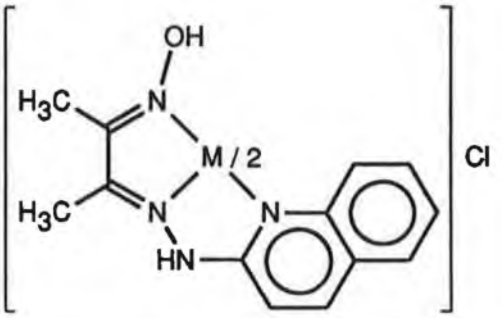
Compound **(178)** forms coloured chelates with heavy metal ions such as, Zn(II), Cd(II), In(III), Pd(II), Ni(II), Cu(II), Fe(II), Fe(III) and Co(II). On comparing diacetylmonothiosemicarbazone(α-pyridyl)hydrazone **(178)** with diacetylmono-(α-pyridyl)hydrazone **(174)**, the ligand **(174)** shows greater sensitivity but less reactivity than **(178)**.

The palladium complex of diacetyldi(α-pyridyl)hydrazone **(165)** was also prepared by Mc Kenzie *et al.*(100,101).

Some other unusual tridentate hydrazone complexes described by Chiswell and Litster in 1978(102,103) are illustrated below. The manganese diacetylmonoximemonohydrazone derivative **(179)** occurs as a pale pink compound.

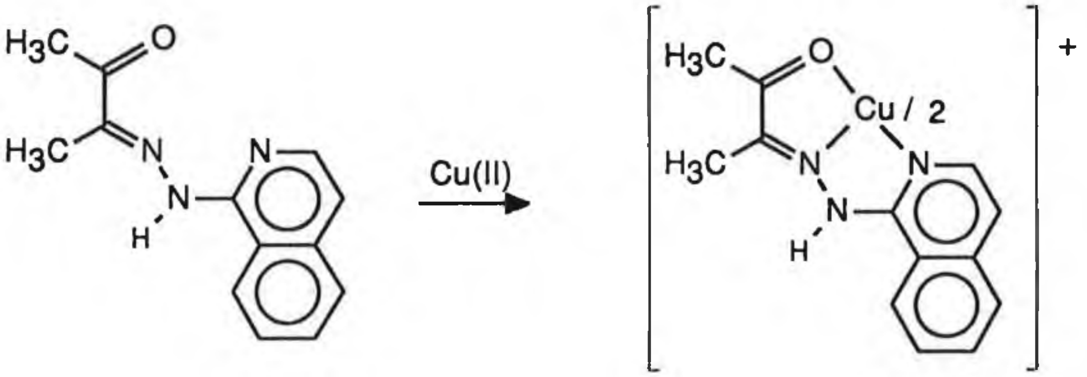


(179)



(180) M = Mn(II)
(181) M = Co(II)

Diacetylmonoximequinolylhydrazone forms a complex with manganese **(180)** and cobalt **(181)**. In later studies, Singh *et al.* in 1981^{104} have demonstrated that diacetylmonoquinoylhydrazone **(182)** can be used for the spectrophotometric determination of copper(II), as described by scheme [1.26]. The complex **(183)** formed exhibits maximum absorption at 570 nm, and can be used successfully for the selective determination of copper(II) in the presence of other metals.

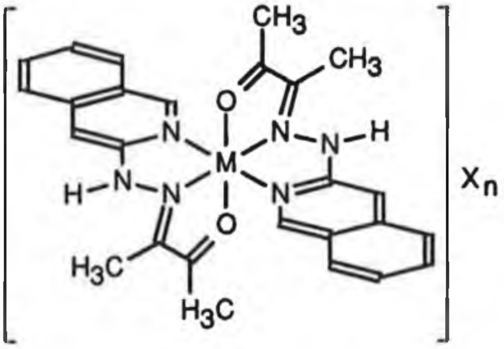


(182) **(183)**

Scheme [1.26]

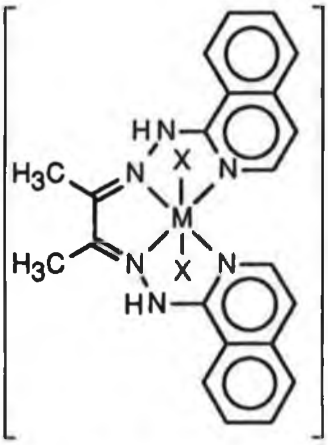
However, serious interferences occur from cyanide, EDTA, Fe(II), Ni(II), Pd(II), Zn(II) and Co(II).

Singh *et al.* in 1984^{105}, reported the copper(II) **(183) - (184)**, cobalt(II) **(185)**, manganese(II) **(186)** and iron(III) **(187)** complexes as having a pseudo-octahedral coordination.



(183) M = Cu(II) X = Cl^- n = 2
(184) M = Cu(II) X = I^- n = 2
(185) M = Co(II) X = Cl^- n = 2
(186) M = Mn(II) X = Cl^- n = 2
(187) M = Fe(III) X = Cl^- n = 3

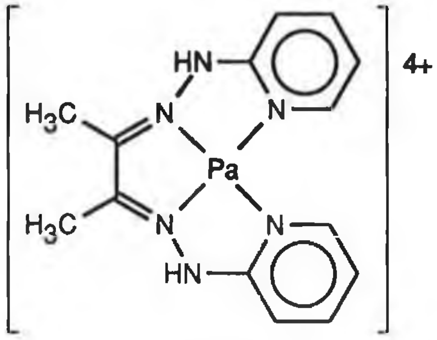
The ligand diacetyldi(quinolylhydrazone) **(188)** gave complexes with copper(II) **(189)** - **(191)**, nickel(II) **(192)** - **(194)**, manganese(II) **(195)** - **(197)** and cobalt(II) **(198)** - **(200)** which were reported the following year by Singh *et al.*[106].



(189) M = Cu(II) X = Cl^-
(190) M = Cu(II) X = Br^-
(191) M = Cu(II) X = SCN^-
(192) M = Ni(II) X = Cl^-
(193) M = Ni(II) X = Br^-
(194) M = Ni(II) X = SCN^-
(195) M = Mn(II) X = Cl^-
(196) M = Mn(II) X = Br^-
(197) M = Mn(II) X = SCN^-
(198) M = Co(II) X = Cl^-
(199) M = Co(II) X = Br^-
(200) M = Co(II) X = SCN^-

To date, only a few protactinium complexes with polydentate ligands have been described. Solache-Rios and Maddock in 1986[107] report the use of diacetyldi(α-pyridylhydrazone) **(161)**, which was one of a series of ligands selected on the basis of tracer experiments, to produce the protactinium 233 complex **(201)**. The complexes were characterised by Infrared and UV/Vis.

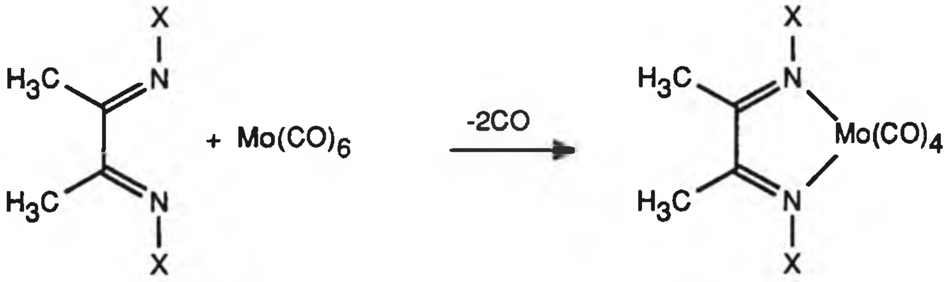
analysis and magnetic measurements. However, on exposure to air the grey complex turned blue, indicating oxidation.



(201)

1.8 METALCARBONYL-DIACETYLHYDRAZONE COMPLEXES

Dieck and coworkers(108,109,110,111) have reported the synthesis of the ligands diacetyldihydrazone **(5)** and diacetyldi(N,N-dimethylhydrazone) **(129)** and their molybdenum complexes **(202)** and **(203)**, according to scheme [2.27].

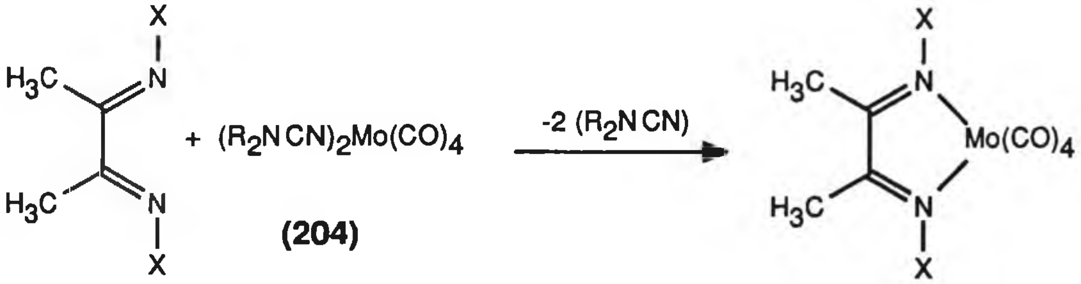


(5) **X = NH_2**
(129) **X = $N(CH_3)_2$**

(202) **X = NH_2**
(203) **X = $N(CH_3)_2$**

Scheme [1.27]

An alternative route for the synthesis of these type of complexes is where di(dialkylcyanamide)molybdenumtetracarbonyl **(204)**, is used as a precursor, as in scheme [1.28].



(204)

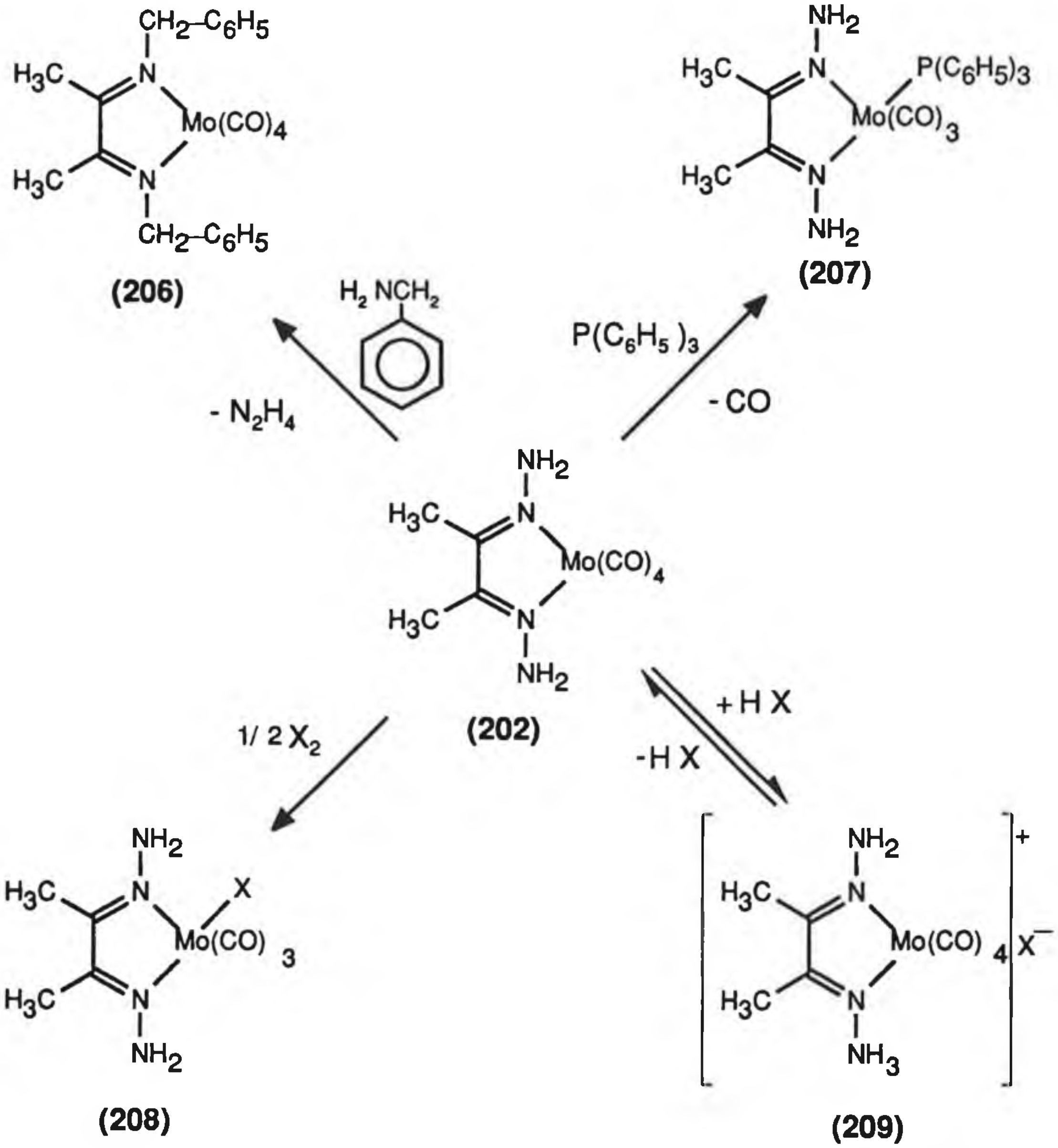
(5) **X = NH_2**
(129) **X = $N(CH_3)_2$**
(149) **X = NH_2/OH**

(202) **X = NH_2**
(203) **X = $N(CH_3)_2$**
(205) **X = NH_2/OH**

Scheme [1.28]

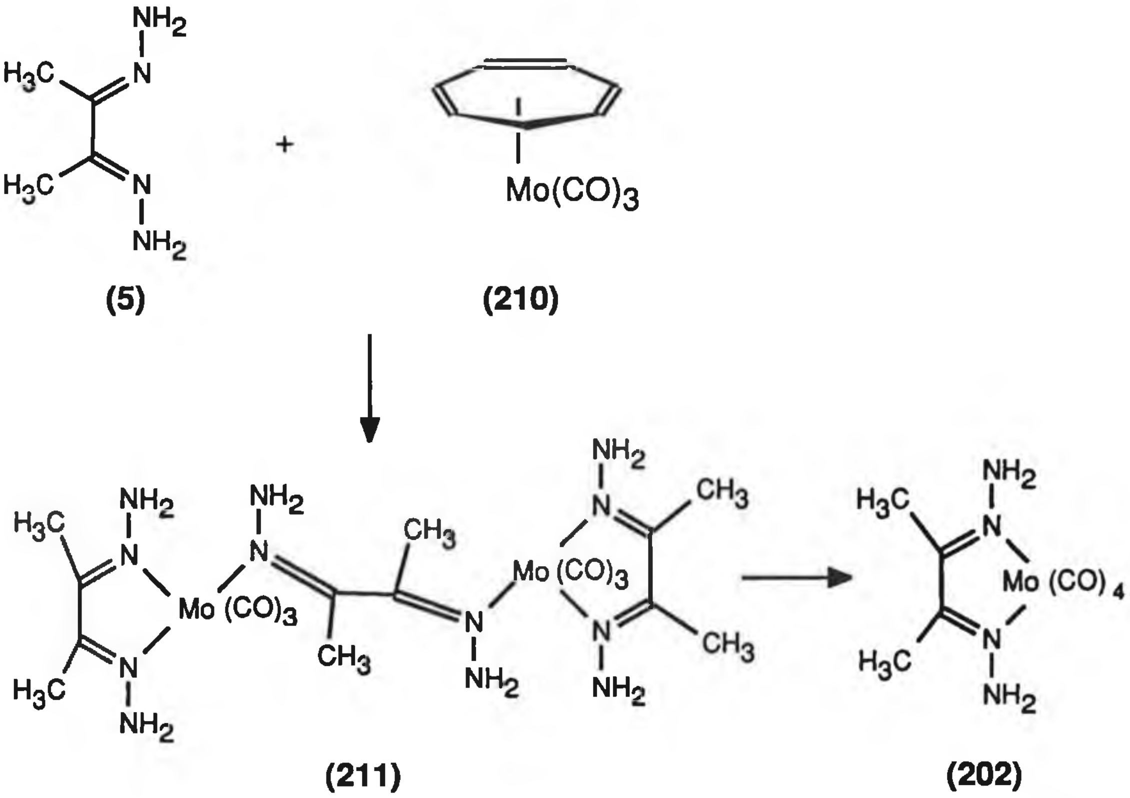
The diacetyloximehydrazone-molybdenumtetracarbonyl complex **(205)** was also prepared by the above method, using the hydrazone-oxime **(149)** as starting material.

Diacetyldihydrazonemolybdenumtetracarbonyl **(202)** undergoes a number of further reactions which are summarized in the reaction scheme [1.29]. Primary amines such as benzylamine react with complex **(202)** to replace the hydrazone group of **(202)**, by an imine group to produce complex **(206)**, with the elimination of hydrazine. Diacetyldihydrazone **(5)** is not removed by triphenylphosphine, but instead yields the tricarbonyl derivative **(207)** with loss of carbonmonoxide. Substitution of one of the CO groups of complex **(202)** by reacting with halogen produces complexes of the type **(208)**. Complex **(202)** is reversibly protonated with concentrated mineral acids (HX), to produce complexes of the type form **(211)**.



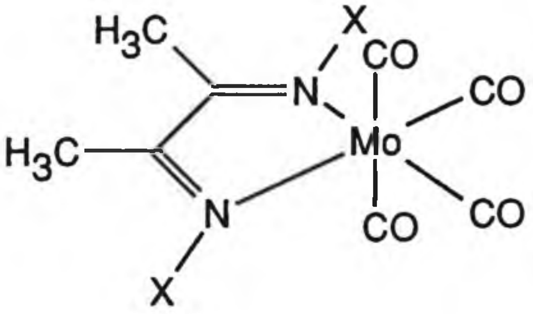
Scheme [1.29]

Diacetyldihydrazone **(5)** on reaction with cycloheptatrienemolbdenumtricarbonyl **(210)** at 80^{o}C, produces a complex with structure **(211)**, according to scheme [1.30]. Complex **(211)** is an example where the ligand diacetyldihydrazone **(5)** acts as a bridging ligand, and coordination of the ligand **(5)** occurs through the imine nitrogens. Complex **(211)** can be reacted further to produce the tetracarbonyl derivative **(202)**.



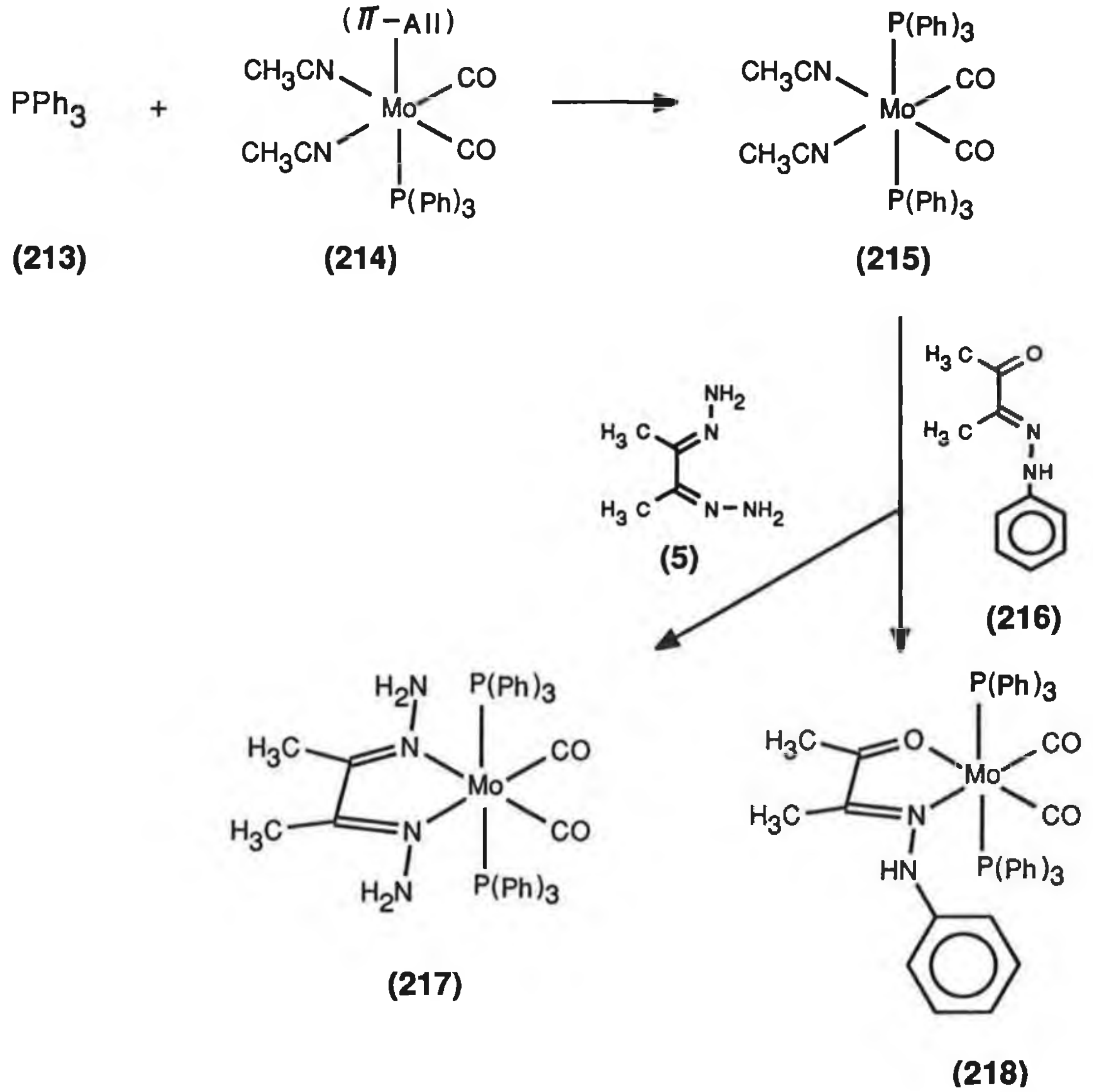
Scheme [1.30]

Dieck and Renk in 1971[112] postulated a (*cis*)-anti-configuration for the structure of diazabutadienemolybdenumtetracarbonyl complexes **(212)** based on IR spectroscopic data and electrochemical analysis of complexes and ligands.



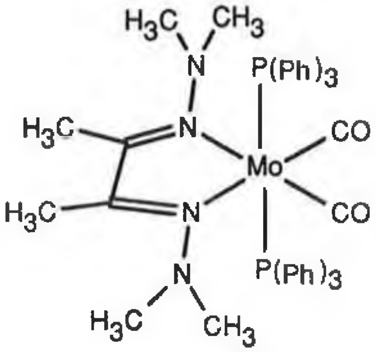
(212)

Dieck and coworkers in 1971[113] describe the reaction of triphenylphosphine **(213)** with π-allyldicarbonyl-molybdenum complex **(214)** to give, the tetra substituted molybdenum carbonyl complex **(215)** from which the complexes of the ligands diacetyldihydrazone **(5)** and diacetylmonophenylhydrazone **(216)** were prepared, **(217)** and **(218)** respectively according to scheme [1.31]. Evidence for the structures of complexes **(214)** to **(217)** was based on IR spectra and elemental analysis.



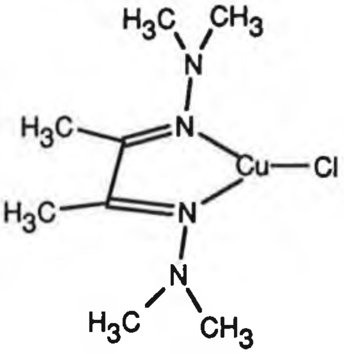
Scheme [1.31]

The diacetyldi(N,N-dimethylhydrazone), derivative **(219)** was reported by Dieck and Renk in 1972[114].

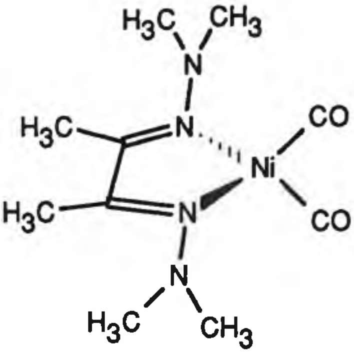


(219)

Dieck and Renk[115] have characterised the complex of diacetyldi(dimethylhydrazone) **(129)** with copper(I)chloride, a strongly coloured monomeric 1:1 adduct **(220)**. Evidence for the formation of complex **(220)** included IR, resonance Raman (RR), UV/Vis. spectroscopy and elemental analysis.



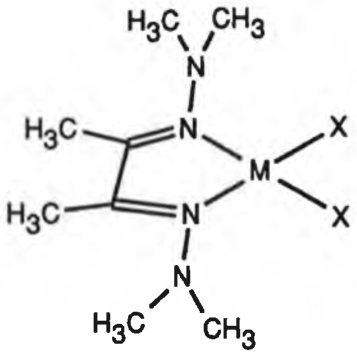
(220)



(221)

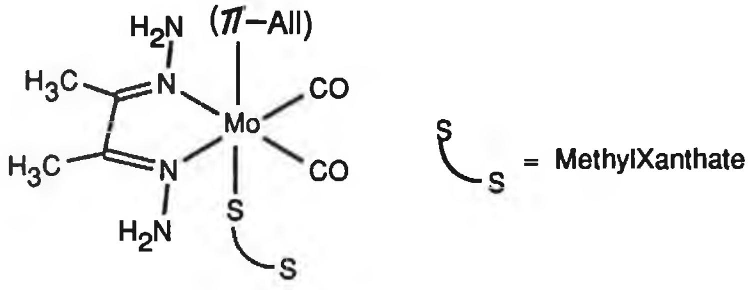
A nickel dicarbonyl complex **(221)** of diacetyldi(dimethylhydrazone) **(129)** has been prepared and characterised, by Hausen and Krogmann in 1972[116]. From the crystal structure data, complex **(221)** has tetrahedral geometry around the nickel atom centre.

Nicholls *et al.* in 1982 reported related complexes of diacetyldi-(dimethylhydrazone) with iron(II), cobalt(II), nickel(II), copper(II) and zinc(II) salts **(222)** - **(237)**[117]. The tetrahedral complexes, which have a metal-to-ligand ratio of 1:1, have the following structure.



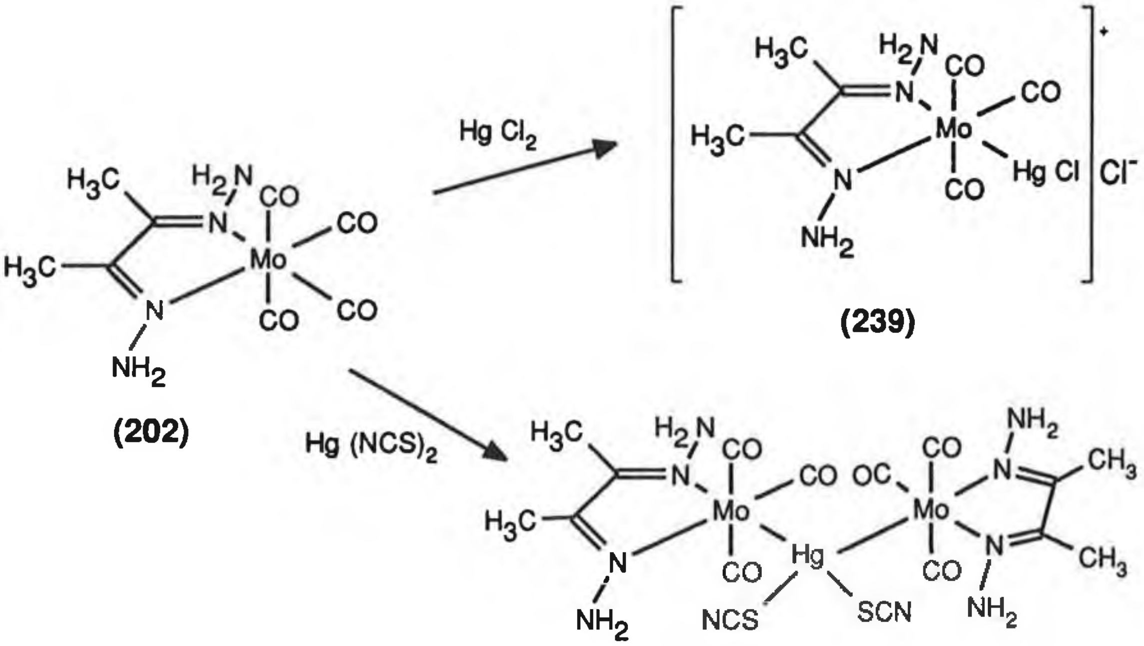
(222) M = Fe X = Cl
(223) M = Fe X = Br
(224) M = Cu X = Cl
(225) M = Cu X = Br
(226) M = Cu X = NCS
(227) M = Co X = NCS
(228) M = Co X = Cl
(229) M = Co X = Br
(230) M = Zn X = Cl
(231) M = Zn X = Br
(232) M = Zn X = NCS
(233) M = Ni X = Cl
(234) M = Ni X = Br
(235) M = Ni X = NCS
(236) M = Ni X = NO_3
(237) M = Ni X = I

The dicarbonylmolybdenum complex **(238)** of diacetyldihydrazone was prepared by Perpinan and Ballester in 1983(118), and characterised by IR, UV/Vis., NMR and elemental analysis.



(238)

Reactions of the complex $[Mo(CO)_4(ddh)]$ **(202)** with HgX_2, (X = Cl, I, SCN) and $SnCl_4$ were studied by Santos and coworkers(119). The reaction of $[Mo(CO)_4(ddh)]$ **(202)** with $HgCl_2$ or $Hg(SCN)_2$ in molar ratio 1:1, give the products **(239)** and **(240)**, according to scheme [1.32]. The products are formed as a result of oxidative addition with the loss of CO. The most useful characterisation technique for the identification of the products was IR spectroscopy. Data for the UV/Vis. spectra was also reported.



(202)

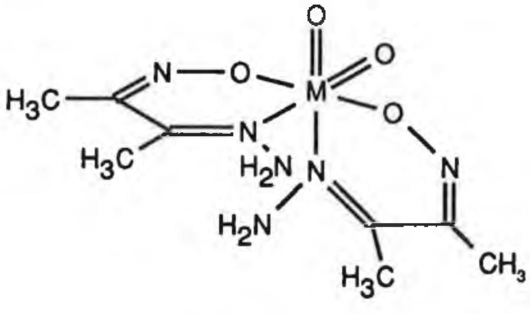
(239)

(240)

Scheme [1.32]

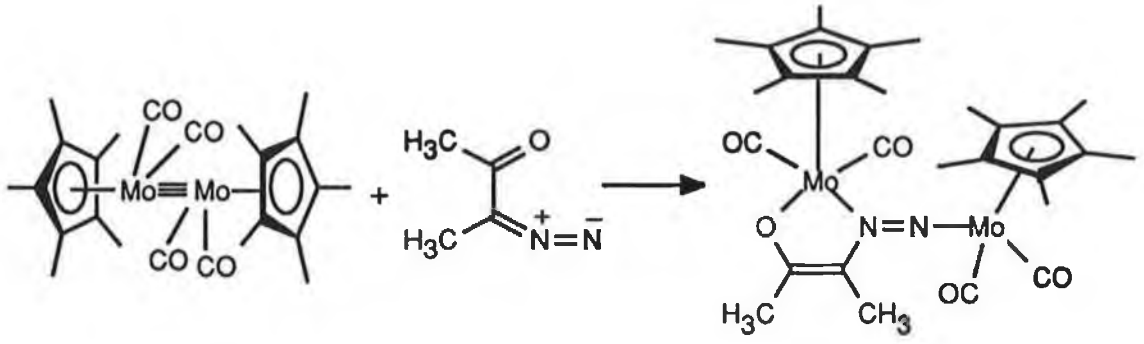
Santos *et al.* in 1984[120] described the oxidative addition reactions of [Mo(CO)$_4$(ddh)] **(202)** with Cl$_2$, Br$_2$ and I$_2$ under mild conditions. CO is eliminated, and seven coordinate molybdenum(II) species containing halogen are formed.

Felin in 1986[121] reported the dioxomolybdenum and dioxotungsten complexes of di(diacetyloximehydrazone), given by **(241)** and **(242)** respectively.



(241) M = Mo
(242) M = W

Herrmann and coworkers in 1982[122,123] described the unusual insertion reaction of 1,2-diazo ketones into a metal-metal triple bond. 3-oxo-2-diazobutane **(243)** reacts with di[dicarbonyl(η^5-pentamethylcyclopentadienyl)molybdenum] **(244)** to produce the complex **(245)**, according to scheme [1.33].



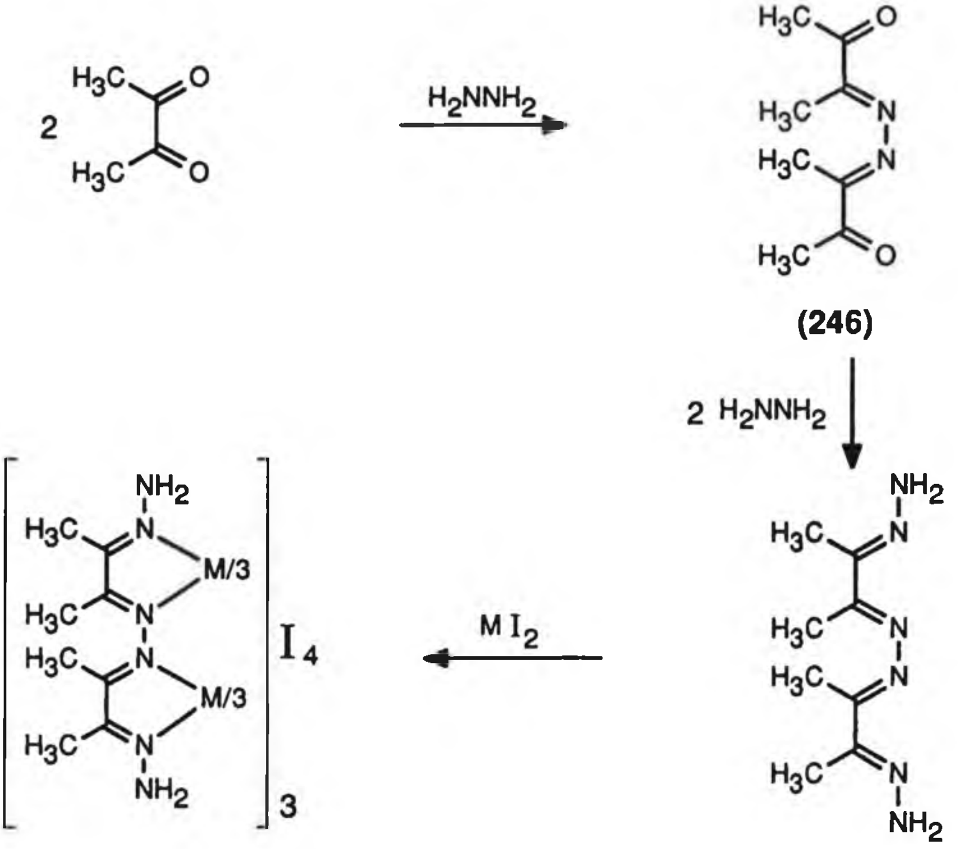
(244) **(243)** **(245)**

Scheme [1.33]

The structure of complex **(245)** was elucidated based on IR and ^{1}H NMR spectroscopy.

1.9 COMPLEXES OF DIACETYLAZINEDIHYDRAZONES

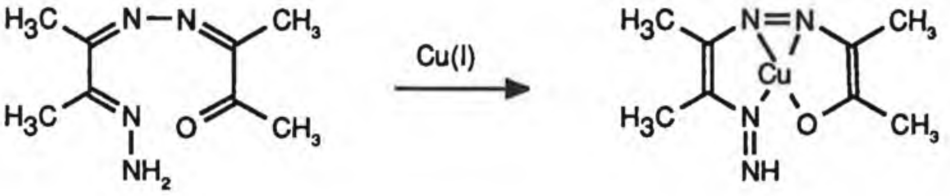
The ligand diacetylazinedihydrazone **(247)** was first synthesized from diacetylazine **(246)** by Stratton and Busch in 1960[124], and its chelating properties were studied briefly. Studies with diacetylazinedihydrazone **(247)** revealed that this ligand forms bridged dinuclear complexes of the type **(248)** and **(249)**, according to scheme [1.34].



(248) **M = Fe(II)**
(249) **M = Ni(II)**

Scheme [1.34]

Valcarcel and coworkers in 1977[125] described the synthesis, characteristics and analytical applications of diacetylhydrazoneazine **(250)**. Its reaction with metal ions, provides a method for the spectrophotometric determination of copper by extraction. Ligand **(250)** forms a complex **(251)** with copper(I), in a ratio of 1:1, according to scheme [1.35].

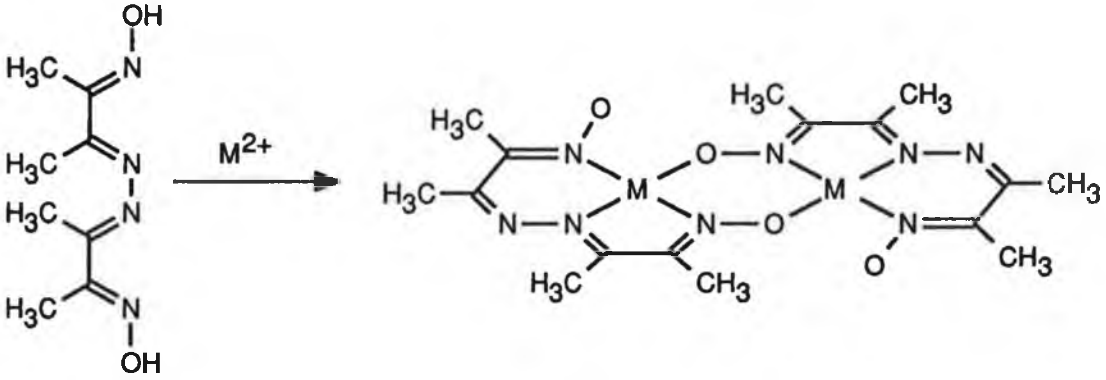


(250) **(251)**

Scheme [1.35]

The complex can be used for spectrophotometric estimation of traces of copper. The method is selective to copper over such metals as Al(III), Cd(II), Zn(II), Hg(I), Hg(II), Ni(II), Co(II), Fe(II), Fe(III), Mn(II), Ag(I), Pd(II) and Pt(IV).

Sahoo and Satpathy in 1971[126] reported that diacetylazinedioxime **(252)** forms chelate complexes with copper(II) and nickel(II) in a bidentate manner, to form di(diacetylazine-dioximato)dicopper(II) **(253)**, and di(diacetylazinedioximato)-dinickel(II)tetrahydrate **(254)**, according to scheme [1.36]. The IR spectra and magnetic properties of these new compounds are described. The crystal structure of the copper complex, Bremard *et al.* in 1985[127], demonstrated that the complex is in fact a dimer as depicted below.

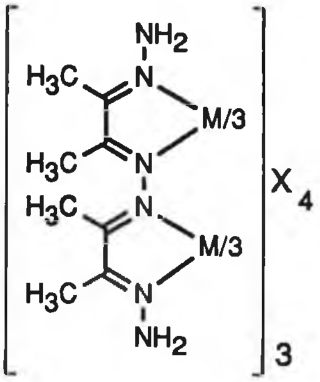


(252)

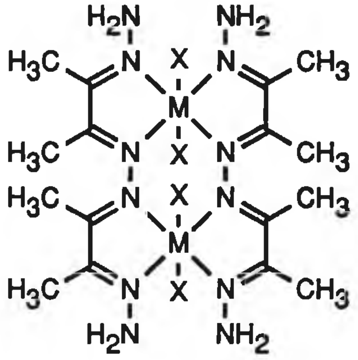
(253) **M = Cu**
(254) **M = Ni**

Scheme [1.36]

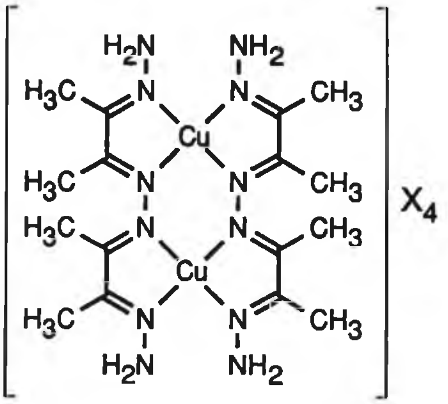
Sahoo and Mohapatra in 1982[128] isolated and characterised a series of Ni(II) **(255)** - **(258)**, Co(II) **(259)** - **(262)**, Fe(II) **(263)** - **(265)** and Cu(II) **(266)** - **(268)** complexes of the ligand **(247)**.



(255) M = Ni $X = Cl^-$
(256) M = Ni $X = Br^-$
(257) M = Ni $X = NO_3^-$
(258) M = Ni $X = ClO_4^-$

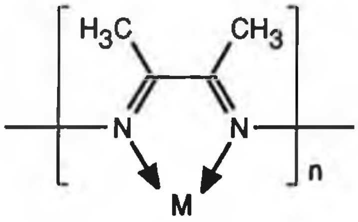


(259) M = Co $X = Cl^-$
(260) M = Co $X = Br^-$
(261) M = Co $X = NCS^-$
(262) M = Co $X = NO_3^-$
(263) M = Fe $X = NCS^-$
(264) M = Fe $X = Br^-$
(265) M = Fe $X = ClO_4^-$



(266) $X = Cl^-$
(267) $X = Br^-$
(268) $X = ClO_4^-$

Graciani Constante and Olias Jimenez(129) report the spectrophotometric determination of iron(II) by polyazine ligands **(269)** prepared "in situ". Diacetyl on reacting with hydrazine and heating to 60°C at pH 9.4, in the presence of iron(II) produces coloured solutions which can be used for the spectrophotometric determination of iron(II).

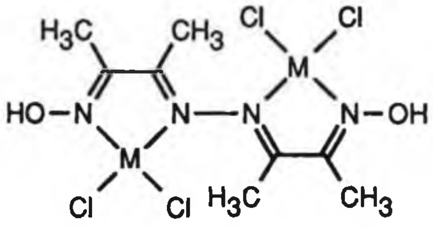


(269)

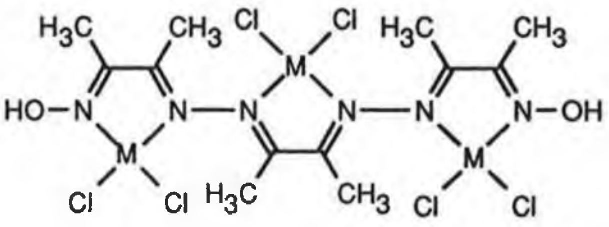
On monitoring at the appropriate wavelength, the method is specific to iron over numerous metals including Al(III), Mn(II), Zn(II), Ni(II) and Cd(II).

Graciani Constante(130) subsequently described the determination of the molecular weight of a polymer of diacetyl and hydrazine, by similar "in situ" synthesis between Fe(II), hydrazine and diacetyl. Attempts to determine polymer molecular weights using uv/visible and infrared spectroscopy and elemental composition are discussed. Molecular weights of up to 1,400 are reported.

In an effort to prepare polymetallic complexes of macromolecules, for use as conducting materials etc., Bremard and coworkers(131,132) report on the vibrational and electronic properties of poly-aza chain molecules of diacetyl and their copper(II) and zinc(II) complexes characterised by IR, Raman, EPR spectroscopies and also magnetic measurements. The copper(II) and zinc(II) complexes **(270)** - **(271)** and **(272)** - **(273)** respectively were prepared from their corresponding ligands, and copper(II)chloride and zinc(II)chloride.



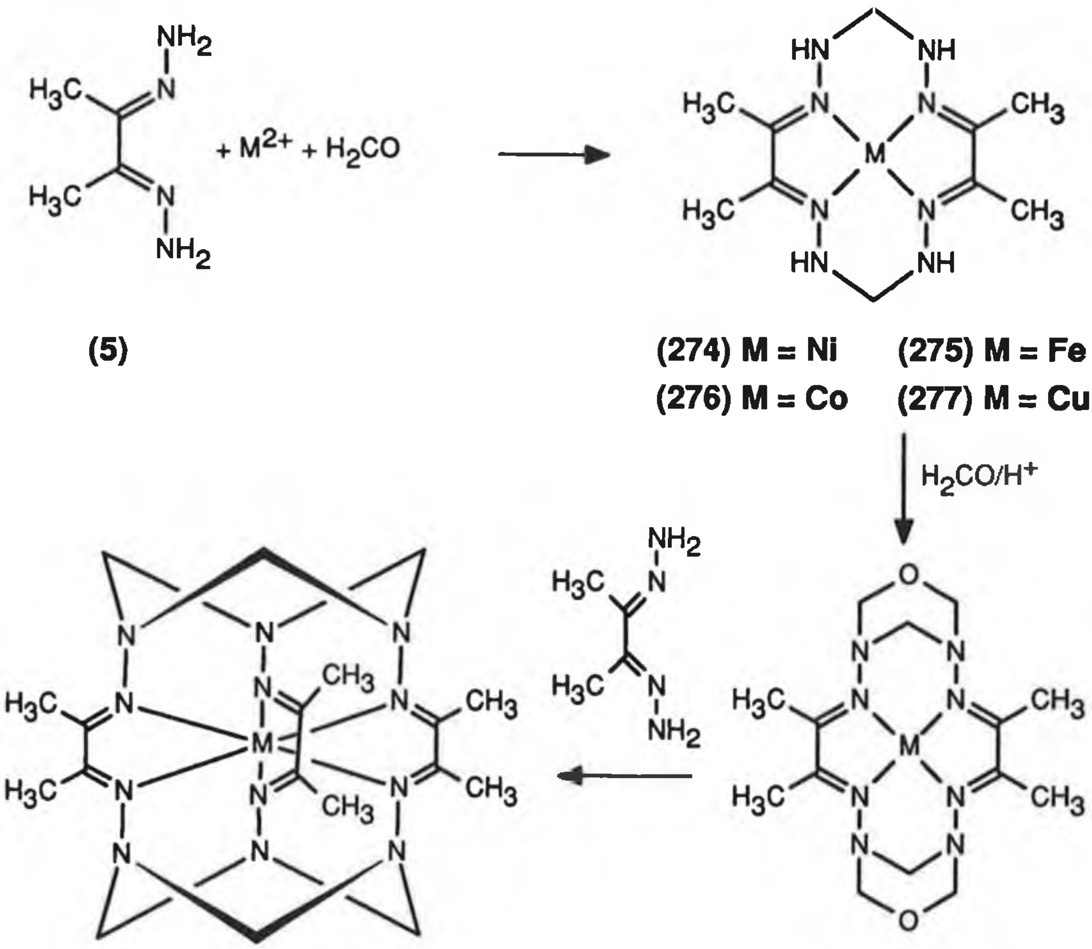
(270) M = Cu(II)
(272) M = Zn(II)



(271) M = Cu(II)
(273) M = Zn(II)

1.10 Template Condensation Reactions of Dihydrazone Complexes

Template condensations reported by Goedken *et al.*[133 - 137] describe metal directed synthesis of macrocyclic, tricyclic, and quadricyclic metal complexes from diacetyldihydrazone **(5)** and formaldehyde. The free amino groups of the coordinated diacetyldihydrazone are ideally oriented for ring closure giving six membered chelate rings and ultimately fourteen membered ring octa-aza-macrocyclic ligand complexes, **(274)** - **(277)** which can undergo further condensation with formaldehyde to yield tricyclic ligand complexes, **(278)** - **(281)**, or react again with another molecule of diacetyldihydrazone **(5)** to yield the quadricyclic ligand complexes **(282)** - **(285)**, scheme [1.37].



(5)

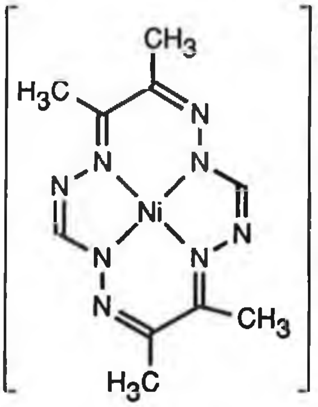
(274) M = Ni **(275) M = Fe**
(276) M = Co **(277) M = Cu**

(282) M = Ni
(283) M = Fe
(284) M = Co
(285) M = Cu

(278) M = Ni
(279) M = Fe
(280) M = Co
(281) M = Cu

Scheme [1.37]

Oxidation of the nickel complex **(274)** by molecular oxygen in acetonitrile solution, results in the formation of isomers **(286) - (288)**.



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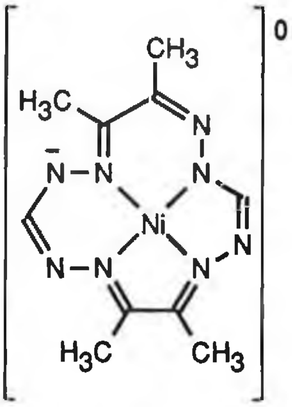

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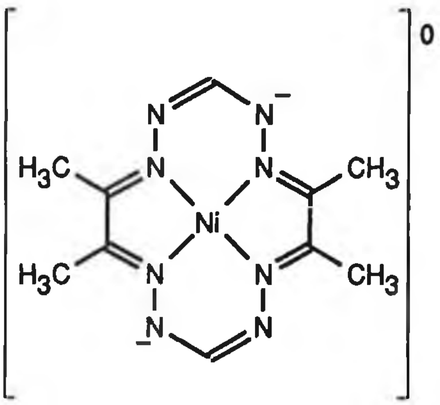
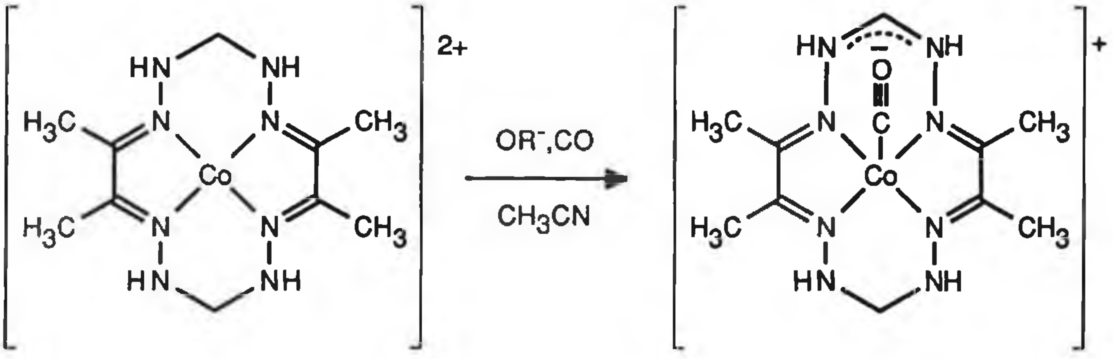


(288)

The carbonmonoxide derivative **(289)** of the cobalt macrocycle **(276)** was synthesised and characterised including X-ray crystallographic analysis by Goedken and Peng in 1974[138], given by scheme [1.38].

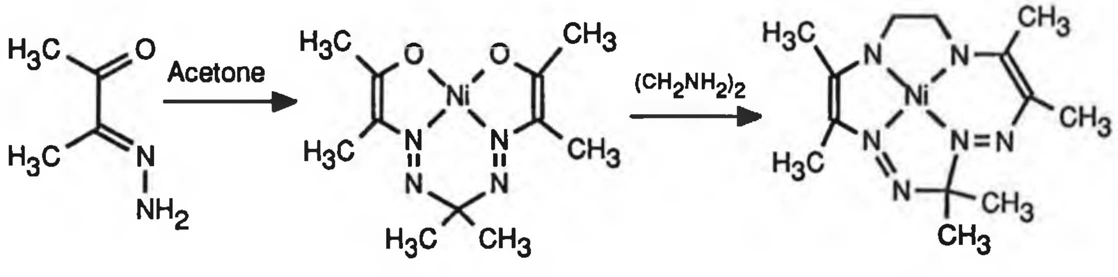


(276)

(289)

Scheme [1.38]

The reaction between diacetylmonohydrazone **(290)** and acetone in the presence of nickel(II) ions to produce a red-brown microcrystalline product **(291)** was studied by Melson and Bonfoey in 1973[139]. Reaction of **(291)** with anhydrous ethylenediamine results in the formation of an orange red product **(292)**, according to scheme [1.39].

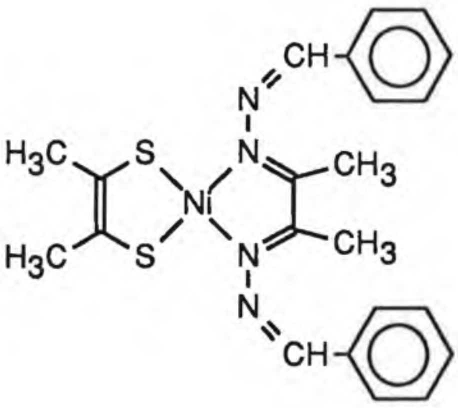


(290) **(291)** **(292)**

Scheme [1.39]

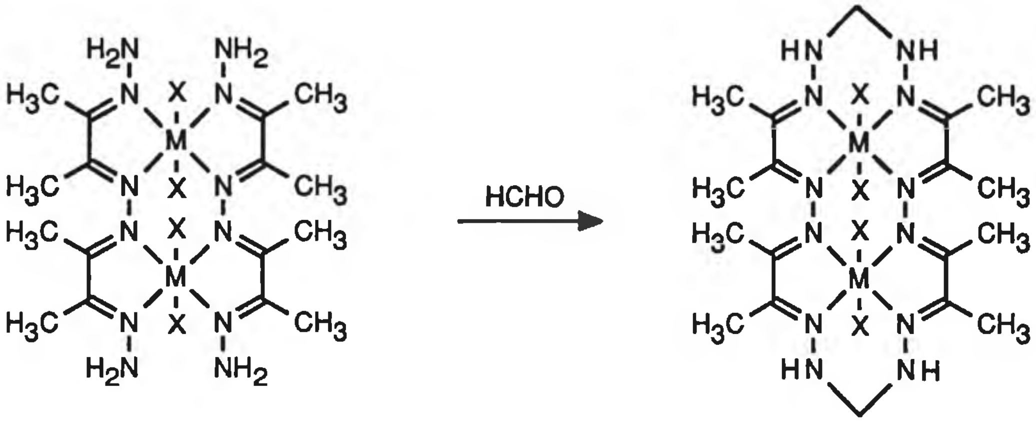
In both complexes **(291)** and **(292)** nickel(II) is in a square planar environment.

Dance and Miller in 1973[140] reported a four coordinate square planar nickel(II) complex **(293)** which contains one dithiolene and one 1,2-diimine ligand.



(293)

By the action of formaldehyde on the diacetylazinedihydrazone complexes **(248)**, **(249)**, **(259)** - **(261)** and **(268)**, a series of binuclear macrocyclic complexes, **(294)** - **(299)** respectively, have been prepared by Sahoo and Mohapatra in 1983[141]. The uncoordinated terminal NH_2 groups of the hydrazone complexes are suitably orientated so that these react with structurally different ketonic functions to yield macrocyclic and encapsulated chelates enclosing two metal centres, according to scheme [1.40].

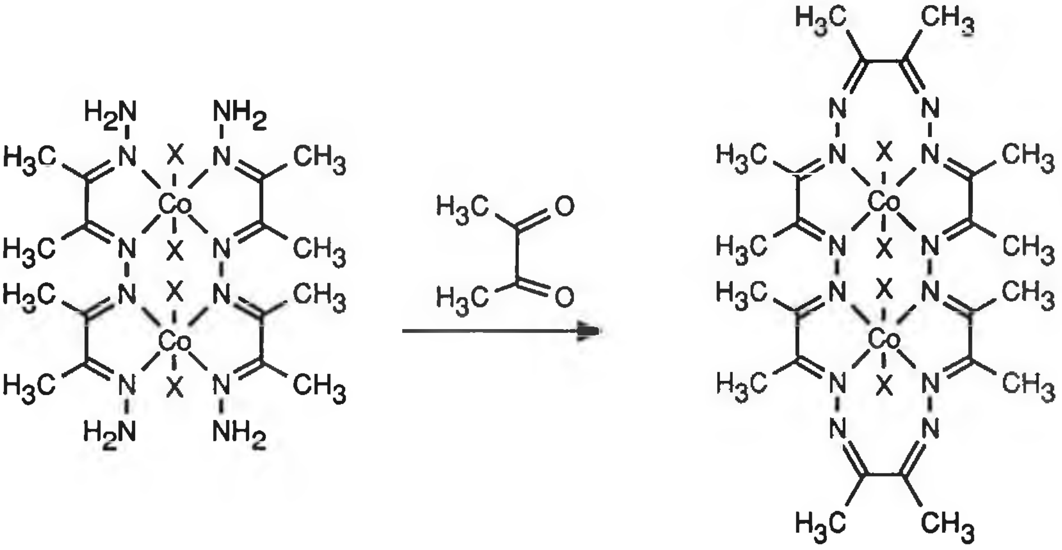


(248) **M = Fe(II) X = NCS$^-$**
(249) **M = Ni(II) X = NCS$^-$**
(259) **M = Co(II) X = Cl$^-$**
(260) **M = Co(II) X = Br$^-$**
(261) **M = Co(II) X = NCS$^-$**
(268) **M = Cu(II) X = ClO$_4^-$**

(294) **M = Fe(II) X = NCS$^-$**
(295) **M = Ni(II) X = NCS$^-$**
(296) **M = Co(II) X = Cl$^-$**
(297) **M = Co(II) X = Br$^-$**
(298) **M = Co(II) X = NCS$^-$**
(299) **M = Cu(II) X = ClO$_4^-$**

Scheme [1.40]

The authors subsequently reported(142) that the cobalt complexes of the type **(260)**, **(261)** and **(300)** react with diacetyl to give twenty four membered binuclear macrocyclic complexes, **(301) - (303)**, according to scheme [1.41].

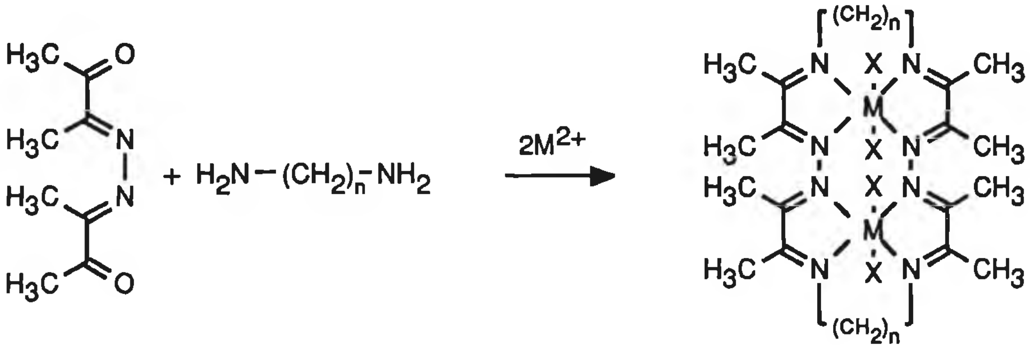


(260) **X = Br$^-$**
(261) **X = NCS$^-$**
(300) **X = I$^-$**

(301) **X = Br$^-$**
(302) **X = NCS$^-$**
(303) **X = I$^-$**

Scheme [1.41]

Sahoo *et al.* in 1985[143] described the template condensations of diacetylazine **(246)** with 1,2-diaminoethane and 1,3-diaminopropane in the presence of Co(II) and Ni(II) ions to form binuclear macrocyclic complexes **(304)** - **(310)**, according to scheme [1.42].



(246)

(304) $M = Ni$ $n=2$ $X=NCS^-$
(305) $M = Ni$ $n=3$ $X=NCS^-$
(306) $M = Co$ $n=2$ $X=NCS^-$
(307) $M = Co$ $n=2$ $X=NO_2^-$
(308) $M = Co$ $n=3$ $X=NCS^-$
(309) $[Ni_2(C_{20}H_{32}N_8)(H_2O)_4][ClO_3]_4$
(310) $[Ni_2(C_{22}H_{36}N_8)(H_2O)_4][ClO_3]_4$

Scheme [1.42]

1.11 Summary

It was clear from the review of the literature that a considerable body of work exists on the complexation of diacetyl derivatives with a variety of metals. This includes examples such as the metal complexes of diacetyldi(benzoylhydrazone) **(42)** and diacetyldi(thiobenzoylhydrazone) **(85)** where coordination to the metal occurs through both the imine nitrogens and the oxygen atoms of the ligand in **(42)**, and through the imine nitrogens and the sulphur atoms of the ligand **(85)**. Furthermore, there exists a large number of reports of complexes of diacetyldi(α-pyridylhydrazone) bound to metals such as Cu(II), Co(II), Ni(II), Zn(II), Pd(II), Mn(II) and Protactinium(IV) in a ratio of 1:1, *via* the imine nitrogens and the nitrogens of the pyridine ring.

In contrast, the phenyl hydrazone derivatives of diacetyl may complex initially *via* either the imino or amino nitrogen, complexes of diacetyldi-(phenylhydrazone) **(29)** forming the dichloride complexes **(31)** with Pd(II) and diacetyldi(N-methyl,N-phenylhydrazone) **(33)** forming the dichloride complexes **(34)** and **(37)** with Pd(II) and Pt(II) respectively. These complexes **(31)**, **(34)** and **(37)**, with bonding through two nitrogens, can be transformed into ortho-metallated phenyl derivatives **(32)**, **(53)** and **(38)** respectively. Diacetyldihydrazone **(5)**, the simplest of the series was reported to complex metals including Fe(II), Fe(III), Cu(II), Co(II), Ni(II), Pt(II), Pd(II), Hg(II), Rh(III), Zn(II), Mn(II) and finally molybdenum which forms metal carbonyl complexes.

The terminal amino groups of complexes of diacetyldihydrazone **(5)** can be joined together, by template condensation reactions of the metal complexes containing two or three ligands **(5)**, by reacting the complexes with either formaldehyde or diacetyl. The complexes produced contain macrocyclic "cage-type" ligands. These reports indicate that the terminal amino groups of **(5)** when complexed to a metal have the potential to react with carbonyl groups, suggesting that it may be possible to construct large oligomeric or polymeric complexes by reacting complexes containing **(5)** with dicarbonyl compounds.

Metal complexes of the dimer, diacetylazinedihydrazone **(247)**, reported include the Fe(II), Ni(II), Co(II) and Cu(II) complexes. An exact configuration (*cis-* or *trans-*) for the ligands of these complexes has not been established. Although a polymer of diacetyl dihydrazone **(269)** was complexed to Fe(II), with very little characterisation carried out on the iron polymer complex, no larger dihydrazone oligomers or polymers of diacetyldihydrazone other than those of the diacetylazinedihydrazone **(247)** have been reported. Similar to the template condensation reactions of the complexes of **(5)**, template condensation reactions can be carried out on the dinuclear complexes of diacetylazinedihydrazone **(247)** to produce dinuclear complexes containing large coordinating macrocycles.

No examples of ruthenium complexation either to dihydrazones or to azines have been reported to date despite the large number of reports on diimines and related ligands. This absence of reports for ruthenium prompted us to examine the coordination of substituted (aryl and alkyl) dihydrazones of diacetyl to the rutheniumbis(bipyridyl) moiety. Furthermore we hoped to investigate the possibility of preparing discrete diacetyldihydrazone oligomers of the type $-N-[-N=C(CH_3)-C(CH_3)=N-]_n-N-$ for n = 1,2,3 *etc.* where n is the number of repeat units, with a view to complexing these azine oligomers to different metals including ruthenium. We aimed to produce and characterise complexes of different lengths with a discrete number of repeat units.

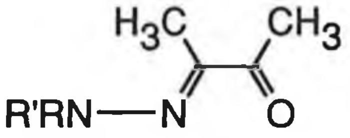
CHAPTER II

SYNTHESIS & CHARACTERISATION OF SUBSTITUTED DIHYDRAZONES, DIHYDRAZONES AND AZINES OF DIACETYL

2.1 INTRODUCTION

This chapter describes the preparation and characterisation of the hydrazone and substituted hydrazone derivatives of diacetyl, most of which are subsequently used to form metal complexes. The compounds prepared may be divided into four main classes.

Class (I) compounds can be described as mono- and di- hydrazones of diacetyl, **(311)** and **(312)** respectively, where R = H, CH_3; R' = H, alkyl, aryl.



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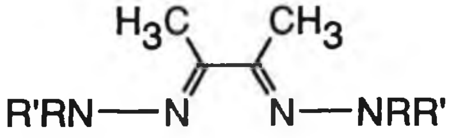


(312)

The disubstituted hydrazones **(312)** contain a diimine functional class, and differ from the more common diazobutadiene **(3)** ligands because of the second nitrogen atom attached to the imine classes. Before we examined the chemistry of larger oligomeric or polymeric hydrazones, we examined compounds of class (I), which are in effect the building blocks of larger hydrazone derivatives. Many substituted dihydrazones of this type have been previously reported but with incomplete methods for their synthesis. A complete description of the synthesis and characterisation of both old and new substituted dihydrazones is described, in most cases isolating the intermediate monohydrazone.

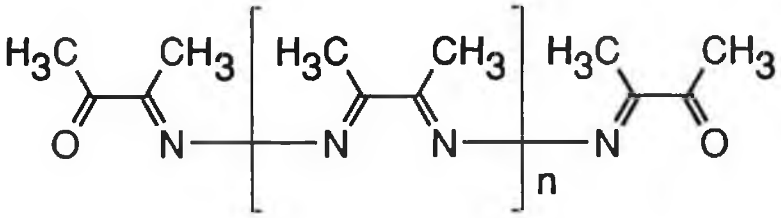
Class (II) compounds can be described as a series of diketone-diacetylazine oligomers **(313)**. Reasons for our interest in this class of compounds include;

(i) They contain a repeating diimine unit;

(ii) They may be end-capped easily using the carbonyl group, with a large number of molecules including amines and hydrazones;

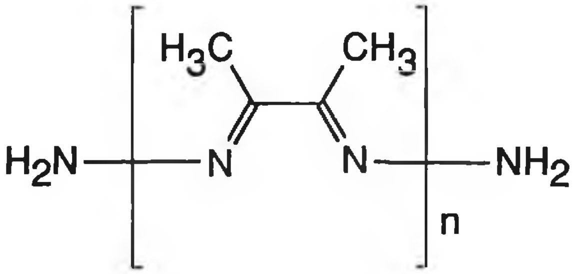
(iii) They act as precursors for the synthesis of oligomeric substituted dihydrazones of class (III) and (IV);

(iv) They possess alternating single and double bonds (a nitrogen containing analogue of polyacetylene) forming a conjugated π-system which may form the basis for an electrically conducting molecule.



(313)

Class (III) and class (IV) compounds are in effect the dihydrazone and diphenylhydrazone derivatives of class (II) compounds given by **(314)** and **(315)** respectively. Their properties and advantages are similar to those described for class(II) compounds.



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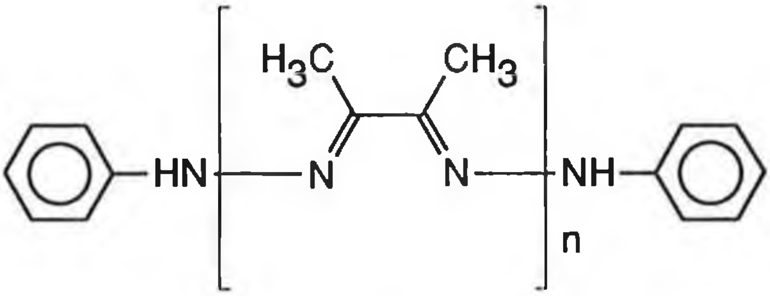


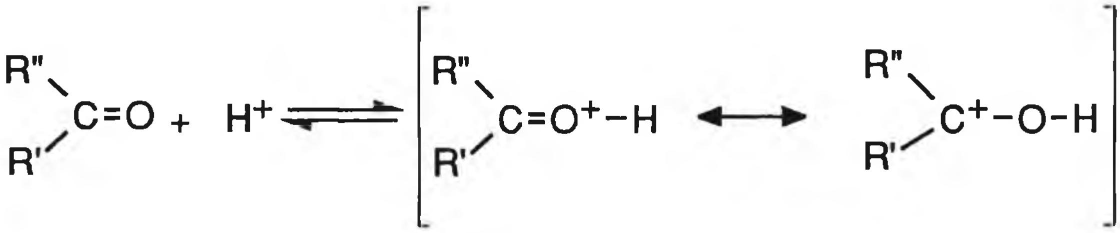
(315)

Class (III) compounds possess a reactive amino group on either end which may be potentially useful in the formation of polymers, or as an anchoring tool, or as a molecular spacer. Class (IV) compounds are similar to the previous dihydrazone oligomers except with the introduction of a phenyl group replacing one of the terminal hydrogens, which in effect end-caps the compounds.

Aldehydes and ketones react readily with compounds containing primary amino groups. The carbonyl is converted to the imine Schiff base, with loss of water, according to scheme [2.1].

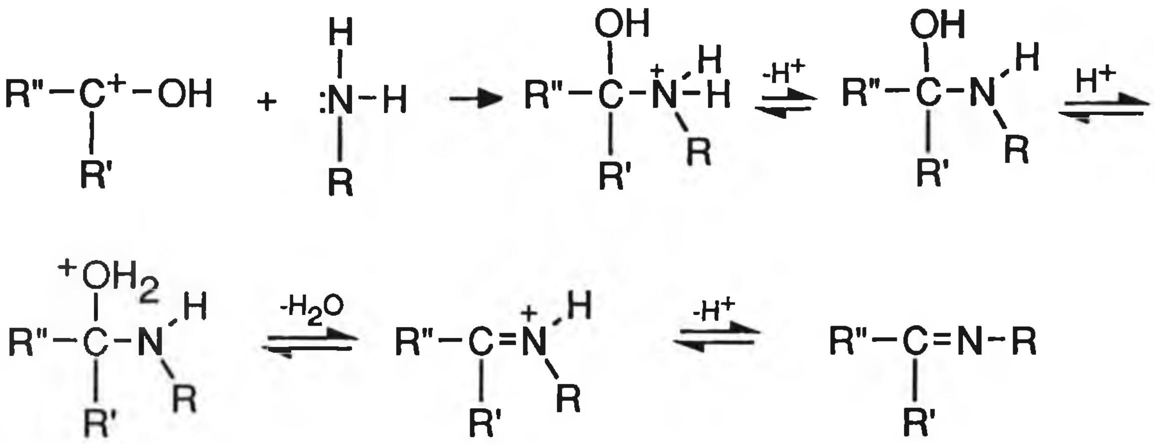
Scheme [2.1]

The reaction is acid catalysed, scheme [2.2], but the reaction mixture must not be too acidic (max. pH = 5), otherwise the nucleophilic amine is protonated.



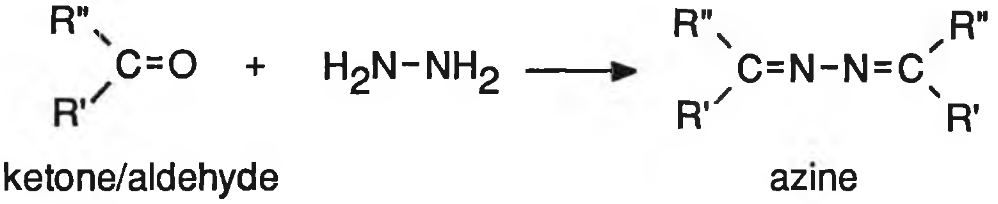
Scheme [2.2]

Nucleophilic addition of the basic nitrogen to the protonated carbonyl and abstraction of a proton yields an unstable alpha-hydroxy amine as intermediate, according to scheme [2.3].

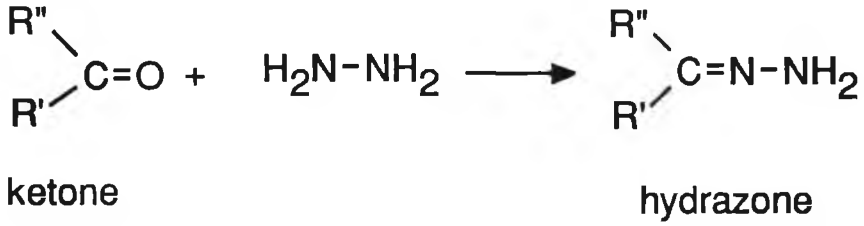


Scheme [2.3]

Hydrazine, $H_2N\text{-}NH_2$, the simplest diamine and parent of innumerable derivatives, is highly reactive at both ends. Both primary amines can act as nucleophiles, and undergo many of the reactions of primary amines. Once used chiefly as a rocket propellant, hydrazine and its derivatives are now used mainly as blowing agents for foamed plastics, as agricultural pesticides and for water treatment(144,145,146). In general, aldehydes and ketones with small substituents react with hydrazine to form azines, as in scheme [2.4]; some ketones, in particular with bulky R groups, react with hydrazine to form hydrazones exclusively, scheme [2.5].



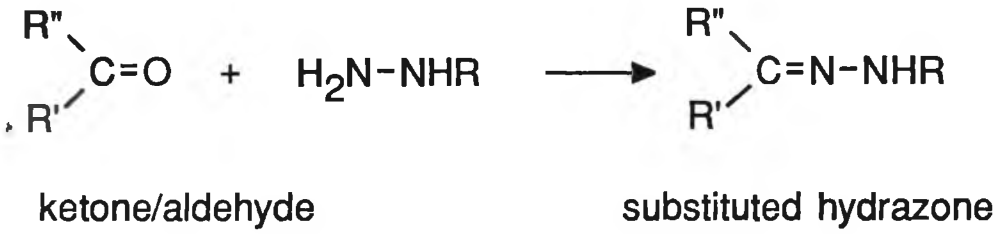
Scheme [2.4]



Scheme [2.5]

Two major influences govern the formation of either the azine or hydrazone, namely steric hindrance and the electron donating effect of substituents on the carbon atom of the carbonyl group.

Substituted hydrazine derivatives react with aldehydes and ketones to yield hydrazones as in scheme [2.6].



Scheme [2.6]

Clearly in the case of dicarbonyl compounds, the preparation of hydrazones is complicated by the presence of two carbonyl groups, and consequently the possibility of polymerisation.

2.2 RESULTS AND DISCUSSION

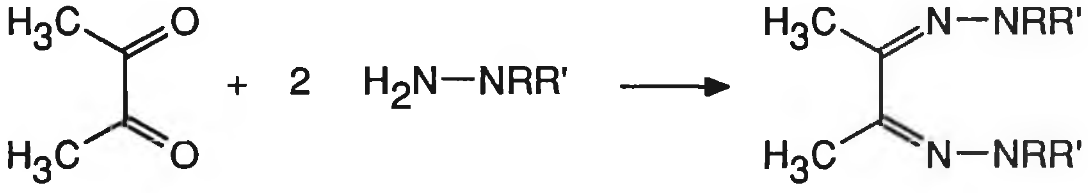
A series of compounds derived from the reaction between diacetyl and a variety of hydrazines has been prepared for use as ligands. As seen in the introduction to this chapter, the compounds have been divided into four main groups.

2.2.1 CLASS (I) COMPOUNDS

Class (I) compounds include monosubstituted hydrazones **(311)** and disubstituted hydrazones (symmetric **(312)** and asymmetric **(316)** hydrazones) of diacetyl. These represent the simplest examples for synthesis as the hydrazines are substituted on one of the amino groups, and thus complication due to azines or polymerisation do not arise.

2.2.2 PREPARATION OF SYMMETRIC DIHYDRAZONES

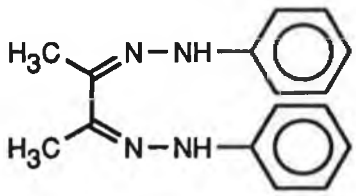
Symmetric dihydrazones **(312)** were prepared by mixing a solution of the particular hydrazine with a solution containing a half molar equivalent of diacetyl with acetic acid present to catalyse the reactions, represented by scheme [2.7].



(312)

Scheme [2.7]

Occasionally, it was necessary to heat the reactions. The products normally precipitated from solution. Using variations of previous procedures in the literature, the following diacetyldihydrazine derivative were prepared; diacetyldi(phenylhydrazone) **(29)** following a procedure reported by George *et al.* in 1975[147] and Chapman *et al.*[22], diacetyldi(p-nitrophenylhydrazone) **(317)** reported by Butler and Cunningham[148], diacetyldi(p-toluenesulphonylhydrazone) **(318)** reported by Bamford and Stevens in 1952[149], diacetyldi(o-tolylhydrazone) **(319)**, and diacetyldi(N-methyl,N-phenylhydrazone) **(320)** reported by Cattalini *et al.* in 1973[28].



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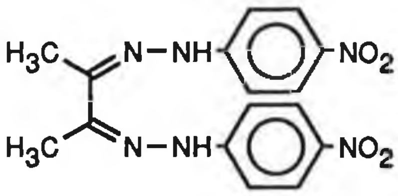

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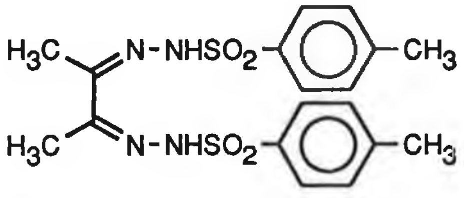

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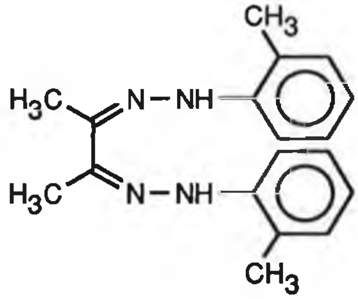

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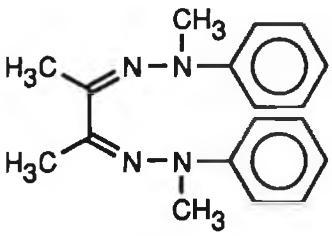
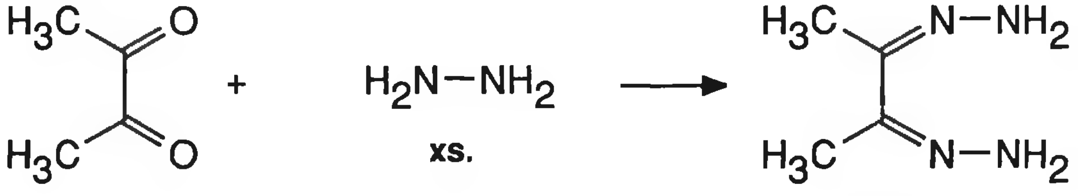


(320)

Analysis of the products isolated by infrared spectroscopy (IR), reveals no absorption peaks between 1700 cm^{-1} and 1600 cm^{-1}, indicating no C=O stretching frequencies, thus the absence of any diacetyl or monosubstituted-hydrazone. Compounds **(29)**, **(317)**, **(318)**, and **(319)** show N-H stretching frequencies at 3341cm^{-1}, 3314 cm^{-1}, 3330 cm^{-1}, 3385 cm^{-1}, respectively whereas the N-methylated dihydrazone **(320)**, shows no N-H stretching vibrations.

Diacetyl dihydrazone **(5)** was prepared by a variation of a method by Busch and Bailar[45]. In order to prevent formation of the azine, an excess of hydrazine hydrate was used, according to scheme [2.8].

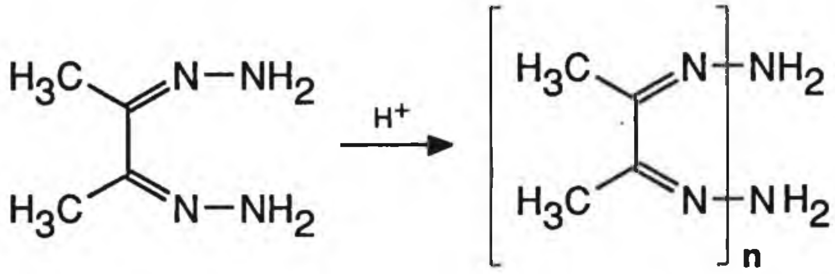


(5)

Scheme [2.8]

Crystals of the diacetyldihydrazone **(5)** form as long white needles from the reaction mixture on standing for 3-4 days. The IR spectrum of diacetyldihydrazone **(5)** has a peak at 3300cm^{-1} due to the asymmetric stretching of the N-H bonds, a symmetric N-H stretching band at 3193 cm^{-1}, and at 1636 cm^{-1} due to the internal deformation of the NH_2 group.

Diacetyl dihydrazone is not very stable and in acidic solution, readily forms yellow azine oligomers, according to scheme [2.9].

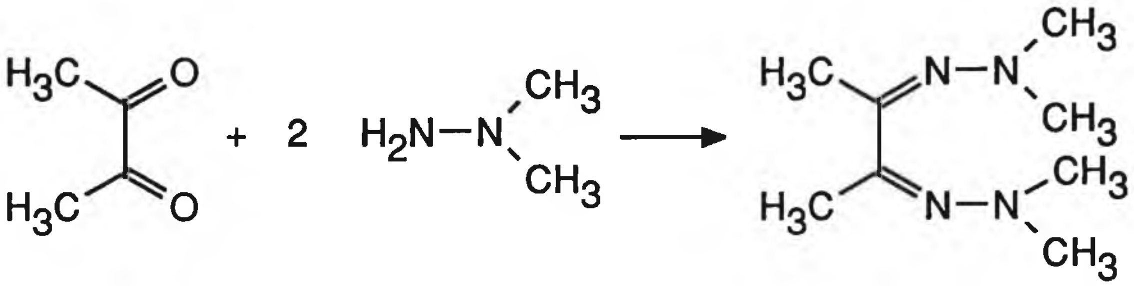


for n = 2,3,4 etc.

(5) **(321)**

Scheme [2.9]

Diacetyl di(N,N-dimethylhydrazone) **(129)** was prepared following a procedure reported by Dieck and Bock[109], by mixing a solution of diacetyl with a solution containing a two molar equivalent of N,N-dimethyl hydrazine, given by [2.10].



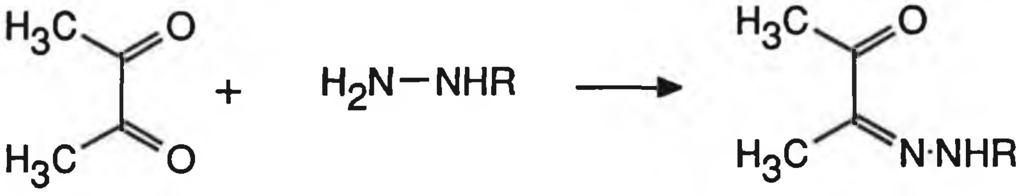
(129)

Scheme[2.10]

Because the product remains as a liquid at room temperature, the diacetyldi(N,N-dimethylhydrazone) **(129)** was isolated using a Kugelrohr distillation apparatus, with the distillate being collected at a temperature of 110°C. Purity was confirmed by using thin layer chromatography (TLC), IR and NMR analysis.

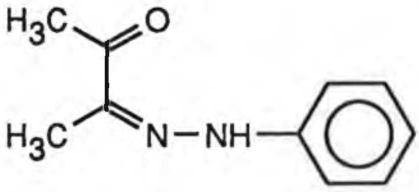
2.2.3 PREPARATION OF MONOHYDRAZONES

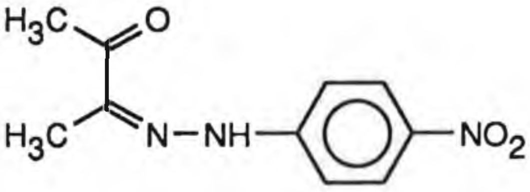
Diacetyl reacts with substituted hydrazines in a one-to-one molar ratio to yield monohydrazones. In the preparation of the monohydrazones **(311)** of diacetyl, it was essential to maintain an excess of the diacetyl in the reaction mixture, in order to prevent formation of the dihydrazone **(312)**. This was achieved by the addition of a solution of the particular hydrazine dropwise from a separation funnel to a stirred solution of diacetyl in an equimolar ratio, according to scheme [2.11].

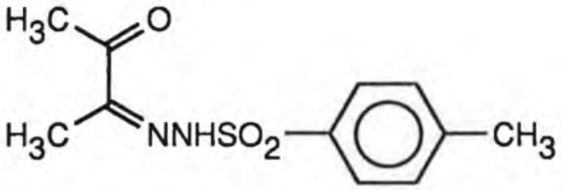

(311)

Scheme [2.11]

Using modifications of reported procedures[1,150], the following diacetyl monosubstituted hydrazones were prepared. Diacetylmono(phenylhydrazone) **(322)** reported by Yoder *et al.* in 1978[151], diacetylmono(p-nitrophenylhydrazone) **(323)** reported by Willey *et al.* in 1985[152] and diacetylmono(p-toluenesulphonylhydrazone) **(324)** were prepared by the dropwise addition of each hydrazine to a solution of diacetyl.


(322)


(323)


(324)

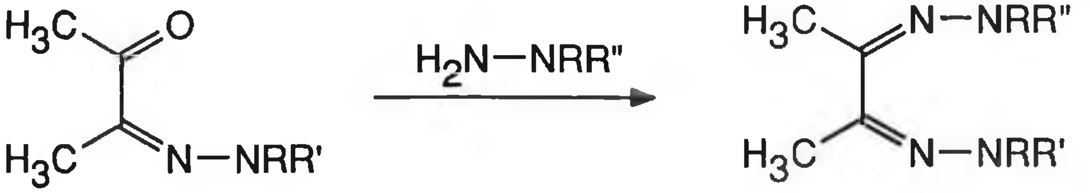
Formation of the monohydrazones was easily detected using thin layer chromatography (TLC) on silica plates. Assignment of the main IR bands was as follows; diacetylmonophenylhydrazone **(322)** has an N-H stretch at 3256 cm^{-1}, C=O at 1649 cm^{-1}; diacetylmono(p-nitrophenylhydrazone) **(323)** has an N-H stretch at 3294 cm^{-1}, C=O stretch at 1668 cm^{-1}; and diacetylmono(p-toluenesulphonylhydrazone) **(324)**, N-H at 3218 cm^{-1}, C=O at 1630 cm^{-1}. The N-H and C=O frequencies of the p-nitrophenylhydrazone derivative **(323)** are both higher than those of the phenylhydrazone derivative **(322)**, with the N-H and C=O frequencies of the p-toluenesulphonylhydrazone derivative **(324)** being the lowest. This phenomenon can be explained in terms of the electron withdrawing capacity of the respective functional groups. The p-nitrophenyl group, a strong electron withdrawing group, draws electron density from the rest of the molecule, causing a decrease in the N-H and C=O bond lengths, leading to higher frequencies. The reverse is true for the p-toluenesulphonyl group, a good electron donor, which feeds in electrons to the rest of the molecule, causing an increase in the bond lengths of N-H and C=O, thus a decrease in their respective frequencies.

The NMR spectra of the monosubstituted hydrazones were also obtained and assigned.

2.2.4 PREPARATION OF ASYMMETRIC DIHYDRAZONES

The isolation of monohydrazones allows the synthesis of asymmetric dihydrazones of the type **(316)**, where the two hydrazone groups attached to a diacetyl compound are different.

The asymmetric dihydrazones **(316)** are prepared by synthesising the monosubstituted hydrazone **(311)** first, and then reacting it with an alternative hydrazine[153], according to scheme [2.12].

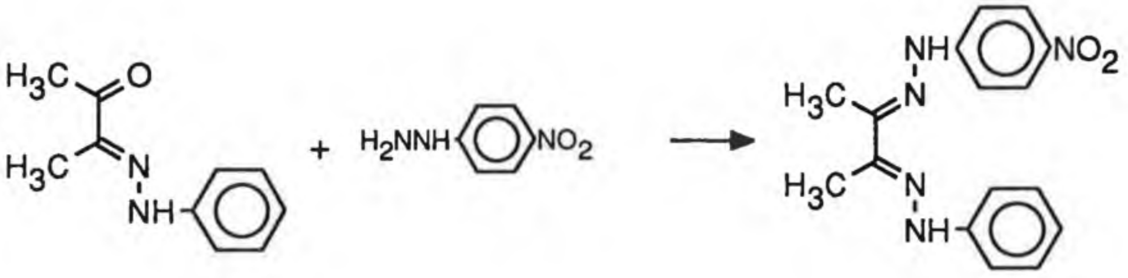


(311) **(316)**

Scheme [2.12]

No examples on asymmetric dihydrazones of this type has been published to date. This is despite the potential that these compounds have as cyclic precursors to nitrogen heterocycles[149]. Comparison of the oxidation products from these compounds with those from both of the corresponding symmetric hydrazones should be worthwhile.

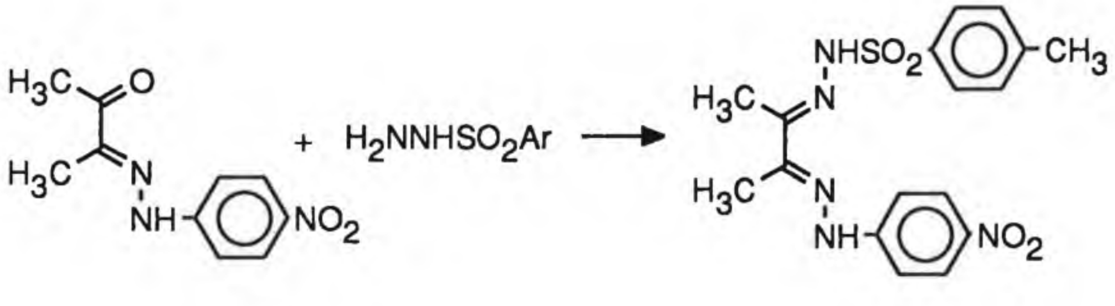
The conversion of a monohydrazone **(311)** into a dihydrazone **(316)** with a different substituent on the amino nitrogen is not trivial. Disproportionation can occur unless mild conditions are employed. Diacetylmonophenylhydrazone-mono(p-nitrophenyl)hydrazone **(325)** was prepared by the addition of p-nitrophenylhydrazine to a diacetylmonophenylhydrazone solution **(322)** according to scheme [2.13].



(322) **(325)**

Scheme [2.13]

The reaction was followed by TLC and an IR spectrum of the brown product indicated the absence of any C=O stretching frequencies. A second asymmetric dihydrazone **(326)** was also prepared by reaction of diacetylmonop-nitrophenylhydrazone **(323)** with toluenesulphonylhydrazine, scheme [2.14].



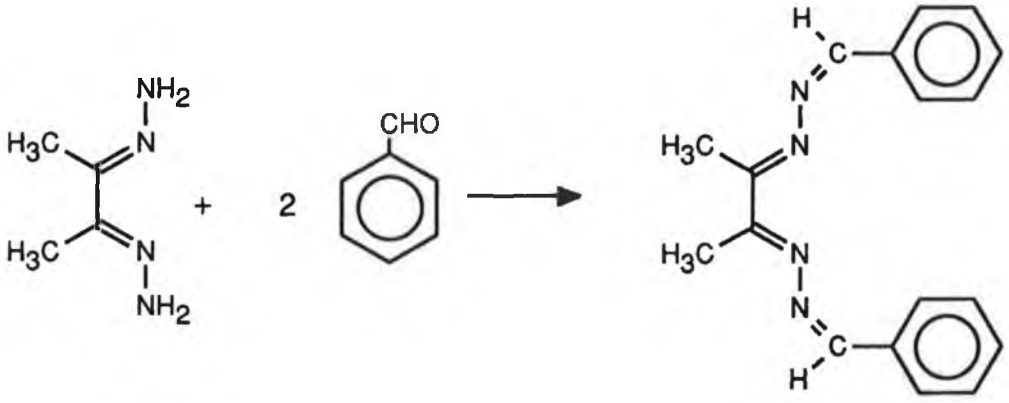
(323) **(326)**

Scheme [2.14]

The IR spectrum of diacetylmono(p-nitrophenylhydrazone)mono(p-toluenesulphonylhydrazone) **(326)** exhibits no C=O stretching frequencies, and a single broad peak at 3300 cm^{-1} for the N-H stretching frequencies. Compounds **(325)** and **(326)** are both new compounds and represent the first reported case of asymmetric substituted dihydrazones of diacetyl.

2.2.5 Formation of Diacetyldibenzilazine

The final compound of this class to be synthesised was diacetyldi(benzilazine) **(327)**, previously reported without a synthetic procedure or physical data by Dance and Miller in 1973[140]. Strictly **(327)** is not a dihydrazone, but is in fact a diazine. However, for convenience, **(327)** has been grouped with the substituted dihydrazones of class (I). Diacetyldi(benzylazine) is prepared by reacting diacetyl dihydrazone **(5)** with benzaldehyde in a one-to-two molar ratio, as in scheme [2.15].



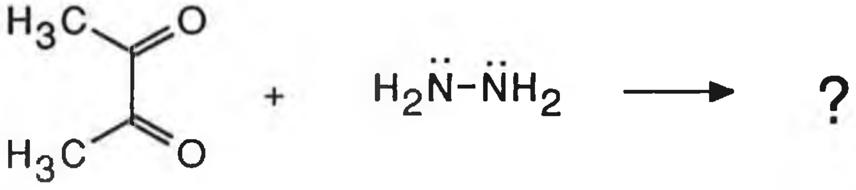
(5) **(327)**

Scheme [2.15]

The IR spectrum of the diazine **(327)** indicated no NH stretching frequencies. From the NMR data, a singlet at 8.25 ppm indicated the presence of the CH resonance of the CH=N. Purity was verified by TLC analysis.

2.3 CLASS (II), (III) & (IV) COMPOUNDS

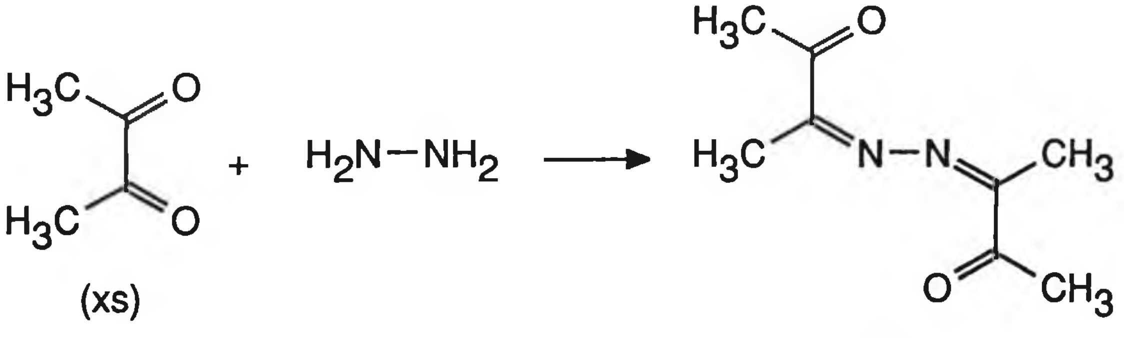
The main starting materials for the synthesis of compounds of class (II), class (III) and class (IV) are diacetyl and hydrazine hydrate. As described in the introduction of Chapter II, hydrazine is highly reactive with both nitrogens having the ability to react as nucleophiles. Diacetyl is also bifunctional with two ketone groups open to nucleophilic attack. Thus on reacting diacetyl with hydrazine, scheme [2.16], a large number of reactions are possible, including the formation of oligomers.



Scheme [2.16]

We have developed a method whereby rigourous control of the chemistry has been achieved on mixing a solution of diacetyl with a solution of hydrazine. The method enables one to build oligomers of diacetylazines in a step-wise manner up to five times. The fundamental basis of this method is maintaining one of the reactants in excess throughout the course of the reaction. Thus, as for the preparation of diacetyldihydrazone **(5)**, described earlier in scheme [2.8], addition of a solution of diacetyl to a solution containing excess hydrazine produces diacetyldihydrazone **(5)**.

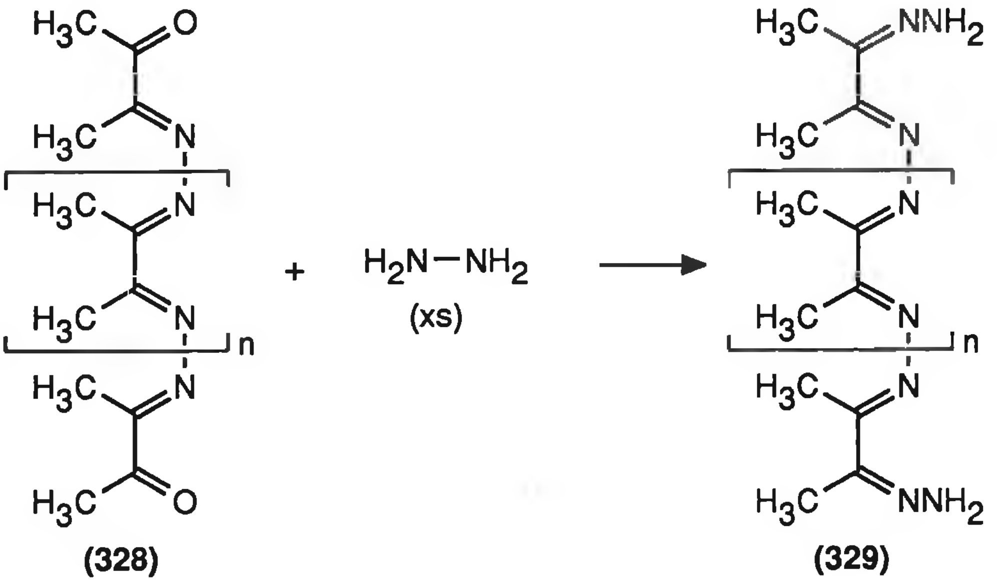
Alternatively a solution of hydrazine can be taken, and added to a solution containing an excess molar equivalent of diacetyl, which produces diacetyl azine **(246)**, according to scheme [2.17].



(246)

Scheme [2.17]

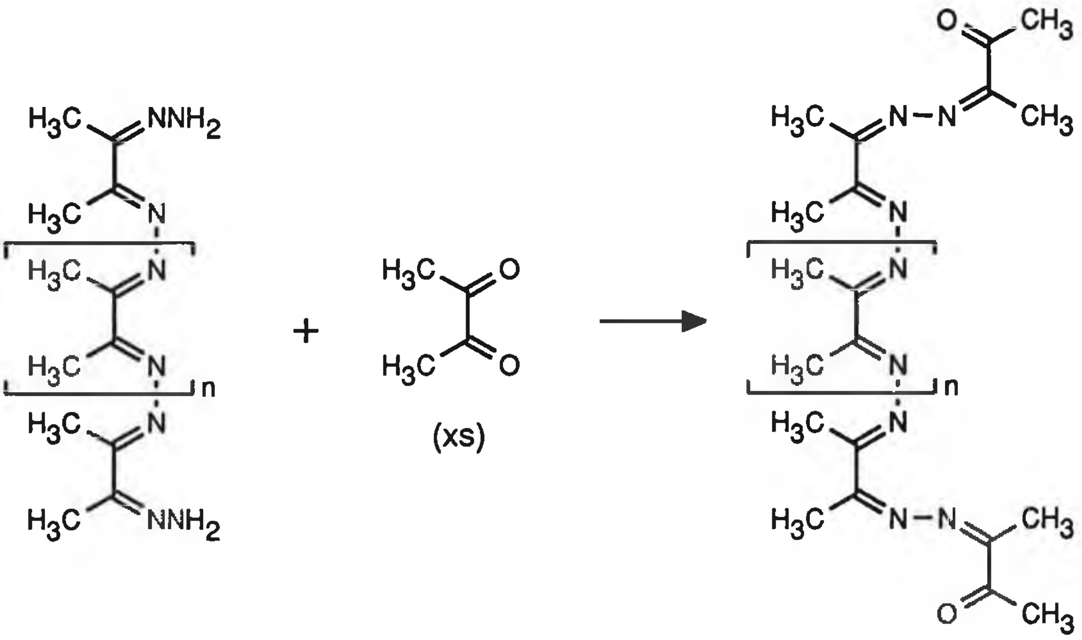
It was found that in general, a solution of diketo-(polydiacetylazine) **(328)** added to a solution containing an excess of hydrazine, produces the corresponding dihydrazone **(329)**, scheme [2.18], for values n from 0 to 3.



(328) **(329)**

Scheme [2.18]

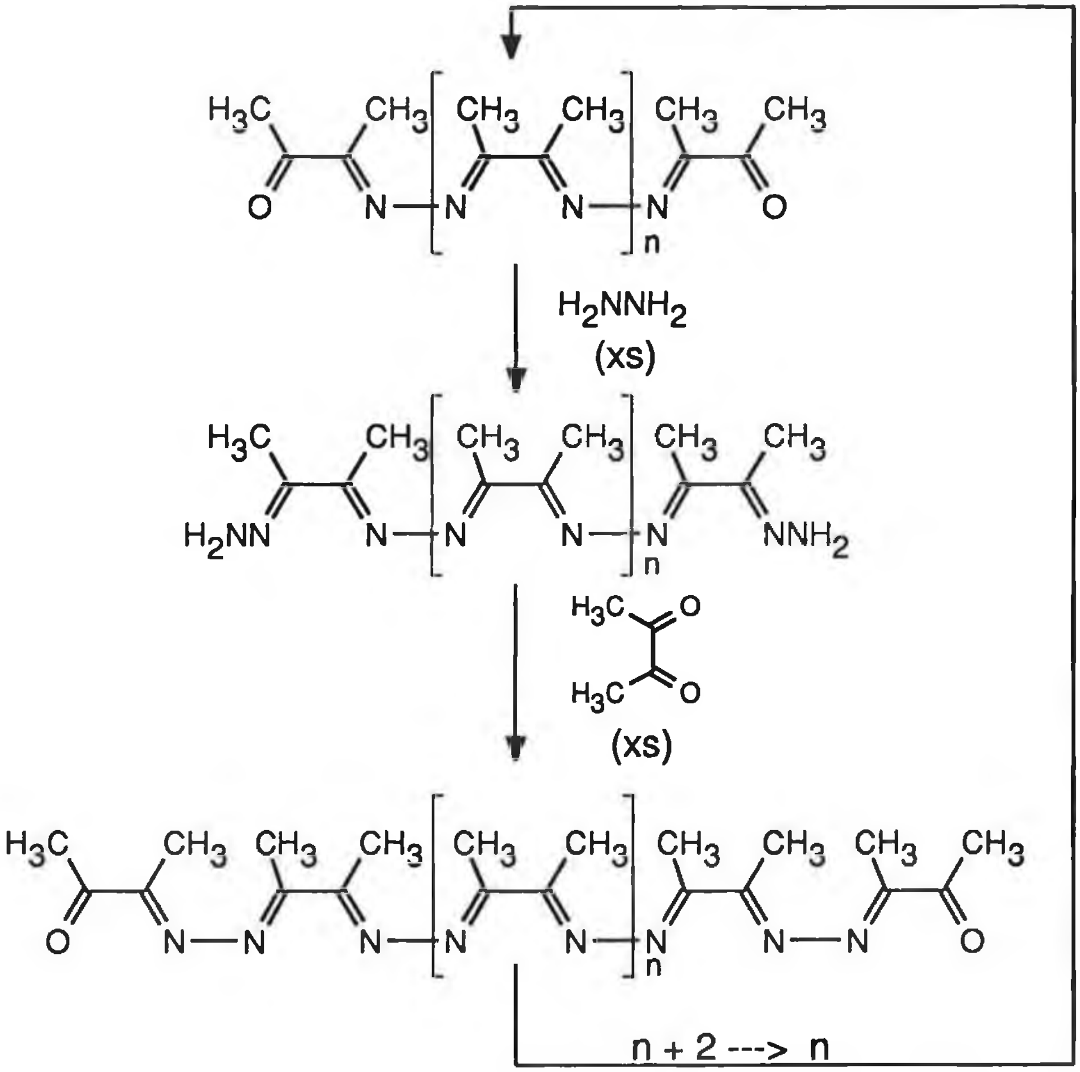
Adding this dihydrazone **(329)** to a solution containing an excess of diacetyl produces a diketo-(polydiacetylazine) **(330)**, which is two units longer than the original diketone, scheme [2.19].



(329) **(330)**

Scheme [2.19]

Repeating this process facilitates the construction of homogeneous oligomers with a definite number of repeat units, according to the cycle depicted in scheme [2.20]. The method works well up to five repeat units, (n=5).

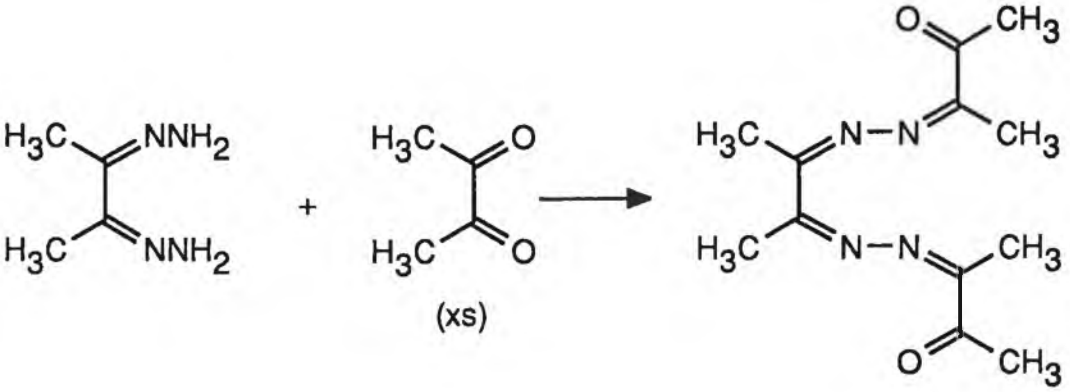


Scheme [2.20]

2.3.1 PREPARATION OF CLASS (II) COMPOUNDS

The simplest compound of class (II), diacetylazine **(246)**, was prepared using a variation of the method by Stratton and Busch(124). In order to prevent the hydrazone or the dihydrazone being formed, it was necessary to ensure that the diacetyl was in excess, throughout the reaction. Thus the addition of a solution of hydrazine to a solution containing a two molar equivalent of diacetyl, scheme [2.17] produces diacetyl azine **(246)**. The reaction was carried out at 0°C in water to prevent further reaction taking place. A catalytic amount of acetic acid is used. After refrigeration overnight, a mixture of yellow and white crystals form. Analysis of both types of crystals by thin layer chromatography reveals that both consisted of the same pure material. Infrared analysis produces a band at 1697 cm^{-1} which is assigned to the C=O stretching frequency. ^{1}H NMR shows the two methyl groups attached to the carbonyl groups occur at 2.40 ppm, whereas the two methyl groups attached to the imine groups occur at 1.75 ppm.

The diketo-trimer **(331)** was obtained by the addition of a solution containing an excess of diacetyl, according to [2.21].

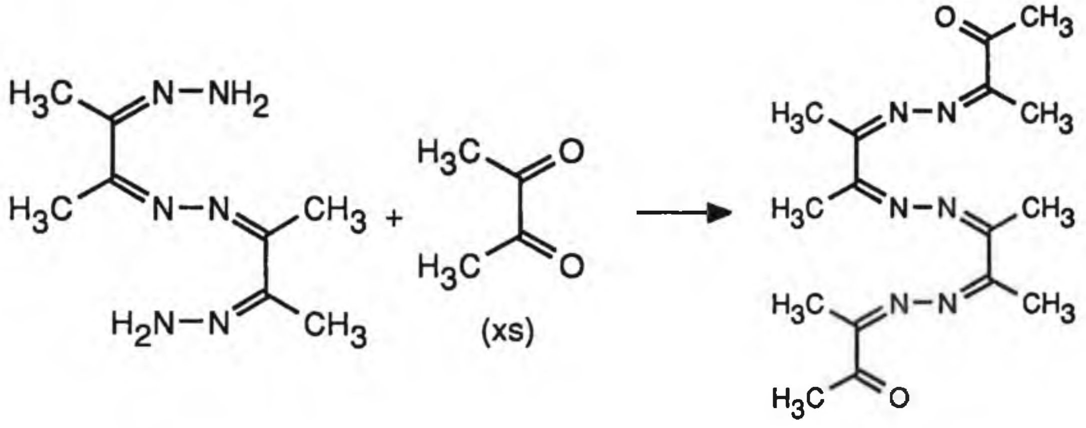


(5) **(331)**

Scheme [2.21]

This compound **(331)** has not been reported in the literature to date. IR analysis reveals a carbonyl stretching band at 1697 cm^{-1}, with the absence of any N-H stretching frequencies. Three peaks of equal intensities for the methyl groups occur in the NMR spectrum, acetyl groups appear at 2.40 ppm, the methyl groups adjacent to the acetyl groups occur at 1.80 ppm, being slightly deshielded by the carbonyl groups, and finally, the remaining methyl groups occur at 2.12 ppm.

The new compound tetra(diacetyl)triazine **(332)** was prepared by reacting diacetylazine dihydrazone **(247)** with a solution containing an excess of diacetyl, according to the scheme [2.22].

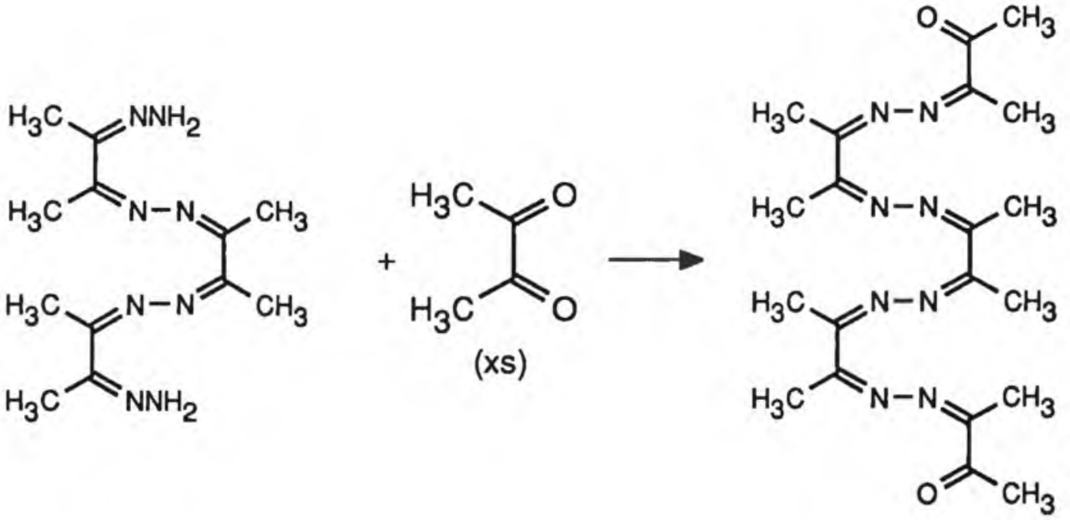


(247) **(332)**

Scheme [2.22]

Analysis of the IR spectrum indicates the presence of carbonyl groups, the peak occurring at 1697 cm^{-1}. The ^{1}H NMR spectrum reveals three peaks, the intensities in the ratio of 1:2:1. The singlet at 2.50 ppm is due to the two acetyl groups, the peaks at 2.10 ppm represents four imine methyl groups farthest away from the carbonyl groups, and finally, the methyl groups of the imine adjacent to the carbonyl groups show a resonance at 1.92 ppm.

The final oligomer of this class, penta(diacetyl)tetra-azine **(333)**, was synthesised by the addition of tri-(diacetyl)diazinedihydrazone **(334)**, to a solution containing a two molar equivalent of diacetyl, as in scheme [2.23].



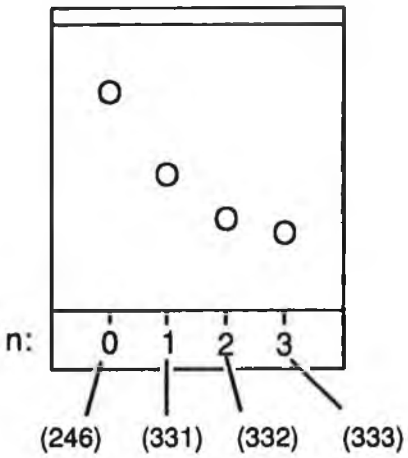
(334) **(333)**

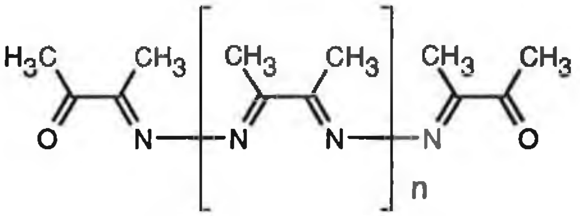
Scheme [2.23]

Penta(diacetyl)tetra-azine **(333)** is also a new compound, and its IR spectrum indicates a carbonyl stretching frequency at 1696 cm^{-1}. ^{1}H NMR analysis shows three main peaks, with intensity ratios 1:3:1. The singlet at 2.52 ppm is due to the acetyl groups, the peak at 1.90 ppm is due to the two imine groups adjacent to the acetyl groups and the multiplet at 2.10 ppm is due to the six remaining methyl groups.

2.3.2 PURITY ASSESSMENT OF CLASS (II) COMPOUNDS

Two main approaches to the assessment of the purity of compounds **(246), (331) - (333)**, was carried out. The first method of characterisation, was TLC on silica plates. Using chloroform/pet. ether (40-60^{o}C) (50/50 v/v) as a mobile phase, only a good separation of the smaller components was obtained, illustrated in figure [2.1].





(246) n = 0
(331) n = 1
(332) n = 2
(333) n = 3

Figure [2.1] **Illustration of TLC plate for separation of class (II) oligomers**

Considerably more success was achieved with high performance liquid chromatography (HPLC). The mobile phase used was methanol/water (80/20 v/v) with a flow rate of 1.5 ml/min., using a C_{18} column as a stationary phase. Sample preparation involved dissolving the compounds in mobile phase. A very good separation of the compounds was achieved. The HPLC technique proved extremely valuable in the determination of the purity of these compounds. Using an on-line photodiode array detector, allowed a UV/Vis. spectrum for each compound to be obtained.

Traces of the chromatograms for each of the compounds **(246), (331) - (333)** are shown superimposed in figure [2.2]. A mixture of the compounds **(246), (331), (332)** and **(333)** was also analysed and the same separation of the compounds was achieved.

Overlaying the UV/Vis. spectra of the compounds of class (II), **(246), (331), (332)** and **(333)**, a shift to longer wavelength for (λ_{max}) was observed for an increase in the length of the oligomers, figure [2.3].

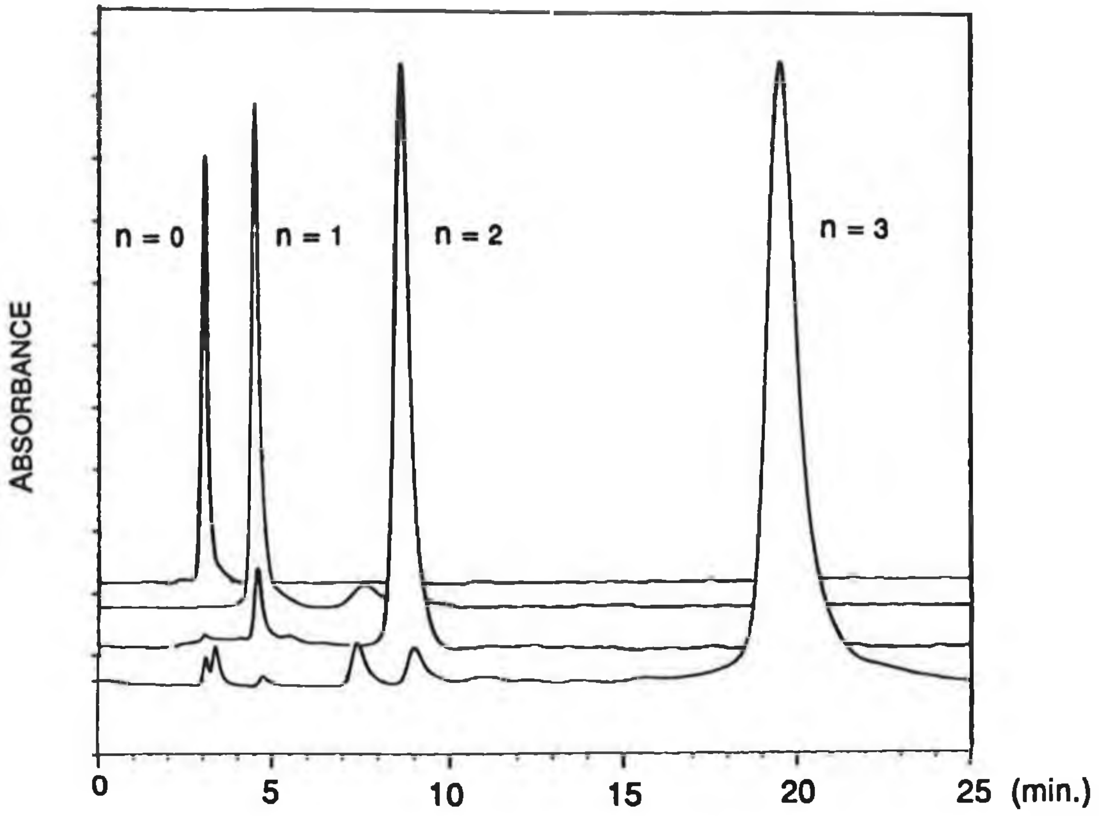


Figure [2.2] **HPLC chromatogram traces for class (II) oligomers**

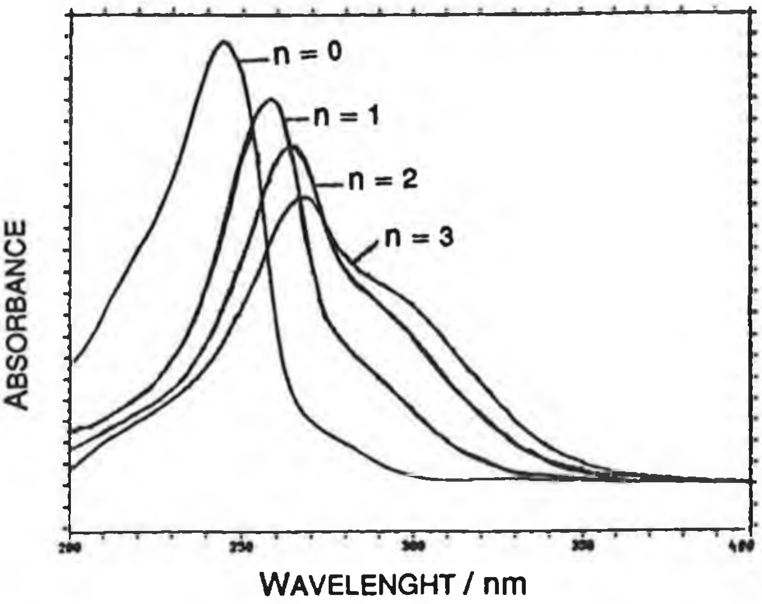


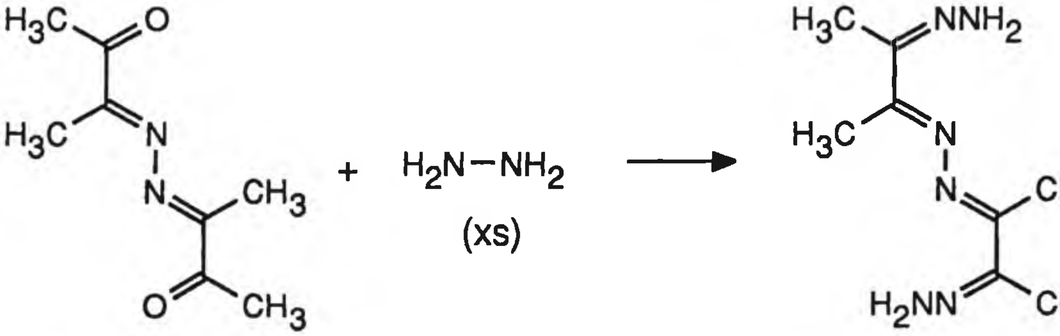
Figure [2.3] **Traces of UV/Vis. spectra for class (II) oligomers in CH_3CN**

The UV/Vis. data parallels the situation for the incorporation of additional C=C bonds into a conjugated molecule where, an increase of 30 nm is observed in the UV/Vis. spectrum, for each additional conjugated double bond(154).

2.3.3 PREPARATION OF CLASS (III) COMPOUNDS

This series of hydrazones includes dihydrazone diacetylazine oligomers, of structure **(314)**, and are prepared from the corresponding diketo-azine oligomer of class (II) compounds, according to scheme [2.19]. These class (III) compounds are the hydrazone analogues of the class (II) keto compounds. The simplest dihydrazone of this series, diacetyl dihydrazone **(5)**, has been discussed earlier with class (I) dihydrazones, according to scheme [2.8].

A modification of the procedure by Stratton and Busch[124] was used to prepare diacetylazinedihydrazone **(247)**, obtained by the addition of a solution of diacetylazine **(246)**, to a solution containing an excess of hydrazine, according to scheme [2.24].

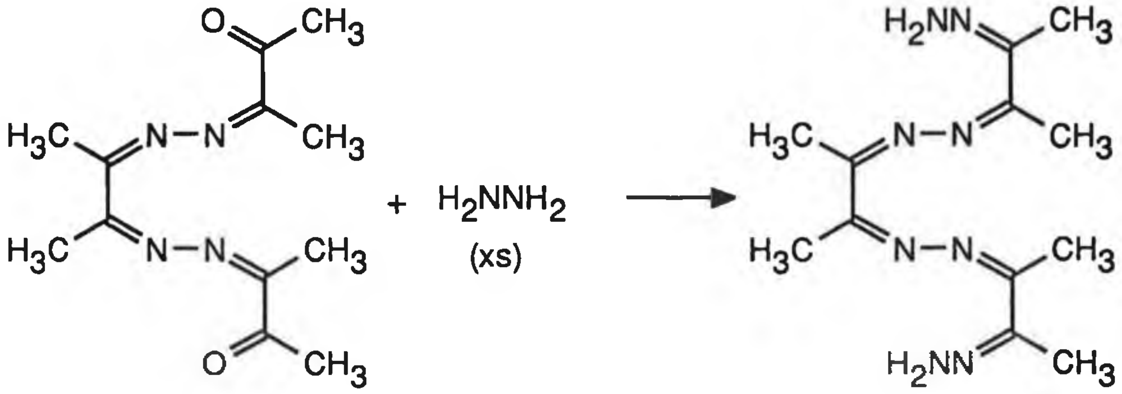


(246) **(247)**

Scheme [2.24]

The melting point (146°C) agrees with the value quoted in the literature, (mp = 147°C). From infrared analysis, asymmetric stretching of the N-H bond occurs at 3347 cm^{-1}, the symmetric N-H stretching occurring at the lower frequency of 3206 cm^{-1}. The ^{1}H NMR spectrum (400 MHz in $CDCl_3$) shows two singlets, 1.91 ppm represents the methyl group attached to the azine moiety, whereas the peak at 1.93 ppm represents the methyl group attached to the hydrazone carbon. In the ^{13}C NMR spectrum the methyl carbons attached to the azine appear at 13.2 ppm, the terminal methyl carbons occur at 10.0 ppm. The hydrazone carbon appears at 143.6 ppm and the azine carbon at 159.0 ppm.

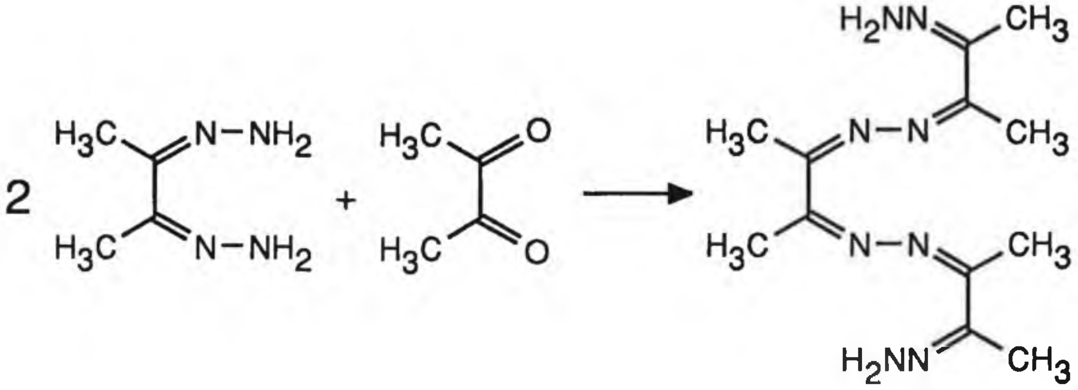
The dihydrazone trimer **(334)** was prepared by the addition of a solution of tri(diacetyl)diazine **(313)** to a solution containing an excess of hydrazone, as in scheme [2.25].



(313) **(334)**

Scheme [2.25]

Tri(diacetyl)diazinedihydrazone **(334)** has been reported previously, by Hauer *et al.* in 1987(155), in a synthesis which involved the addition of diacetyldihydrazone **(5)** to a half molar equivalent of diacetyl, according to [2.26].

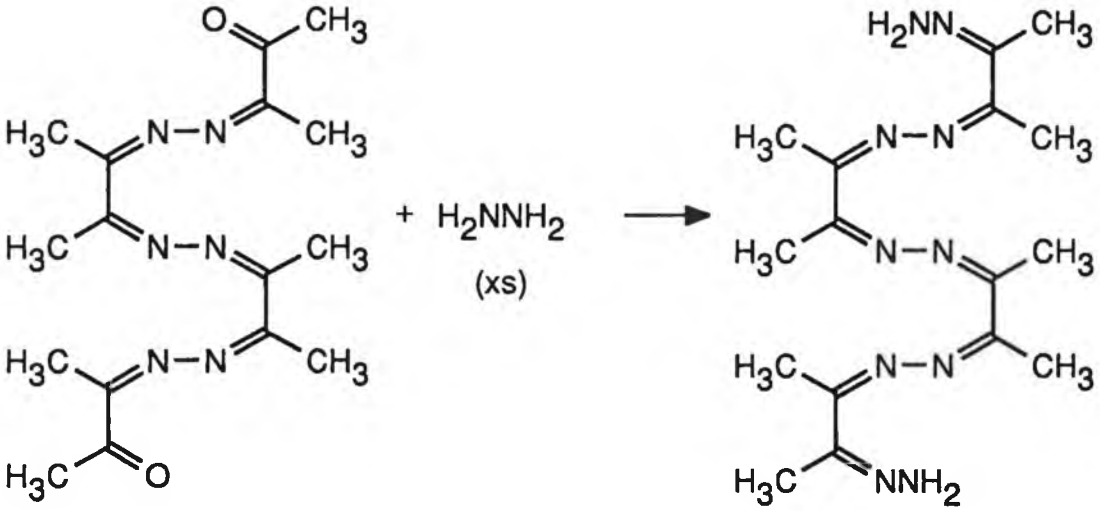


(5) **(334)**

Scheme [2.26]

Our attempts to repeat this were unsuccessful and resulted in a mixture of products. Hauer prepared a series of oligomeric dihydrazones and characterised them by infrared spectroscopy and microanalysis. We found that microanalysis does not serve as a satisfactory method for the determination of the purity of these compounds, because the elemental composition of the various oligomers are quite similar and also because the elemental analysis of a pure oligomer of a discrete size may coincidentally be the same as that of a mixture of different sized oligomers. The melting point of the trimer dihydrazone **(334)** which we prepared was 150-156°C compared to 140-147°C reported by Hauer(155). Infrared analysis shows an N-H asymmetric stretching frequency at 3361 cm^{-1}, and the N-H symmetric stretching frequency occurring at 3221 cm^{-1}. No carbonyl stretching frequency was observed in the spectrum. ^{1}H NMR reveals three peaks with intensity ratios of 3:6:2; a singlet at 2.00 ppm due to the two methyl groups attached to the hydrazone carbons, a singlet at 2.10 ppm due to the four methyl groups attached to the azine groups, and a singlet at 5.60 ppm for to the two terminal amino groups.

The dihydrazone tetramer **(335)** was prepared by the addition of the diketo-compound **(332)** to a solution containing an excess of hydrazine, according to scheme [2.27].

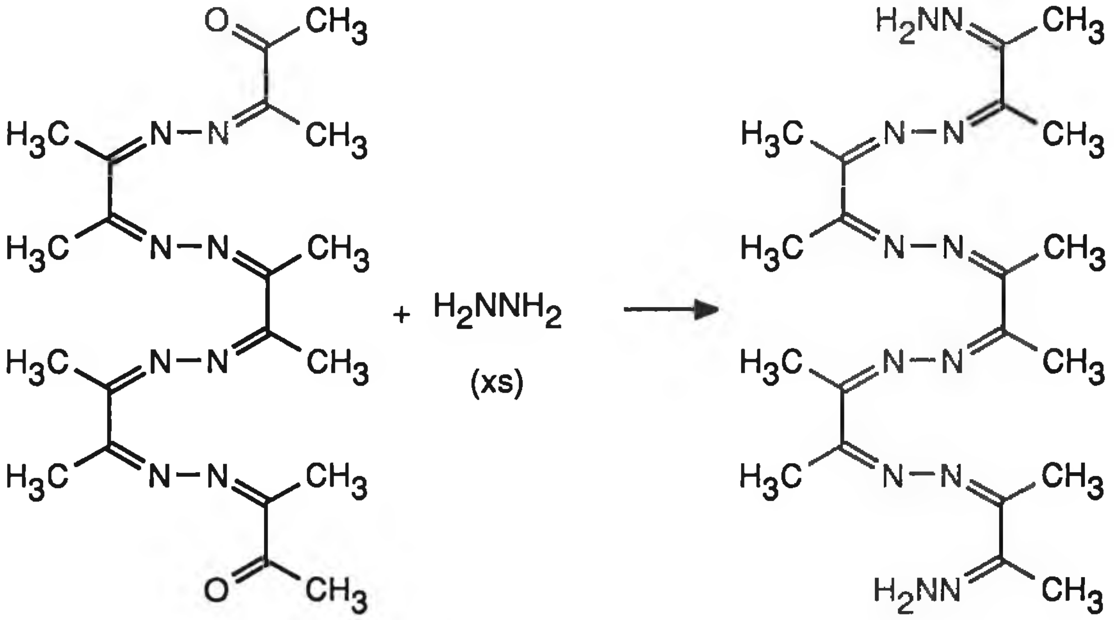


(332) **(335)**

Scheme [2.27]

Tetra(diacetyl)triazine dihydrazone **(335)** has not been reported previously, was found to have a melting point of 280-285°C. IR analysis shows the N-H asymmetric stretching frequency at 3397 cm^{-1}, and the symmetric stretching at 3238 cm^{-1}. ^{1}H NMR shows three peaks with intensities 3:9:2, a singlet at 2.02 ppm for the two methyl groups attached to the hydrazone carbons, a multiplet at 2.10 ppm for to the six methyl groups attached to the azine groups and finally a singlet at 5.60 ppm for the NH_2 group. The chemical shifts are identical to the trimer **(334)**.

The final hydrazone of this particular series of compounds, is penta(diacetyl)tetra(azine)dihydrazone **(336)**, prepared from the diketo-pentamer **(333)** and excess hydrazine, according to scheme [2.28].



(333) **(336)**

Scheme [2.28]

IR analysis shows an asymmetric N-H stretching frequency at 3379 cm^{-1}, and an N-H symmetric frequencies at 3235 cm^{-1}. ^{1}H NMR reveals a multiplet at 2.10 ppm representing ten methyl groups and a singlet at 5.60 ppm for the terminal amino groups.

2.3.4 ASSESSMENT OF PURITY OF CLASS (III) COMPOUNDS

TLC was useful in method development for following the reactions and determining purity. However the separation factor decreases for the larger oligomers, figure [2.4], and the results became ambiguous for oligomers with four or more repeating units. The mobile phase used was chloroform.

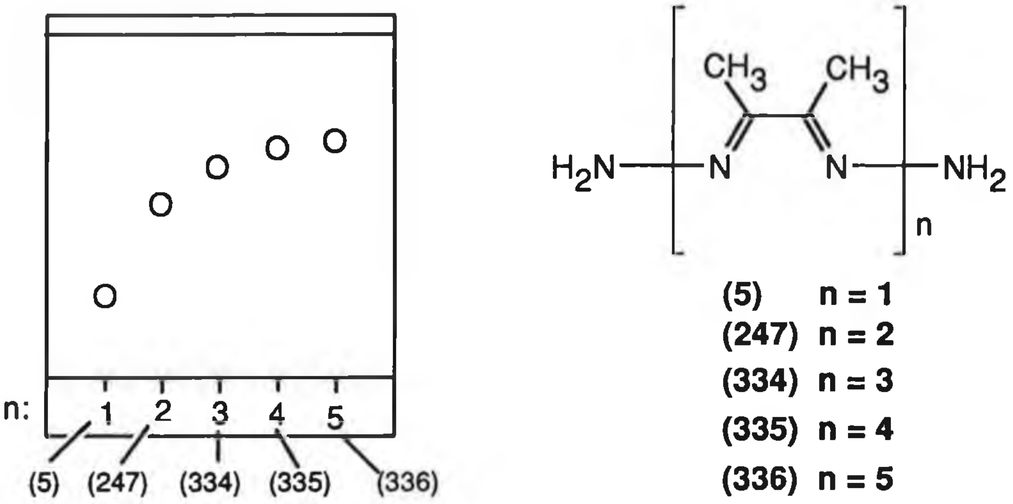


Figure [2.4] **Illustration of TLC plate for separation of class (III) oligomers**

HPLC analysis was carried out on class (III) compounds, with a mobile phase of methanol/water (80/20), and a C_{18} column stationary phase. The flow rate was 1.5 ml/min and a photodiode array detector was used. A good separation of compounds **(247)**, **(334)**, **(335)** and **(336)** was achieved. Their chromatograms are depicted in figure [2.5].

A mixture of **(247)**, **(334)**, **(335)** and **(336)** was analysed by the HPLC system and a good separation was observed. However, the monomer **(5)** elutes at a very similar retention time as the dimer **(247)** using this mobile phase (80/20). A mobile phase of methanol/water (50/50 v/v) separates monomer **(5)** from the dimer **(247)**.

A UV/Vis. spectrum for each compound was obtained. The λ_{max} for each moves to a longer wavelength with an increase in compound size, figure [2.6]. The UV/Vis. spectra of the dihydrazone oligomers display a similar λ_{max} increase as for the di-keto oligomers **(246)**, **(331)** - **(333)**, except the spectra for the dihydrazones are broader . The increase in wavelength is most likely due to the increase in conjugation as the length of the oligomer increases(154).

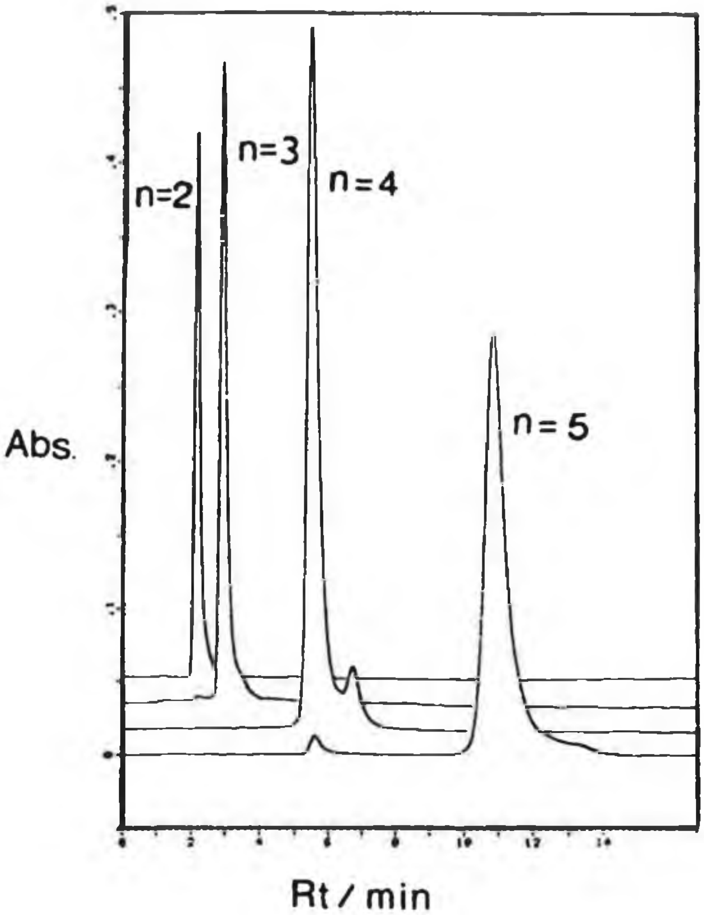


Figure [2.5] HPLC chromatogram traces for class (III) oligomers

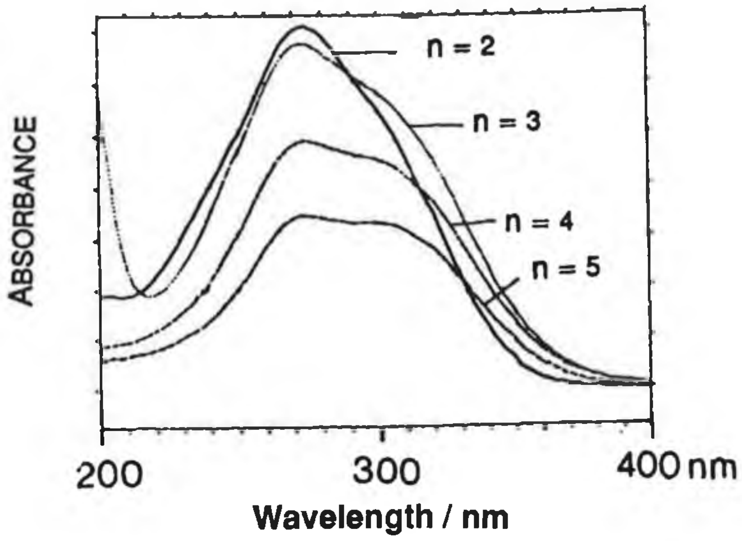
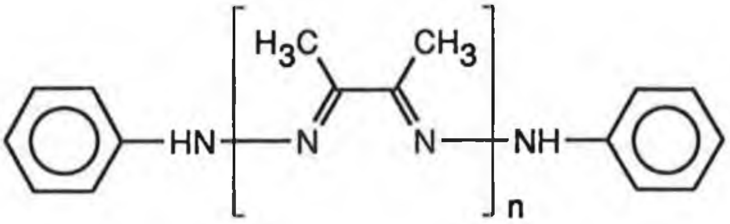


Figure [2.6] Traces of UV/Vis. spectra for class (III) oligomers

2.3.5 PREPARATION OF CLASS (IV) COMPOUNDS

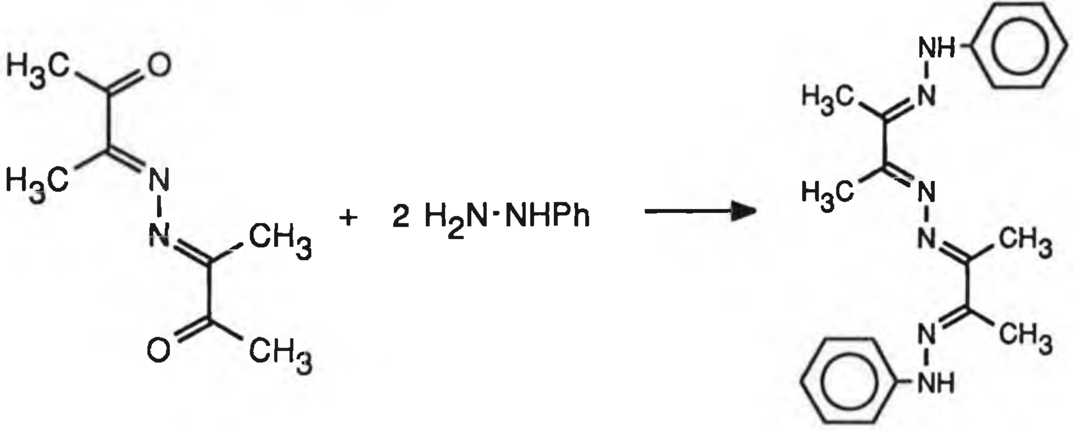
The final set of compounds prepared is class (IV), a series of oligomeric diacetylazine diphenylhydrazone derivatives corresponding to structure **(315)**.



(315)

The properties of these compounds are similar to those of class (III), the difference being that one of the hydrogens of the amino groups is replaced by a phenyl group. Class (IV) compounds are in effect end-capped derivatives of class (III) and do not possess reactive terminal amino groups. Similar to the preparation of class (III) compounds, class (IV) compounds are prepared by reacting the corresponding diketo-azine with a two molar equivalent of phenylhydrazine.

The smallest of this series , diacetyldiphenylhydrazone **(29)**, was already discussed as part of class (I). The next in the series is the new compound diacetylazinediphenylhydrazone **(337)**, which was prepared by reacting a solution of diacetylazine **(246)** with a two molar equivalent of phenylhydrazine, according to scheme [2.29].



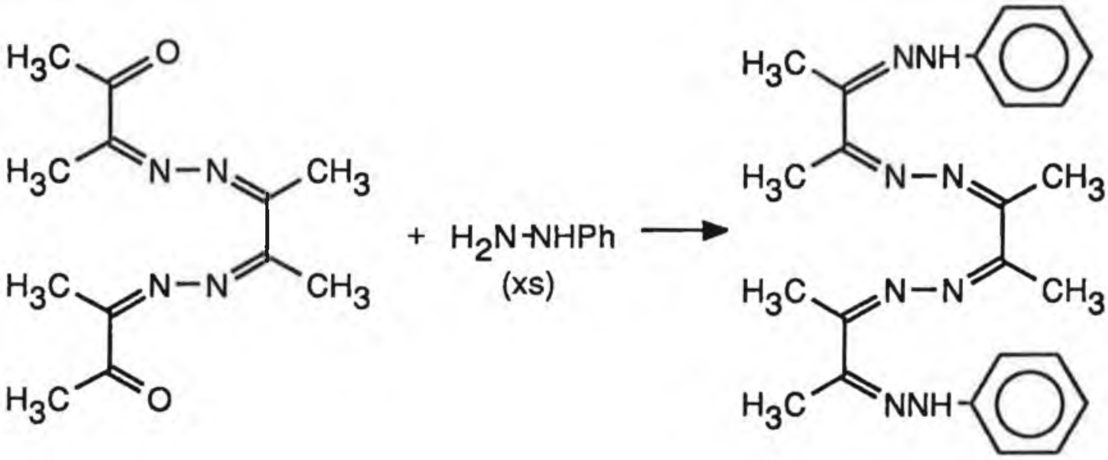
(246) **(337)**

Scheme [2.29]

Examining the orange product by IR analysis reveals an N-H stretching frequency at 3361 cm^{-1}, and the absence of any carbonyl peak.

^1H NMR data indicates four methyl groups at a chemical shift of 2.20 ppm, the phenyl group appears as a multiplet at a chemical shift 7.20 ppm and the N-H hydrogens appear at 7.60 ppm.

The trimer diphenylhydrazone **(338)** was prepared by reacting two moles of phenylhydrazine with tri(diacetyl)di(azine) **(331)**, according to scheme [2.30].



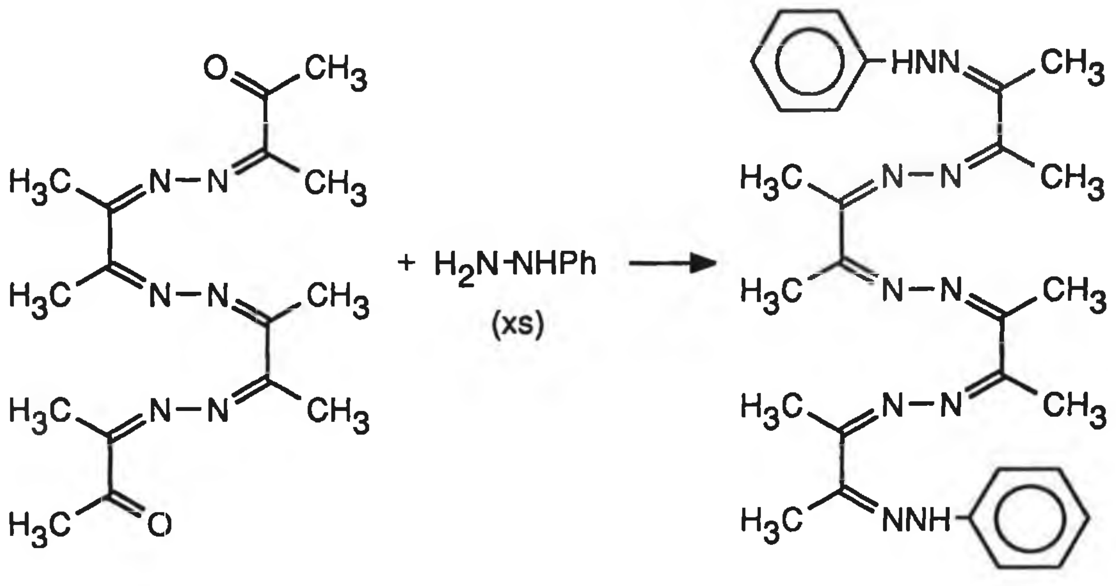
(331) **(338)**

Scheme [2.30]

This previously unreported compound tri(diacetyl)di(azine)diphenylhydrazone **(338)**, has a bright orange appearance, and IR analysis reveals the N-H stretching frequency at 3355 cm^{-1}, and the absence of any carbonyl peak.

The ^1H NMR spectrum exhibits a singlet at 2.21 ppm for the methyl groups, the aromatic hydrogens as a multiplet at 7.20 ppm and the amino groups at 7.60 ppm.

Finally, the new compound tetra(diacetyl)tri(azine)diphenylhydrazone **(339)**, was prepared by adding a solution of the diketo-tetramer **(332)** to a solution containing an excess of phenylhydrazine, according to [2.31].



(332)

(339)

Scheme [2.31]

An N-H stretching frequency of 3351 cm^{-1}, was observed in the IR spectrum. The ^1H NMR spectrum has three peaks, a singlet at 2.15 ppm for the methyl groups, a multiplet at 7.22 ppm due to the aromatic protons and a singlet at 7.61 ppm for the N-H protons.

2.4 EXPERIMENTAL

2.4.1 INSTRUMENTATION & TECHNIQUES

Infrared Spectra in the 4000 - 200 cm^{-1} region were obtained on a Perkin-Elmer 983-G spectrometer from pressed KBr disks.

^{1}H NMR Spectra were recorded on a JEOL GX-FT 270 MHz or on a Bruker AC 400 MHz instrument, and referenced to residual solvent hydrogen. Measurements on the ligands and complexes were normally carried out in the solvents $CDCl_3$, Acetone-d_6 or DMSO-d_6.

UV/Vis. Spectra were obtained using either a Waters 990 photodiodearray spectrometer or on a Shimadzu OPI-1 spectrometer.

Elemental Analysis on C, H and N were determined at the microanalytical laboratory, University College, Dublin.

Thin Layer Chromatography (TLC) was carried out on silica gel with fluorescent indicator 254 nm on alumina cards, 0.2 mm thickness and visualised using an ultraviolet lamp.

Analytical High Performance Liquid Chromatography (HPLC) experiments were performed using a Waters 501 HPLC pump, a Waters 990 Photodiode Array HPLC system with a NEC PAC III computer and a 20 µL injector loop. A standard C_{18} column was used to analyse the ligands, with a detector wavelength of 300 nm using a mobile phase of methanol/water (80/20 v/v), flow rate 1.5 ml/min.

2.4.2 CLASS (I) COMPOUNDS

Diacetyldi(phenylhydrazone) (29)

To a solution of 5.00 g (0.058 mol) of diacetyl in 50 ml acetic acid, 12.3 g of phenylhydrazine in 50 ml acetic acid was added. The reaction mixture was stirred at room temperature for 1 h. The product was filtered, washed with ethanol, pet. ether (40-60°C) and dried: yield, 11.1 g (0.044 mol), 76%; mp = 249-253°C (Lit.[147] mp = 254°C). IR (KBr) 3341 cm^{-1}. ^{1}H NMR (60 MHz, DMSO-d_6) δ 2.1(s,6H), 6.9-7.1(m,10H), 9.1(s,2H).

Diacetyldi(p-nitrophenylhydrazone) (317)

To a stirred solution of 1.00 g (0.012 mol) of diacetyl in 10 ml acetic acid, 3.60 g (0.024 mol) of p-nitrophenylhydrazine in 100 ml acetic acid was added. The reaction mixture was refluxed for 15 min. The red product precipitates after a few seconds, and was hot filtered, washed with acetic acid, pet. ether (40-60°C) and recrystallised from ethanol: yield, 4.10 g (0.011 mol), 90%; mp = 305-308°C (Lit.[148] mp = 311-312°C). IR (KBr) 3160 cm^{-1}. ^{1}H NMR (60 MHz, DMSO-d_6) δ 2.1(s,6H), 7.2(d,4H), 8.0(d,4H), 9.1(s,2H).

Diacetyldi(p-toluenesulphonylhydrazone) (318)

To a stirred solution of 2.00 g (0.023 mol) of diacetyl in 20 ml ethanol, 8.6 g (0.047 mol) of p-toluenesulphonylhydrazine in 50 ml ethanol was added. The reaction mixture was refluxed for 15 min. The white product precipitates on cooling, was washed with ethanol, pet. ether (40-60°C) and recrystallised from ethanol: yield, 3.6 g (0.0085 mol), 37%; mp = 180-185°C, (Lit.[149] mp = 198-199°C). IR (KBr) 3280 cm^{-1}. ^{1}H NMR (60 MHz, DMSO-d_6) δ 2.0(s,6H), 7.4(d,4H), 7.8(d,4H), 10.3(s,2H).

Diacetyldi(o-tolylhydrazone) (319)

To a solution of 1.00 g (0.0116 mol) of diacetyl in 20 ml ethanol, 2.93g (0.0240 mol) of o-tolylhydrazine in 50 ml ethanol was added. The solution was stirred at 55°C for 30 min., refluxed for a further 2 min. On cooling, the cream coloured product was filtered, washed with pet. ether (40-60°C) and dried: yield, 86%; mp = 199-202°C. IR(KBr) 3385 cm^{-1}. ^{1}H NMR (270 MHz, DMSO-d_6) δ 2.2(s,6H), 2.4(s,6H), 6.9(t,2H), 7.2(m,10H), 7.7(t,2H).

Diacetyldi(N-methylphenylhydrazone) (320)

To a solution of 1.00 g (0.0082 mol) of N-methyl,N-phenylhydrazine in 10 ml of methanol, 0.352 g (0.004 mol) of diacetyl in 10 ml of methanol was added. The reaction mixture was refluxed gently for 2 h. The yellow/orange product was filtered, washed with pet. ether (40-60°C) and dried: yield, 0.92 g (0.0031 mol), 78%; mp = 90-92°C. ^{1}H NMR (270MHz, DMSO-d_6) δ 2.2(s,6H), 3.2(s,6H), 6.9(t,2H), 7.05(m,10H), 7.29(t,4H), 9.1(s,2H).

Diacetyldihydrazone (5)

To a stirred solution of 30.0 g (0.08 mol) of hydrazinehydrate (85%) in 200 ml of ethanol, 10 g (0.116 mol) of diacetyl in 30 ml of ethanol was added dropwise over an hour at room temperature. The resulting solution was stirred at room temperature for another two hours, stoppered and refrigerated overnight. Long white crystals were filtered, washed with ethanol, pet. ether (40-60°C) and dried under vacuum: yield, 9.4 g (0.082 mol), 71%; mp = 158-161°C, (Lit.[45] mp = 159-160°C). IR (KBr) 3300, 3193, 1636 cm^{-1}. ^{1}H NMR (60MHz, DMSO-d_6) δ 2.0(s,6H), 5.8(s,4H).

Diacetyldi(N,N-dimethylhydrazone) (129)

To a stirred solution of 3.0 g (0.05 mol) of N,N-dimethylhydrazine in 20 ml of ethanol, 2 g (0.0232 mol) of diacetyl in 20 ml of ethanol was added dropwise over ten minutes. The resulting solution was stirred at room temperature for another two hours. Using a Kugelrohr short-path distillation apparatus, the product was isolated as a fraction 90-110°C: yield, 2.0 g (0.012 mol), 51%. IR (KBr) 1600 cm^{-1}. ^{1}H NMR (60MHz, $CDCl_3$) δ 2.1(s,6H), 2.55(s,12H).

Diacetylmonophenylhydrazone (322)

To a stirred solution of 5.00 g (0.058 mol) of diacetyl in 40 ml ethanol/water, (10/90v/v), 6.2 g (0.058 mol) of phenylhydrazine in 10 ml ethanol/water, (30/70v/v) was added. The reaction mixture was stirred at room temperature for 30 min. The white precipitate was filtered, washed with pet. ether (40-60°C) and recrystallised from methanol: yield, 7.60 g (0.042 mol), 72%; mp = 132-134°C (Lit.[151] mp = 136°C). IR (KBr) 3256 cm^{-1}. ^{1}H NMR (60MHz, DMSO-d_6) δ 1.7(s,3H), 2.1(s,3H), 6.5-7.1(m,5H), 9.1(s,1H).

Diacetylmono(p-nitrophenyl)hydrazone (323)

To a stirred solution of 3.00 g (0.034 mol) of diacetyl in 20 ml acetic acid, 5.00 g (0.033 mol) of p-nitrophenylhydrazine in 160 ml acetic acid was added dropwise over 1 h. The yellow product was filtered, washed with water, pet. ether (40-60^{o}C) and recrystallised from ethanol: yield, 6.54 g (0.022 mol), 90%; mp = 134-135^{o}C (Lit.[152] mp = 138^{o}C). IR (KBr) 3294, 1668 cm^{-1}. ^{1}H NMR (60 MHz, DMSO-d_6) δ 1.7(s,3H), 2.1(s,3H), 7.2(d,2H), 8.0(d,2H), 10.0(s,1H).

Diacetylmono(p-toluenesulphonyl)hydrazone (324)

To a solution of 2.00 g (0.023 mol) of diacetyl in 10 ml ethanol stirred at 55^{o}C, 2.00 g (0.010 mol) of p-toluenesulphonylhydrazine in 10 ml of ethanol was added dropwise from a separation funnel. The reaction was stirred at 50-60^{o}C for 24 h. 20 ml of water was then added and on cooling a white precipitate forms. The product was filtered, washed with pet. ether (40-60^{o}C) and dried: yield, 1.71 g (0.0031 mol), 31%; mp = 134-135^{o}C. IR (KBr) 3218 cm^{-1}, 1630 cm^{-1}. ^{1}H NMR (60MHz, DMSO-d_6) δ 2.0(d,6H), 7.4(d,2H), 7.8(d,2H), 10.0(s,1H).

Diacetyl(p-nitrophenyl)hydrazonephenylhydrazone (325)

To a stirred solution of 1.00 g (0.057 mol) of diacetyl-phenylhyrazone **(29)** in 50 ml ethanol, (10/90 v/v), 6.2 g (0.058 mol) of p-nitrophenylhydrazine in 100 ml ethanol/acetic acid, (90/10 v/v) was added. The reaction mixture was stirred at 50^{o}C for 30 min . 100 ml of water was then added. On cooling, a dark red precipitate forms. The product was filtered, washed with water, pet. ether (40-60^{o}C) and dried under vacuum: yield, 1.30 g (0.0042 mol), 73%; mp = 222-226^{o}C. IR (KBr) 3325 cm^{-1}. ^{1}H NMR (60 MHz, DMSO-d_6) δ 2.1(d,6H), 7.1(m,7H), 8.0(d,2H), 9.25(s,1H), 10.0(s,1H).

Diacetyl(p-toluenesulphonyl)hydrazone(p-nitrophenyl)hydrazone (326)

To a solution of 1.00 g (0.0045 mol) of diacetylmono(p-nitrophenyl)hydrazone **(323)** in 100 ml acetic acid stirred at room temperature, 0.85 g (0.0046 mol) of p-toluenesulphonylhydrazine in 20 ml of acetic acid was added dropwise. The reaction was refluxed for 10 min. On cooling, an orange coloured product precipitates. The precipitate was filtered, washed with pet. ether (40-60^{o}C) and recrystallised from ethanol: yield, 1.47 g (0.0035 mol), 79%;

mp = 183-186°C. IR (KBr) 3300 cm^{-1}. ^{1}H NMR (60 MHz, DMSO-d_6) δ 2.0(s,3H), 2.1(s,3H), 2.4(s,3H), 7.3(d,H), 7.4(d,2H), 7.8(d,2H), 8.1(d,2H) 10.3(s,1H), 10.6(s,1H).

Diacetyldi(benzylazine) (327)

To a solution of 10.0 g (0.094 mol) of benzaldehyde in 50 ml of ethanol, 5 drops of acetic acid, 5.0 g (0.044 mol) of diacetyldihydrazone **(5)** in 50 ml of ethanol was added. The reaction mixture was stirred at 60°C for 30 min. On cooling the yellow product was filtered, washed with a small amount of cold ethanol, pet. ether (40-60°C) and dried under vacuum: yield, 10.2 g (0.035 mol), 80%; mp = 120-122°C. ^{1}H NMR (60 MHz, DMSOd_6) δ 2.25(s,6H), 7.4(m,6H) 7.7(m,4H), 8.25(s,2H).

2.4.3 CLASS (II) COMPOUNDS

Diacetylazine ($C_8H_{12}N_2O_2$) (246)

To a stirred solution of 15.0 g (0.174 mol) of diacetyl in 10 ml water at 0°C, 3.0 g (0.08 mol) of hydrazinehydrate (85%) in 5 ml of water was added dropwise over 30 min. The solution was then added to 100 ml water, stoppered and refrigerated overnight. The product was filtered, washed with a small amount of cold water and dried in a vacuum oven at 30°C: yield, 4.4 g (0.026 mol), 33%; mp = 33-34°C, (Lit.[155] mp = 32-35°C). IR (KBr) 1697 cm^{-1}. ^1H NMR (60 MHz, DMSO-d_6) δ 1.75(s,6H), 2.4(s,6H).

Tri(diacetyl)diazine ($C_{12}H_{18}N_4O_2$) (331)

To a stirred solution of 30.0 g (0.349 mol) of diacetyl in 200 ml ethanol/water (50/50), 10.7 g (0.094 mol) of diacetyldihydrazone **(5)** was added as a solid. The suspension was stirred at room temperature for 2 h. The product was filtered, washed with pet. ether (40-60°C) and dried under vacuum at 30°C: yield, 18.8 g (0.075 mol), 80%; mp = 101-103°C. IR (KBr) 1697 cm^{-1}. ^1H NMR (60 MHz, $CDCl_3$) δ 1.9(s,6H), 2.1(s,6H), 2.5(s,6H).

Tetra(diacetyl)triazine ($C_{16}H_{24}N_6O_2$) (332)

To a stirred solution of 10.0 g (0.12 mol) of diacetyl in 100 ml ethanol/water (50/50), 2.08 g (0.011 mol) of diacetylazinedihydrazone **(247)** was added as a solid. The suspension was stirred vigorously at room temperature for 2 h. The product was filtered, washed with water, pet. ether (40-60°C) and dried under vacuum at 30°C: yield, 2.77 g (0.0083 mol), 79%; mp = 111-113°C. IR (KBr) 1697 cm^{-1}. ^1H NMR (60 MHz, $CDCl_3$) δ 1.9(s,6H), 2.1(m,12H), 2.5(s,6H).

Penta(diacetyl)tetraazine ($C_{20}H_{30}N_8O_2$) (333)

To a stirred solution of 6.0 g (0.07 mol) of diacetyl in 100 ml ethanol/water (50/50), 2.0 g (0.0072 mol) of tri(diacetyl)diazinedihydrazone **(334)** was added as a solid. The suspension was stirred at room temperature overnight. The product was filtered, washed with water, pet. ether (40-60°C) and dried under vacuum at 30°C: yield, 2.85 g (0.0069 mol), 95%; mp = 133-137°C. IR (KBr) 1696 cm^{-1}. ^1H NMR (60 MHz, $CDCl_3$) δ 1.9(s,6H), 2.1(m,18H), 2.5(s,6H).

2.4.4 GROUP (III) COMPOUNDS

Diacetylazinedihydrazone ($C_8H_{16}N_6$) (247)

To a stirred solution of 3.0 g (0.08 mol) of hydrazinehydrate (85%) in 20 ml of water, a solution of 1.0 g (0.006 mol) of diacetylazine **(246)** in 10 ml of ethanol was added dropwise over 30 min. The solution was stoppered and refrigerated overnight. The yellow product was filtered, washed with pet. ether (40-60°C), and recrystallised from hot ethanol: yield, 0.47 g (0.0024 mol), 34%; mp = 144-146°C, (Lit.[155] mp = 146-158°C). IR (KBr) 3347, 3206 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.91(s,6H), 1.93(s,6H), 6.83(s,4H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 10.0, 13.2, 143.6, 159.0.

Tri(diacetyl)diazinedihydrazone ($C_{12}H_{22}N_8$) (334)

To a stirred solution of 20.0 g (0.53 mol) of hydrazinehydrate (85%) in 50 ml of water, a solution of 10.0 g (0.035 mol) of tri(diacetyl)diazine **(331)** in 50 ml of ethanol was added. The resultant solution was stirred overnight. The product was filtered, washed with pet. ether (40-60°C), and recrystallised from hot chloroform and ethanol: yield, 6.1 g (0.022 mol), 55%; mp = 152-156°C, (Lit.[155] mp = 140-147°C). IR (KBr) 3361, 3221 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.0(s,6H), 2.1(m,12H), 5.63(s,4H).

Tetra(diacetyl)triazinedihydrazone ($C_{16}H_{28}N_{10}$) (335)

To a stirred solution of 10.0 g (0.27 mol) of hydrazinehydrate (85%) in 50 ml of water, a suspension of 1.0 g (0.003 mol) of tetra(diacetyl)triazine **(332)** in 50 ml of ethanol was added. The resultant solution was stirred for 48 h. The product was filtered, washed with ethanol, pet. ether (40-60°C), and recrystallised from hot chloroform and ethanol: yield, 0.47 g (0.013 mol), 43%; mp = 280-285°C. IR (KBr) 3397, 3238 cm^{-1}. ^{1}H NMR (60 MHz, $CDCl_3$) δ 2.0(s,6H), 2.1(m,18H), 5.6(s,4H).

Penta(diacetyl)tetraazinedihydrazone ($C_{20}H_{34}N_{12}$) (336)

To a stirred solution of 10.0 g (0.27 mol) of hydrazinehydrate (85%) in 40 ml of water, a suspension of 1.0 g (0.0024 mol) of penta(diacetyl)tetraazine **(333)** in 100 ml of ethanol was added. The resultant mixture was stirred for 48 h. The product was filtered, washed with ethanol, pet. ether (40-60°C), and dried at 35°C under vacuum: yield, 0.54 g (0.0023 mol), 51%; mp = 310-315°C, (Lit.[155] mp = 315-320°C). IR (KBr) 3379, 3235 cm^{-1}. ^{1}H NMR (60 MHz, $CDCl_3$) δ 2.1(m,30H), 5.6(s,4H).

2.4.5 CLASS (IV) COMPOUNDS

Diacetylazinediphenylhydrazone ($C_{20}H_{24}N_6$) (337)

To a stirred solution of 6.0 g (0.055 mol) of phenylhydrazine in 25 ml of ethanol, a solution of 2.5 g (0.015 mol) of diacetylazine **(246)** in 25 ml of ethanol was added. The solution was boiled gently for 20 min. to give a reduced volume of 25 ml. The orange product was filtered, washed with pet. ether (40-60°C) and dried under vacuum: yield, 2.41 g (0.007 mol), 46%; mp = 190-193°C. IR (KBr) 3361 cm^{-1}. ^{1}H NMR (60 MHz, $CDCl_3$) δ 2.2(s,12H), 7.2(m,10H), 7.6(s,2H).

Tri(diacetyl)diazinediphenylhydrazone ($C_{24}H_{30}N_8$) (338)

To a stirred solution of 12.0 g (0.11 mol) of phenylhydrazine in 20 ml of ethanol, a suspension of 3.0 g (0.012 mol) of tri(diacetyl)diazine **(331)** in 80 ml of ethanol was added. The reaction mixture was refluxed gently for 30 min. The product was filtered, washed with cold ethanol, pet. ether (40-60°C), and dried at 35°C under vacuum: yield, 4.0 g (0.0093 mol), 78%; mp = 204-206°C. IR (KBr) 3355 cm^{-1}. ^{1}H NMR (60 MHz, $CDCl_3$) δ 2.2(s,18H), 7.2(m,10H), 7.6(s,2H).

Tetra(diacetyl)triazinediphenylhydrazone ($C_{28}H_{36}N_{10}$) (339)

To a stirred solution of 10.0 g (0.092 mol) of phenylhydrazine in 25 ml of ethanol, a suspension of 1.7 g (0.0051 mol) of tetra(diacetyl)triazine **(332)** in 25 ml of ethanol was added. The reaction mixture was refluxed gently for 20 min. The product was filtered, washed with ethanol, pet. ether (40-60°C), and dried at 35°C under vacuum: yield, 2.1 g (0.0041 mol), 80%; mp = 180-182°C. IR (KBr) 3351 cm^{-1}. ^{1}H NMR (60 MHz, $CDCl_3$) δ 2.15(d,24H), 7.2(m,10H), 7.6(s,2H).

2.5 SUMMARY

The synthesis and characterisation of a number of potential compounds suitable as ligands have been described. Included are a number of symmetrically substituted dihydrazones **(312)** and monohydrazones **(311)** of diacetyl. All of these compounds have been reported previously in the literature, with the exception of the diacetyldi(o-tolylhydrazone) **(319)**. However, the reported procedures for their preparation are not complete. A full description of the synthesis of the substituted dihydrazones is presented.

From the monohydrazones **(311)**, asymmetric substituted dihydrazones **(325)** and **(326)** were prepared. To the best of our knowledge, no examples of substituted dihydrazones of diacetyl with different hydrazone moieties have been reported in the literature. A rigorous synthetic route for the preparation of asymmetric substituted hydrazones is described and should have potential in areas such as in the formation of nitrogen heterocycles(147,148).

The unsubstituted diacetyldihydrazone **(5)**, was prepared by literature methods and the reactivity of the terminal amino groups investigated. It was found that the amino groups could readily react with aldehyde groups, and allow azine formation. As will be discussed later, this azine formation was found to occur even after complexation of the dihydrazone.

A new route for the synthesis of a series of discrete polyazine oligomers using diacetyl and hydrazine as starting materials to form **(313)**, **(314)** and **(315)** is also described. This method contrasts with the literature method(155), which in our hands gave spurious results. The method developed by us allows the step by step synthesis of azine oligomers with complete control. This method allows the isolation of the corresponding keto compounds, the first report of such compounds in the case of **(332)** and **(333)**. In addition these keto compounds were reacted to give previously unreported phenylhydrazones.

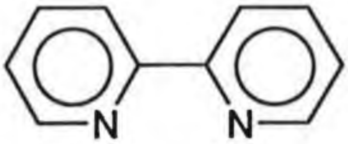
In order to circumvent limitations associated with TLC , a HPLC method was also developed for the analysis of these type of oligomers, which was invaluable as other methods of identification of purity of the oligomers are limited. At least in the case of the smaller azines, the HPLC method allows an unambiguous determination of the number of repeat units. A number of these azine oligomers have not been previously reported, and the route for their synthesis may possibly be extended to a variety of polymeric starting materials and facilitate the synthesis of other types of oligomers of discrete sizes.

CHAPTER III

SYNTHESIS AND CHARACTERISATION OF RUTHENIUMBIS(BIPYRIDYL) DERIVATIVES OF SUBSTITUTED DIHYDRAZONES OF DIACETYL

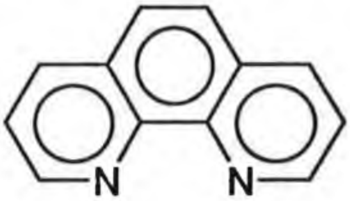
3.1 INTRODUCTION

Ruthenium is a member of a family of rare elements, with a natural abundance in the earths crust of approximately 10^{-3} ppm(156). One of the more interesting features of ruthenium chemistry is that as many as nine oxidation states are known, [Ru(0) to Ru(VIII)]. Much of the current research involves the (II) and (III) oxidation states. Ruthenium (III) shows an extensive coordination chemistry, forming many stable cationic, neutral and anionic monomeric species. A considerable amount of research has been carried out on ruthenium (II) complexes containing three 2,2'-bipyridine (bipy) **(4)** or 1,10-phenanthroline ligands **(340)**, not least because $[Ru(bipy)_3]^{2+}$ **(341)** has been recognised as a potential photo-catalyst (156,157,158).



2,2'-bipyridine (bipy)

(4)



1,10-phenanthroline (phen)

(340)

$[Ru(bipy)_3]^{2+}$ was prepared for the first time by Burstall in 1936(159). Its luminescence was first reported in 1959 by Paris(160). $[Ru(bipy)_3]^{2+}$ is one of the few metal complexes which may be used as a catalyst for solar energy conversion, because of its unique electrochemical and photophysical properties(156-166).

The more important photophysical properties of $[Ru(bipy)_3]^{2+}$ may be explained with the aid of Figure [3.1]. The absorption spectrum of $[Ru(bipy)_3]^{2+}$ exhibits an intense absorption band at 452 nm, which is assigned to a metal-to-ligand charge transfer (MLCT) transition(166-169). Fast intersystem crossing (ISC), occurs from the ^{1}MLCT state, to four closely spaced triplet states, ^{3}MLCT, with an efficiency close to unity(170 -171). Emission from the triplet state to the ground state (K_r) or radiationless deactivation to the ground state (K_{nr}) can take place(166). Another deactivation pathway is thermal population of the metal centred (^{3}MC) excited state, giving rise to either radiationless deactivation (K_o) or to photodecomposition of the complex(172-174).

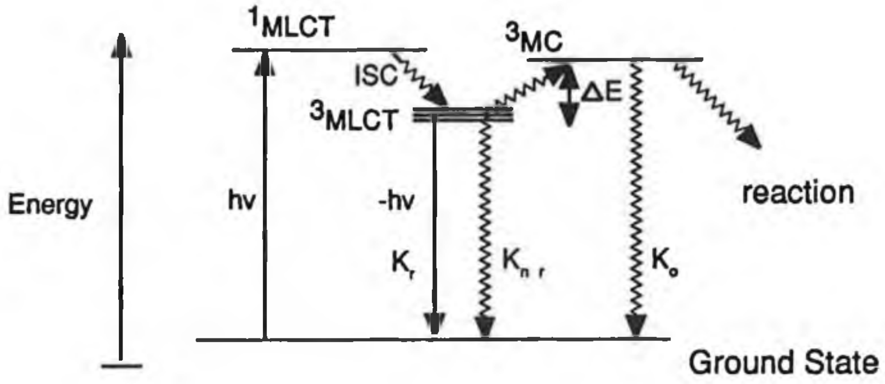


Figure [3.1] **Scheme of the photophysical processes of $[Ru(bipy)_3]^{2+}$ (341)**

$[Ru(bipy)_3]^{2+}$ is a potential photocatalyst for the photodecomposition of water by irradiation of solar light[158]. The splitting of water into hydrogen and oxygen is given by the two half cell reactions.

$$H_2O + e^- \longrightarrow {}^1/_2 H_2 + OH^-$$

$$ {}^1/_2 H_2O \longrightarrow {}^1/_2 O_2 + H^+ + e^-$$

The redox potentials for these reactions at pH = 0 are 0.0 V and 1.23 V respectively (*versus* Normal Hydrogen Electrode, NHE). The conversion of light into electrical energy, (*via* intermediate conversion into chemical energy), is possible using $[Ru(bipy)_3]^{2+}$, which meets the necessary requirements for a light absorption sensitizer[166]. The oxidation potential of a good photocatalyst must be higher than 1.23 V, while the reduction potential of the complex must be lower than 0.0 V. $[Ru(bipy)_3]^{2+}$ has an oxidation potential of 1.26 V and a reduction potential of -1.35 V *versus* SCE, (Saturated Calomel Electrode; 0.2415 V *versus* NHE). When $[Ru(bipy)_3]^{2+}$ absorbs a photon of light, the complex in its excited state is both a better reductor and oxidant than in the ground state. The reason for this is because the excited state electron is located at one of the bipy ligands and is thus easily transferred to the compound that has to be reduced[166]. Furthermore, after excitation, the metal centre charge is formally 3+, so there is an electron hole present at the metal ion and the excited complex becomes a strong oxidant. Another important requirement for a good photocatalyst is its stability. Not only is $[Ru(bipy)_3]^{2+}$ stable but its oxidised and reduced species are also stable.

However, $[Ru(bipy)_3]^{2+}$ is not the most suitable photocatalyst, because it is not photochemically inert towards ligand substitution, and population of the ^3MC state leads to photodecomposition of the complex, see Figure [3.1]. Furthermore, due to the rather narrow absorption band at 452 nm for $[Ru(bipy)_3]^{2+}$, only a small part of the solar spectrum can be used.

By changing the ligand systems around the ruthenium (II) centre, it is possible to alter the ground-state and the excited-state properties of the complexes(166). The properties of ruthenium (II) complexes are governed by the σ-donor and π-acceptor properties of the ligands. Strong π-acceptor ligands stabilise the filled metal orbitals giving rise to high oxidation potentials and low reduction (less negative) potentials(175-184). The difference in energy between the filled d-orbitals and the lowest empty ligand-based orbital is related to the absorption and emission energies of the complexes. The energy of the MLCT excited states depends on;

(i) the π-acceptor properties (related to reduction potential) of the ligand involved in the MLCT transition,
(ii) the oxidation potential of the metal in the complex,
(iii) the charge separation caused by the transition(166).

Thus, by changing the nature of the ligands, not only are the redox potentials altered, but also the energies of the absorption and emission bands(166,175,177-183).

The mixed ligand complexes of the type $[Ru(bipy)_2(LL)]^{2+}$, (where LL represents a strong π-accepting ligand) display a red shift of the absorption and emission energies. Due to lower energies of the absorption bands, a larger portion of the solar energy can be harvested. However, a disadvantage of these ligands is that often, the strong π-accepting ligands are weak σ-donor ligands. As a result, the ligand-field splitting of Ru (II) is much smaller and after excitation of the complex, the ^3MC state becomes very easily populated and the emission yield is diminished. In addition the complexes are often less photostable than the parent $[Ru(bipy)_3]^{2+}$(166). However, this is not always the case, because the π^* levels of the LL ligand are stabilised compared to those of $[Ru(bipy)_3]^{2+}$ and in some complexes the energy gap between the ^3MLCT states and the ^3MC states is then larger than in $[Ru(bipy)_3]^{2+}$ producing a photostable complex.

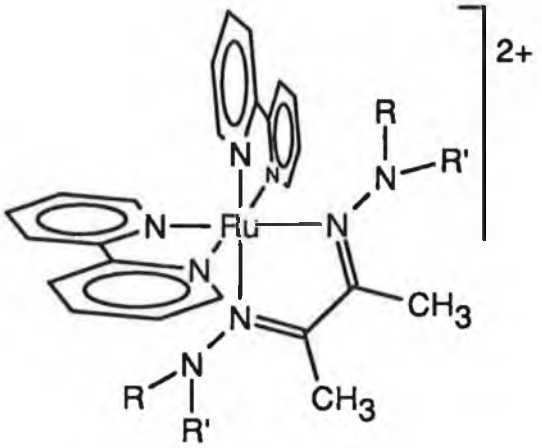
On the other hand, complexes containing strong σ-donor ligands donate much electron density into the d-orbitals, causing lower oxidation potentials and more negative reduction potentials(175). The stronger σ-donor capacities may result in larger ligand-field splitting thus preventing photodecomposition of the complex. Strong σ-donors are often weak π-acceptors which can be a disadvantage as the energy difference between the filled d-orbitals of the metal and the empty π*-orbitals of the ligand is then larger, which causes a blue shift in the absorption and emission spectra, thus reducing the amount of the solar energy that can be harvested.

One way to circumvent this problem is to use mixed-ligand complexes, *e.g.* containing two bipy ligands and one strong σ-donating ligand(166). In these cases, the lowest π* level is still bipy based (causing a red shift in the spectrum), but the d-filled orbitals are destabilised by the strong σ-donor ligands (lower oxidation potential) potentially producing a more photostable complex.

In this chapter, the preparation and characterisation of new complexes of rutheniumbis(2,2'-bipyridyl) with some of the substituted dihydrazones of diacetyl are described. To our knowledge, substituted hydrazones of this type coordinated to ruthenium have not been reported in the literature.

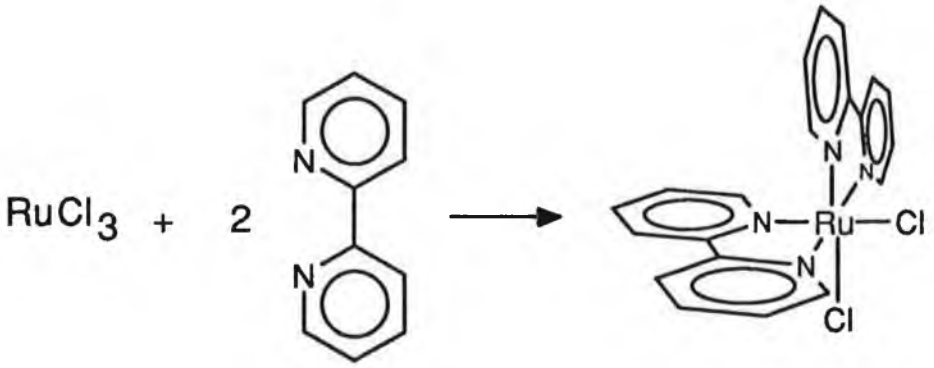
3.2 RESULTS AND DISCUSSION

A series of Ruthenium(II)bis(2,2'-bipyridyl)diacetyldi(hydrazones) **(342) - (347)** was prepared from [Ru(bipy)$_2$Cl$_2$] **(348)** and characterised, summarised below.



(342)	**R = H,**	**R' = Ph**	**(345)**	**R = CH$_3$,**	**R' = CH$_3$**
(343)	**R = CH$_3$,**	**R' = Ph**	**(346)**	**R = H,**	**R' = H**
(344)	**R = H,**	**R' = o-methylphenyl**	**(347)**	**R/R' =**	**=CH-Ph**

Rutheniumbis(2,2'-bipyridyl)dichloride **(348)**, was used as starting material for the formation of [Ru(bipy)$_2$(LL)]$^{2+}$ substituted dihydrazone complexes **(342) - (347)**. The chloride ligands are good leaving groups, and are easily displaced by free ligands in aqueous ethanol solution. [Ru(bipy)$_2$Cl$_2$].2H$_2$O **(348)** was obtained following a literature procedure, by reacting ruthenium(III)trichloride **(349)** with a two molar equivalent of bipyridyl **(4)**$^{(185)}$, according to scheme [3.1].



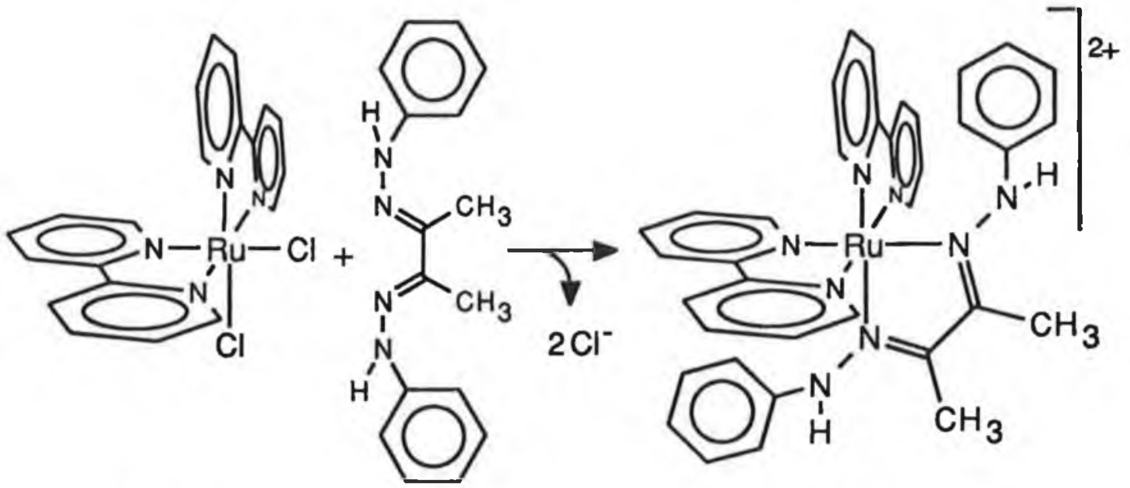
(349) **(4)** **(348)**

Scheme [3.1]

(348) was determined by cation exchange HPLC, with an on-line photodiode array detector. The product has an absorption maximum of 520 nm.

3.2.1 PREPARATION AND CHARACTERISATION OF [RU(BIPY)$_2$(DDPH)](PF$_6$)$_2$ (342)

Refluxing [Ru(bipy)$_2$Cl$_2$] **(348)** with a 1.2 molar excess of diacetyldiphenylhydrazone **(29)** in aqueous ethanol produces the complex **(342)** according to scheme [3.2].



(248) **(29)** **(342)**

Scheme [3.2]

The reaction progress was monitored by HPLC using an on-line PDA detector. The product was found to have a maximum absorption at 450 nm, indicative of the six coordination sites of the ruthenium atom being filled by nitrogen ligands. Removal of the solvent and reconstituting the residue into distilled water, followed by ether extraction removes excess diacetyldiphenylhydrazone **(29)**. Addition of the aqueous solution of complex dropwise to an aqueous solution of ammonium hexafluorophosphate, precipitates the product as a complex with PF_6^- as the counter ion, given by [Ru(bipy)$_2$(ddph)](PF$_6$)$_2$ **(342)**.

UV/Vis. Analysis

A UV/Vis. spectrum (200-550 nm) of the complex [Ru(bipy)$_2$(ddph)](PF$_6$)$_2$ **(342)** is displayed in Figure [3.2].

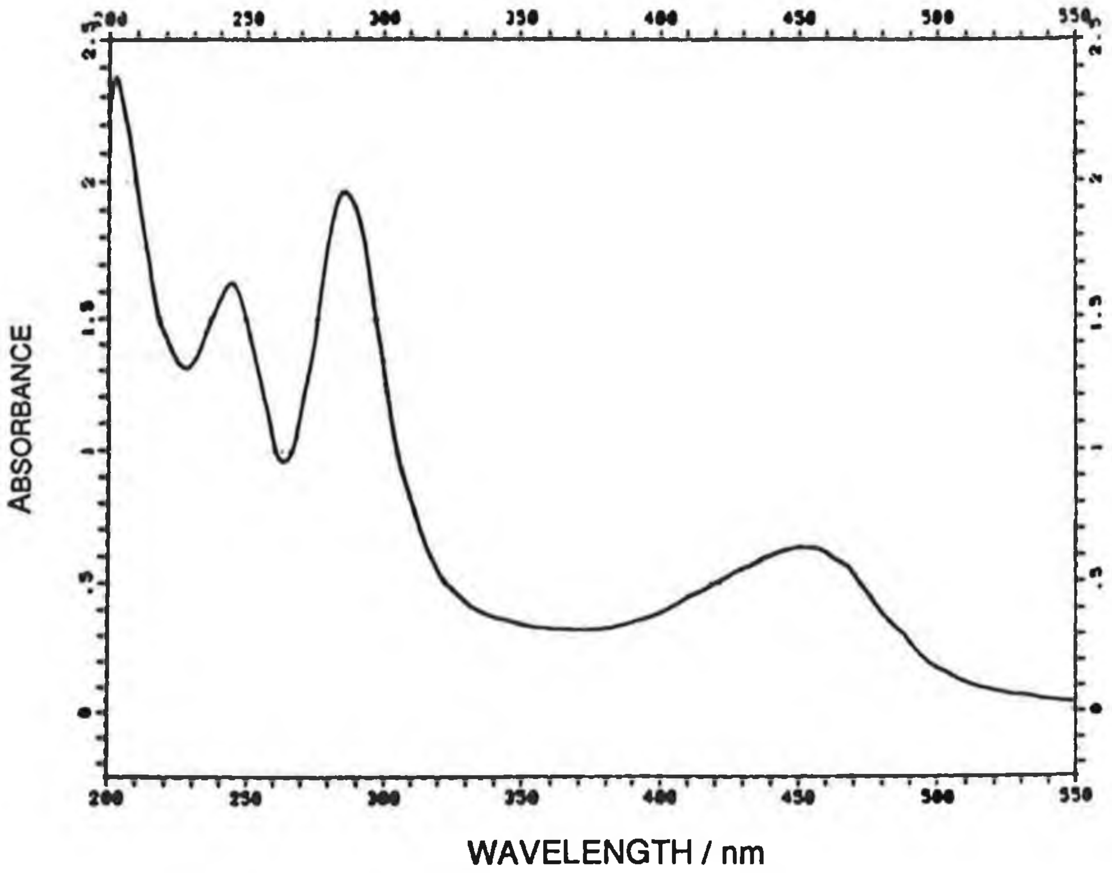


Figure [3.2] UV/Vis. spectrum of $[Ru(bipy)_2(ddph)](PF_6)_2$ in CH_3CN (342)

The band at 285 nm is assigned to the ligand centred (LC) π to π* transitions. The π - π* transitions of the free ligand (ddph) occur at 360 nm which is not observed in the spectrum of the complex. The intense absorption band at 240 nm and the low energy absorption band at 450 nm was assigned to the metal to ligand charge transfer (MLCT), d to π* transitions[166]. The position of the lowest energy maximum in $[Ru(bipy)_2(LL)]^{2+}$ complexes is generally taken as a measure of the metal to ligand interaction[182]. If ligand (LL) is a good π-acceptor ligand, then back donation of electron density from the filled t_{2g} orbitals of ruthenium to the unoccupied π-antibonding orbitals of the ligand occurs, resulting in a reduced energy difference between filled d-orbitals and empty π* orbitals. Consequently, lower energy bands of the absorption spectrum, due to strong π-acceptor ligands, cause a red shift of the absorption maximum to occur. Strong σ-donor ligands causes the energy difference between the filled d-orbitals to be larger, thus causing a blue shift in the absorption and emission spectra[166,175]. $[Ru(bipy)_3]^{2+}$ **(341)** exhibits an intense absorption band at 452 nm[166-169]. Thus, the UV/Vis. data suggests that the ligand **(29)** has similar π-acceptor electronic characteristics to 2,2'-bipyridyl **(4)**.

Emission Analysis

Excitation of $[Ru(bipy)_2(ddph)](PF_6)_2$ **(342)**, at 450 nm, and scanning from 480 - 800 nm for emission, showed no emission bands. To eliminate the possibility of thermal population of the metal centred triplet state ^3MC, (see Figure [3.1]), which might result in radiationless decay, low temperature emission studies were carried out at 77 K, but still no emission bands were observed. No emission was observed for the complex **(342)**, for a range of common solvents, including conditions where the amine groups would be protonated, (scanning at pH as low as pH1).

Photolysis of $[Ru(bipy)_2(ddph)](PF_6)_2$ (342)

To examine the possibility of photodecomposition, $[Ru(bipy)_2(ddph)](PF_6)_2$ **(342)** was photolysed by irradiation (500 W, white light) of a solution of the complex in 0.05M BTEAC in dichloromethane (BTEAC = Benzyltriethylammonium-chloride, a source of Cl^- soluble in CH_3CN), and the reaction mixture was monitored at various time intervals using cation exchange HPLC. The data show that the complex $[Ru(bipy)_2(ddph)](PF_6)_2$ **(342)** is photostable for at least 5 h, as the strongly coordinating chloride anions do not displace ligands of the complex. Under the same conditions, $[Ru(bipy)_3](PF_6)_2$ **(341)** shows significant photodecomposition after thirty min.

These results indicate that the energy gap between the ^3MLCT triplet state and the ^3MC state, (see Figure [3.1]), is large enough to prevent population of the ^3MC state thus preventing photodecomposition[166,175]. The energy of the ^3MC excited states depends on the ligand field strength, which in turn depends on the σ-donor and π-acceptor properties of the ligands, and the steric crowding around the metal[166]. Thus, the results suggest that the ligand diacetyldiphenylhydrazone **(29)** is a strong π-acceptor, as the complex **(342)** is photostable compared to $[Ru(bipy)_3](PF_6)_2$ **(341)**.

Electrochemical Analysis

Cyclic voltammetry was carried out on both the ligand (ddph) **(29)** and the complex $[Ru(bipy)_2(ddph)](PF_6)_2$ **(342)**. A cyclic voltammogram (CV) of $[Ru(bipy)_2(ddph)](PF_6)_2$ **(342)** using 0.1 M TEAP in acetonitrile as electrolyte, (TEAP = tetrabutylammoniumperchlorate, potentials *versus* SCE) is given in Figure [3.3].

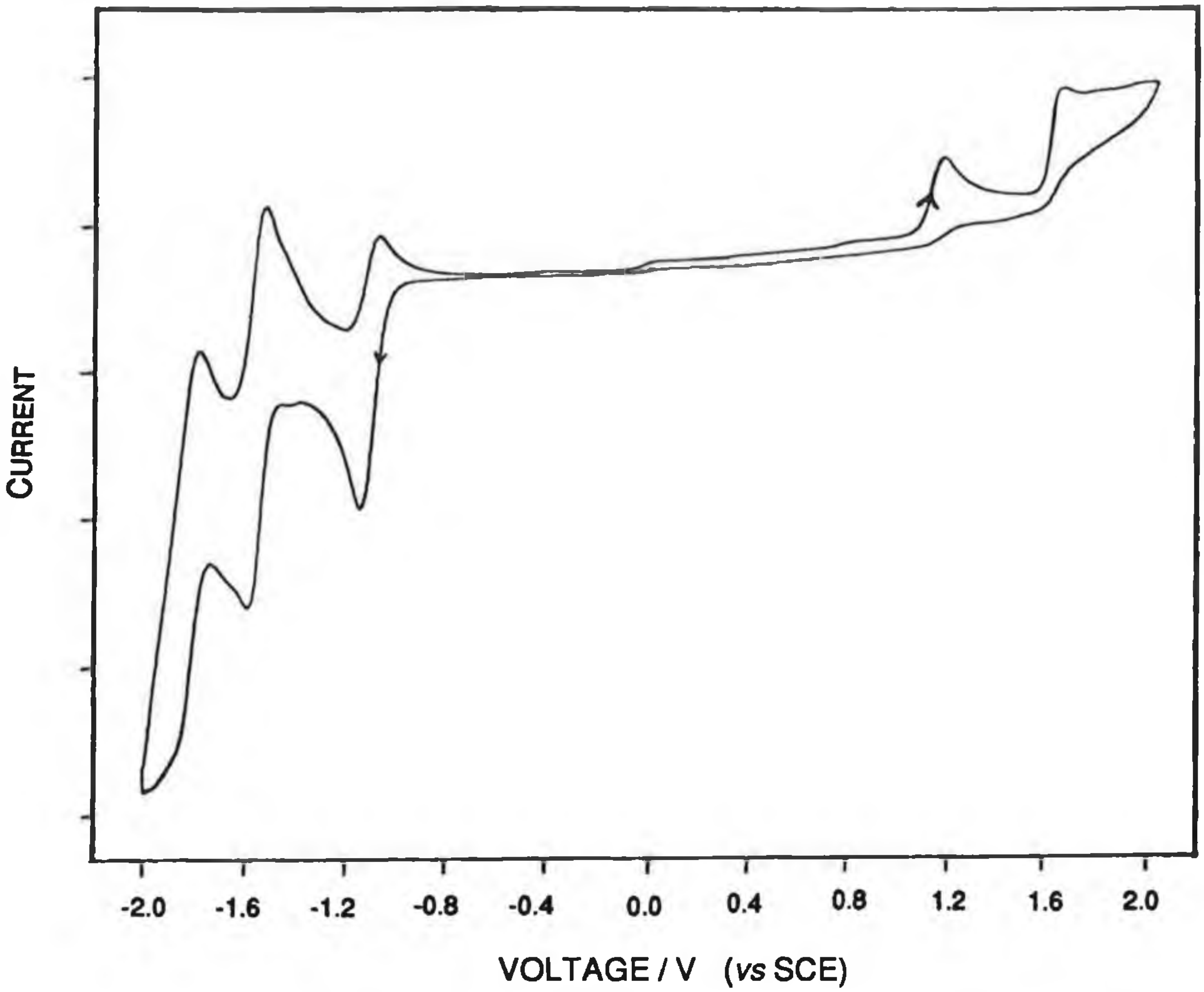


Figure [3.3] Cyclic Voltammogram of complex (342) in 0.1 M TEAP in CH_3CN

Oxidation of the free ligand **(29)** shows an irreversible oxidation process occurring at 1.1 V. The oxidation potentials of $[Ru(bipy)_2(ddph)](PF_6)_2$ **(342)** occur at 1.1 V and 1.60V *versus* SCE. A metal based oxidation potential at 1.26 V has been reported for $[Ru(bipy)_3]^{2+}$ **(341)** under the same conditions(166). Reduction of the free ligand **(29)** shows no reduction processes occurring between 0 V and -2.0 V. The first reduction potential for $[Ru(bipy)_2(ddph)](PF_6)_2$ **(342)**, observed at -1.10 V, is assigned to the reduction of the ligand ddph **(29)**. The remaining reduction potentials at -1.55 V and -1.85 V are likely to be bipy based, (reduction potentials of bipy in $[Ru(bipy)_3]^{2+}$ **(341)** under the same conditions(166), are -1.35 V and -1.60 V). These reduction potentials indicate that the ligand ddph **(29)** is a stronger π-acceptor than bipy, being reduced at relatively low negative potentials, and consequently the energy of the ^{3}MLCT level is reduced compared to $[Ru(bipy)_3]^{2+}$ **(341)** producing a photostable complex, (see page 101).

^{1}H NMR Analysis

A ^{1}H NMR spectrum and a 2D-COSY spectrum of [Ru(bipy)$_2$(ddph)](PF$_6$)$_2$ **(342)**, were obtained. The aromatic region shows eight separate multiplets for the bipy resonances consistent with the symmetry of the molecule. These are assigned as a set of primed 3', 4', 5', 6' and a set of non-primed signals 3, 4, 5, 6. The phenyl resonances occur as a doublet for the ortho hydrogens and a multiplet for the meta and para resonances. Aromatic peaks with a chemical shift as low as 5.9 ppm were observed, as shown in Figure [3.4].

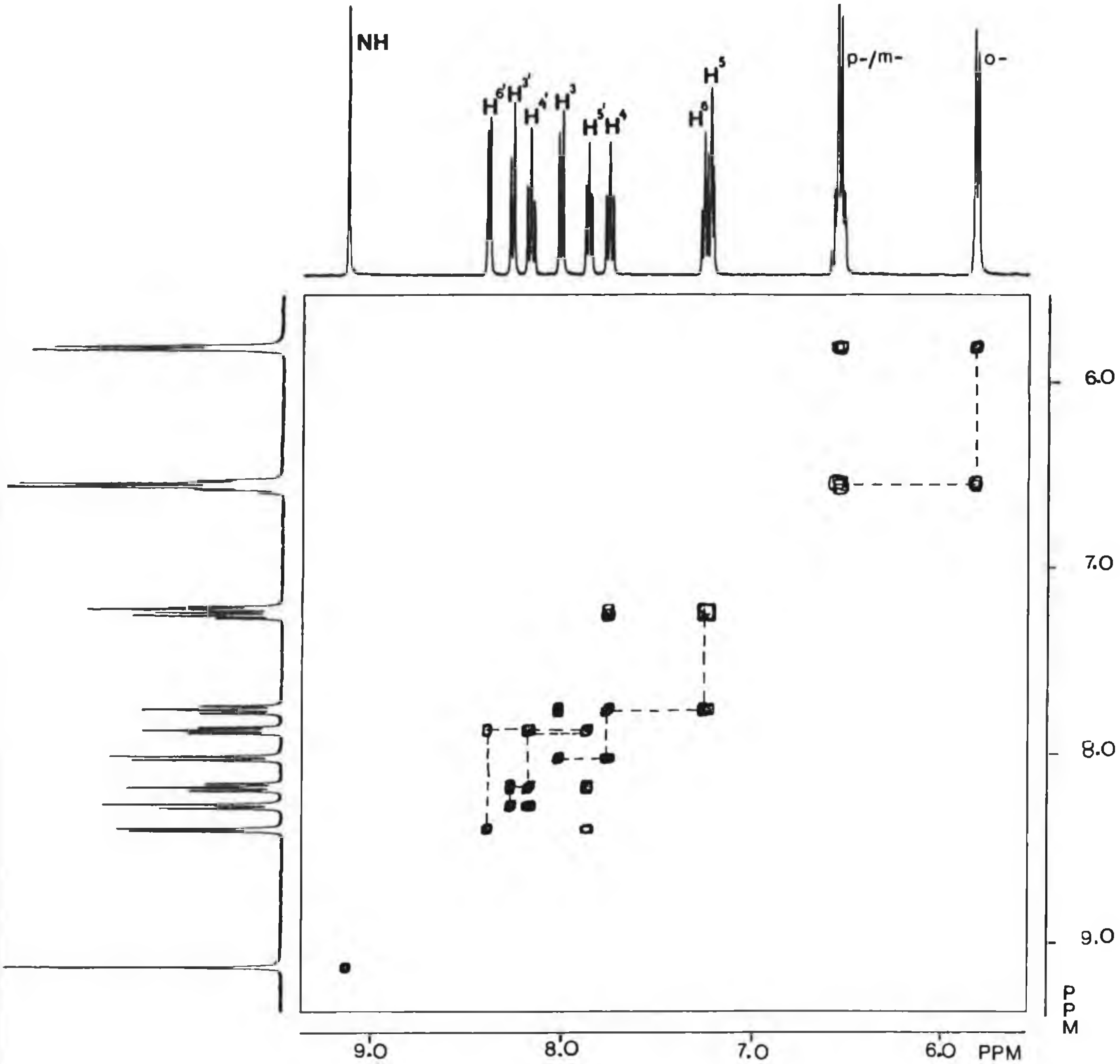
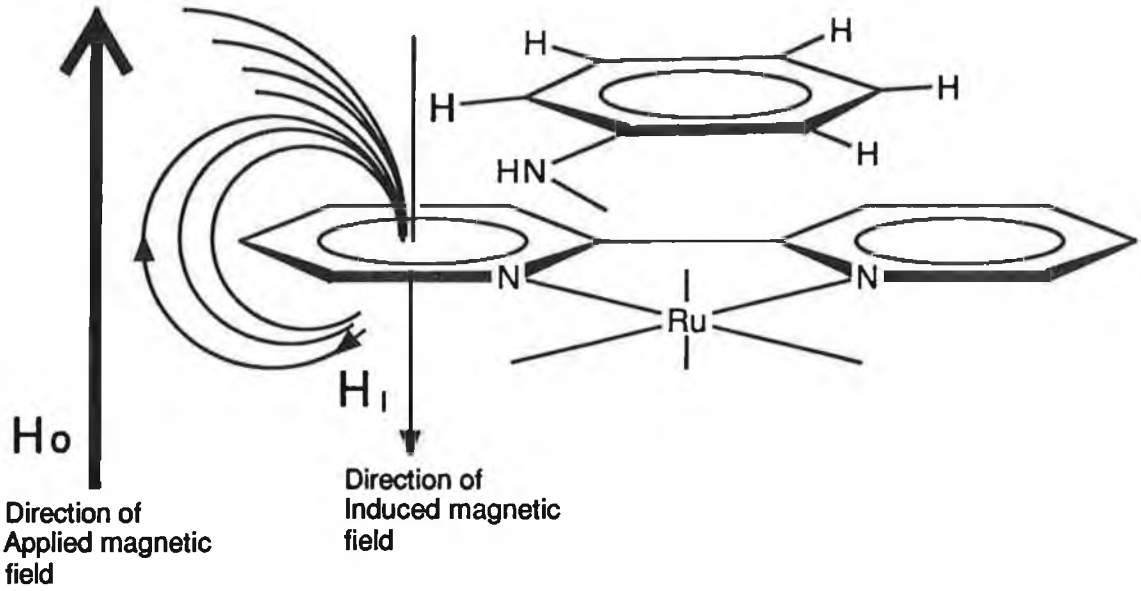


Figure [3.4] ^{1}H NMR 2D COSY of [Ru(bipy)$_2$(ddph)](PF$_6$)$_2$ (342) in DMSO-d$_6$

To explain the high field aromatic resonances, a molecular structure for the complex is proposed, in which hydrogens of the phenyl groups are in close proximity to the 2,2'-bipyridyl groups. These hydrogens are orientated in such a way that they are lying directly over the 2,2'-bipyridyl groups causing them to be shielded by the induced magnetic field of the 2,2'-bipyridyl groups. Circulation of electrons about the bipy groups, generates a field H_I at the ortho phenyl proton(s), aligned in such a way that it opposes the applied field H_o, thus protons are shielded, causing an upfield shift.

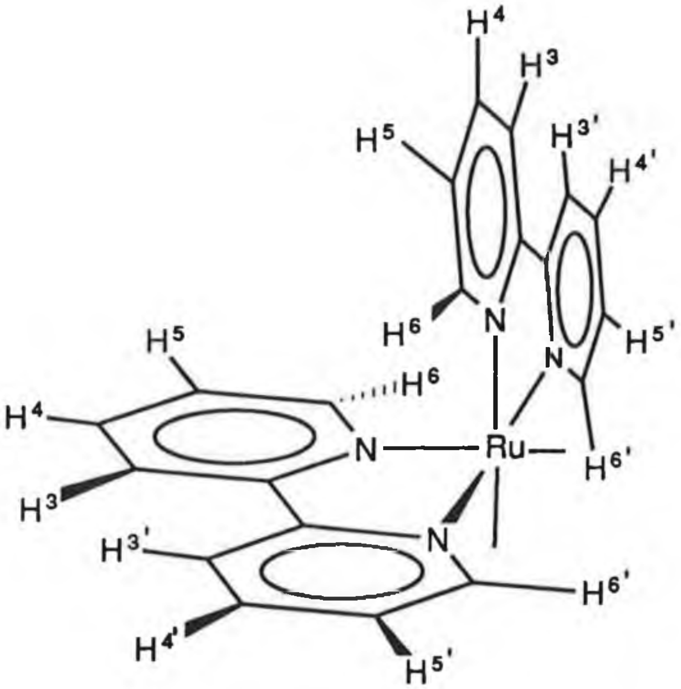


The doublet at 5.90 ppm is assigned to the ortho hydrogens of the phenyl rings being heavily shielded by the induced magnetic field of the bipyridyl rings, while the multiplet, at 6.5 ppm is assigned to the meta and para hydrogens of the phenyl rings.

The bipyridyl protons are assigned using the COSY spectrum. In general for complexes of this type, the lowest field bipyridyl peak, if a doublet is generally assumed to be the $H^{6'}$ proton. Both $H^{6'}$ protons of *cis-* bis(bipyridyl) ruthenium complexes are orientated away from the pyridine ring systems causing them to be the most deshielded protons, illustrated below. For the $[Ru(bipy)_2(ddph)](PF_6)_2$ **(342)** complex, the $H^{6'}$ appears as a doublet with a chemical shift of 8.40 ppm, coupled to a triplet at 7.90 ppm, ($H^{5'}$), which is coupled to a second triplet at 8.20 ppm, ($H^{4'}$), which in turn is coupled to a doublet at 8.25 ppm representing the proton $H^{3'}$, illustrated in Figure [3.4].

To assign the remaining protons of the bipyridyl, the doublet at 8.10 ppm is assigned to the H^3 proton. H^3 and $H^{3'}$ proton doublets generally have a larger

J splitting constant than the H^6 and $H^{6'}$ doublets. A triplet at 7.80 ppm coupled to the H^3 proton is assigned to the H^4 proton. The H^4 proton is coupled to a second triplet at 7.30 ppm (H^5), which in turn is coupled to a doublet at 7.20 ppm assigned to the H^6 protons.



Difference Nuclear Overhauser Effect (NOE) Studies

In order to investigate the contention that the phenyl protons are close in space to the bipyridyl rings, difference NOE experiments were carried out on the complex **(342)**. On applying the decoupler on the ortho hydrogens of the phenyl ring (saturating the signal at 5.8 ppm), a 2.5% diff. NOE is observed to the $H^{6'}$ protons of the bipyridyl ring, and a 1.8% diff. NOE is observed to the H^6 protons of the bipy ring. A 4% diff. NOE is also observed to the NH protons, (see Figure [3.5]). The lower trace shows the normal ^1H NMR spectrum whereas the middle trace shows the difference after subtraction of the spectrum resulting from irradiation of the ortho phenyl protons. The upper trace is a repeat of the difference spectrum at an increased sensitivity. A similar result was obtained at both 250 MHz and 400 MHz. Figure [3.6] shows the normal ^1H NMR spectrum and the difference after subtraction of the decoupled spectrum experiment at 400 MHz.

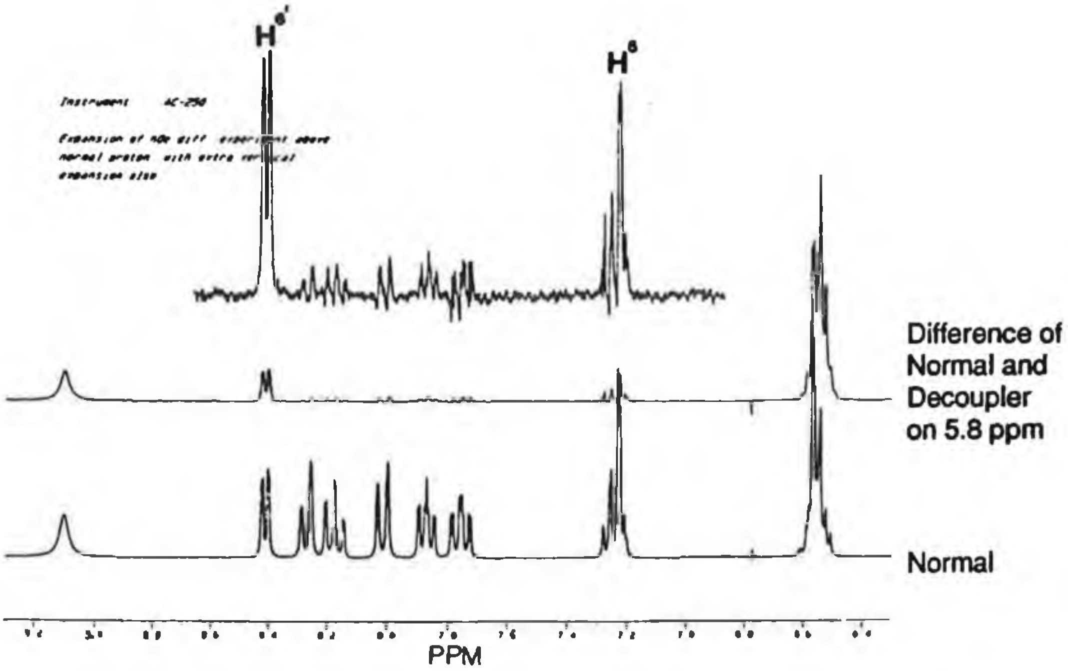


Figure [3.5] Difference NOE Spectrum for $[Ru(bipy)_2(ddph)](PF_6)_2$ (342) in DMSO-d_6 at 250 MHz

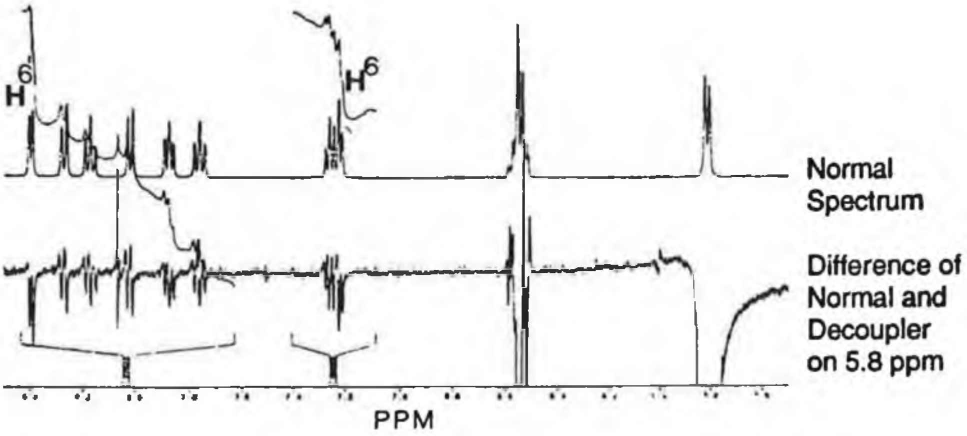


Figure [3.6] Difference NOE Spectrum for $[Ru(bipy)_2(ddph)](PF_6)_2$ (342) in DMSO-d_6 at 400 MHz

These results indicate that the ortho protons of the phenyl ring are close in space, (< 3Å) to the hydrogens of the bipyridyl system. This supports the contention that at least in solution, the phenyl ring lies in close proximity over the bipy system.

Resonance Raman Spectroscopy Studies

To reinforce the proposal that the ligand (ddph) **(29)** is involved in the lowest energy MLCT band of complex **(342)**, resonance Raman spectra of complex **(342)** were obtained. Excitation into an allowed Ru to π^* transition to one of the ligands gives rise to enhancement of the symmetrical stretching modes of that ligand(186). By study of the wavelength dependence of the spectra, resonance Raman allows different electronic transitions underneath one absorption band to be detected and identified.

RR spectra (500 to 1600 cm^{-1}) of the complex **(342)** were recorded at 457 nm and 488 nm in both acetonitrile and acetone. A spectrum was also recorded at 383.8 nm in acetonitrile. In addition to the bipy features displayed in the spectra recorded at 457 nm and 488 nm, both spectra show some hydrazone linked features as well. Figure [3.7] shows the RR spectra of [Ru(bipy)$_2$(ddph)](PF$_6$)$_2$ **(342)** in acetone obtained by excitation with a wavelength at 457.9 nm. Comparison with the literature data of similar rutheniumbis(bipyridyl) derivatives(186) indicates that the enhanced bands at 1608, 1564, 1493, 1322, 1278, 1178, 1029 cm^{-1} are bipy based vibrations. The bands at 1469 cm^{-1} and 1351 cm^{-1} are assigned to be hydrazone ligand based. Excitation at 488.0 nm yielded the same spectrum. The bands at 1421 cm^{-1} and 1438 cm^{-1} are thought to be due to residual solvent in the sample. Spectra recorded at 363.8 nm (not illustrated) are noisier but show similar features.

These results support the data obtained from the electrochemical measurements which indicate that the lowest energy MLCT band of Ru(bipy)$_2$(ddph)](PF$_6$)$_2$ **(342)** can be explained by Ru --> $\pi^*_{(ddph)}$ MLCT transitions. If the ligand (ddph) **(29)** was a poor π-acceptor, the absence of any hydrazone based peaks in the RR spectra would be expected(186). Because the spectra observed are very similar and the relative intensities of the hydrazone and bipy peaks do not change significantly, at different excitation wavelengths, suggests that there is a large overlap between the dπ --> $\pi^*_{(ddph)}$ and dπ --> $\pi^*_{(bipy)}$ transitions in the absorption spectrum of [Ru(bipy)$_2$(ddph)](PF$_6$)$_2$ **(342)**. The RR data confirm that the transitions between the ground state and the excited state of the bipy ligands and the hydrazone ligands are similar which may explain radiationless deactivation of the excited states.

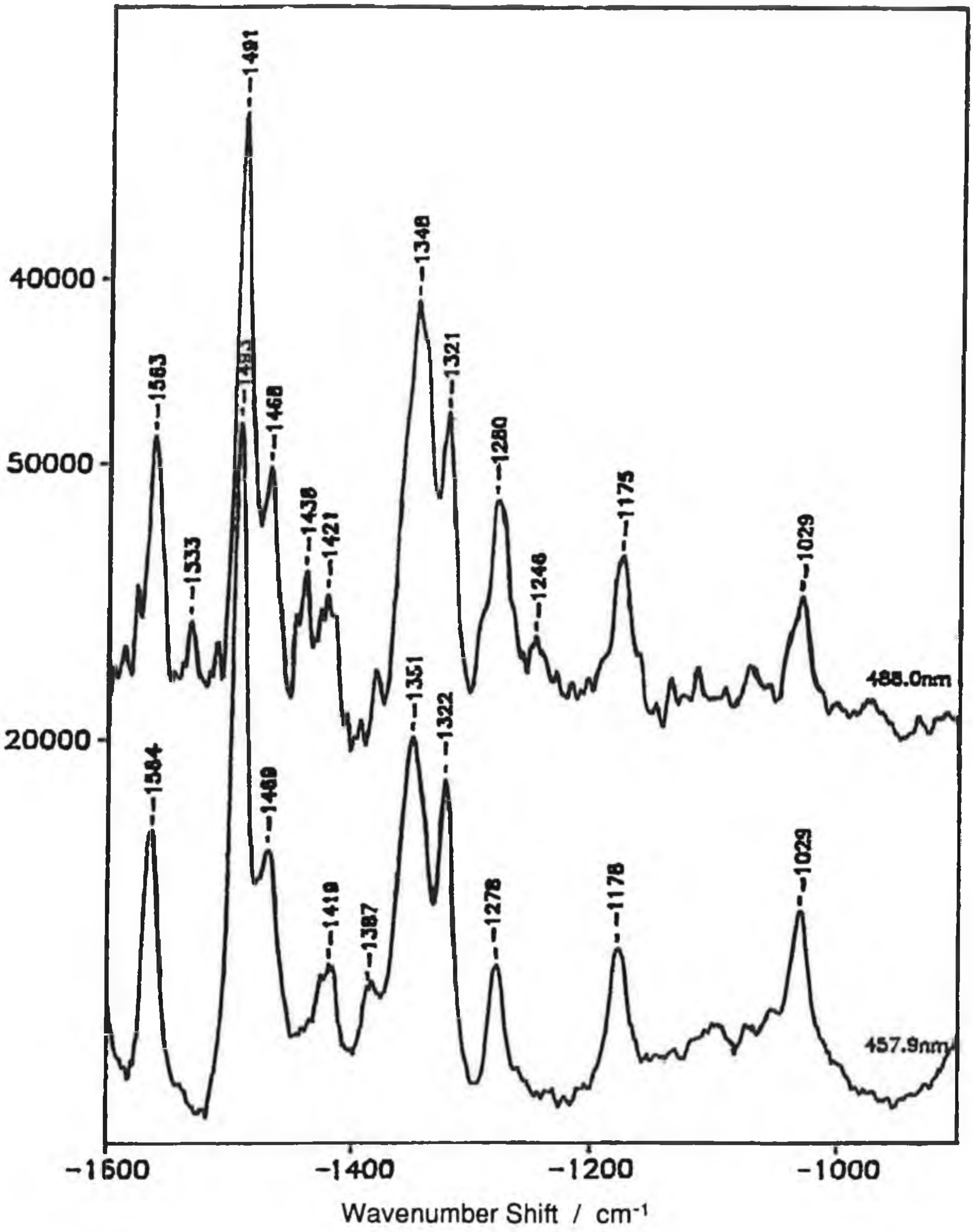


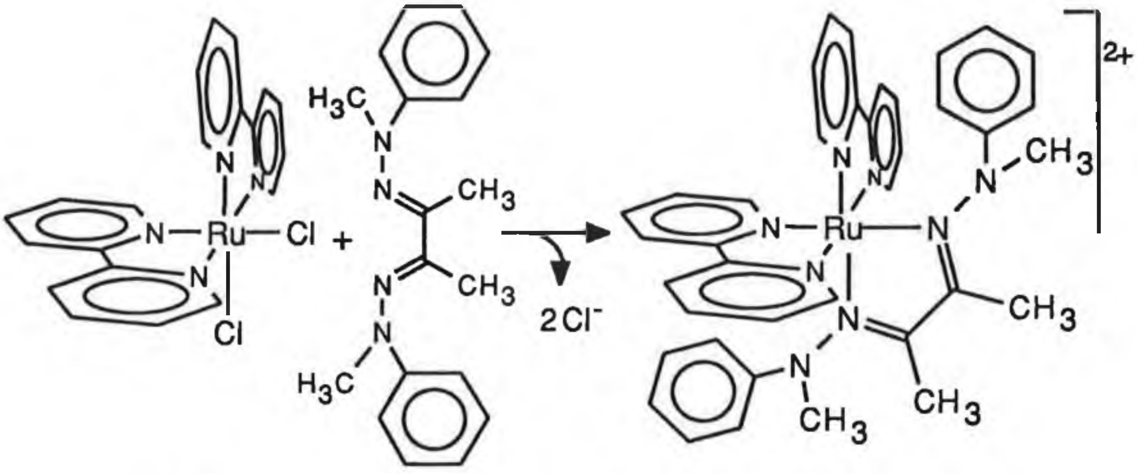
Figure [3.7] **Resonance Raman Spectra of Complex (342) in Acetone excited at; (i) 488 nm and (ii) 457 nm**

The resonance Raman spectra were obtained by Dr. J. J. McGarvey at the Chemistry Department, Queens University, Belfast, and experiments were performed by Dr. R. A. McNicholl.

3.2.2 PREPARATION AND CHARACTERISATION OF [RU(BIPY)$_2$(DDMPH)](PF$_6$)$_2$ (343)

In an attempt to further explore the configuration of the phenyl groups, in the complex [Ru(bipy)$_2$(ddph)](PF$_6$)$_2$ **(342)**, and to try to "move" the phenyl rings away from the 2,2'-bipyridyl units, the complex rutheniumbis(2,2'-bipyridyl)-diacetyldi(N-methyl,N-phenylhydrazone)bis(hexafluorophosphate) **(343)** was prepared where the N-H hydrogens of the hydrazone ligand in complex **(342)** were replaced by a methyl group. It was anticipated that the methyl group, due to increased size might possibly rotate the hydrazone group away from the 2,2'-bipyridyl units.

Refluxing [Ru(bipy)$_2$Cl$_2$] **(348)** with a 1.2 molar excess of diacetyldi(N-methyl,N-phenylhydrazone) (ddmph) **(320)** in aqueous ethanol for a reaction period of 48 hours produces the complex [Ru(bipy)$_2$(ddmph)](PF$_6$)$_2$ **(343)** according to scheme [3.3].



(348) **(320)** **(343)**

Scheme [3.3]

The reaction was monitored using cation exchange HPLC. After the reaction goes to completion, the excess ligand was removed by extraction, and the product was isolated as the PF$_6^-$ complex from water. Good yields (74%) were recovered after recrystallisation. Analysis of the isolated product by HPLC indicates that the product was pure.

UV/Vis. Analysis And Emission studies

A UV/Vis. absorption spectrum of [Ru(bipy)$_2$(ddmph)](PF$_6$)$_2$ **(343)** in acetonitrile, is dominated by an intense metal-to-ligand charge transfer band

(MLCT) at 455 nm. The band at 285 nm is assigned to the LC π to π* transitions[166]. In the UV/Vis. spectrum of the free ligand (ddmph) **(320)**, bands were observed at 205 nm, 260 nm and 370 nm.

On excitation of $[Ru(bipy)_2(ddmph)](PF_6)_2$ **(343)** in ethanol at 455 nm and scanning for emission from 480-800 nm, no emission peaks were observed. Low temperature (77 K) emission studies also revealed no emission bands.

Photolysis of $[Ru(bipy)_2(ddmph)](PF_6)_2$ (343)

Irradiation of a solution of $[Ru(bipy)_2(ddmph)](PF_6)_2$ **(343)** in 0.05 M BTEAC in dichloromethane, using a white light source, and monitoring at various time intervals using cation exchange HPLC, indicates that the complex is photostable under these conditions for at least five hours. This result is as expected, since the introduction of a methyl group onto the nitrogen would not be expected to significantly alter the donor-acceptor characteristics relative to the complex **(342)**.

Electrochemical Analysis of $[Ru(bipy)_2(ddmph)](PF_6)_2$ (343)

Oxidation (0 to +2.0 V) and reduction (0 to -2.0 V *versus* SCE) cyclic voltammetry was carried out on the free ligand (ddmph) **(320)** and on the complex $[Ru(bipy)_2(ddmph)](PF_6)_2$ **(343)** in 0.1 M TEAP in CH_3CN. Oxidation potentials of 1.10 V and 1.30 V are observed for the free ligand **(320)** with the absence of reduction potentials. For the complex **(343)**, the first two oxidation potentials of the CV occur at 1.10 V and 1.30 V which are most likely due to the oxidation of the ligand **(320)**. Based on the electrochemistry of the free ligand, the irreversible oxidation wave at potential 1.90 V is thought to be due to oxidation of the metal, Ru(II) to Ru(III).

The first reduction potential observed at -1.00 V for $[Ru(bipy)_2(ddmph)](PF_6)_2$ **(343)** is assigned to the reversible reduction of the ligand (ddmph) **(320)**. The remaining reduction potentials at -1.60 V and -1.90 V are likely to be bipy based[166], indicating that the ligand (ddmph) **(320)** is a stronger π-acceptor than bipy[175,177-184], being reduced at a lower potentials. Hence, the MLCT transition involves excitation of an electron from the d-orbitals of the metal centre to the empty π*-orbitals of the ligand (ddmph) **(320)**.

^1H NMR Analysis of $[Ru(bipy)_2(ddmph)](PF_6)_2$ (343)

Because of extensive broadening, the ^1H NMR spectrum of $[Ru(bipy)_2(ddmph)](PF_6)_2$ **(343)** collected at room temperature was not suitable for assigning the protons of the complex, the reasons for this will be discussed later in the variable temperature NMR studies section. A ^1H NMR and a 2D-COSY NMR spectrum of $[Ru(bipy)_2(ddmph)](PF_6)_2$ in DMSO-d_6 were obtained at 363 K, figure [3.8].

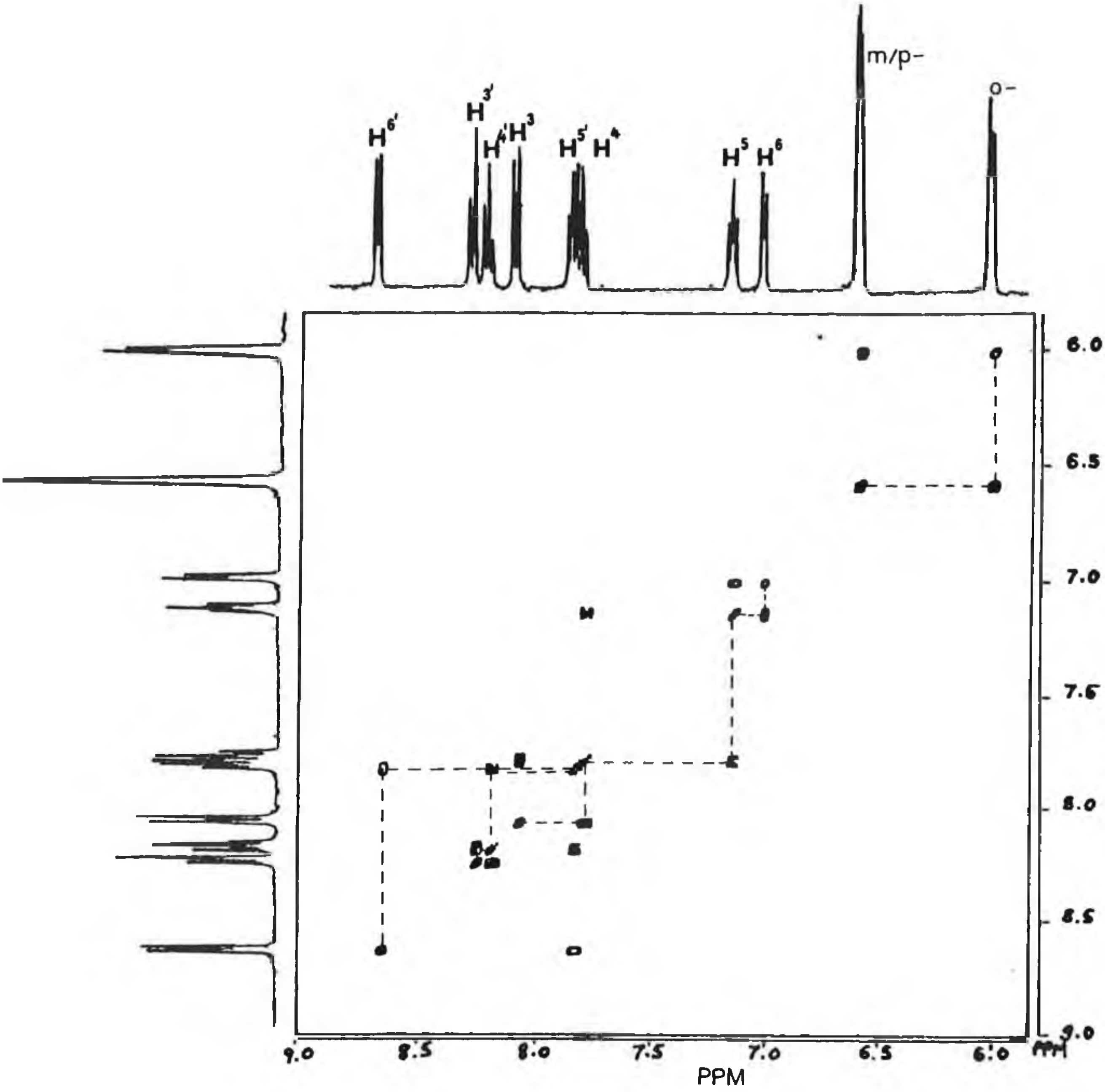


Figure [3.8] 2D-COSY spectrum of $[Ru(bipy)_2(ddmph)(PF_6)_2$ in DMSO-d_6 @ 363 K

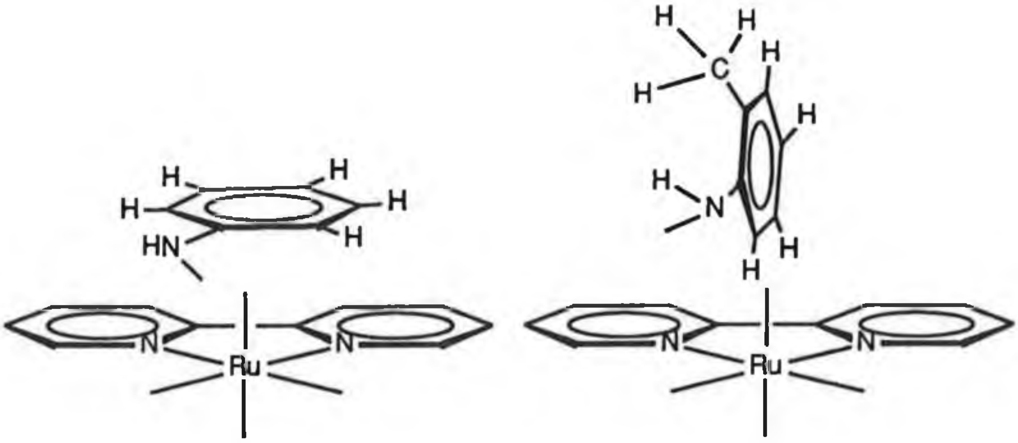
The diacetyl-methyl groups appear as a singlet at 2.86 ppm, ($\delta_{(free\ ligand)}$ = 2.2 ppm). This increase in chemical shift on complexing is most likely explained by the decrease in electron density around the protons caused by the σ donation of electrons by the ligand. The N-methyl hydrogens appear as a sharp singlet at 3.10 ppm, ($\delta_{(free\ ligand)}$ = 2.50 ppm), which also displays a increase in the chemical shift on complexing.

A notable feature of the ^{1}H NMR spectra of [Ru(bipy)$_2$(ddmph)](PF$_6$)$_2$ **(343)** is the presence of two peaks with peak intensities of 4:6, which are assigned as the ortho hydrogens at 6.01 ppm and the meta and para hydrogens at 6.58 ppm, ($\delta_{(free\ ligand)}$ = 7.2 ppm). The chemical shift values of the phenyl protons indicate that the phenyl groups are positioned close to the (bipy) groups.

The 2,2'-bipyridyl protons of [Ru(bipy)$_2$(ddmph)](PF$_6$)$_2$ **(343)** were assigned using the COSY technique. The H^6 doublet at a chemical shift 7.03 ppm is coupled to the H^5 triplet at 7.17 ppm, which is in turn coupled to a second H^4 triplet at 7.82 ppm which is coupled to the H^3 doublet at 8.08 ppm. The H$^{6'}$ protons (facing away the bipy ring system), appear as a doublet at 8.86 ppm, coupled to the H$^{5'}$ triplet at 7.86 ppm, which is coupled to a second H$^{4'}$ triplet at 8.22 ppm which is coupled to a H$^{3'}$ doublet at 8.27 ppm.

3.2.3 PREPARATION AND CHARACTERISATION OF [RU(BIPY)$_2$(DDOTH)](PF$_6$)$_2$ (344)

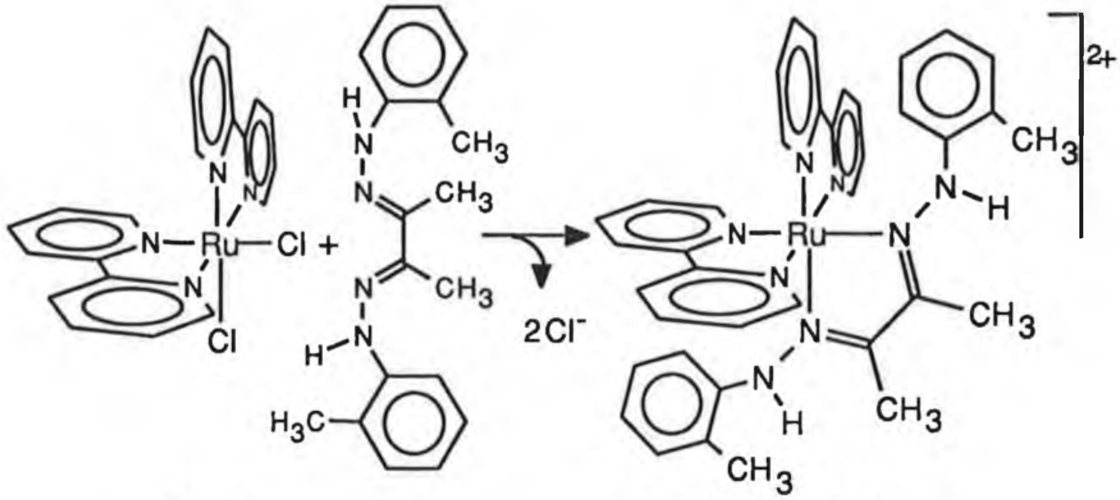
In a further investigation of the orientation of the phenyl groups with respect to the 2,2'-bipyridyl units, one of the ortho- protons of each phenyl group of complex [Ru(bipy)$_2$(ddph)](PF$_6$)$_2$ **(342)** was replaced by a methyl group. On steric grounds, the methyl may cause the phenyl ring to be rotated away from the 2,2'-bipyridyl groups as depicted below.



(342) **(344)**

Proposed orientation of phenyl groups with respect to 2,2'-bipyridyl groups

[Rutheniumbis(2,2'-bipyridyl)diacetyldi(o-tolylhydrazone)]$^{2+}$ **(344)** was prepared by refluxing a solution of [Ru(bipy)$_2$Cl$_2$] **(348)** with a 1.2 molar equivalent of diacetyldi(o-tolylhydrazone) (ddoth) **(319)**, according to scheme [3.6].



(348) **(319)** **(344)**

Scheme [3.6]

After extraction of excess ligand the product was isolated as the PF$_6^-$ complex. The reaction went to completion, with a single product obtained.

UV/Vis. Analysis and Emission Studies

UV/Vis. absorption bands at 205 nm and 345 nm occur for the free ligand (ddoth) **(319)**. The intense band at 285 nm is assigned to the ligand centred, π to π^* electronic transitions[166]. The main peak at lower frequency in the spectrum, assigned to the metal-to-ligand charge transfer, occurs at 450 nm, very similar to the MLCT band caused by bipy groups, in $[Ru(bipy)_3](PF_6)_2$ **(341)**. $[Ru(bipy)_2(ddoth)](PF_6)_2$ **(344)** on excitation at 450 nm shows no emission between 480 nm to 800 nm, both at room temperature and at 77 K.

Photolysis of $[Ru(bipy)_2(ddoth)](PF_6)_2$ (344)

A solution of $[Ru(bipy)_2(ddoth)](PF_6)_2$ **(344)** in 0.05 M BTEAC in dichloromethane was photolysed for five hours. The reaction mixture was monitored by HPLC. Results indicate that the complex is photostable for at least five hours in these conditions, in a similar manner to complexes **(342)** and **(343)**.

Electrochemical Analysis of $[Ru(bipy)_2(ddoth)](PF_6)_2$ (344)

Cyclic voltammograms were obtained for the free ligand (ddoth) **(319)** and for the complex $[Ru(bipy)_2(ddoth)](PF_6)_2$ **(344)** in 0.1 M TEAP in CH_3CN. Oxidation CV's were scanned from 0 V to +2.0 V and reduction from 0 to -2.0 V (*versus* SCE). The ligand **(319)** displays irreversible oxidation wave potentials at 0.80 V and at 1.70 V. No reduction potential peaks were observed for the free ligand **(319)**. The first oxidation potential of the complex **(344)** occurs as an irreversible wave at 1.10 V, and is possibly the oxidation of the NH groups of the ligand **(319)**, ($E^\circ_{\text{free ligand}} = 0.8$ V). An irreversible oxidation peak at 1.60 V is most likely due to oxidation of Ru(II) to Ru(III).

The first reduction potential of $[Ru(bipy)_2(ddoth)](PF_6)_2$ **(344)** observed at -1.10 V, is assigned to the reversible reduction of the ligand (ddoth) **(319)**. The reduction waves at potentials -1.50 V and -1.85 V are thought to be bipy based[166]. These results indicate that the ligand (ddoth) **(319)** is a stronger π-acceptor than bipy, being reduced at lower potentials[175,177-184].

^1H NMR Analysis

A ^1H NMR spectrum of $[Ru(bipy)_2(ddoth)](PF_6)_2$ **(344)** in DMSO-d_6 was obtained at room temperature but the peaks at 5.50 ppm and 6.30 ppm are very broad, (see section 3.4). A suitable ^{1}H NMR and a 2D-COSY spectrum of the complex **(344)** in DMSO-d_6 was obtained at 373 K, as depicted in figure [3.9].

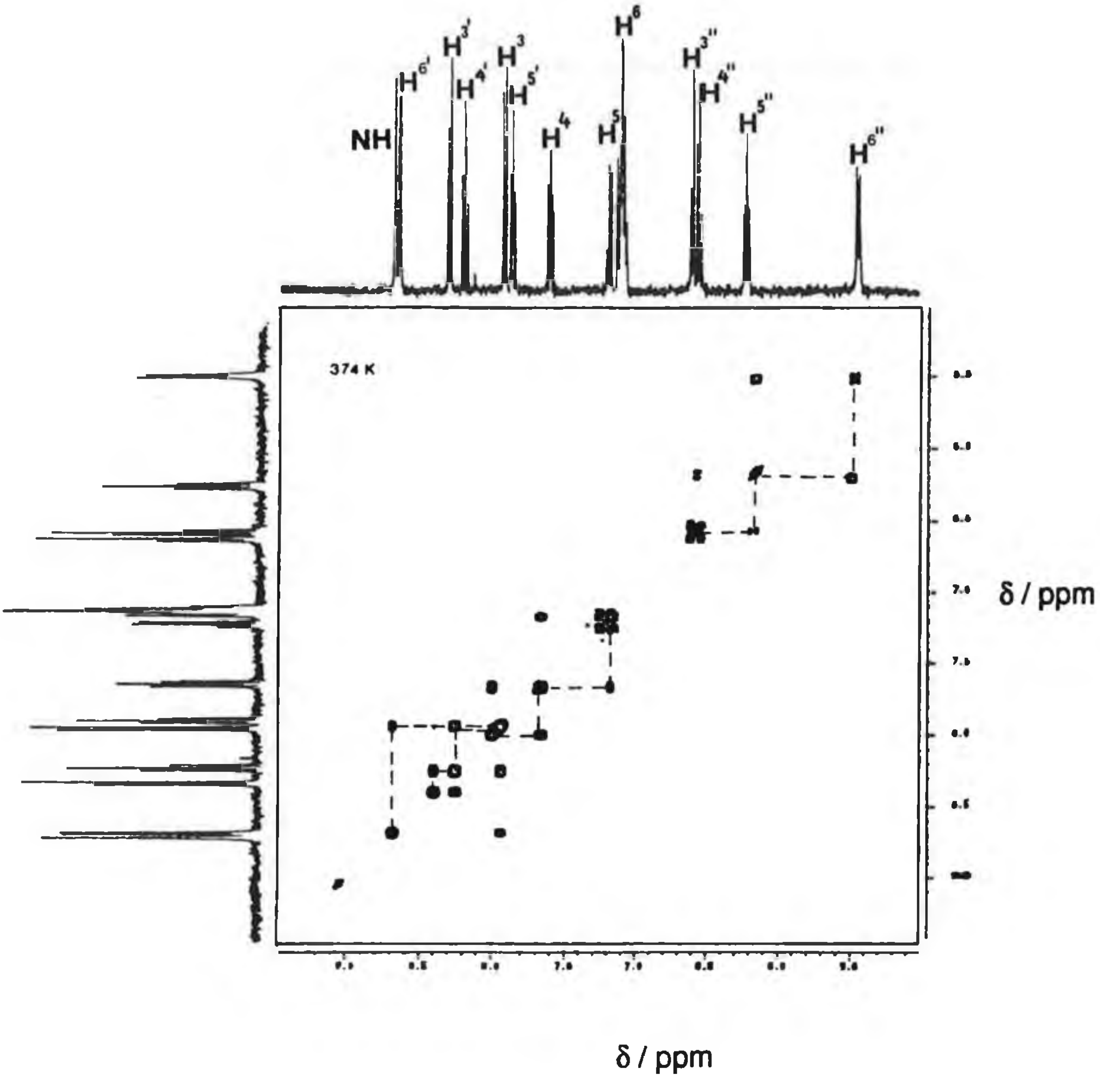


Figure [3.9] **2D-COSY spectrum of $[Ru(bipy)_2(ddoth)](PF_6)_2$ in DMSO-d_6 @ 373 K**

The diacetyl methyl groups appear as a singlet at 2.71 ppm, ($\delta_{(free\ ligand)}$ = 2.20 ppm), and the ortho methyl groups of the phenyl group appear as a sharp resonance at 1.84 ppm. A proton resonance at a chemical shift of 5.51 ppm is assigned to the ortho-proton $H^{6''}$ of the o-tolyl groups, again showing a low chemical shift value for the $H^{6''}$ proton, ($\delta_{(free\ ligand)}$ = 7.26 ppm). Again it is believed that the tolyl-groups are situated directly over the 2,2'-bipyridyl groups, similar to the structure of the complex [Ru(bipy)$_2$(ddph)](PF$_6$)$_2$ **(342)**, despite the introduction of a methyl group onto the phenyl ring.

This is supported by the chemical shift of the $H^{5''}$ proton of the o-tolyl group, which occurs as a triplet at $\delta = 6.26$ ppm, compared to 6.91 ppm for the free ligand **(319)**. From the 2D-COSY, the $H^{5''}$ triplet is coupled to the $H^{6''}$ doublet (5.51 ppm). The $H^{5''}$ triplet is also coupled to the $H^{4''}$ triplet at a chemical shift of 6.64 ppm, which is coupled to the $H^{3''}$ doublet at 6.66 ppm, $H^{4''}$ and $H^{3''}$ being shielded to a lesser degree by the ring currents of the 2,2'-bipyridyl groups. The 2,2'-bipyridyl protons of [Ru(bipy)$_2$(ddoth)](PF$_6$)$_2$ **(344)**, were assigned using the 2D-COSY NMR spectrum. The H^5 triplet at 7.24 ppm is coupled to both the H^6 doublet at a chemical shift at 7.14 ppm and also H^4 triplet at 7.65 ppm. The H^4 triplet is in turn coupled to the H^3 doublet at 7.95 ppm. The $H^{6'}$ proton appears as a doublet at 8.69 ppm, coupled to the $H^{5'}$ triplet at 7.90 ppm, which is coupled to a second triplet, ($H^{4'}$ at 8.23 ppm) which is also coupled to a $H^{3'}$ doublet at 8.35 ppm. The singlet at 8.74 ppm represents the NH protons. The singlet at 2.3 ppm and the multiplet between 7.1 ppm and 7.3 ppm is due to toluene which remained in the solid after recrystallisation, from toluene/acetone.

Difference NOE Studies

To investigate whether the methyl group of the tolyl group was positioned over a particular ring of the bipy groups, difference NOE experiments were performed on complex **(344)**. When the ortho methyl resonance signal is decoupled (saturating the signal at 1.84 ppm), a small NOE is observed through space for the H^6, H^5, and $H^{6'}$ protons, as depicted in figure [3.10]. Larger NOE's are observed for the $H^{3''}$ and $H^{4''}$ of the phenyl ring to which the irradiated methyl is attached, and for the NH proton.

These results suggest that the ortho methyl group may be positioned close in space to the "non-primed" pyridyl ring, (*i.e.* the pyridyl ring which faces into the second bipyridyl ring), as depicted in figure [3.11].

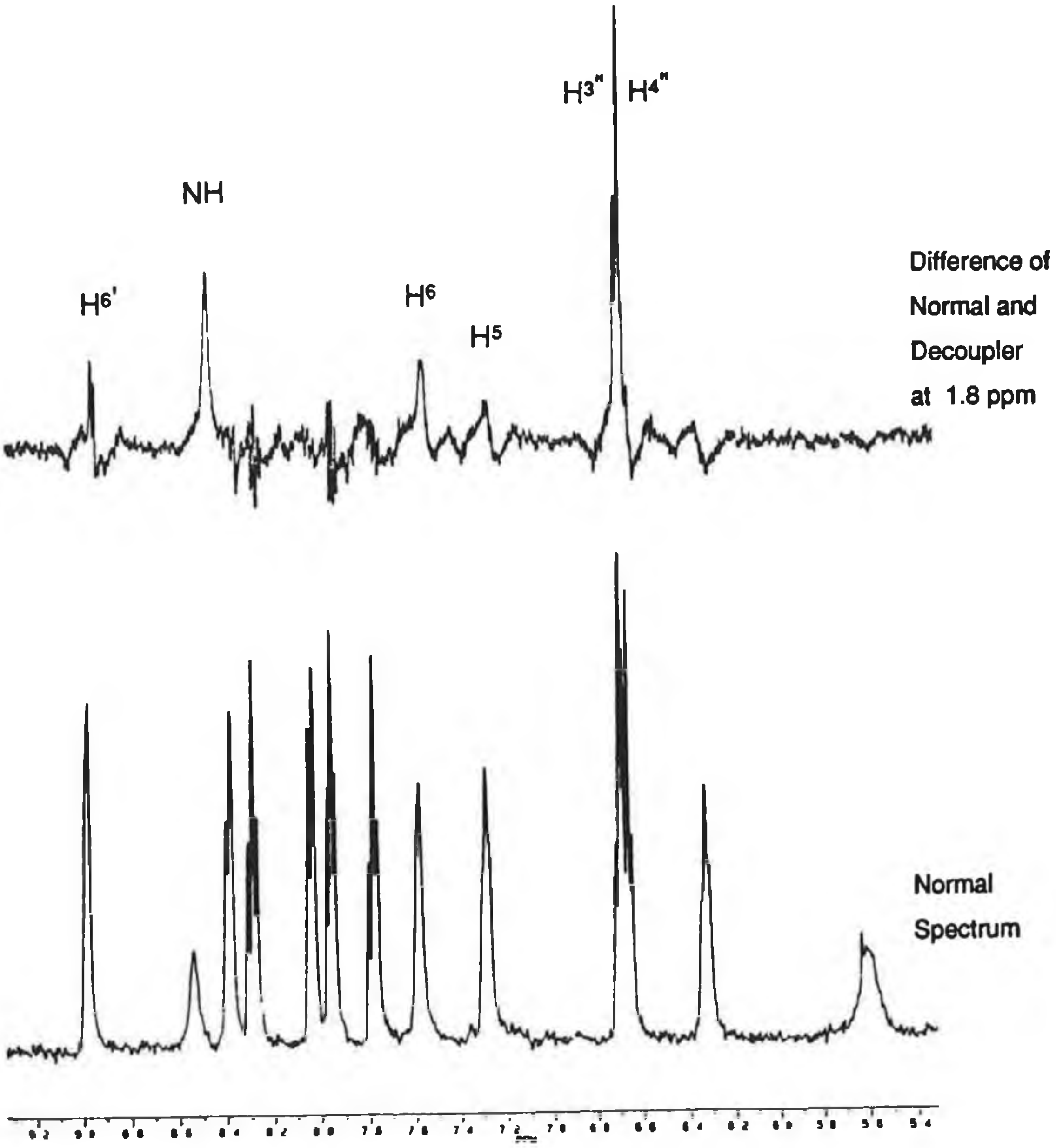


Figure [3.10] Difference NOE Spectrum for $[Ru(bipy)_2(ddoth)](PF_6)_2$ (344) (Acetone-d_6)

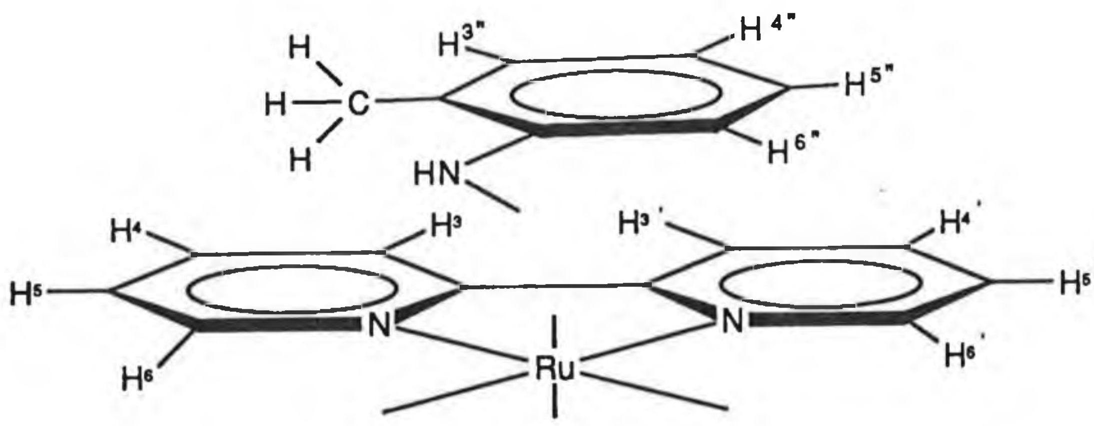
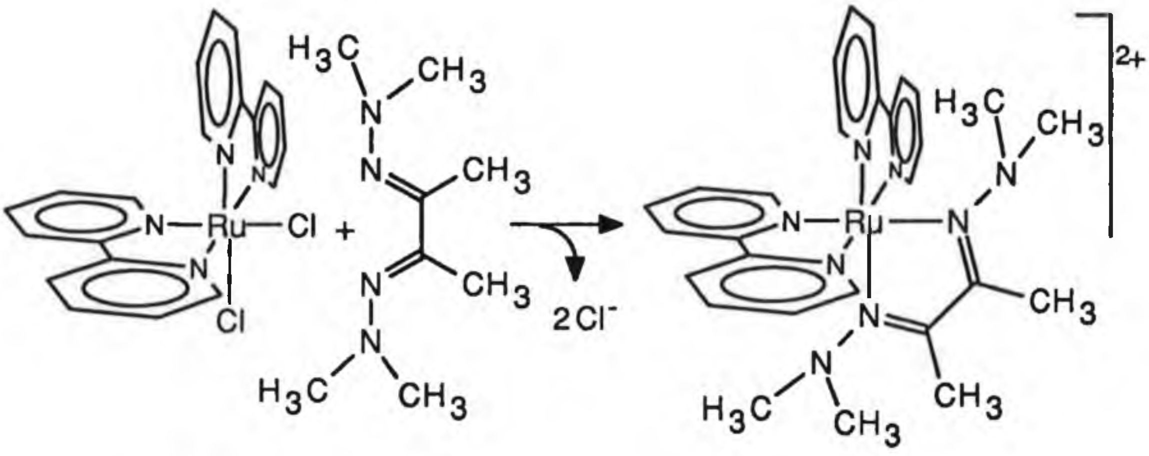


Figure [3.11] Orientation of o-tolyl groups with respect to bipyridyl groups

3.2.4 PREPARATION AND CHARACTERISATION OF [RU(BIPY)$_2$(DDMH)](PF$_6$)$_2$

The ligand **(129)** which contains no aromatic moiety allowed the preparation of a complex not possessing phenyl rings. Diacetyldi(N,N-dimethylhydrazone) (ddmh) **(129)** refluxed with rutheniumbis(2,2'-bipyridyl)dichloride for 48 hours produces rutheniumbis(bipyridyl)diacetyldi(N,N-dimethylhydrazone)bis(hexafluorophosphate) **(345)**, according to scheme [3.5].



(348) **(129)** **(345)**

Scheme [3.5]

The reaction was monitored by HPLC, and after removal of excess ligand by extraction, the product was precipitated into water solution as the PF_6^- complex. The product was found to be HPLC pure with satisfactory elemental analysis.

UV/Vis. Analysis and Emission Analysis

UV/Vis. spectra of the free ligand (ddmh) **(129)** and the complex [Ru(bipy)$_2$(ddmh)](PF$_6$)$_2$ **(345)** in acetonitrile were obtained. For the free ligand (ddmh) **(129)**, absorption bands were observed at 220 nm and 320 nm. For the complex, the ligand centred π to π^* transitions are found to occur at 285 nm[166]. The band at wavelength 455 nm is assigned to the MLCT transition. [Ru(bipy)$_2$(ddmh)](PF$_6$)$_2$ **(345)**, displayed no emission on excitation at 455 nm and scanning from 480-800 nm.

Photolysis of $[Ru(bipy)_2(ddmh)](PF_6)_2$ (345)

A solution of $[Ru(bipy)_2(ddmh)](PF_6)_2$ **(345)** in 0.05 M BTEAC (Cl^-) in dichloromethane was photolysed by irradiation of the sample using a white light source. Monitoring the reaction by HPLC analysis indicates that the complex **(345)** is **not** photostable under these conditions, and decomposes to free ligand and chloride complexes, which contrasts with the previous photostable complexes **(342)**, **(343)** and **(344)**.

The ligand **(129)** is a weaker π-acceptor, (small alkyl groups), than the phenyl containing ligands of complexes **(342)**, **(343)** and **(344)**, which reduces the energy gap between the ^{3}MLCT excited state and the ^{3}MC state. Population of the ^{3}MC state may lead to deactivation of the excited state through thermal processes or photodecomposition of the complex by ligand substitution, (see figure [3.1]).

Electrochemical Analysis of $[Ru(bipy)_2(ddmh)](PF_6)_2$ (345)

Cyclic voltammograms of the ligand (ddmh) **(129)** and of the complex $[Ru(bipy)_2(ddmh)](PF_6)_2$ **(345)** were obtained. Oxidation potentials range from 0 V to +2.0 V and reduction from 0 V to -2.0 V (*versus* SCE). An oxidation potential of 1.30 V is observed for the free ligand (ddmh) **(129)**, whereas no reduction wave potentials are observed. The oxidation CV of the complex **(345)** displays an irreversible wave at a potential +1.30 V .

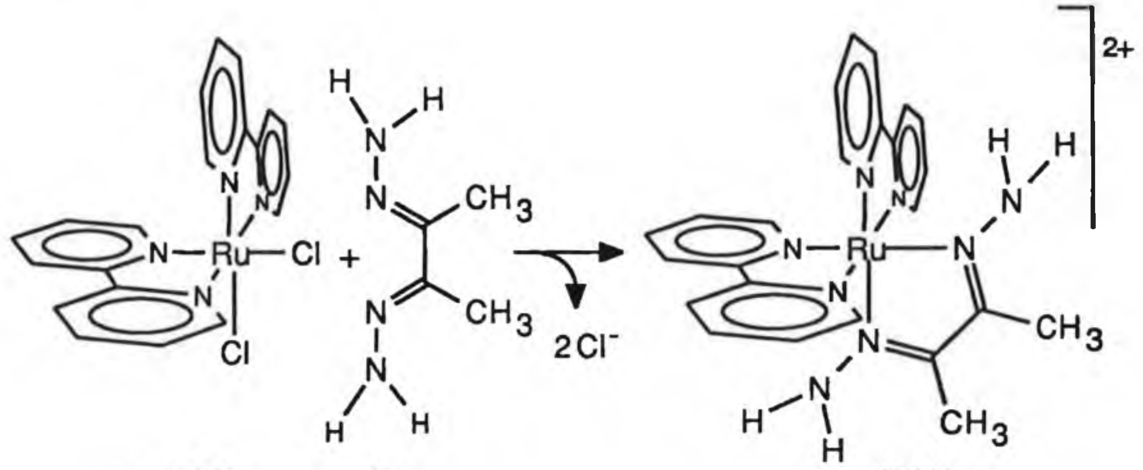
The first reduction wave for $[Ru(bipy)_2(ddmh)](PF_6)_2$ **(345)** is observed at a potential of -1.15 V and is attributed to the reversible reduction of the ligand (ddmh) **(129)**. The reduction potentials at -1.55 V and -1.90 V are assigned to bipy ligands[166]. The ligand (ddmh) **(129)** is a stronger π-acceptor than bipy[175,177-183], but a weaker π-acceptor than the ligands (ddph) **(29)**, (ddmph) **(320)** and (ddoth) **(319)**. Thus the MLCT transition involves excitation of an electron from the d-orbitals of the metal centre to the empty π* orbitals of the ligand (ddmh) **(129)**.

^{1}H NMR Analysis

A ^{1}H NMR and a 2D-COSY NMR spectrum of the complex $[Ru(bipy)_2(ddmh)](PF_6)_2$ **(345)** were obtained in DMSO-d_6. For the hydrazone ligand, the two methyl groups attached to the imine groups appear as a singlet with a chemical shift of 2.73 ppm ($\delta_{(free\ ligand)}$ = 1.90 ppm). This increase in chemical shift between the ligand and the complex is due to the σ-donation to the metal. The four methyl groups attached to the nitrogens of the hydrazone groups appear as a singlet at a chemical shift of 1.90 ppm, ($\delta_{(free\ ligand)}$ = 2.75 ppm), indicating a relatively large change in the proton chemical shift of the methyl groups on complexation to ruthenium. This change in chemical shift may be due to the shielding effect of the bipyridyl groups on the methyl hydrogens, which is in agreement with earlier results where the phenyl hydrogens of the disubstituted hydrazones were also shielded upfield by the bipyridyl groups. Therefore, it can be concluded that the di-hydrazone methyl groups are close in space to the bipyridyl groups. The bipyridyl protons are assigned with the aid of the 2D-COSY spectrum. The H^5 triplet at 7.33 ppm is coupled to both the H^6 proton doublet at 7.67 ppm and the H^4 triplet at 8.05 ppm which is coupled to the H^3 doublet at 8.73 ppm. The $H^{3'}$ doublet at 8.22 ppm is coupled to the $H^{4'}$ triplet at 7.78 ppm, coupled to a second $H^{5'}$ triplet at 8.33 ppm which is coupled to the $H^{6'}$ doublet at 8.88 ppm. No broadening of the spectrum was observed for complex **(345)** from temperatures ranging from 353 K to -243 K.

3.2.5 PREPARATION AND CHARACTERISTICS OF $[RU(BIPY)_2(DDH)](PF_6)_2$

Rutheniumbis(2,2'-bipyridyl)diacetyldihydrazonebis(hexafluorophosphate) **(346)** was prepared by refluxing rutheniumbis(bipyridyl)dichloride with diacetyldihydrazone **(5)** in aqueous ethanol solution, according to scheme [3.6].



(348) **(5)** **(346)**

Scheme [3.6]

The reaction was refluxed for 24 hours, and on completion, the excess ligand was removed by ether extraction. The product was obtained as the (PF_6) complex, followed by recrystallisation from acetone/water to produce relatively large crystals. The complex was found to be HPLC pure, and gave satisfactory elemental analysis.

IR Analysis

The asymmetric and symmetric N-H stretching frequency appear as strong bands at 3330 cm^{-1} and 3193 cm^{-1} respectively, ($\upsilon_{(free\ ligand)}$ = 3398, 3310 cm^{-1}).

UV/Vis. Analysis and Emission Studies

UV/Vis. spectra of the ligand (ddh) **(5)** and the complex $[Ru(bipy)_2(ddh)](PF_6)_2$ **(346)** in acetonitrile were obtained. A band at 265 nm is observed in the spectrum of the free ligand (ddh) **(5)** and is assigned to the π - π^* transitions. In the UV/Vis. spectrum of complex **(346)**, the band at 285 nm is attributed to the ligand centred π to π^* transitions. The intense absorption band at 240 nm and the low energy absorption maximum at 420 nm are assigned to MLCT d to π^* transitions of the complex **(346)**. The band at 420 nm is about 30 nm lower in wavelength, compared to the other substituted dihydrazone derivatives of rutheniumbis(bipyridyl) prepared. This blue shift of the MLCT band suggests that diacetyldihydrazone is a stronger σ-donor than the previous ligands (ddph) **(29)**, (ddmph) **(320)**, (ddoth) **(319)** and (ddmh) **(129)** investigated[166].

No emission was observed either at room temperature or 77 K for $[Ru(bipy)_2(ddh)](PF_6)_2$ **(346)**, and is most likely due to non-emitting properties of the ligand **(5)**.

Photolysis of $[Ru(bipy)_2(ddh)](PF_6)_2$ (346)

Photolysis of a solution of $[Ru(bipy)_2(ddh)](PF_6)_2$ **(346)** in 0.05 M BTEAC (Cl^-) in dichloromethane was carried out by irradiating the sample with a white light source, and monitoring the reaction mixture at thirty minute intervals using cation exchange HPLC. From the results it was found that the complex **(346)** is not photostable under these conditions, and decomposes to free ligand and chloride complexes. This contrasts with the phenyl ring containing complexes **(342)**, **(343)** and **(344)**.

From the electrochemistry data, the ligand (ddh) **(5)** is shown to be a weaker π-acceptor than the ligands (ddph) **(29)**, (ddmph) **(320)**, (ddoth) **(319)** and (ddmh) **(129)**, which causes a decrease in the energy gap between the ^3MLCT π^* excited state and the ^3MC state. Population of the ^3MC state may be responsible for photodecomposition of the complex **(346)**, (see Figure 3.1)[166,175].

Electrochemical Analysis of $[Ru(bipy)_2(ddh)](PF_6)_2$ (346)

Cyclic voltammograms (Oxidation 0 V to +2 V; Reduction 0 V to -2 V *versus* SCE) of the ligand (ddh) **(5)** and of the complex $[Ru(bipy)_2(ddh)](PF_6)_2$ **(346)** are obtained in 0.1 M TEAP in CH_3CN. The free ligand (ddh) **(5)** shows an oxidation potential at 1.30 V, but no reduction wave potentials were observed. The metal based oxidation potential of the complex $[Ru(bipy)_2(ddh)](PF_6)_2$ **(346)** occurs at 1.20 V and is lower than that of $[Ru(bipy)_3]^{2+}$ **(341)**, which has an oxidation potential of 1.26 V *versus* SCE[166]. Oxidation of the coordinated ligand (ddh) **(5)** in the complex $[Ru(bipy)_2(ddh)](PF_6)_2$ **(346)** occurs at 1.40 V, which is 100 mV higher than that of the free ligand. This increase in potential on complexing is due to electron donation by the ligand (ddh) **(5)** to the metal in the complex **(346)** making it more difficult to oxidise (ddh) **(5)**.

The first reduction potential for $[Ru(bipy)_2(ddh)](PF_6)_2$ **(346)** is observed at a potential of -1.30 V and assigned to the irreversible reduction of the ligand (ddh) **(5)**. The reduction potentials at -1.45 V and -1.70 V are assigned to the bipy ligands(166). Diacetyldihydrazone **(5)** is a weaker π-acceptor than the previously discussed hydrazone derivatives, (ddph) **(29)**, (ddmph) **(320)**, (ddoth) **(319)** and (ddmh) **(129)** which possibly explains the 30 nm blue shift of the MLCT band observed in the UV/Vis. spectrum of $[Ru(bipy)_2(ddh)](PF_6)_2$ **(346)**.

^{1}H NMR Analysis

A singlet at a chemical shift of 2.50 ppm is assigned to the two methyl groups, ($\delta_{\text{(free ligands)}}$ = 2.00 ppm). This increase in the chemical shift on complexing to ruthenium is due to the decrease in electron density around the methyl groups after the σ-donation by the ligand. The N-H protons appear as a singlet at a chemical shift of 6.54 ppm, ($\delta_{\text{(freeligand)}}$ = 5.80 ppm), demonstrating that there is also a decrease in electron density around the N-H region of the ligand. This coincides with the fact that the λ_{max} of the UV/Vis. spectrum was low, suggesting that the ligand was a good σ-donor and a poor π-acceptor. The bipyridyl protons are identified from a 2D-COSY spectrum, figure [3.12].

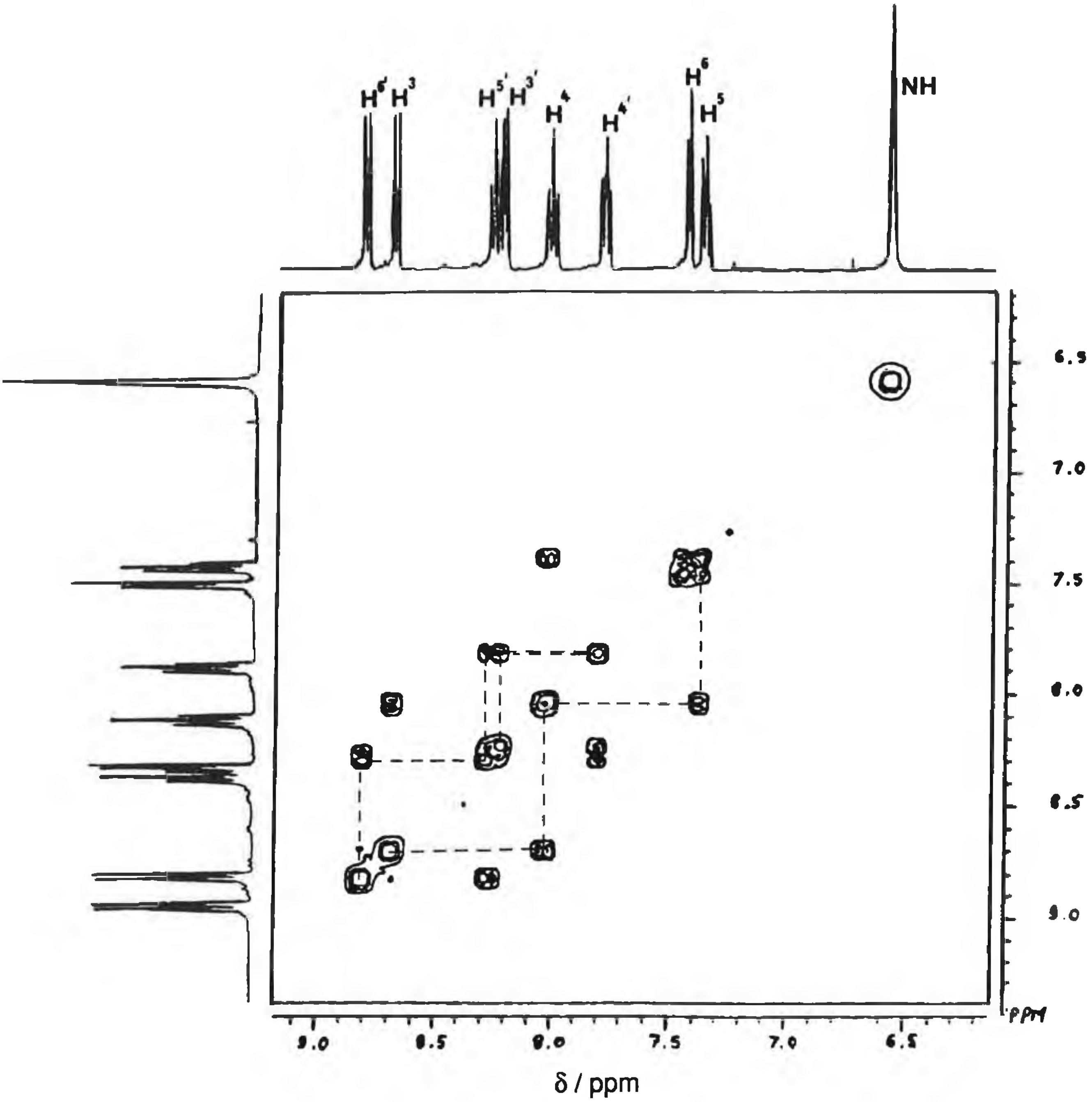


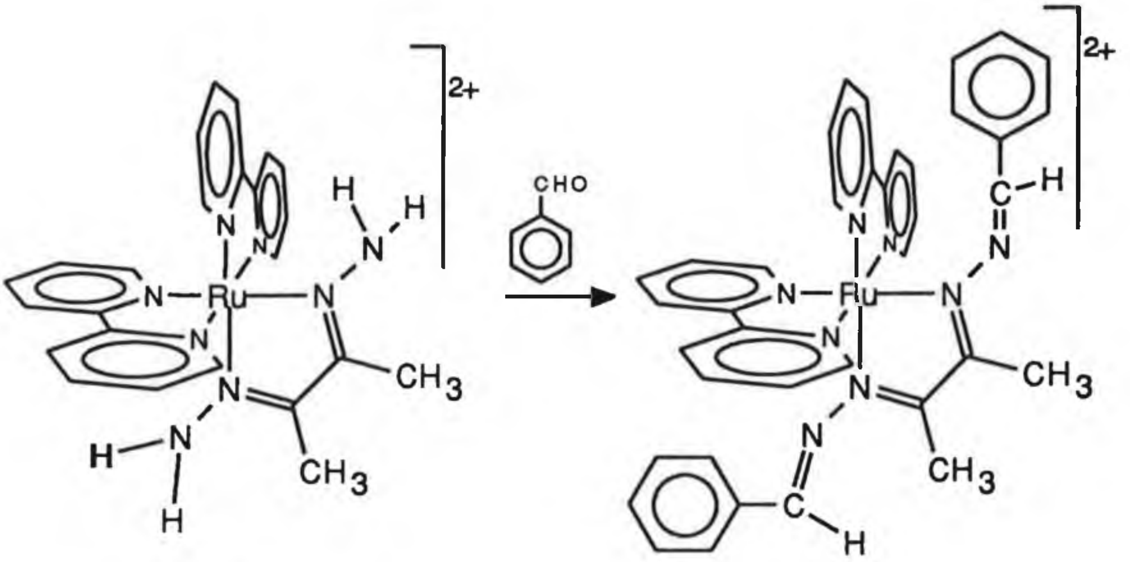
Figure [3.12] COSY Spectrum of [Ru(bipy)$_2$(ddh)](PF$_6$)$_2$ in DMSO-d$_6$ @ 293 K

The H^6 doublet at 7.44 ppm is coupled to the H^5 triplet at 7.36 ppm, coupled to H^4 triplet at 8.02 ppm, which is coupled to the H^3 doublet at 8.68 ppm. The $H^{6'}$ doublet at 8.80 ppm is coupled to the $H^{5'}$ triplet at 8.26 ppm, coupled to $H^{4'}$ triplet at 7.78 ppm coupled to the $H^{3'}$ doublet at 8.22 ppm.

3.2.6 PREPARATION AND CHARACTERISATION OF [Ru(bipy)$_2$(ddba)](PF$_6$)$_2$

The possibility of reacting the two primary amine groups of [Ru(bipy)$_2$(ddh)](PF$_6$)$_2$ **(346)**, with a carbonyl group and thus allow the diacetyldihydrazone ligand to serve as an anchoring ligand was investigated. Potential applications might be its use as a tool for binding catalysts to an insoluble polymeric material, which would facilitate recovery of catalysts or to bind diacetyldihydrazone to a radioactive metal such as ^{97}Ru, which could be bound to biological materials and act as a marker.

A simple method to test the reactivity of the amino groups of [Ru(bipy)$_2$(ddh)](PF$_6$)$_2$ **(346)**, was by examining their reaction with benzaldehyde. Refluxing a solution of [Ru(bipy)$_2$(ddh)](PF$_6$)$_2$ **(346)** with benzaldehyde in ethanol/acetonitrile/acetic acid, (3:2:2) for 120 hours produces rutheniumbis(bipyridyl)diacetyldi(benzylazine)bis(hexafluorophosphate) **(347)**, which show that the amino groups of the complex [Ru(bipy)$_2$(ddh)](PF$_6$)$_2$ **(346)** were capable of reacting with carbonyl groups, according to scheme [3.7].

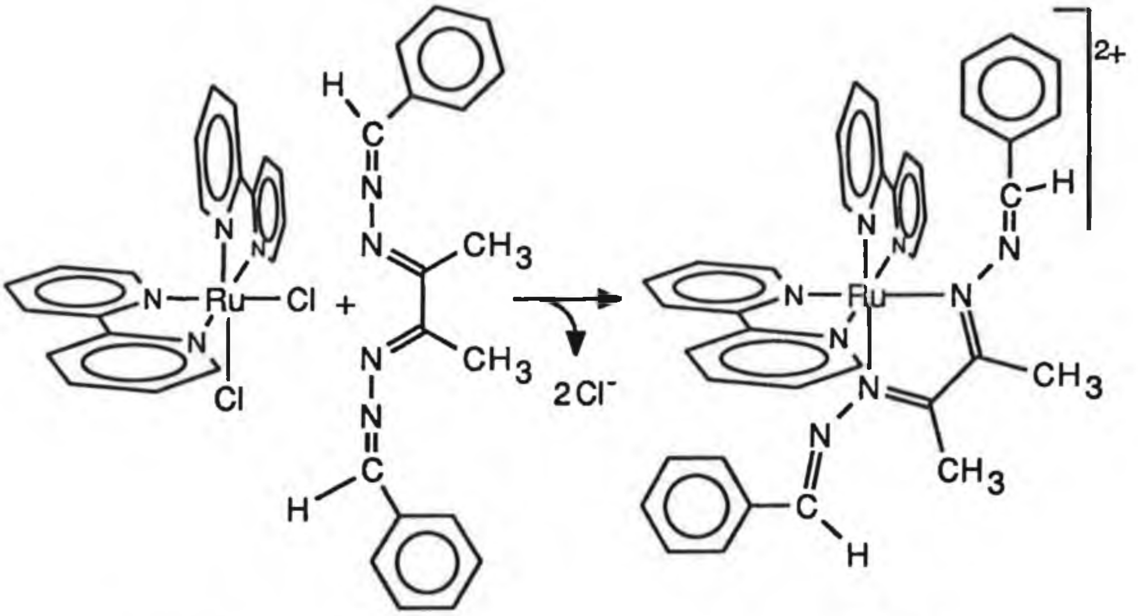


(346) **(247)**

Scheme [3.7]

The reaction was carried out in less polar solvents as the starting material [Ru(bipy)$_2$(ddh)](PF$_6$)$_2$ **(346)** was insoluble in water/ethanol mixture. Acetone was not used as a reaction solvent for fear of the amino groups of the complex reacting with acetone on refluxing. The reaction was monitored by cation exchange HPLC, and the decrease in the peak intensity of the starting material **(346)** (retention time = 5.1 min.), was observed with concomitant increase in the peak intensity of the product $[Ru(bipy)_2(ddba)](PF_6)_2$ **(347)** (retention time = 2.2 min.). The product was isolated as the (PF_6) complex, and satisfactory microanalysis results were obtained.

An alternative route to the complex **(347)** was using diacetyldi(benzylazine) **(327)** as starting ligand. Refluxing diacetyl(dibenzylazine) with rutheniumbis(bipyridyl)dichloride produces the complex $[Ru(bipy)_2(ddba)](PF_6)_2$ **(347)**, according to scheme [3.8].



(348) **(327)** **(347)**

Scheme [3.8]

The reaction mixture was refluxed for 120 h, and the excess ligand was removed by extraction. The product was isolated as the (PF_6) complex, and analysis of the product at this stage by HPLC, indicated that there was an impurity in the product. The product was purified using semi-preparative cation exchange HPLC.

The product obtained from semipreparative HPLC was isolated by removing the solvents under vacuum, dissolving the residue in a minimum amount of acetone and precipitating into an aqueous NH_4PF_6 solution. Following satisfactory C,H,N elemental analysis results for the product, comparison of the UV/Vis. data, infrared spectrum, NMR spectrum showed the product was identical to **(347)** as obtained by [3.7]. Thus, the amine groups of diacetyldihydrazone have the potential to react with carbonyl groups both before and after complexation to ruthenium.

UV/Vis. and Emission Analysis of [Ru(bipy)$_2$(ddba)](PF$_6$)$_2$ (347)

UV/Vis. spectra of the ligand (ddba) **(327)** and of the complex [Ru(bipy)$_2$(ddba)](PF$_6$)$_2$ **(347)** in acetonitrile were obtained. The bands at 200 nm and 340 nm of the ligand **(327)** were assigned to π to π^* transitions. The peak at 285 nm in the spectrum of the complex **(347)** is assigned to the π to π^* transitions of the (bipy) ligands of **(347)**(166). The main lower energy peak at 450 nm in the UV/Vis. spectrum of the complex **(347)**, is assigned to the MLCT band. A change from 420 nm in the precursor complex **(346)** to 450 nm in complex **(347)** demonstrates how the characteristics of the complexes could easily be altered by the conversion of the hydrazone ligand (ddh) **(5)** into the azine ligand **(327)**. The reason for this 30 nm red shift of the MLCT band is because the ligand (ddba) **(327)** of complex **(347)** is a stronger π-acceptor than the ligand (ddh) **(5)** of complex **(346)**.

Ru(bipy)$_2$(ddba)](PF$_6$)$_2$ **(347)** does not exhibit any emission at room temperature or at 77 K after excitation at 450 nm, scanning for emission between 480 nm and 800 nm.

Photolysis of [Ru(bipy)$_2$(ddba)](PF$_6$)$_2$ (347)

Photolysis of a solution of [Ru(bipy)$_2$(ddba)](PF$_6$)$_2$ **(347)** in 0.05 M BTEAC (Cl$^-$) in dichloromethane by irradiation of the sample using a white light source, and monitoring the reaction mixture by HPLC indicates that the complex **(347)** is photostable under these conditions for at least 5 hours.

From the electrochemistry of the complex **(347)**, the ligand (ddba) **(327)** is a strong π-acceptor, which would cause a decrease in the energy of the ^{3}MLCT. This may possibly lead to a larger energy gap between the ^{3}MLCT and the ^{3}MC, thus preventing population of the ^{3}MC state which is normally responsible for photodecomposition of complexes(166), (see figure 3.1).

Electrochemical Analysis of [Ru(bipy)$_2$(ddba)](PF$_6$)$_2$ (347)

Cyclic voltammetry (Oxidation 0 V to +2 V; Reduction 0 V to -2 V *versus* SCE) was carried out on the ligand (ddba) **(327)** and on the complex [Ru(bipy)$_2$(ddba)](PF$_6$)$_2$ **(347)** in 0.1 M TEAP in CH$_3$CN. No oxidation potential was observed for the free ligand (ddba) **(327)**. The metal based oxidation potential of [Ru(bipy)$_2$(ddba)](PF$_6$)$_2$ **(347)** occurs as a reversible wave at

1.40 V which is 0.17 V higher than that of $[Ru(bipy)_3]^{2+}$ **(341)** under the same conditions[166].

The ligand (ddba) **(327)** is the only ligand of the series studied which displays a reduction potential between 0 V and -2.0 V. An irreversible reduction wave is observed at a potential of -1.50 V for the free ligand (ddba) **(327)**, suggesting that the ligand is a much better π-acceptor than bipy, which has a reduction potential of -2.22 V under the same conditions.

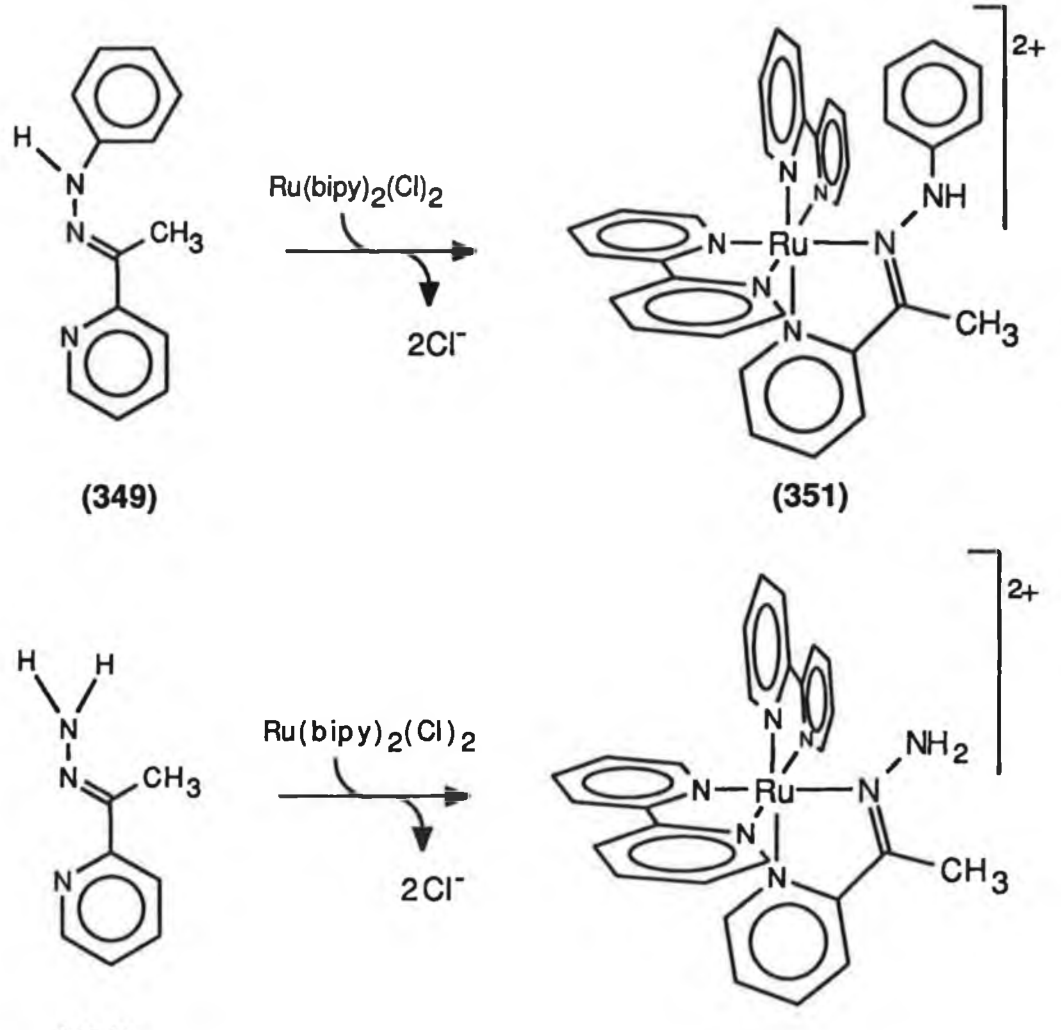
The first reduction potential for $[Ru(bipy)_2(ddba)](PF_6)_2$ **(347)** is observed at a potential of -0.95 V and is attributed to the reversible reduction of the ligand (ddba) **(327)**. The reduction potentials at -1.45 V and -1.70 V are assigned to the bipy ligands[166]. These results indicate that the ligand (ddba) **(327)** is a stronger π-acceptor than both bipy[175,177-184] and (ddh) **(5)** being reduced at lower potentials, ($E_{(ddh)}$ = -1.3 V) which accounts for the 30 nm red shift of the MLCT band observed in the UV/Vis. spectrum of $[Ru(bipy)_2(ddba)](PF_6)_2$ **(347)**, prepared from $[Ru(bipy)_2(ddh)](PF_6)_2$ **(346)**.

^{1}H NMR Analysis

A ^{1}H NMR and a 2D COSY spectrum of the complex $[Ru(bipy)_2(ddba)](PF_6)_2$ **(347)** in DMSO-d_6 was obtained. The singlet at 2.60 ppm is assigned to the two methyl groups, ($\delta_{\text{(free ligand)}}$ = 2.25 ppm). This increase in chemical shift value on complexing is due to the σ-donation by the ligand to ruthenium reducing the electron density around the methyl groups. A multiplet at a chemical shift of 7.3-7.5 ppm is attributed to the ten phenyl protons of the diacetyldibenzylazine **(327)**. A singlet at a chemical shift of 7.70 ppm is attributed to the =CH- moiety of the (ddba). From the 2D COSY the bipyridyl proton resonances were assigned. The H^6 doublet at 7.63 ppm is coupled to H^5 triplet at 7.28 ppm, coupled to H^4 triplet at 7.82 ppm, which is coupled to the H^3 doublet at 8.54 ppm. The $H^{6'}$ doublet at 8.78 ppm is coupled to the $H^{5'}$ triplet at 8.36 ppm, coupled to the $H^{4'}$ triplet at 7.89 ppm, which is in turn coupled to $H^{3'}$ doublet at 8.67 ppm.

3.2.7 RELATED RUTHENIUM DERIVATIVES

In a study to explore the contribution of the hydrazone ligands to the properties of ruthenium complexes **(342)** - **(347)** described, complexes of the type **(351)** and **(352)** were synthesised. The ligand **(349)** is effectively a "half" bipy, "half" hydrazone ligand having both an acetylphenylhydrazone and a bipyridyl group. 2-acetylpyridine-phenylhydrazone (apph) **(349)** and 2-acetylpyridinehydrazone (aph) **(350)** were prepared followed by the synthesis of their rutheniumbis(bipyridyl) complexes [Ru(bipy)$_2$(apph)](PF$_6$)$_2$ **(351)** and [Ru(bipy)$_2$(aph)](PF$_6$)$_2$ **(352)**, according to schemes [3.9].



(349) **(351)**

(350) **(352)**

Scheme [3.9]

The synthesis and characterisation of the complexes **(351)** and **(352)** was carried out in collaboration with A. Fernandez Martinez. The results have been submitted as part component for an M.Sc. in Instrumental Analysis at DCU.

Complexes **(351)** and **(352)** were fully characterised, by IR, NMR, UV/Vis. and emission spectroscopy and C,H,N elemental analyses.

UV/Vis. and Emission Analysis of [Ru(bipy)$_2$(apph)](PF$_6$)$_2$ (351)

UV/Vis. absorption spectra of the ligand (apph) **(349)** and of the complex [Ru(bipy)$_2$(apph)](PF$_6$)$_2$ **(351)** were obtained in acetonitrile. The $\pi - \pi^*$ transitions of the free ligand (apph) **(349)** occur at 350 nm. For complex **(351)**, the absorption band at 285 nm is assigned to the LC π to π^* transitions[166]. The metal-to-ligand charge transfer band (MLCT) is observed at 445 nm, and a shoulder at 345 nm is assigned to the MC transitions.

On excitation of [Ru(bipy)$_2$(apph)](PF$_6$)$_2$ **(351)** at 445 nm and scanning for emission from 480-800 nm, emission peaks are observed at 670 nm, (293 K). Low temperature (77 K) emission studies show emission at 595 nm.

Photolysis of [Ru(bipy)$_2$(apph)](PF$_6$)$_2$ (351)

Photolysis of [Ru(bipy)$_2$(apph)](PF$_6$)$_2$ **(351)** in 0.05 M BTEAC in dichloromethane, indicates that the complex is not photostable under these conditions, most likely due to population of the ^{3}MC state which leads to photodecomposition of the complex **(351)**.

Progress of the photolysis was monitored by cation exchange HPLC, using a mobile phase of (80/20 v/v) acetonitrile/water 0.08 M LiClO$_4$. The chromatograms of the reaction mixture after various time intervals; **(a)** 0 min., **(b)** 30 min. and **(c)** 120 min. are displayed in figure [3.13]. These traces, **(a)** to **(c)** of figure [3.13], are a typical representation of the degradation of these types of complexes. Trace **(a)** shows a single peak, (peak 3), for complex **(351)** before photolysis. After 30 min. of irradiation of the sample, trace **(b)** shows that significant decomposition of [Ru(bipy)$_2$(apph)](PF$_6$)$_2$ **(351)** (peak 3) has occurred, degrading into free ligand (peak 1) and rutheniumchloride derivative (peak 2). After 120 min. of photolysis, trace **(c)** shows that most of the complex (peak 3) has decomposed.

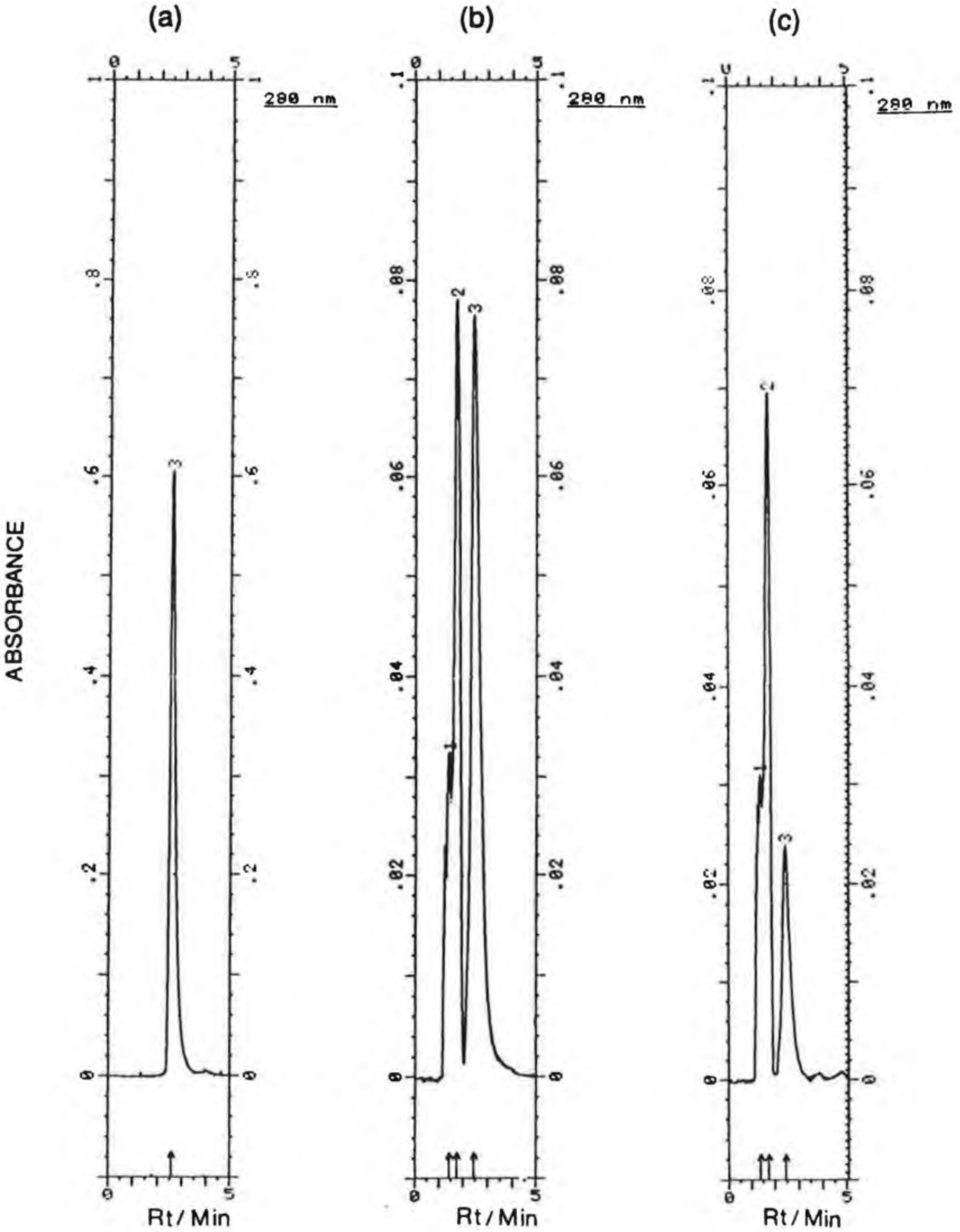


Figure [3.13] **HPLC Chromatograms of Photolysis of (351) in 0.005 M Cl^- in CH_2Cl_2 at; (a) 0 min., (b) 30 min. and (c) 120 min.**

Electrochemical Analysis of $[Ru(bipy)_2(apph)](PF_6)_2$ (351)

Oxidation (0 to +2.0 V) and reduction (0 to -2.0 V *versus* SCE) cyclic voltammetry was carried out on (apph) **(349)** and on the complex $[Ru(bipy)_2(apph)](PF_6)_2$ **(343)** in 0.1 M TEAP in CH_3CN. No reduction potential waves are observed for the free ligand **(349)**. For the complex **(343)**, the first oxidation potentials of the CV occurs at 1.15 V which is most likely due to irreversible oxidation of the amino group of the ligand (apph) **(349)**. The reversible oxidation wave potentials at 1.65 V is thought to be the reversible oxidation of Ru(II) to Ru(III).

The first reduction potential observed for $[Ru(bipy)_2(apph)](PF_6)_2$ **(351)** occurred at -1.20 V is assigned to the reversible reduction of the ligand (apph) **(349)**. The remaining reduction potentials at -1.60 V and -1.90 V are likely to be bipy based[166]. The ligand (apph) **(349)** is a stronger π-acceptor than bipy, being reduced at less negative potentials. Thus the energy level of the lowest ^{3}MLCT state of the complex **(351)**, (see Figure [3.1]), is lower than that of $[Ru(bipy)_3]^{2+}$ **(341)** but higher than the complexes containing the ligands (ddph) **(29)**, (ddmph) **(320)**, (ddoth) **(319)**, (ddmh) **(129)** and (ddba) **(327)**. This small difference in the energy of the MLCT excited state may account for the photodecomposition of the complex $[Ru(bipy)_2(apph)](PF_6)_2$ **(351)**, and the small blue shift in the absorption spectrum.

UV/Vis. and Emission Analysis of $[Ru(bipy)_2(aph)](PF_6)_2$ (352)

A UV/Vis. absorption spectrum of $[Ru(bipy)_2(aph)](PF_6)_2$ **(352)** in acetonitrile was obtained. The LC π to π* transitions are assigned to the band at 285 nm. A metal-to-ligand charge transfer band at 440 nm is observed, a 15 nm blue shift compared to complexes **(342)** - **(345)** and **(347)** is possibly due to the weaker π-accepting properties of the ligand (aph) **(350)** in complex **(352)**.

Excitation of $[Ru(bipy)_2(aph)](PF_6)_2$ **(352)** at 440nm produces an emission band at 660 nm, (293 K), and at low temperature (77 K) an emission band is observed at 604 nm. The emission spectrum (480 - 800 nm) at 77 K is depicted in figure [3.14].

Photolysis of $[Ru(bipy)_2(aph)](PF_6)_2$ (352)

Photolysis of $[Ru(bipy)_2(aph)](PF_6)_2$ **(352)** in 0.05 M Cl^- in dichloromethane, indicates that the complex is not photostable under these conditions. Population of ^{3}MC excited state its likely to be responsible for the photodecomposition of the complex **(352)**, (see Figure [3.1]), as the ligand (aph) **(350)** is a weaker π-acceptor than the previous ligand examined, (apph) **(349)**.

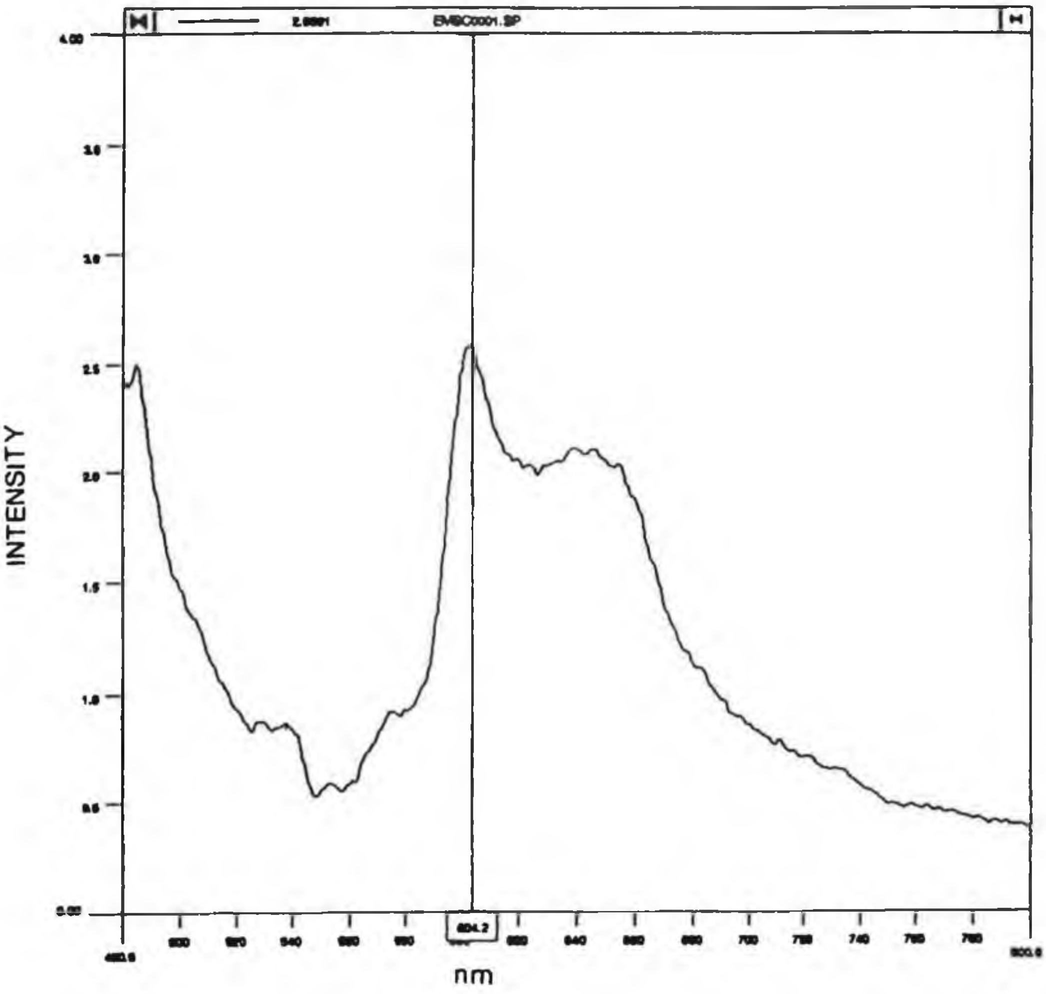


Figure [3.14] **Emission Spectrum of Complex (352) at 77 K in Ethanol**

Electrochemical Analysis of [Ru(bipy)$_2$(aph)](PF$_6$)$_2$ (352)

Cyclic voltammetry ranging from oxidation 0 V to +2.0 V and reduction 0 V to -2.0 V (*versus* SCE), was carried out on the free ligand (aph) **(350)** and on the complex [Ru(bipy)$_2$(aph)](PF$_6$)$_2$ **(352)**. A single oxidation potential of the CV occurs at 1.30 V which is most likely metal based oxidation of Ru(II) to Ru(III). Reversible reduction of the ligand (aph) **(350)** is observed for [Ru(bipy)$_2$(aph)](PF$_6$)$_2$ **(352)** at -1.30 V. The reduction potentials at -1.50 V and -1.75 V are most likely to be bipy based[166]. The ligand (aph) **(350)** is a stronger π-acceptor than bipy[175], causing the energy level of the ^{3}MLCT excited state to be only slightly lower than that of [Ru(bipy)$_3$]$^{2+}$ **(341)**.

3.3 X-ray Crystal Structure Of $[Ru(bipy)_2(ddph)](PF_6)_2$ (342)

The crystal structure of the cation is illustrated in figure [3.15] and crystal data, atomic coordinates, bond lengths, bond angles, anisotropic and isotropic thermal parameters are given in the appendix. The crystal used for analysis was formed by slow recrystallisation of a dilute solution of the complex $[Ru(bipy)_2(ddph)](PF_6)_2$ **(342)** from acetone/toluene. The crystal diffracted very strongly and to a high Bragg angle.

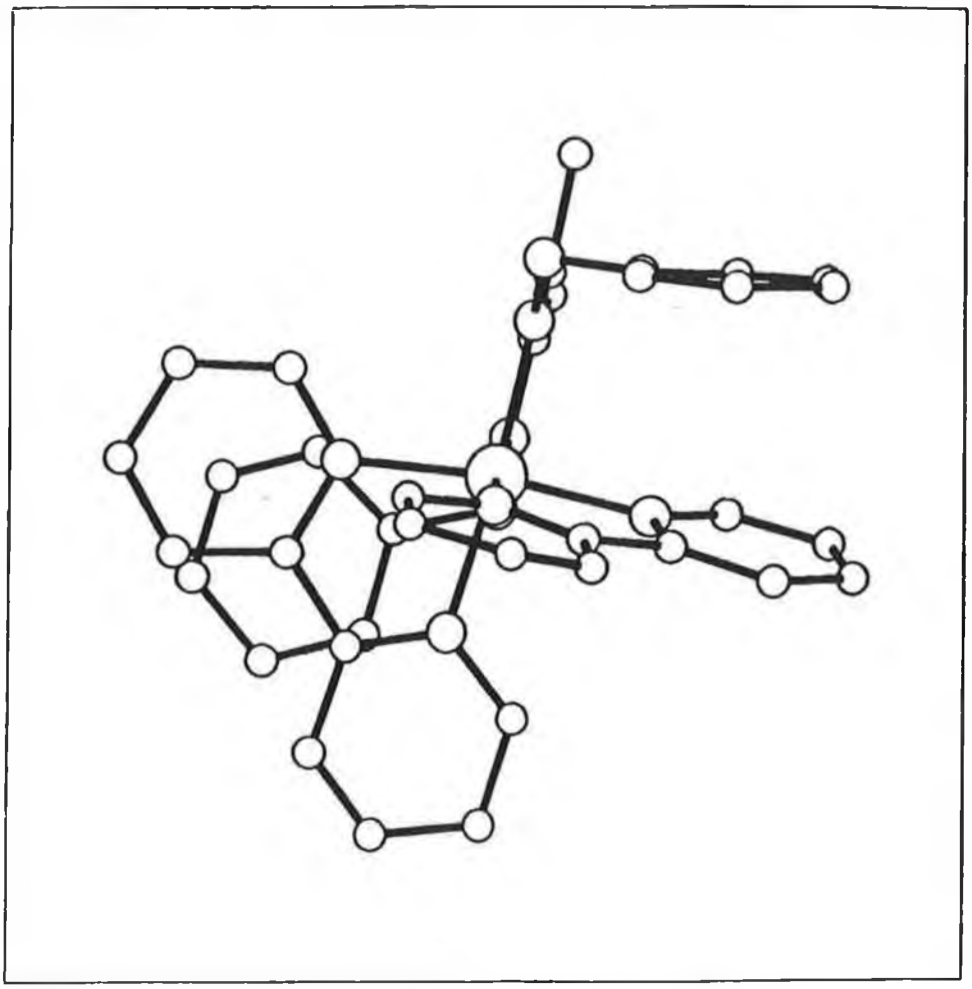


Figure [3.15] **Structure Of $[Ru(bipy)_2(ddph)](PF_6)_2$ with thermal ellipsoids shown**

The crystal structure was determined by;

Professor P. Mc Ardle of Chemistry Department, University College, Galway, and
Professor G. Ferguson of Chemistry Department, University of Guelph, Guelph, Ontario, Canada, N1G 2W1.

The asymmetric unit consists of half of the cation, one anion (with 9:1 disorder about one of the F-P-F directions), and one toluene of solvation with a site occupancy of 0.5. The complex exhibits pseudo-octahedral geometry with the ruthenium ion bound to two bipyridyl rings orientated in a *cis*-configuration along with diacetyldiphenylhydrazone coordinated by the N(1) nitrogens. The complex is symmetric with one of the phenyl rings lying directly over each bipyridyl ring. A selection of the relevant bond lengths are listed in table [3.1]

Table [3.1] **Selected Bond Lengths (Å) of $[Ru(bipy)_2(ddph)](PF_6)_2$**

Ru(1) --N(1)	2.013(3)	Ru(1) --N(3)	2.060(3)
Ru(1) --N(4)	2.081(3)	N(1) --N(2)	1.444(3)
N(1) --C(1)	1.296(5)	N(2) --C(11)	1.439(5)
N(3) --C(32)	1.349(5)	N(3) --C(36)	1.347(5)
N(4) --C(22)	1.323(5)	N(4) --C(26)	1.350(5)
C(1) --C(2)	1.490(5)	C(1) --C(1)	1.487(6)
C(11) --C(12)	1.374(5)	C(11) --C(16)	1.378(5)
C(12) --C(13)	1.371(6)	C(13) --C(14)	1.374(8)
C(14) --C(15)	1.380(9)	C(15) --C(16)	1.376(7)
C(22) --C(23)	1.398(6)	C(22) --C(32)	1.461(6)
C(23) --C(24)	1.348(8)	C(24) --C(25)	1.390(8)
C(25) --C(26)	1.385(6)	C(32) --C(33)	1.393(6)
C(33) --C(34)	1.359(7)	C(34) --C(35)	1.403(8)
C(35) --C(36)	1.363(6)		

The bond lengths for the diacetyldiphenylhydrazone **(29)** to ruthenium are significantly shorter, Ru-N(1) = 2.013(3) Å, compared to the ruthenium-nitrogen bond lengths of the bipy which together with electrochemical data indicates that the phenylhydrazone **(29)** has stronger π-acceptor capacities than 2,2'-bipyridyl **(4)**. The bond lengths for the ruthenium to bipyridyl ligands are Ru-N(3) = 2.060(3) Å, and Ru-N(4) = 2.081(3) Å; in good agreement with the value Ru-N = 2.056 Å for $[Ru(bipy)_3](PF_6)_2$(185) and other similar rutheniumbisbipyridyl complexes reported(187-191) indicating that the bipyridyl ligands show little sign of strain or distortion.

Relevant bond angles are listed in table [3.2]. The bite angle of the (ddph) **(29)** coordinating dihydrazone ligand, N(1)-Ru(1)-N(1) is 75.9(2)° compared to a bond angle of 78.1(1)° for the bipyridine chelation to ruthenium N(3)-Ru(1)-N(4), which is normal for these type of compounds.

Table [3.2] **Selected Bond Angles (Degrees) of [Ru(bipy)$_2$(ddph)](PF$_6$)$_2$ (342)**

N(3)	--Ru(1)	--N(1)	97.9(1)	N(4)	--Ru(1)	--N(1)	173.7(1)
N(4)	--Ru(1)	--N(3)	78.1(1)	N(2)	--N(1)	--Ru(1)	124.9(2)
C(1)	--N(1)	--Ru(1)	119.5(2)	C(1)	--N(1)	--N(2)	115.5(3)
N(1)	--Ru(1)	--N(1)	75.9(2)	C(11)	--N(2)	--N(1)	113.4(3)
C(32)	--N(3)	--Ru(1)	115.3(3)	C(36)	--N(3)	--Ru(1)	125.5(3)
C(26)	--N(4)	--Ru(1)	124.4(3)	C(22)	--N(4)	--Ru(1)	115.5(3)
N(4)	--Ru(1)	--N(4)	86.1(1)	C(2)	--C(1)	--N(1)	126.6(3)

Viewing the structure from an alternative angle, figure [3.16], demonstrates how the phenyl ring lies directly over and in the same plane as the bipyridyl groups in solid state and corresponds well with the proposed structure of the complex in solution based on NMR analysis. The hydrogen atoms and numbering scheme have been omitted for clarity.

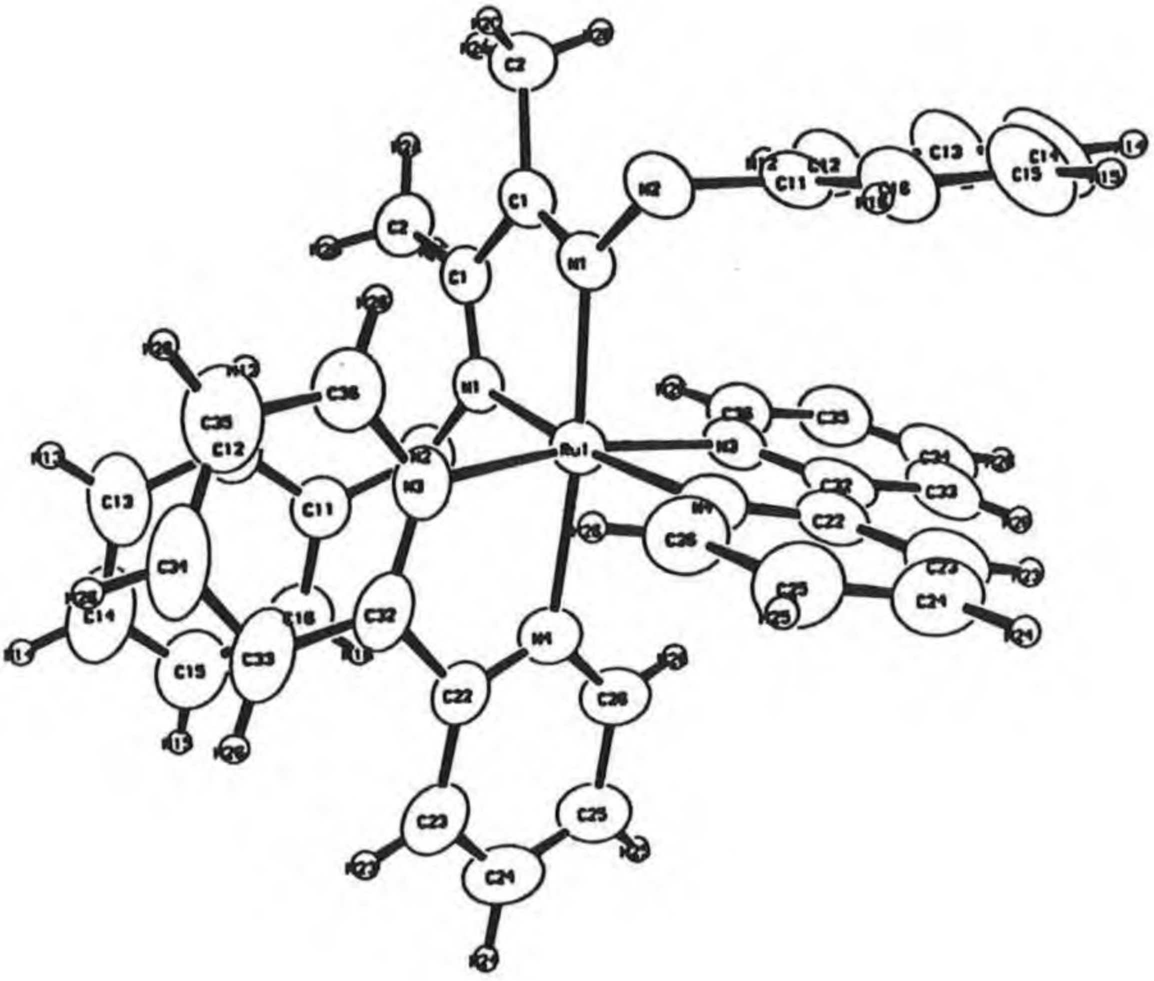


Figure [3.16] **X-ray Crystal Structure Of [Ru(bipy)$_2$(ddph)](PF$_6$)$_2$ (342)**

3.4 VARIABLE TEMPERATURE ^{1}H NMR ANALYSIS OF COMPLEXES

There have been a number of reports on the temperature dependence of NMR spectra of complexes containing an aromatic ring which is free to rotate[192,193]. Pertinent examples include the temperature dependence of the ^{1}H NMR spectra of Ru(diacetyldi(p-tolylimine))Cl_2 where the aromatic group is free to rotate about the N-C bond[192], and the temperature dependence of $[Ru(bipy)_2(p\text{-tolylbipy})](PF_6)_2$ with a freely rotating tolyl ring[193]. The use of dynamic NMR in the characterisation of organometallic compounds is described by Crabtree *et al.*[194,195,196]

Variable Temperature ^{1}H NMR of $[Ru(bipy)_2(ddph)](PF_6)_2$ (342)

^{1}H NMR analysis of the complex $[Ru(bipy)_2(ddph)](PF_6)_2$ **(342)** in DMSO-d_6 was carried out at ten degree intervals in temperature, ranging from 293 K to 403 K. The ortho hydrogens of the phenyl group exhibit a change of 0.12 ppm in chemical shift, appearing as a doublet at 5.80 ppm at 293 K, and a multiplet at 5.92 ppm at 403 K. The meta and para hydrogens also exhibit a similar change in chemical shift, ranging from 6.50 ppm at 293 K, to 6.62 ppm at 403 K. These changes in chemical shift suggest that there is no significant change in orientation of the phenyl ring. Only small changes in the chemical shifts of the bipyridyl protons were observed. The NH broad peak at 293 K, ($\delta = 9.1$ ppm), coalesces to baseline with increase in temperature.

Low temperature NMR studies of complex $[Ru(bipy)_2(ddph)](PF_6)_2$ **(342)** were carried out in acetone-d_6. ^{1}H NMR spectra were collected at temperatures ranging from 293 K to 193 K, and a selection of the aromatic regions of these spectra are depicted in figure [3.17].

On lowering the temperature in ten degree intervals ranging from 293 K to 193 K the ortho phenyl proton resonance broadens significantly (and to a lesser extent the meta/para proton resonances), while undergoing only a small downfield shift. No significant change occurred in the bipyridyl resonances.

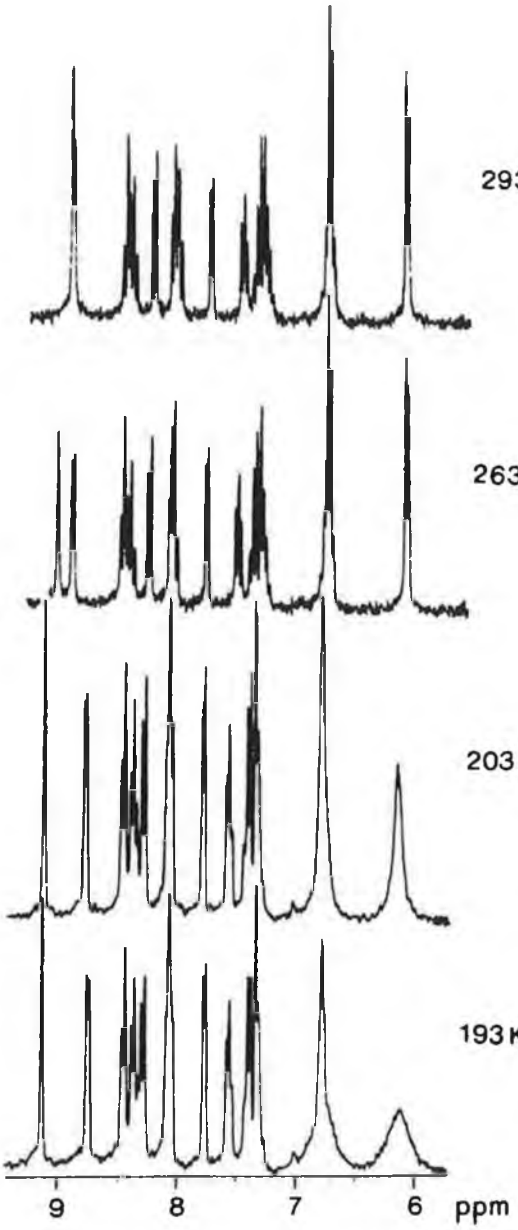


Figure [3.17] Low temperature ^1H NMR spectra of $[Ru(bipy)_2(ddph)](PF_6)_2$ (342)

Variable Temperature ^1H NMR of $[Ru(bipy)_2(ddoth)](PF_6)_2$ (344)

^1H NMR analysis was carried out also on the complex $[Ru(bipy)_2(ddoth)](PF_6)_2$ **(344)** in DMSO-d_6 at temperature intervals, from 293 K to 363 K. No significant change in chemical shift for the diacetyl methyl (2.65 ppm) was observed. The ortho methyls of the phenyl groups of the complex appear as a broad/baseline peak at 1.78 ppm at 293 K. As the temperature is increased (333 K) , the peak becomes sharper. At 373 K, a sharp peak at 1.78 ppm was observed. The broadening of the methyl peak in DMSO occurs within the same temperature region as the aromatic resonance broadening.

A selection of the aromatic regions of the spectra at different temperatures have been overlaid and are displayed in figure [3.18]. Within this temperature range a number of the aromatic peaks exhibit broadening in the lower temperature region. At 303 K, the $H^{6''}$ and $H^{5''}$ phenyl ring proton resonances show broadening at 6.20 ppm and 5.27 ppm, and the H^5 and H^6 at 7.25 ppm of the bipy system also show broadening, the rest of the spectrum remaining sharp. At 333 K, the $H^{5''}$ phenyl proton resonance (6.23 ppm) sharpens to a triplet at the higher temperature, whereas the $H^{6''}$ broad resonance at 5.30 ppm sharpens slightly. At 363 K, the broad peak at 5.30 ppm is resolved into a sharp doublet and the H^5 and H^6 bipy resonance at 7.30 ppm changes from a broad peak at 294 K to a sharp doublet and triplet at 363 K.

Low temperature NMR analysis was also carried out on the complex $[Ru(bipy)_2(ddoth)](PF_6)_2$ **(344)**, at ten degree intervals ranging from 303 K to 213 K, using acetone-d_6 as a solvent. The aromatic region of selected low temperature spectra are also displayed in figure [3.18]. At 303 K, the diacetyl methyl group proton resonance occurs at 2.85 ppm, ($\delta_{(free\ ligand)}$ = 2.22 ppm). This sharp peak does not broaden with decreasing temperature, but does however undergo a small change in chemical shift. At 293 K, the ortho methyl resonance peak appears as a slightly broadened peak at 1.83 ppm. As the temperature is reduced, the peak broadens to baseline, 293 - 273 K. At 253 K, the peak begins to sharpen and is fully resolved at 213 K. A change in chemical shift is observed with reduction in temperature ranging from 1.83 ppm (303 K) to 1.76 ppm (213 K). This decrease in chemical shift with lower temperature may be due to the phenyl group lying closer to the bipy groups causing the ortho methyl group to experience more of the shielding effect.

At 293 K, a number of broad peaks are observed in the aromatic region including the $H^{6''}$ (5.5 ppm) and $H^{5''}$ (6.3 ppm) phenyl proton resonance and the H^6 (7.6 ppm) and H^5 (7.3 ppm) bipy proton resonances and the remaining peaks are relatively sharp. As the temperature is decreased to 273 K, a broadening of a number of peaks occurs. Broadened resonances at 273 K include the $H^{6''}$ and $H^{5''}$ phenyl proton peaks and the $H^{6'}$,$H^{3'}$, H^5 and H^6 bipy resonances. As the temperature is reduced, the peaks begin to resolve and at 253 K, all of the broad peaks are nearly fully resolved, and are completely resolved at 213 K.

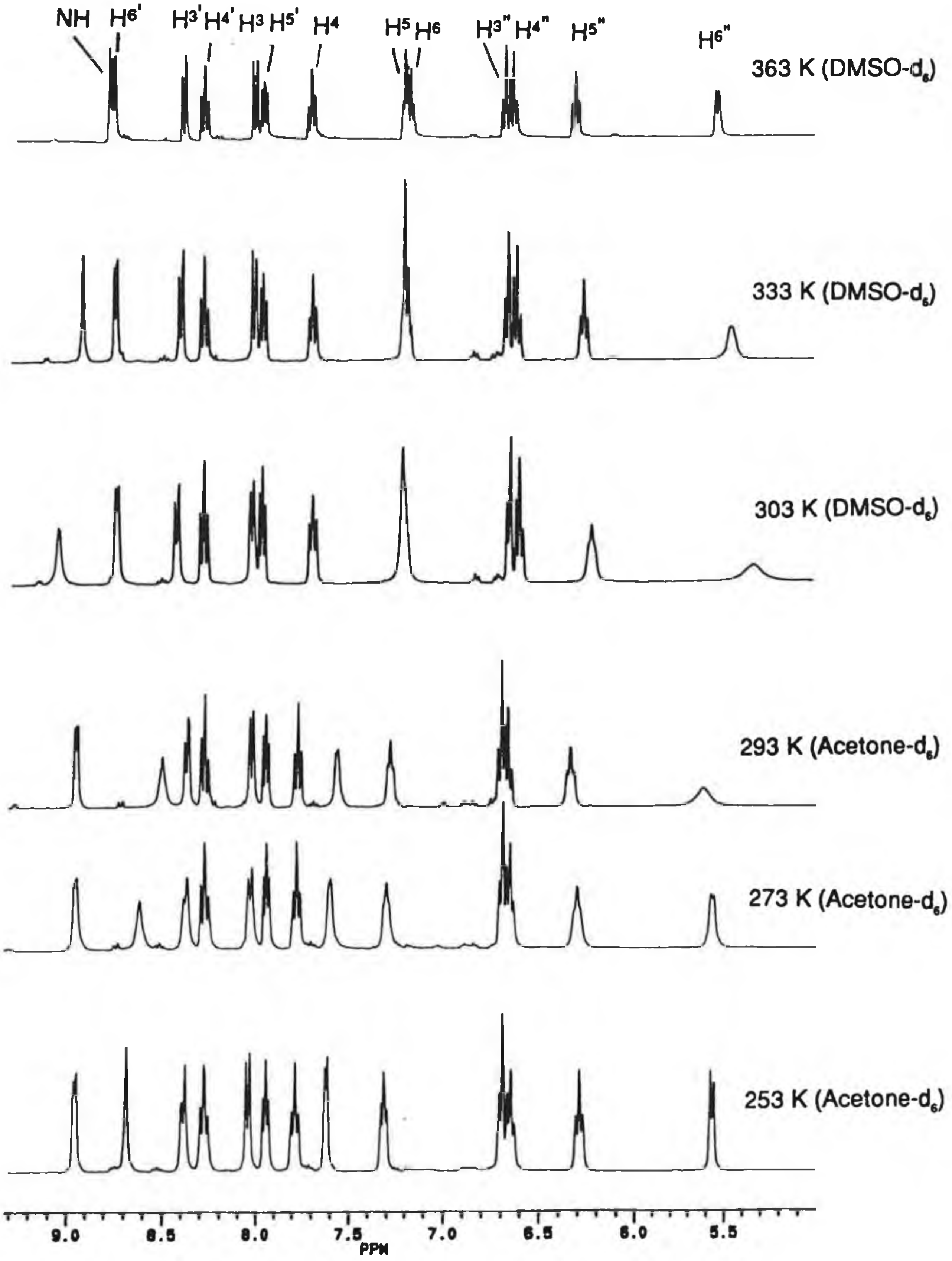


Figure [3.18] ^{1}H NMR of $[Ru(bipy)_2(ddoth)](PF_6)_2$ (344) at various temperatures; Higher Temperatures in DMSO-d_6, Lower Temperatures in Acetone-d_6

Variable Temperature ^{1}H NMR's of [Ru(bipy)$_2$(ddmph)](PF$_6$)$_2$ (343)

The ^{1}H NMR spectrum of the N-methyl containing complex **(343)** at room temperature, (293 K) shows that most of the aromatic peaks are very broad or reduced to baseline for both the bipyridyl and the phenyl groups, with the exception of the $H^{5'}$ and the H^4 bipyridyl proton resonances which occur as the only sharp peaks. For this reason, a number of ^{1}H NMR spectra of [Ru(bipy)$_2$(ddmph)](PF$_6$)$_2$ **(343)** in DMSO-d$_6$ were collected, at various temperature intervals ranging from 293 K to 373 K.

At 293 K, the diacetyl methyl groups appear as a sharp singlet at 2.86 ppm whereas the methyl groups attached to the hydrazone nitrogens, 3.10 ppm are very broad/baseline. At 323 K the broad/baseline peak at 3.10 ppm begins to emerge as a broad peak, and as the temperature is increased, the peak sharpens and is fully resolved at 363 K. The chemical shifts of both methyl resonances do not change significantly. Broadening of the N-methyl peaks occurs at the same temperature (293 K) as the broadening of the bipyridyl and the phenyl resonance peaks. The aromatic regions of the NMR spectra at the various temperatures were overlaid as depicted in figure [3.19].

At 303 K, some of the proton resonances begin to resolve including the $H^{6'}$ and $H^{4'}$ bipyridyl proton peaks, whilst the $H^{3'}$, H^3, H^5 and H^6 of the bipy rings and the phenyl proton resonances remain broad. Between 303 K and 373 K, all the remaining broad peaks are resolved and are fully resolved at 373 K. Only small changes (~0.18) in chemical shift where observed for the spectra at different temperatures. A COSY spectrum was obtained at 363 K and was used to assign the signals.

Low temperature NMR analysis was also carried out on the complex [Ru(bipy)$_2$(ddmph)](PF$_6$)$_2$ **(343)** in Acetone-d$_6$. NMR spectra were collected at ten degree intervals over a temperature range of 313 K to 203 K. At 313 K, the methyl groups of the diacetyl group appears as a singlet at 3.04 ppm, ($\delta_{\text{(free ligand)}}$ = 2.2 ppm). As the temperature is reduced to 203 K, the peak remains sharp without any significant change in chemical shift. At 313 K, the N-methyl resonance occurs as a sharp peak at 3.30 ppm and as the temperature is reduced, the peak at 3.30 ppm broadens and becomes baseline. The peak remains very broad from 293 K to 243 K, at which temperature the peak begins to sharpen and is fully resolved at 203 K. There is also a marginal increase in the chemical shift of the peak with a reduction in temperature changing from 3.30 ppm at 313 K to 3.45 ppm at 203 K.

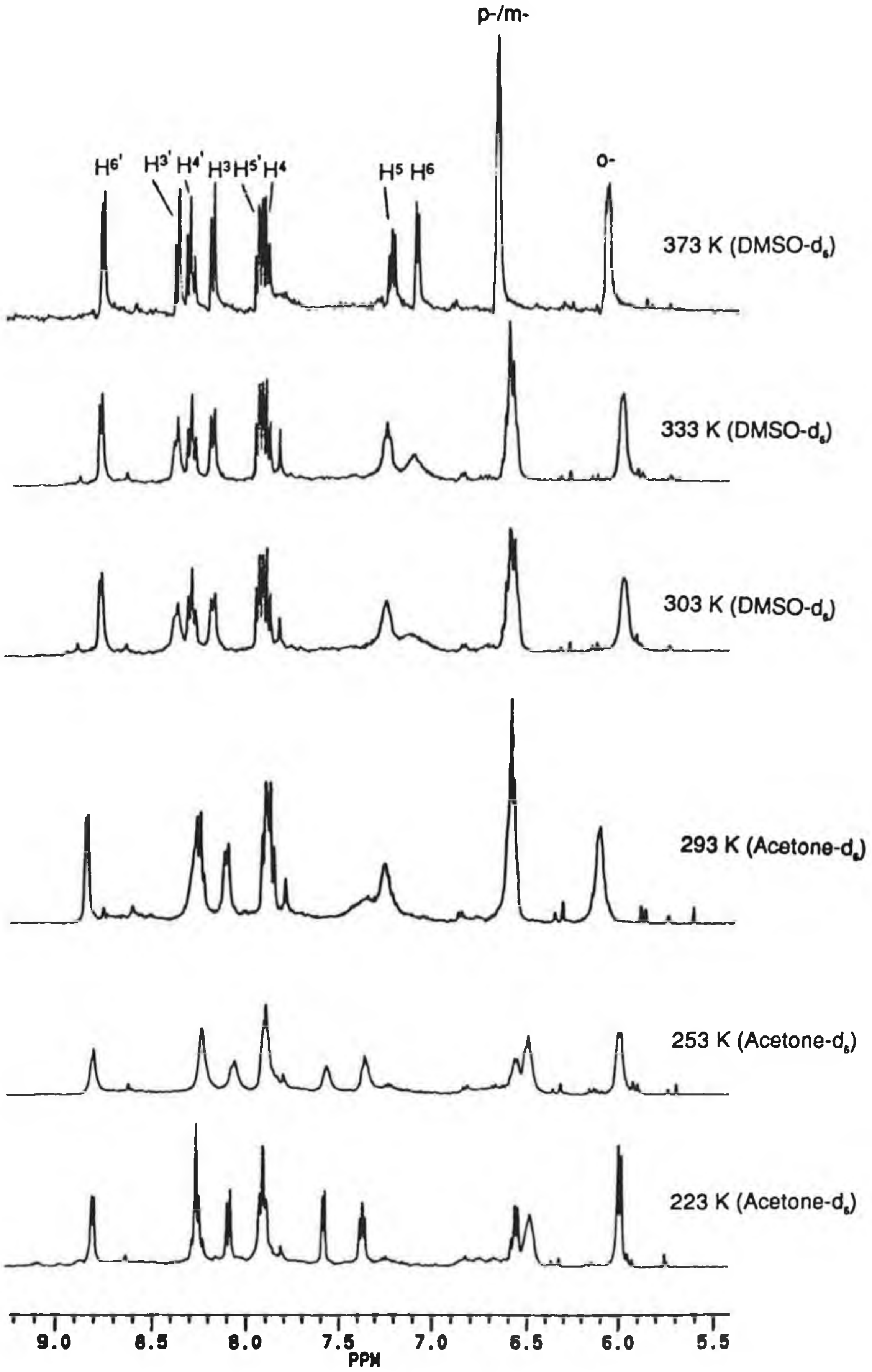
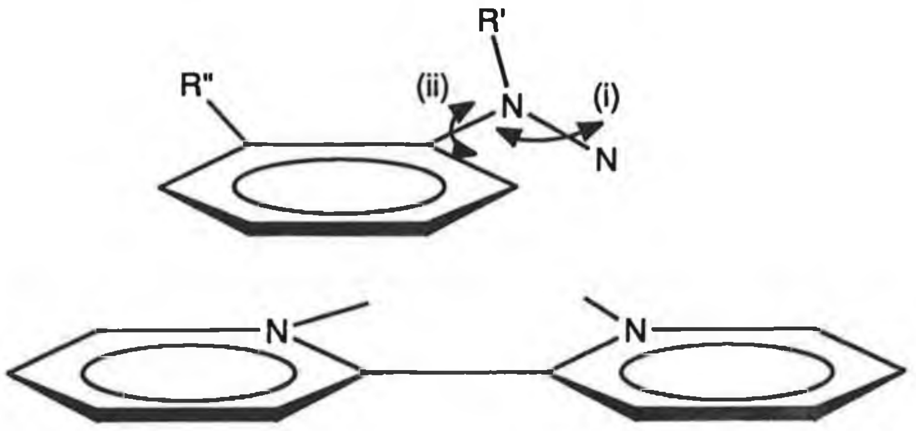


Figure [3.19] ^{1}H NMR of [Ru(bipy)$_2$(ddmph)](PF$_6$)$_2$ (343) at various temperatures; Higher Temperatures in DMSO-d$_6$, Lower Temperatures in Acetone-d$_6$

A selection of the aromatic regions of the ^1H NMR spectra were overlaid and are displayed in figure [3.19]. At 293 K most of the phenyl and bipyridyl protons resonances are nearly fully resolved. However, as the temperature is reduced the majority of the peaks begin to broaden, and at 293 K the only remaining sharp peak is the $H^{6'}$ doublet at 8.87 ppm. At the temperature 253 K, all peaks are very broad or baseline. At 223 K, the peaks begin to sharpen, and two peaks emerge at 6.52 ppm and 6.55 ppm, from what was originally a broad multiplet and were assigned to the meta and para protons of the phenyl groups respectively.

The broadening of resonances for the complexes **(342)**, **(343)** and **(344)** may be attributed to the exchange of the phenyl ring proton environments resulting from rotation about either the N-N bond or C-N bond, (see (i) and (ii) in figure [3.20]). From examination of molecular models, it is clear that rotation about the N-C bond is severely restricted on steric grounds. Rotation about the N-N bond is possible for ± 15° and leads to movement across the bipyridyl ring system. When restricted to a small rotation about the N-N bond, this may result in a shallow potential energy well. Concomitant small rotations about the N-C bond may also be taken into account but will only have a slight effect on the position of the phenyl ring. Fast (on the NMR time scale) rotation with increased temperature leads to sharp signals corresponding to the averaged proton environment. Even with high temperature, the phenyl ring is not displaced from this potential energy well since ortho protons maintain their chemical shift.

The introduction of a methyl group onto the amino nitrogen would not alter rotation about the N-C bond significantly whereas it would have a significant effect on the N-N rotation. The effect on the NMR spectra is significant including broadening of the bipyridyl resonances in particular H^5 and H^6 and phenyl resonances. (See figure [3.19]). For the room temperature spectrum of the ortho methylphenyl analogue **(344)**, the single ortho hydrogen occurs at 5.5 ppm as a broad singlet which sharpens with increasing temperature (see 363 K in figure [3.18]) and decreasing temperature (see 253 K in figure [1.18]) At high and low temperature eight signals for the bipyridyl system and four for the tolyl group are observed. The sharp signals with increased temperature results from the averaged proton environment experienced by each molecule due to rotation about the N-N bond whereas the sharp signals at low temperature result from the average signal for each molecule within the potential well.



(342) R' = H , R" = H

(343) R' = CH_3 , R" = H

(344) R' = H , R" = CH_3

Figure [3.20] **Movement of Phenyl Groups of Complexes (342), (343) and (344) with Respect to Bipyridine Groups**

The introduction of a methyl onto the nitrogen of the amino group gives a similar temperature range over which broadening of signals occurs. For the N-methyl substituted complex **(343)** at room temperature almost all of the aromatic resonances are broadened, in particular H^6 and H^5 of the bipyridyl rings are broad and baseline respectively. (See 293 K in figure [3.19]). On elevation of the temperature, all of the aromatic signals sharpen and give the expected eight bipyridyl signals at 373 K. Also on lowering the temperature one obtains a sharpening of signals without any increase in the number of signals or significant changes in chemical shift, (see 223 K in figure [1.19]). The broadening of signals occurs at higher temperature for both **(343)** and **(344)** compared to **(342)** is consistent with replacement of hydrogen by methyl.

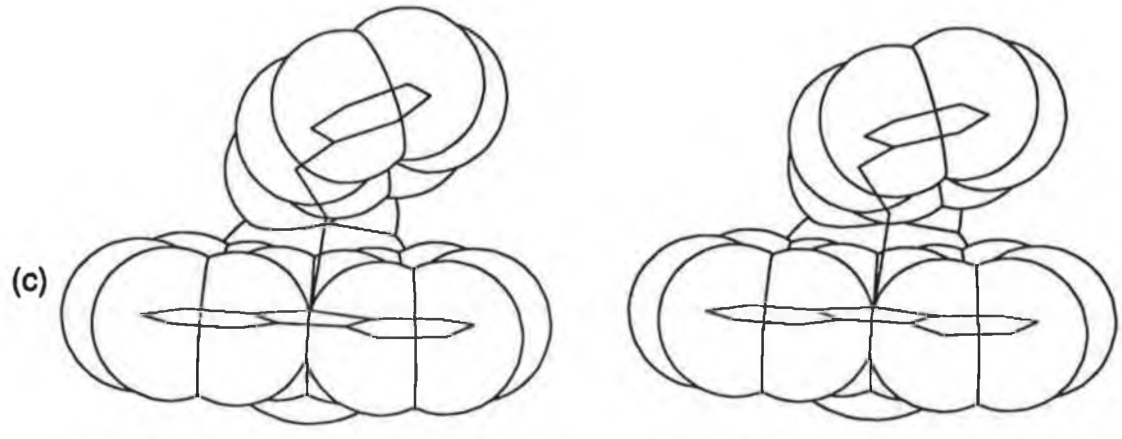
The suggestion of a phenyl ring lying close in space (<3Å) over a bipyridyl group is supported by a difference Nuclear Overhauser Effect (NOE) study on **(342)**. On irradiation the ortho hydrogens (signal at 5.8 ppm) show a 2.5% NOE to the $H^{6'}$ and a 1.8% NOE to the H^6 protons of the bipyridyl system in addition to a 4.0% NOE to the NH proton. Similarly the ortho methyl of **(344)** gives small NOE's to $H^{6'}$, H^6 and H^5 of the bipy moiety, the bipyridyl resonances which experience greatest broadening.

Broadening of peaks is thought to be due to the molecules **(342)**, **(343)** and **(344)** being nonrigid, so that the phenyl groups of the substituted dihydrazone ligands exchange positions (oscillate over the bipy groups) within the complex. At higher temperatures, the rate of oscillation of the phenyl rings over the bipy rings increase to a rate faster than the NMR timescale and a fully averaged spectrum is observed.

At low temperatures, the movement of the phenyl rings is slowed down so that the rate of exchange of the environments of the nuclei involved takes place at a rate less than that of the NMR timescale, and the corresponding static spectrum observed is sharp. Normally in dynamic NMR one would observe signals representing the most favourable isomers(194,195,196). In the case of complexes **(342)**, **(343)** and **(344)**, movement of the phenyl rings is restricted within a shallow potential energy well. If energy minima were present, one might expect to observe structural isomers for the o-tolyl group depending on the orientation of the o-methyl group, and consequently different sets of phenyl protons. We consider that the static spectrum corresponds to a tolyl group orientated in such a way to have the methyl group lying over the "nonprimed" pyridyl ring of the bipy system. At intermediate temperatures, the phenyl rings move over the bipy groups at a rate comparable to that of the NMR time scale, and causes the NMR proton resonances of the nuclei involved to broaden to baseline.

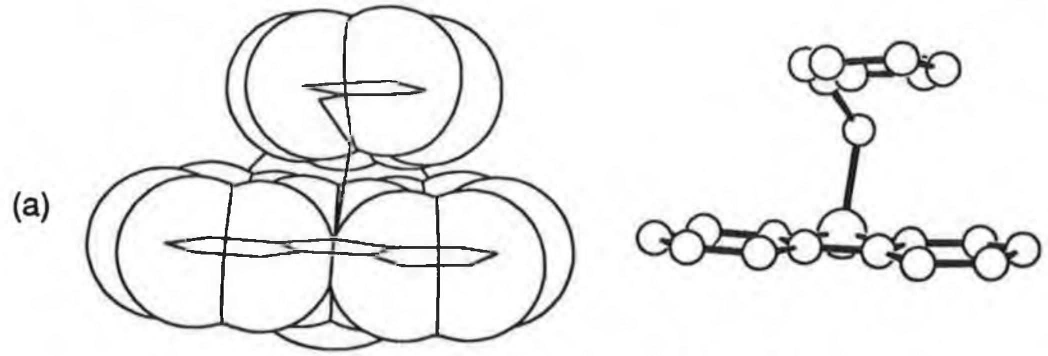
Consideration of the orientation of the phenyl group with respect to the bipyridyl system is possible using the atomic coordinates (Appendix 1) for the complex **(342)** obtained for the X-ray crystal structure determination. Using the SCHAKAL program(197,198) and presenting the structure with the Van der Waals radius included, it is clear ((a) in figure [3.21]) that a favourable interaction exists between the π system of the phenyl group and the bipy system.

When the structure is "unlocked" and the phenyl group is free to rotate about the N-N bond, two limiting situations arise. The first involves a "crash" of the phenyl group and the bipy system ((b) in figure [3.21]), and occurs at approximately - 15° rotation away from the position in the crystal. Rotation in the opposite direction leads to a loss of the favourable interaction between the π-system, ((c) in figure [3.21]). Rotation about the N-C bond may also be taken into account but will not alter significantly the degree of rotation allowed. Thus one could envisage a situation occurring where the phenyl group is oscillating over the bipy group within a shallow potential energy well system.

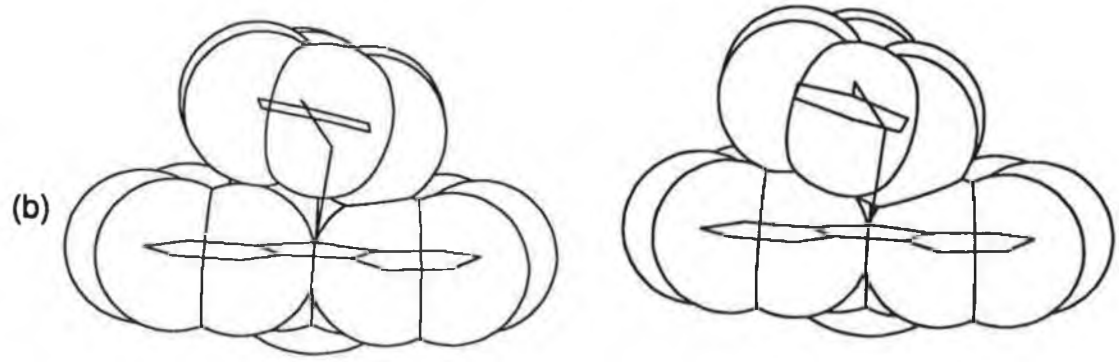


+ 30° Rotation about N-N Bond

+ 20° Rotation about N-N Bond



Normal Position of Phenyl Ring Above Bipy System



- 20° Rotation about N-N Bond

- 30° Rotation about N-N Bond

Figure [3.21] Molecular models of rotation about N-N bond a single phenyl ring Over a Bipy Ring in Complex (342) Based On Crystal Structure Data with Van der Waals Radii Shown

3.5 GENERAL DISCUSSION

3.5.1 Reasons for lack of emission in the complexes (342) - (347)

The complexes **(342)** - **(347)** do not emit either at room temperature or at low temperature. At the outset, it was hoped that the complexes would display emission properties which would possibly render them useful in areas such as photosensitisers, photocatalysts or biological applications(166,175,177-183). Table [3.3] list some of the electrochemical and photochemical properties of the complexes **(342)** - **(347)**.

Table [3.3] **Electrochemical and Photochemical properties of Complexes (342) - (347)**

	Absorption	Photostable	Electrochemistry *vs.* SCE	
	$\lambda_{max.}$ / nm		Oxid. $E_{1/2}$/ V	Red. $E_{1/2}$/ V
[Ru(bipy)$_2$(ddph)](PF$_6$)$_2$ (342)	450	+	1.6*, 1.1	-1.1, -1.5, -1.8
[Ru(bipy)$_2$(ddmph)](PF$_6$)$_2$ (343)	445	+	1.9*, 1.3, 1.1	-1.0, -1.6, -1.9
[Ru(bipy)$_2$(doth)](PF$_6$)$_2$ (344)	450	+	1.6*, 1.1	-1.1, -1.5, -1.8
[Ru(bipy)$_2$(ddmh)](PF$_6$)$_2$ (345)	450	-	1.3*	-1.1, -1.5, -1.9
[Ru(bipy)$_2$(ddh)](PF$_6$)$_2$ (346)	420	-	1.4, 1.2*	-1.3, -1.5, -1.7
[Ru(bipy)$_2$(ddba)](PF$_6$)$_2$ (347)	450	+	1.4*	-0.9, -1.5, -1.8
[Ru(bipy)$_2$(apph)](PF$_6$)$_2$ (351)#	445	-	1.6*, 1.1, 0.9	-1.2, -1.5, -1.7
[Ru(bipy)$_2$(aph)](PF$_6$)$_2$ (352)#	440	-	1.3*	-1.3, -1.5, -1.7

* Metal based oxidation process
# Complexes emit

The high aromatic proton resonances in the ^{1}H NMR spectrum of the complex **(342)** indicate that the ortho hydrogens of the phenyl group are shielded upfield due to the phenyl rings lying close to the bipyridyl groups. It was initially thought that the presence of the phenyl groups and their interaction with the bipyridyl groups may be responsible for the lack of emission in this complex. Emission in these type of complexes is normally bipy based, (*i.e.* an electron transition from the bipyridyl excited state to the metal centred ground state). However, the electrochemical data for complex **(342)**, the first reduction potential is observed at -1.0 V and is assigned to the reduction of (ddph) **(29)**, indicating that the ligand (ddph) **(29)** is a stronger π-acceptor than bipy. Hence excitation of the complex **(342)** most likely involves an electron transfer from the metal to the lower ^{3}MLCT energy level of the ligand (ddph) **(29)**. In addition it was found that the complex **(342)** is photostable in strong coordinating solvents, implying that the energy gap between the ^{3}MLCT excited state and the ^{3}MC state is sufficiently large to prevent population of the ^{3}MC level, (see Figure [3.1]). This suggests that for complex **(342)**, relaxation of the excited electrons on the ligand (ddph) **(29)** does not occur through the ^{3}MC state but through a radiationless deactivation pathway from the ^{3}MLCT to the ground state, (see K_{nr} figure [3.1]). The delocalised π-electron system of the phenyl groups and the bipyridyl groups may facilitate deactivation of the excited state.

To examine this proposed theory for lack of emission, attempts were made to prepare similar complexes which had the phenyl rings positioned away from the bipyridyl groups. By replacing the N-H protons of the complex **(342)** with methyl groups as in complex **(343)**, it was hoped that this increase in steric crowding would cause the phenyl groups to be rotated away from the bipyridine groups.

Characterisation of $[Ru(bipy)_2(ddmph)](PF_6)_2$ **(343)**, indicates that there are also highfield aromatic peaks in the NMR spectrum of **(343)**. The ortho protons of **(343)** appear at 6.01 ppm indicating that the phenyl rings are positioned close to the bipy rings. It was concluded, based on the NMR data, that the presence of a methyl group on the amino nitrogen in complex **(343)** does not cause the phenyl group to be positioned away from the bipyridine system. Electrochemical data for complex **(343)** indicates that the ligand (ddmph) **(320)** is a stronger π-acceptor than bipy. This suggests that the MLCT transition involves excitation of an electron from the d-orbitals of the metal centre to the empty π^*-orbitals of (ddmph) **(320)**. $[Ru(bipy)_2(ddmph)](PF_6)_2$ **(343)** does not emit in common solvents at room temperature or at low temperature, and is photostable in strong coordinating solvents compared to $[Ru(bipy)_3]^{2+}$ **(341)**.

In a second attempt to displace the phenyl rings away from the bipyridyl systems, $[Ru(bipy)_2(ddoth)](PF_6)_2$ **(344)** was prepared. It was hoped that by replacing one of the hydrogens of the phenyl groups of the complex **(342)** with a methyl group, as in **(344)**, would cause the phenyl rings to be positioned away from the bipy groups. Similar to the NMR data for complexes **(342)** and **(343)**, the NMR spectrum of complex **(344)** shows highfield aromatic proton resonances for the phenyl protons indicating that the phenyl rings remain close to the bipy groups. Again, no emission properties are observed for complex **(344)** which suggests a large energy gap between the ^{3}MLCT level and the

^{3}MC level. Electrochemical data for complex **(344)** indicate that (ddoth) **(319)** is a stronger π-acceptor than bipy, suggesting that the MLCT transition involves excitation of an electron to the ^{3}MLCT of the hydrazone ligand **(319)**. Thus if complexes **(342)** - **(344)** were to emit, they would have to emit from the hydrazone ligand.

To further investigate this hypothesis $[Ru(bipy)_2(ddmh)](PF_6)_2$ **(345)** which contains an N,N-dimethyl hydrazone group instead of an NH-phenyl hydrazone group, was synthesised. Complex **(345)** does not show any emission properties nor do the complexes $[Ru(bipy)_2(ddh)](PF_6)_2$ **(346)** and $[Ru(bipy)_2(ddba)](PF_6)_2$ **(347)**. One could argue that in the complexes **(345)** and **(346)** the emitting state is deactivated through population of the ^{3}MC state. However, complex **(347)** is photostable suggesting that the most likely reason for the apparent lack of emission in complexes **(342)** to **(347)** is that in these type of hydrazone complexes, the hydrazone based ^{3}MLCT does not emit.

Differences in the electrochemical properties of the dihydrazone ligands of complexes **(342)** to **(347)** may be attributed to the functional groups of the hydrazones, particularly with respect to the π-accepting properties of the complexed ligands. Those ligands which contain functional groups capable of stabilising a negative charge have less negative reduction potentials when complexed, (*i.e.* more easily reduced). Table [3.4] lists the complexes, hydrazone substituents and the first reduction potentials.

Table [3.4] List of Hydrazone Substituents of and First Reduction Potentials

	Hydrazone Ligand Substituents	First Red. Pot. $E_{1/2}$ / V
$[Ru(bipy)_2(ddph)](PF_6)_2$ **(342)**	NHPh (x 2)	-1.1
$[Ru(bipy)_2(ddmph)](PF_6)_2$ **(343)**	$N(CH_3)Ph$ (x 2)	-1.0
$[Ru(bipy)_2(doth)](PF_6)_2$ **(344)**	NH(o-$PhCH_3$) (x 2)	-1.1
$[Ru(bipy)_2(ddmh)](PF_6)_2$ **(345)**	$N(CH_3)_2$ (x 2)	-1.1
$[Ru(bipy)_2(ddh)](PF_6)_2$ **(346)**	NH_2 (x 2)	-1.3
$[Ru(bipy)_2(ddba)](PF_6)_2$ **(347)**	N=CH-Ph (x 2)	-0.9
$[Ru(bipy)_2(apph)](PF_6)_2$ **(351)**	pyridine / NHPh	-1.2
$[Ru(bipy)_2(aph)](PF_6)_2$ **(352)**	pyridine / NH_2	-1.3

From the data, the ligands (ddph) **(29)**, (ddmph) **(320)**, (ddoth) **(319)** and (dbba) **(327)** are the strongest π-acceptors, (more easily reduced), which can be attributed to the presence of the phenyl rings on the ligands. An extra electron is more stabilised by a conjugated phenyl ring system of ligands (ddph) **(29)**, (ddmph) **(320)**, (ddoth) **(319)** and (dbba) **(327)** compared to the ligands (ddmh) **(129)** and (ddh) **(5)** which contain only methyl groups and hydrogens. The ligands (apph) **(349)** and (aph) **(350)** are weaker π-acceptors due to the pyridine moieties, which is also evident by the more negative reduction potentials of the bipy groups of the complexes.

Although complexes **(342)** - **(347)** do not exhibit emission properties they have potential in this field of research as rutheniumbis(bipyridyl) derivatives which are photostable are relatively uncommon. Research in this area was initiated by the quest for a more photostable analogue of $[Ru(bipy)_3]^{2+}$(166). Differences in the photostability properties of the complexes **(342)** - **(347)**, **(351)** and **(352)** can be related to the first reduction potentials of the complexes. Complexes **(342)** - **(344)** and **(347)** which have low reduction potentials (> - 1.1 V) are photostable whereas, complexes **(345)**, **(346)**, **(351)** and **(352)** which have a first reduction potential less than -1.1 V (more negative) decompose when irradiated by white light in the presence of Cl^- ions. Photodecomposition occurs through population of the ^{3}MC energy level from the ^{3}MLCT level, (see figure [3.1])(166). If ligand (LL) of a complex is easily reduced, the energy of its empty π^* energy level, ^{3}MLCT, will be relatively low, thus causing the energy gap between the lowest ^{3}MLCT level and the ^{3}MC level to be greater. This increased energy gap prevents population of the ^{3}MC state which results in the complex being more photostable. The reverse situation arises if the first reduction potential of the complex is relatively negative causing the lowest ^{3}MLCT energy level to be increased. Thus the energy gap between the ^{3}MLCT and the ^{3}MC is reduced resulting in population of the ^{3}MC level which may lead to photodecomposition of the complex.

In a further study, in collaboration with A. Fernandez Martinez, to examine the contribution of the ligands to the lack of emission, complexes of the type $[Ru(bipy)_2(apph)](PF_6)_2$ **(351)** and $[Ru(bipy)_2(aph)](PF_6)_2$ **(352)** were prepared from the ligands 2-acetylpyridinephenylhydrazone **(349)** and 2-acetylpyridinehydrazone **(350)** respectively. The ligand **(349)** is effectively a " half " bipy, half " hydrazone ligand " having both an acetylphenylhydrazone and a pyridine ring and similarly the ligand **(350)** has both a hydrazone group and a pyridine group. These complexes represent "half-way" stage between $[Ru(bipy)_3]^{2+}$ **(341)** and the complexes **(342)** and **(346)**. Both complexes **(351)** and **(352)** display emission properties both at room temperature and at 77 K, indicating that the presence of hydrazone groups in these type of complexes does not result in lack emission in the complexes. The absorption and emission properties are listed in table [3.5].

Table [3.5] **Maximum Absorption & Emission Wavelengths of (351) and (352)**

	Absorption MLCT λ_{max}	Emission λ_{max} (293 K)	Emission λ_{max} (77 K)
$[Ru(bipy)_2(apph)](PF_6)_2$ **(351)**	445 nm	670 nm	595 nm
$[Ru(bipy)_2(aph)](PF_6)_2$ **(352)**	440 nm	660 nm	604 nm

A likely reason why complexes **(351)** and **(352)** emit is because their ligands (apph) **(349)** and (aph) **(350)** possess a higher degree of conjugation due to the presence of the pyridine ring, compared to the substituted dihydrazone ligands of complexes **(342)** to **(347)**.

Resonance Raman spectra of $[Ru(bipy)_2(apph)](PF_6)_2$ **(351)**, (see Appendix II), excited at 457.9, 488.0, 514.5 nm show both bipy and hydrazone ligand features suggesting that the lowest MLCT transitions includes Ru --> $\pi^*_{(apph)}$ transitions, confirming electrochemical data. The RR spectra indicate a change in the relative intensities of the hydrazone and bipy peaks at *ca.* 1475 nm and 1491 nm, which suggest there might be more than one transition involved in the absorption spectrum of $[Ru(bipy)_2(apph)](PF_6)_2$ **(351)**, most likely an overlap between the dπ --> $\pi^*_{(ddph)}$ and dπ --> $\pi^*_{(bipy)}$ transitions.

Preliminary results indicate that a ΔA plot (*i.e.* excited state absorbance difference spectrum, see Appendix II), for complex $[Ru(bipy)_2(apph)](PF_6)_2$ **(351)** shows a 35-40 nano second transient in acetonitrile.

Combining the photostable properties of the complexes containing the phenyl ring substituted dihydrazones of diacetyl, complexes **(342)** - **(344)** and **(347)**, with the emission properties of the complexes containing the hydrazone and pyridyl moieties, complexes **(351)** and **(352)**, it may be possible to produce a ruthenium complex which is both photostable and shows emission. Further work in this area would be to prepare ligands of a type similar to **(349)** and **(350)**. It should be possible to produce hydrazone derivatives of 2-acetylpyridine which when complexed to rutheniumbis(bipyridyl) would have a reduction potential greater than -1.0 V. To cause the reduction potential of these ligands to be less negative, one could introduce an electron withdrawing group on the hydrazone moiety quite easily, for example, a p-nitro group on the phenyl ring of complex **(351)**. These easily reduced ligands when complexed would hopefully reduce the ^{3}MLCT level causing the energy gap between this level and the ^{3}MC level to be increased reducing the possibility of decomposition. It would also be hoped that the presence of the pyridyl moiety would cause the ligand to emit when complexed. The results show the conversion of the photolabile complex **(346)** using benzaldehyde to produce the photostable complex **(347)**, and the first reduction potential of the respective complexes changes from -1.3 V to -0.9 V. Based on these observations, it may be possible to produce a photostable complex which emits by reacting the amino group of the photoactive complex **(352)** with aromatic aldehydes.

Although the complexes **(351)** and **(352)** are found not to be photostable in the presence of coordinating ions, the complexes have the potential of being useful in a variety of areas, for example, the use of $[Ru(bipy)_2(aph)](PF_6)_2$ **(352)** by binding it to antibodies *via* the NH_2 group, for use as a biological marker or as a reagent in immuno assays(199,200).

3.5.2 ^{1}H NMR Analysis of the complexes

Some interesting features were observed in the NMR studies. Many of the ^{1}H NMR peaks of the ligands **(5)**, **(29)**, **(129)**, **(319)**, **(320)** and **(327)**, display a marked change in proton chemical shift on complexing to ruthenium bis(bipyridyl), in particular in the case of complexes **(342) - (344).** Table [3.6] lists some of the NMR chemical shift values of the diacetyldihydrazone ligands both prior to and after complexation.

On average, the proton resonances of the acetyl hydrogens undergo a downfield shift of *ca.* 0.6 ppm on coupling to $[Ru(bipy)_2]^{2+}$ ranging from 1.8 - 2.3 ppm for the free ligands to 2.5 - 3.0 ppm for the complexes **(342) - (347)**. This increase in chemical shift on complexing is possibly explained by the decrease in electron density around the ligand due to σ-donation of electrons of the ligand to the metal on complexing.

Table [3.6] **Chemical shifts of Ligands and Complexes**

	Phenyl Protons / ppm					CH_3 / ppm	CH_3' / ppm	NH_2 /ppm
	$H^{2''}$	$H^{3''}$	$H^{4''}$	$H^{5''}$	$H^{6''}$			
(ddph) (29)	7.3	7.3	6.9	7.3	7.3	2.3		
$[Ru(bipy)_2(ddph)]^{2+}$ (342)	5.8	6.6	6.6	6.6	5.8	2.8		
(ddmph) (320)	7.0	7.3	6.9	7.3	7.0	2.2	3.2	
$[Ru(bipy)_2(ddmph)]^{2+}$ (343)	6.1	6.6	6.6	6.6	6.1	2.8	3.0	
(ddoth) (319)		7.7	7.3	6.9	7.3	2.2	2.5	
$[Ru(bipy)_2(ddoth)]^{2+}$ (344)		6.8	6.8	6.6	5.9	3.0	2.2	
(ddmh) (129)						1.9	2.7	
$[Ru(bipy)_2(ddmh)]^{2+}$ (345)						2.7	1.9	
(ddh) (5)						1.8		5.8
$[Ru(bipy)_2(ddh)]^{2+}$ (346)						2.5		6.5
(ddba) (327)	7.7	7.4	7.4	7.4	7.7	2.2		
$[Ru(bipy)_2(ddba)]^{2+}$ (347)	7.5	7.5	7.5	7.5	7.5	2.8		

The proton resonances of the phenyl rings of the ligands **(29)**, **(319)** and **(320)** all undergo an upfield shift on complexing to rutheniumbis(bipyridyl), with the ortho proton resonances experiencing the greatest shift; a change of *ca.* -1.5 ppm for the ortho hydrogens of the ligands **(29)** and **(319)** on complexing. This upfield change in chemical shift is explained in terms of the phenyl groups of the substituted hydrazone ligands lying directly over the bipyridyl rings, causing the phenyl proton resonances to be shielded by the ring currents of the bipy groups. This theory was reinforced by difference NOE experiments carried out on complexes $[Ru(bipy)_2(ddph)](PF_6)_2$ **(342)** and $[Ru(bipy)_2(ddoth)](PF_6)_2$ **(344)**. For complex **(342)**, on saturating the signal of the ortho-hydrogens of the phenyl ring, a 2% diff. NOE is observed for the H^6 and $H^{6'}$ protons of the bipyridyl ring system indicating that the ortho protons of the phenyl ring are close in space, (< 3Å), to the bipyridyl rings in solution. Similarly complex **(344)**, an NOE difference is observed for the H^6, H^5, $H^{6'}$ protons on decoupling the ortho-methyl signal at 1.8 ppm. This observation suggests that the ortho-methyl group of complex **(344)** is positioned over a particular bipy ring, the "non-primed" pyridyl ring and is also close in space (< 3 Å) to the $H^{6'}$ proton of the second bipyridyl ring of the molecule.

An upfield change in chemical shift also occurs for the methyl groups of $[Ru(bipy)_2(ddmh)](PF_6)_2$ **(345)**. The N-methyl protons are shifted upfield to 1.9 ppm, ($\delta_{(free\ ligand)}$ = 2.7 ppm). indicating that the N-methyl groups are also close in space to the bipyridyl ring systems which causes them to be shielded upfield. On the other hand, the diacetyldibenzilazine **(327)** proton resonances do not undergo any major changes in chemical shift on complexing to rutheniumbis(bipyridyl) to form **(347)**. This is due to the increased length of the ligand which causes the phenyl group to be orientated away from the bipyridyl rings.

Not only do the phenyl rings of the complexes **(342) - (344)** experience a shielding effect from the bipy groups, but also the bipyridyl protons experience a concomitant shielding effect from the phenyl groups, which is evident from table [3.7]. On average, the chemical shifts of the bipyridyl protons of the complexes **(342) - (344)** which contain a phenyl ring, are at significantly higher field than the chemical shifts of the bipyridyl protons of the complexes **(345) - (347)** which do not contain a phenyl ring over the bipyridyl groups, with the exception of the $H^{3'}$ and the $H^{4'}$ protons of the bipy groups. Moreover, it was found that the H^6, H^5, H^4, H^3, $H^{6'}$ and $H^{5'}$ protons which are on the opposite end of the bipyridyl molecule are shielded by the phenyl rings of the hydrazone ligands. This suggests that the phenyl rings oscillate over and back across the "non-primed" pyridyl ring of the bipy group. The interaction between the $H^{6'}$ and $H^{5'}$ protons of the bipy rings and the phenyl protons most likely occurs between the phenyl ring and the second bipy group that is at right angles to the phenyl group.

Table [3.7] List of the chemical shifts for bipy protons of complexes

Complex \ bipy proton/ ppm	H^6	H^5	H^4	H^3	$H^{3'}$	$H^{4'}$	$H^{5'}$	$H^{6'}$
$[Ru(bipy)_2(ddph)]^{2+}$ (342)	7.20	7.30	7.81	8.10	8.25	8.20	7.90	8.40
$[Ru(bipy)_2(ddmph)]^{2+}$ (343)	7.03	7.17	7.82	8.08	8.27	8.22	7.86	8.86
$[Ru(bipy)_2(ddoth)]^{2+}$ (344)	7.14	7.24	7.65	7.95	8.35	8.23	7.90	8.69
$[Ru(bipy)_2(ddmh)]^{2+}$ (345)	7.67	7.33	8.05	8.73	8.22	7.78	8.33	8.88
$[Ru(bipy)_2(ddh)]^{2+}$ (346)	7.44	7.36	8.02	8.68	8.22	7.78	8.26	8.80
$[Ru(bipy)_2(ddba)]^{2+}$ (347)	7.63	7.28	7.82	8.54	8.67	7.89	8.36	8.78

3.5.3 Variable temperature ^{1}H NMR Analysis of the complexes

Variable temperature NMR analysis was carried out on the complexes **(342)** - **(344)**. Low temperature NMR analysis of $[Ru(bipy)_2(ddph)](PF_6)_2$ **(342)** (293 K - 193 K) shows broadening of the proton resonances of the ortho hydrogen of the phenyl ring to baseline at 193 K. Variable temperature NMR studies of the complex $[Ru(bipy)_2(ddmph)](PF_6)_2$ **(343)** shows baseline broadening of many of the aromatic proton resonances which occur within the temperature range 334 K - 233 K. At temperatures above and below this range, a very sharp spectrum is observed. Similar results are observed for $[Ru(bipy)_2(ddoth)](PF_6)_2$ **(344)**. Both the phenyl and bipyridyl proton resonances are broadened to baseline at temperatures close to room temperature, whereas very sharp NMR spectra were collected at high temperature (374 K) and at low temperatures (215 K).

High temperature NMR analysis of the complex $[Ru(bipy)_2(ddph)](PF_6)_2$ **(342)** indicated some slight changes in chemical shift resonances and small changes in chemical shifts are also observed for complexes **(343)** and **(344)**, with various proton resonances experiencing an upfield shift with decrease in temperature.

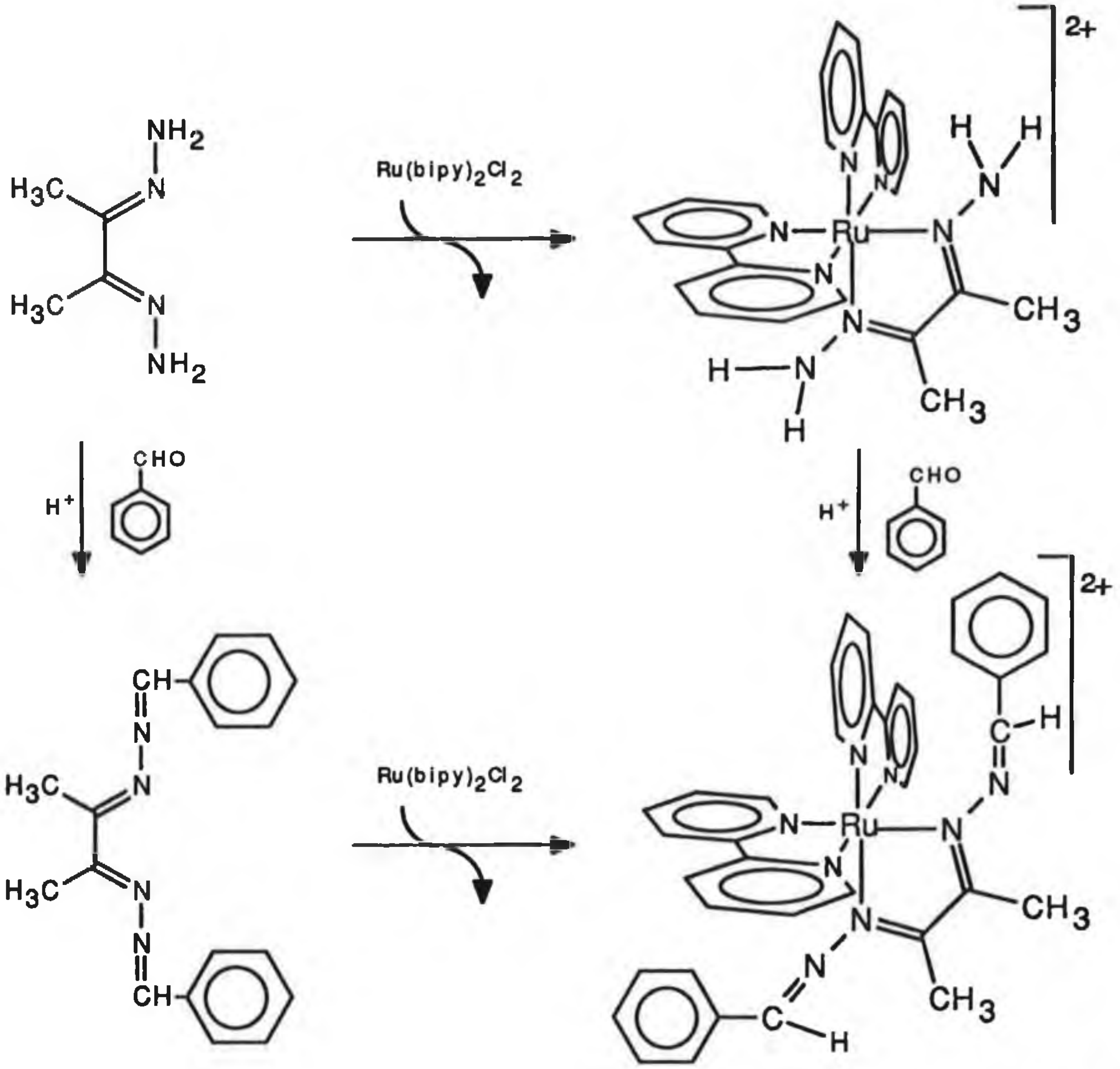
This coalescence to baseline at various temperatures, is thought to be caused by movement of the phenyl rings of complexes **(342)** - **(344)** in a region very close in proximity to the bipyridyl rings. For complex **(342)**, positioning of the phenyl rings directly over the bipy groups causes the protons of the phenyl group to experience an induced magnetic field set up by the bipy groups to oppose the applied magnetic field. The results indicate that the ortho-proton experience the greatest degree of shielding by the induced magnetic field, whereas the meta- and para-protons experience the shielding effect to a lesser degree. Thus any movement of the phenyl ring across the bipy ring should effect the magnetic environment of the phenyl protons. The time taken for the NMR detector to collect a spectrum is of the order of a second, and the average signal of all of the molecules of the sample is displayed.

In the case of complex **(342)** at higher temperatures, the oscillation of the phenyl ring over the bipy groups is fast on the NMR time scale and the spectrum observed is sharp. As the temperature is reduced to 193 K, movement of the phenyl ring across the bipy groups slows down to a timescale comparable to that of the NMR, and causes the signal of the phenyl protons to broaden to baseline.

This phenomenon is greatly enhanced by the presence of a methyl group on the amino nitrogen or on the ortho position of the phenyl group. Complex **(343)** differs from complex **(342)** in that complex **(343)** possesses a methyl group on the amino nitrogen. The presence of this methyl group causes the oscillation of the phenyl group over the bipy group to slow down. From the variable temperature ^{1}H NMR studies of complex **(343)** in solution, a sharp spectrum is observed at temperatures above 353 K and below 223 K. In between this temperature range, many of the aromatic proton resonances are broad or baseline. Similarly for complex **(344)** which differs from complex **(342)** by a methyl group on the 2" position of the hydrazone phenyl ring. Variable temperature NMR studies of **(344)** show that a sharp NMR spectrum is obtained at temperatures above 353 K and below 253 K, and in between this temperature range many of the proton resonances are broadened to baseline. This phenomenon is explained in terms of oscillation of the phenyl groups above the bipy groups. At high temperatures, the phenyl rings move over and back across the bipyridyl rings at a fast rate ($<10^{-1}$ s) compared to the NMR timescale and the sharp signal displayed is an average of all the signals of the protons in different environments. At lower temperatures, the phenyl ring of the complexes **(343)** and **(344)** oscillates over the bipy groups at a rate which is less than that of the NMR timescale (> seconds x 10) and the static spectrum is observed by the NMR detector producing a sharp spectrum. At intermediate temperatures, the phenyl rings of the complexes **(342)** - **(344)** move slowly over and back across the bipy groups causing the aromatic proton environments to be changing slowly at a rate which is similar to the NMR timescale. This causes the data acquisition by the NMR to be "blurred" and the resonance peaks in the NMR spectrum to be broadened to baseline.

3.5.4 Reactivity of Coordinated Diacetyldihydrazone (5)

One of the other complexes of particular interest is $[Ru(bipy)_2(ddh)](PF_6)_2$ **(346)**. Reacting **(346)** with benzaldehyde produces $[Ru(bipy)_2(ddba)](PF_6)_2$ **(347)**. Thus, the amine groups of diacetyldihydrazone have the potential to react with carbonyl groups both prior to and after complexation to ruthenium, summarised in scheme [3.11].



Scheme [3.11]

This reaction is important as it demonstrates how the complexes containing the ligand diacetyldihydrazone **(5)** could be attached to materials containing aldehyde groups such as polymer backbones containing repeating carbonyl groups, biological materials etc. Complexes containing the ligand diacetyldihydrazone **(5)** could also be reacted with dicarbonyl compounds to produce polymers which contain a repeating metal complex unit.

3.6 EXPERIMENTAL

3.6.1 INSTRUMENTATION & TECHNIQUES

Infrared, ^{1}H NMR, UV/Vis. Spectra were obtained using the same instrumentation as described in Chapter II.

Emission Spectra were obtained on a Perkin Elmer L550 Luminescence Spectrometer, in acetonitrile at room temperature and in ethanol at 77 K. Spectra were recorded using an excitation slit width of 10 nm and an emission slit width of 5 nm.

Resonance Raman Spectra were obtained by Dr. J. J. McGarvey at the Chemistry Department, Queens University, Belfast, and experiments were performed by Dr. R. A. McNicholl.

Analytical HPLC experiments were performed using a Waters 501 HPLC pump, a Waters 990 Photodiode Array HPLC system with a NEC PAC III computer, a 20 μL injector loop. A μ Partisil SCX radial PAK cation cartridge was used for the analytical separation of the ruthenium complexes, the detection wavelength was 280 nm and the mobile phase acetonitrile/water (80/20 v/v) or (60/40 v/v), containing 0.08 M $LiClO_4$ at a flow rate of 2.5 ml/min.

Semipreparative HPLC was carried out using a Gilson apparatus with a linear UV/Vis. 203 detector at 215 nm, a pre-column containing Whatman Pellicular Cation Exchange and a Magnum 9 Partisil cation exchange column (10 mm / 25 cm). The mobile phase was acetonitrile/water (80/20) containing 0.1 M KNO_3, with a flow rate of 2.0-3.0 ml/min.

Photolysis of the Complexes was carried out by irradiation of a solution of the complex dissolved in 0.005 M LiCl in CH_2Cl_2. The white light source used was a slide projector lamp (500 W), focused on the sample contained in a stoppered quartz cuvette, with 5 cm of water buffer between the sample and the light source to prevent heat transfer from the lamp to the sample. 20 ml samples were taken and analysed by cation exchange HPLC at time intervals ranging from t = 0, 30, 60, 90, ... , 300 min. UV/Vis. spectra of the photo-decomposition products were obtained on the PDA detector.

Experimental Data for Crystal Structure of [Ru(bipy)$_2$(ddph)](PF$_6$)$_2$ (342)

The structure was solved by direct methods, SHELX86(197), and refined by full matrix least squares using SHELX76(198). Data were corrected for Lorentz and polarization effects but not for absorption. Hydrogen atoms were included in calculated positions with fixed thermal parameters. The non-hydrogen atoms of the cation and the atoms of the major orientations of the anion were refined anisotropically. The thermal parameters were terms U_{ij} of

$$\exp(-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*))$$

The atomic scattering factors for non-hydrogen and hydrogen atoms and the anomalous dispersion correction factors for non-hydrogen atoms were taken from the literature(201,202,203). All calculations were performed on a VAX 8700 computer. The ORTEP program was used to obtain the drawings(204).

Note; Ruthenium(III)trichloride was obtained as a gift from Johnson Mathey.

[Ru(bipy)$_2$Cl$_2$] (348)

Using a variation of a procedure reported previously(185), [Ru(bipy)$_2$Cl$_2$] **(348)** was prepared as follows. To a stirred refluxing solution of 2.8 g of commercial $RuCl_3.3H_2O$ (29.8 mmol), 0.12 g (2.0 mmol) of LiCl in 30 ml DMF, 9.36 g (60.0 mmol) of bipyridine in 20 ml of DMF was added dropwise over a period of 30 min. The reaction mixture was refluxed while stirring for a further 8 h. After the reaction mixture was cooled to room temperature, 250 ml of acetone was added and the resultant solution was cooled to 0°C overnight. Filtering yielded a red to red-violet solution and a dark green/black microcrystalline product. The solid was washed three times with 3 x 25 ml portions of diethyl ether, and dried by suction. Yield; 80%. Purity was established using cation exchange HPLC (photodiode array detector) and comparison with a standard.

[Ru(bipy)$_2$(ddph)](PF$_6$)$_2$ (342)

To a solution of 100 mg (0.19 mmol) of [Ru(bipy)$_2$Cl$_2$].2H_2O in 40 ml water, 61.4 mg (0.23 mmol) of diacetyldiphenylhydrazone in 40 ml ethanol was added. The reaction mixture was refluxed for 24 h. The solvent was removed at 90°C by rotary evaporation. The residue was redissolved into 5 ml water, and added dropwise to a solution of 100 mg of NH_4PF_6 in 20 ml water. The precipitate was filtered, washed well with diethylether, petroleum ether (40-60°C) and recrystallised slowly from acetone/water. Further recrystallisation from toluene/acetone was carried out to grow crystals suitable for X-ray crystallography: yield, 125 mg, 80%. IR(KBr); (NH) 3336 cm^{-1}. UV/Vis. λ_{max} = 450 nm. ^{1}H NMR (400MHz, DMSO-d$_6$) hydrazone ligand; δ 2.8(s,6H), 5.9(m,4H,ortho-), 6.5(s,6H,meta-&para-), 9.1(s,2H,NH). 2,2'-bipyridine ligands; δ 7.2(d,2H^6), 7.3(t,2H^5), 7.8(t,2H^4), 7.9(t,2H$^{5'}$), 8.1(d,2H^3), 8.2(t,2H$^{4'}$), 8.25(d,2H$^{3'}$), 8.4(d2H$^{6'}$). Anal. Calcd. for $C_{36}H_{38}F_{12}N_8O_2P_2Ru$: C,42.98; H,3.78; N,11.14. Found: C,42.79; H,3.50; N,11.02.

[Ru(bipy)$_2$(ddmph)](PF$_6$)$_2$ (343)

To a solution of 100 mg (0.19 mmol) of [Ru(bipy)$_2$Cl$_2$].2H_2O in 40 ml water, 280 mg (0.95 mmol) of diacetyldi(N-methylphenylhydrazone) in 40 ml ethanol was added. The reaction mixture was refluxed for 48 h. The solvent was removed at 90°C by rotary evaporation. The residue was redissolved into 5 ml water, and added dropwise to a solution of 100 mg of NH_4PF_6 in 20 ml water.

The precipitate was filtered, washed well with diethylether, petroleum ether (40-60°C). The product was purified by recrystallizing slowly from acetone/water: yield, 105 mg, (0.14 mmol) 74%. UV/Vis. λ_{max} = 455 nm. ^{1}H NMR (400MHz, DMSO-d_6 @ 363 K) hydrazone ligand; δ 2.87(s,6H), 3.04(s,6H), 6.01(d,4H,ortho-), 6.58(m,6H,meta-&para-). 2,2'-bipyridine ligands; δ 7.03(d,2H^6), 7.17(t,2H^5), 7.82(t,2H^4), 7.86(t,2$H^{5'}$), 8.08(d,2H^3), 8.22(t,2$H^{4'}$), 8.27(d,2$H^{3'}$), 8.86(d,2$H^{6'}$). Anal. Calcd. for $C_{38}H_{38}F_{12}N_8P_2Ru$: C,45.73; H,3.81; N,11.23. Found: C,46.02; H,3.90; N,11.26.

[Ru(bipy)$_2$(ddoth)](PF$_6$)$_2$ (344)

To a solution of 200 mg (0.38 mmol) of [Ru(bipy)$_2$Cl$_2$].2H$_2$O in 40 ml water, 136 mg (0.46 mmol) of diacetyldi(o-tolylhydrazone) in 40 ml ethanol was added. The reaction mixture was refluxed for 120 h. The solvent was removed at 90°C by rotary evaporation. The residue was redissolved into 5 ml water, and added dropwise to a solution of 100 mg of NH_4PF_6 in 20 ml water. The precipitate was filtered and washed with pet. ether (40-60°C). The product was purified by recrystallizing from acetone/toluene: yield, 245 mg, (0.35 mmol) 93%. IR(KBr); (NH) 3320 cm^{-1}. UV/Vis. λ_{max} = 450 nm. ^{1}H NMR (400MHz, DMSO-d_6 @ 373 K) hydrazone ligand; δ 2.00(s,6H), 2.48(s,6H), 5.51(d,2$H^{6''}$), 6.26(t,2$H^{5''}$), 6.58(t,2$H^{4''}$), 6.64(d,2$H^{3''}$). 2,2'-bipyridine ligands; δ 7.14(t,2H^6), 7.24(d,2H^5), 7.65(t,2H^4), 7.90(t,2$H^{5'}$), 7.95(d,2H^3), 8.23(t,2$H^{4'}$), 8.35(d,2$H^{3'}$), 8.69(d,2$H^{6'}$), (s,2H,NH). Anal. Calcd. for $C_{38}H_{38}F_{12}N_8P_2Ru$: C,45.73; H,3.81; N,11.23. Found: C,45.73; H,3.78; N,10.75.

[Ru(bipy)$_2$(ddmh)](PF$_6$)$_2$ (345)

To a solution of 200 mg (0.38 mmol) of [Ru(bipy)$_2$Cl$_2$].2H$_2$O in 40 ml water, 200 mg (1.18 mmol) of diacetyldi(dimethylhydrazone) in 40 ml ethanol was added. The reaction mixture was refluxed for 48 h. The solvent was removed at 90°C by rotary evaporation. The residue was washed well with diethylether, redissolved into 10 ml acetone/water (50:50 v/v), and added dropwise to a solution of 100 mg of NH_4PF_6 in 20 ml water. The precipitate was filtered, washed with petroleum ether (40-60°C) and recrystallised slowly from acetone/water: yield, 140 mg, (0.22 mmol) 60%. UV/Vis. λ_{max} = 450 nm. ^{1}H NMR (400MHz, DMSO-d_6) hydrazone ligand; δ 1.90(s,12H), 2.73(s,6H). 2,2'-bipyridine ligands; δ 7.33(t,2H^4), 7.67(d,2H^3), 7.78(t,2$H^{4'}$), 8.05(t,2H^5), 8.22(d,2$H^{3'}$), 8.33(t,2$H^{5'}$), 8.73(d,2H^6), 8.88(d,2$H^{6'}$). Anal. Calcd. for $C_{28}H_{34}F_{12}N_8P_2Ru$: C,38.48; H,3.89; N,12.83. Found: C,38.43; H,3.73; N,12.56.

[Ru(bipy)$_2$(ddh)](PF$_6$)$_2$ (346)

To a solution of 200 mg (0.38 mmol) of [Ru(bipy)$_2$Cl$_2$].2H$_2$O in 40 ml water, 220 mg (1.93 mmol) of diacetyldihydrazone in 40 ml ethanol was added. The reaction mixture was refluxed for 24 h. The solvent was removed at 90°C by rotary evaporation. The residue was washed well with diethylether, redissolved into 10 ml acetone/water (50:50 v/v), and added dropwise to a solution of 100 mg of NH$_4$PF$_6$ in 20 ml water. The precipitate was filtered, washed with petroleum ether (40-60°C) and recrystallised slowly from acetone/water: yield, 170 mg, (0.23 mmol) 85%. IR(KBr); (NH) 3330, (NH) 3193 cm^{-1}. UV/Vis. λ_{max} = 420 nm. ^{1}H NMR (400MHz, DMSO-d$_6$) hydrazone ligand; δ 2.48(s,6H), 6.54(m,4H). 2,2'-bipyridine ligands; δ 7.36(t,2H^5), 8.02(t,2H^4), 7.44(d,2H^6), 8.26(t,2H$^{5'}$), 7.78(t,2H$^{4'}$), 8.68(d,2H^3), 8.22(d,2H$^{3'}$), 8.80(d2H$^{6'}$). Anal. Calcd. for C$_{24}$H$_{26}$F$_{12}$N$_8$P$_2$Ru: C,35.25; H,3.18; N,13.71. Found: C,35.26; H,3.24; N,13.74.

[Ru(bipy)$_2$(ddba)](PF$_6$)$_2$ (Route I) (347)

To a solution of 200 mg (0.38 mmol) of [Ru(bipy)$_2$(ddh)](PF$_6$)$_2$ **(342)** in ethanol-/acetonitrile/acetic acid (30:20:20 ml), 200 mg (1.90 mmol) of benzaldehyde was added. The reaction mixture was refluxed for 120 h. The solvent was removed at 95°C. The residue was washed with diethylether, redissolved into 5 ml water, 5 ml acetone and added dropwise to a solution of 100 mg of NH$_4$PF$_6$ in 20 ml water. The precipitate was filtered, washed with diethylether and petroleum ether (40-60°C) and recrystallised from acetone/water: yield, 150 mg (0.15 mmol), 60%. UV/Vis. λ_{max} = 450 nm. ^{1}H NMR (270MHz, Acetone-d$_6$) diazine ligand; δ 2.8(s,6H), 7.5(m,10H). 2,2'-bipyridine ligands; δ 7.39(d,2H^6), 7.51(t,2H^5), 7.85(t,2H^4), 7.94(t,2H$^{5'}$), 8.84(d,2H4'), 8.55(t,2H^3), 8.80(d,2H$^{3'}$), 8.93(d2H$^{6'}$). Anal. Calcd. for C$_{38}$H$_{38}$F$_{12}$N$_8$O$_2$P$_2$Ru: C,44.30; H,3.69; N,10.88. Found: C,44.20; H,3.63; N,10.82.

[Ru(bipy)$_2$(ddba)](PF$_6$)$_2$ (Route II) (347)

To a solution of 200 mg (0.38 mmol) of [Ru(bipy)$_2$Cl$_2$](H$_2$O)$_2$ in 40 ml water, 200 mg (0.76 mmol) of diacetyldi(benzylazine) in 40 ml ethanol was added. The reaction mixture was refluxed for 120 h. The solvent was removed at 95°C by rotary evaporation. The residue was washed with diethylether, redissolved into 10 ml water/acetone (50:50) and added dropwise to a solution of 100 mg of NH$_4$PF$_6$ in 20 ml water. The precipitate was filtered and washed with diethylether and petroleum ether (40-60°C). The product was purified using semi-preparative HPLC, (Cation exchange column, mobile phase: acetonitrile/water, 80/20 v/v (0.1MKNO_3)): yield, 100 mg, (0.10 mmol) 40%. UV/Vis. λ_{max} = 450 nm. ^{1}H NMR (270MHz, Acetone-d_6) diazine ligand; δ 2.8(s,6H), 7.42(m,8H), 7.7(s,2H). 2,2'-bipyridine ligands; δ 7.39(d,2H^6), 7.51(t,2H^5), 7.85(t,2H^4), 7.94(t,2$H^{5'}$), 8.84(d,2H4'), 8.55(t,2H^3), 8.80(d,2$H^{3'}$), 8.93(d2$H^{6'}$).

3.7 Summary

This chapter describes the first reported case of substituted dihydrazones of diacetyl being bound to ruthenium. The electrochemical data shows that the substituted dihydrazones of diacetyl **(29)**, **(320)**, **(319)**, **(129)**, **(5)** and **(327)** are all better π-acceptors than 2,2'-bipyridyl which causes them to be reduced more easily. One of the major objectives of this area of research was achieved in that four photostable complexes were produced, complexes **(342)** - **(344)** and **(347)**. Photostable derivatives of rutheniumbis(bipyridyl) are relatively rare and the above complexes were found to be photochemically inert even under extreme conditions. The complexes which contain the smaller substituted dihydrazones of diacetyl, complexes **(345)** and **(346)**, show decomposition when irradiated using white light in the presence of chloride anion in solution, which is explained by the poorer π-acceptor properties of their respective ligands (ddmh) **(129)** and (ddh) **(5)**, compared to the ligands **(29)**, **(320)** and **(319)** for the photostable complexes.

A common feature of the rutheniumbis(bipyridyl) derivatives of the substituted dihydrazones of diacetyl was that none of the complexes exhibit emission properties. The reason behind the apparent lack of emission for **(342)** to **(347)** is believed to be because emission can not occur from the substituted dihydrazone ligands which are the ligands involved in the MLCT transitions.

Complexes **(351)** and **(352)** which contain a hydrazone moiety and a pyridine moiety do however exhibit emission properties which suggests that their respective ligands (apph) **(349)** (aph) **(350)** are capable of emitting, most likely as a result of the increased conjugation in these ligands. Combining the benefical emission properties of these pyridine related ligands with the photostable (good π-acceptors) properties of the substituted dihydrazones of diacetyl, provides a challenge for future research in this area, that is to produce a ligand which forms a photostable emitting rutheniumbis(bipyridyl) complex.

NMR data indicates that for complexes **(342)** - **(344)**, the phenyl groups are positioned directly over the bipy groups causing the phenyl proton resonances to be shielded upfield caused by the induced magnetic fields of the bipy groups. The ortho hydrogen of the phenyl ring of complex **(344)** was shielded from 7.2 ppm in the free ligand to 5.5 ppm when complexed. The orientations of the ligands in the complexes in solution were elucidated based mainly on NMR data. Variable temperature NMR studies were also carried out on complexes **(342)** - **(344)**. For complex **(342)**, it was found that the phenyl proton resonances were broadened to baseline at 193 K. Complexes **(343)** and **(344)** show sharp NMR spectra at high (> 373 K) and low (< 223 K for **(343)**; < 253 K for **(344)**) temperatures. At intermediate temperatures, the NMR spectra of **(343)** and **(344)** are broad/baseline. Broadening of the spectra was attributed to oscillation of the phenyl groups across the bipy groups at a timescale comparable to the NMR timescale.

The X-ray crystal structure of $[Ru(bipy)_2(ddph)](PF_6)_2$ **(342)** supported the interpretations of the NMR data. The structure revealed that the phenyl rings of the complex are positioned directly above the bipyridyl rings in solid state, showing that the proposed conformation of the complex in solution is a favourable one. The crystal structure also indicates that the complex is symmetrical, in that each "arm" of the ligand diacetyldiphenylhydrazone **(29)** is extended over one of the bipyridyl rings. The use of atomic coordinates from the crystal structure data together with consideration of the Van der Waals radii agrees well with examination of molecular models in that the phenyl group was free to oscillate approximately ± 15° by rotation about the N-N bond. This was useful in identifying the behaviour in the the variable temperature NMR studies.

Experiments demonstrated that the NH_2 terminal group of $[Ru(bipy)_2(ddh)](PF_6)_2$ **(346)** could be reacted with carbonyl groups without decomposition of the complex. The use of the active NH_2 groups of complex $[Ru(bipy)_2(ddh)](PF_6)_2$ **(346)** or complex $[Ru(bipy)_2(aph)](PF_6)_2$ **(352)** may prove to be useful as a ligand which can initially be complexed to a metal or complex of interest and then bound to a second target such as the carbonyl group of biological materials, or polymer backbones in areas such as sensors, biological applications, and polymers(10 - 15,199,200).

CHAPTER IV

SYNTHESIS AND CHARACTERISATION OF METAL COMPLEXES OF AZINE OLIGOMERS OF DIACETYL

4.1 INTRODUCTION

The polymetallic complexes of oligomers and polymers play a vital role in many areas ranging from conductive materials technology to biology{141}. Polymetallic macromolecules are involved in a large number of processes including electron transport, metal storage and as substrate or intermediate in redox reactions{132}. Thus, the interaction of metallic ions with large molecules is currently receiving much attention. Among the large molecules of interest, the linear conjugated macromolecules such as polyacetylenes $-[-C=C-]-_n$ and carotenoids are by far the most studied{205-207}. Unfortunately, the interactions of these polyene molecules occur only with low-oxidation state metallic species such as carbonyl complexes, as reported by Bremard and Bariz in 1988{132}. Polyazine $-[-N=C-C=N-]-_n$, is also a linear chain of atoms with alternating single and double bonds, but with pairs of nitrogen atoms substituted for pairs of carbon atoms in the polyacetylene chain. Advantages of polyazines include;

(i) Simple synthesis from inexpensive starting materials;
(ii) Polyazines are often environmentally stable{208};
(iii) Broad variability of substituents;
(iv) Simple theoretical description of the small -N=C-C=N- system{12,13,14};
(v) The π system in polyazines is not degenerate;
(vi) Similar to polyacetylene, polyazines can be doped with iodine and other oxidants to give a highly conducting material{155}.

The synthesis of polyazine oligomers and polymers $-[-N=C-C=N-]-_n$, give the opportunity to generate stable metallic complexes using the nitrogen as donor atoms. Oligomeric ligands which can coordinate two or more metal ions offer the possibility of studying unusual electronic and chemical properties depending upon the proximity of the metal centres{127}. Variation of the ligands allows the separation and disposition of the metal ions to be controlled in a systematic manner{209-210}.

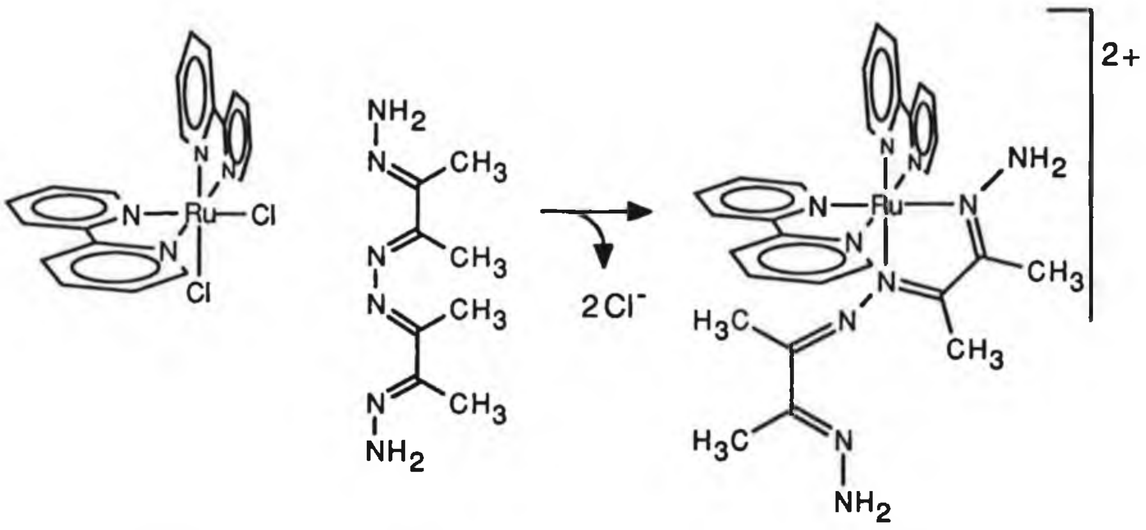
The diacetyl ligands **(5)** and **(247)** described in chapter II and the extension to larger molecules where the structure is unambiguously assigned **(334) - (339)**, should represent ideal model systems for studying complexation of metals to polyazines. Diacetyldihydrazone **(5)** can be regarded as a monomer of polyazines of diacetyl.

To date, numerous metal complexes of diacetyldihydrazone **(5)** have been reported, including the Fe(II), Ni(II), Co(II), Cu(II), Pt(II), Hg(II), Rh(II), W(0) and Mo(0) and more recently Mn(II) and Zn(II) complexes(71). The only reported crystal structure for any of these complexes to our knowledge is the nickel complex, with a metal to ligand ratio 1:3, reported by Pomahehko in 1989(73). The crystal structure of the ligand **(5)** was reported as part of a study of polyazines(155).

Sahoo and Mohapatra in 1982(128) prepared a series of binuclear Ni(II), Co(II), Cu(II) and Fe(II) complexes **(255)** - **(268)** of the dimeric ligand, diacetylazinedihydrazone **(247)**. The exact structure of these complexes is not known, and in particular whether the ligands are complexed in a *cis* or *trans* configuration around the metal centres. In an extension of this work, we report in this chapter the synthesis and characterisation of a number of previously unreported metal complexes of polyazines.

4.2 PREPARATION OF [RU(BIPY)$_2$(DIACETYLAZINEDIHYDRAZONE)](PF$_6$)$_2$ (353)

To investigate the possibility of binding ruthenium to molecules containing multiple diimine sites, such as polyazine dihydrazones, rutheniumbis(bipyridyl) was refluxed with an excess of diacetylazinedihydrazone in aqueous ethanol solution according to scheme [4.1].



(348) **(247)** **(353)**

Scheme [4.1]

Monitoring the reaction by cation exchange HPLC revealed that a large number of side products were also obtained in addition to the main product, [rutheniumbis(bipyridyl)(phenyldiacetylazinedihydrazone)]$^{2+}$ **(353)**. The product was purified using semipreparative HPLC, and was isolated as the PF_6 salt.

IR analysis of the product **(353)** displayed four sharp peaks assigned to the symmetric and asymmetric stretching of the different types of NH_2 groups. The peak at 3634 cm^{-1} due to the symmetric stretch of the terminal NH_2 group bound to the ruthenium; 3388 cm^{-1} due to the asymmetric stretching of the same group. The peak at 3400 cm^{-1} was assigned to the NH_2 groups of the hydrazone not bound to ruthenium and its corresponding asymmetric stretching mode occurring at 3314 cm^{-1}. The NH rocking occurs at 1630 cm^{-1}, and the P-F stretching frequency appears at 556 cm^{-1}.

^{1}H NMR analysis provides more conclusive evidence for the formation of the mono-nuclear complex, with Ru(bipy)$_2$:dimer ligand in a 1:1 ratio. The methyl group closest to the hydrazone not involved in chelation appears as a singlet at a chemical shift of 1.08 ppm, ($\delta_{(\text{free ligand})}$ = 1.93 ppm), and its adjacent methyl group close to the azine group appears as a singlet at 1.81 ppm, ($\delta_{(\text{free ligand})}$ = 1.91 ppm). The methyl group closest to the hydrazone group bound to ruthenium has been assigned to a singlet at a chemical shift of 2.71 ppm, ($\delta_{(\text{free ligand})}$ = 1.93 ppm) and its neighbouring methyl group appears at a chemical shift of 2.55 ppm, ($\delta_{(\text{free ligand})}$ = 1.91 ppm). The fact that the four methyl groups all have very different chemical shift values, is indicative of a mono-nuclear complex, as a dinuclear complex would be symmetric producing only two methyl peaks in the NMR spectrum.

Two peaks were assigned to the terminal NH_2 groups. A singlet occurs at a chemical shift of 7.29 ppm for the complexed hydrazone group, and a second broad singlet appears at a chemical shift of 7.03 ppm for the uncomplexed hydrazone, ($\delta_{(\text{free ligand})}$ = 6.8 ppm). The bipyridyl protons gave 16 multiplets and were assigned with the help of a COSY spectrum, figure [4.1].

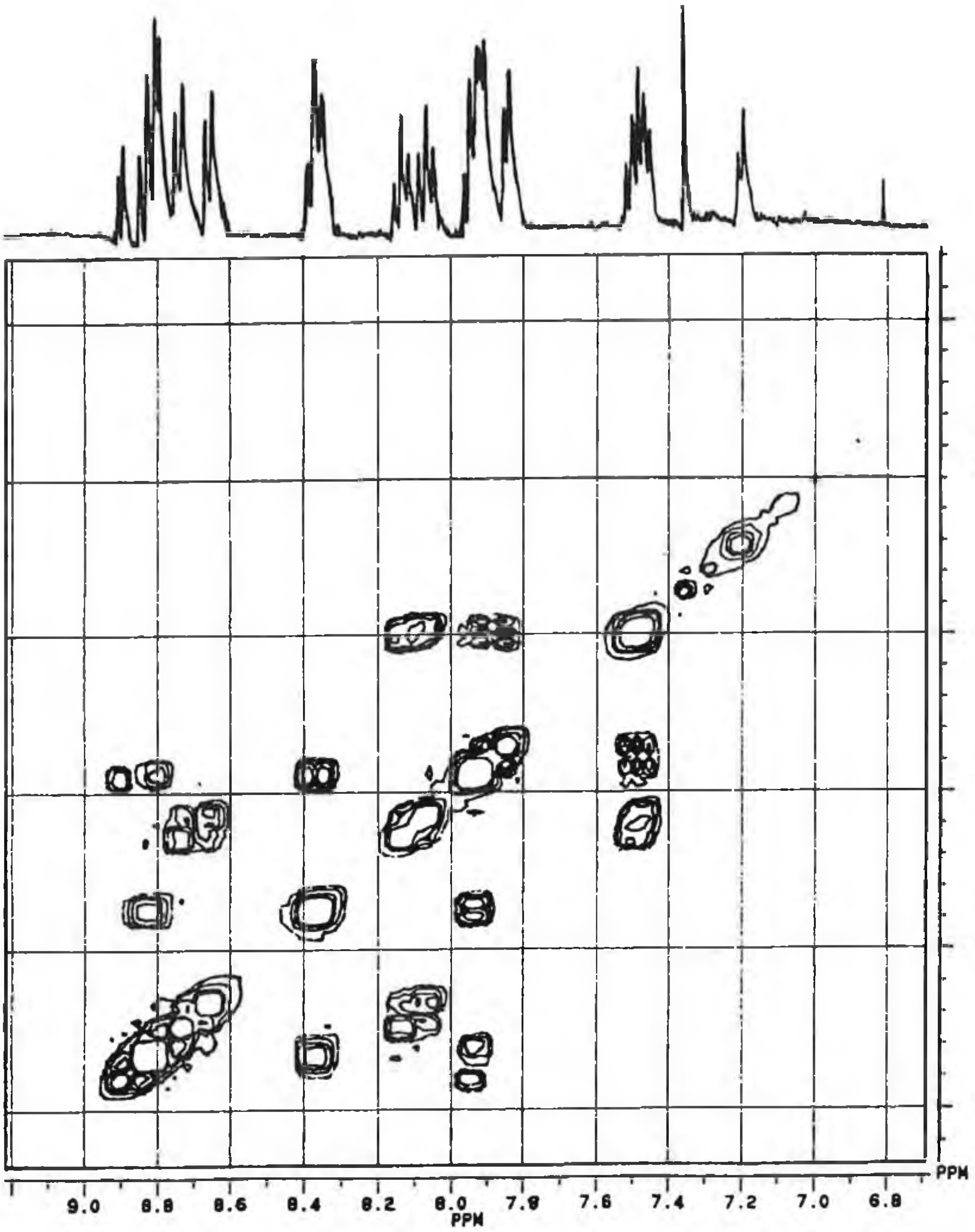
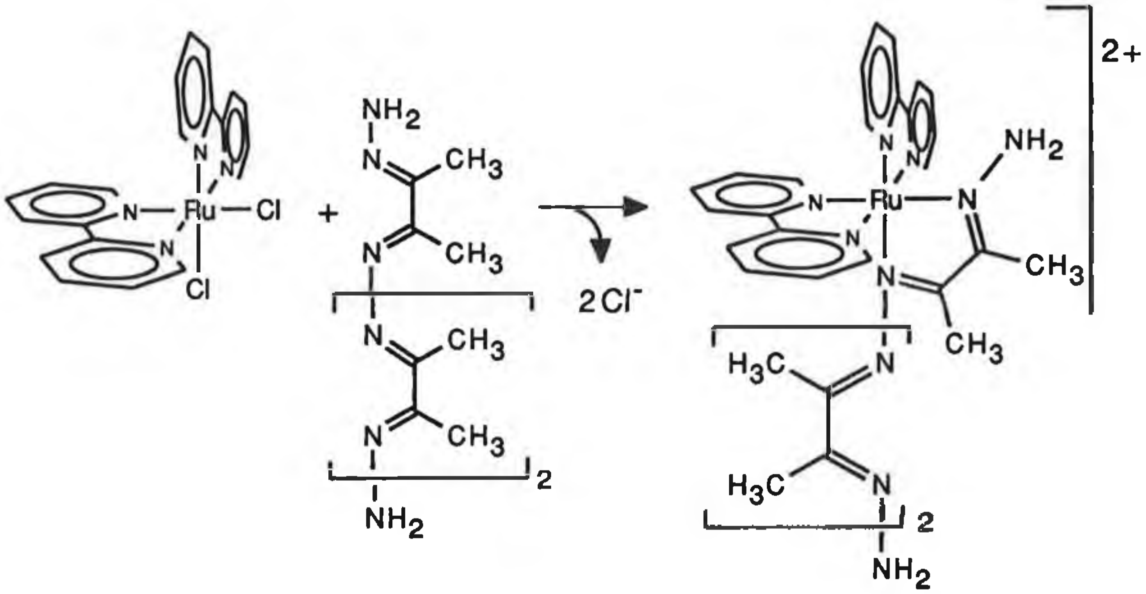


Figure [4.1] ^{1}H NMR 2D COSY of $[Ru(bipy)_2(247)](PF_6)_2$ (353) in DMSO-d_6

A UV/Vis. spectrum (280-600 nm) was obtained for the complex in acetonitrile **(353)** and the lowest energy maximum appears at 420 nm. This band was assigned to the metal-to-ligand charge transfer. No evidence for emission properties was found for the complex both at room temperature and at low temperature.

4.2.1 ATTEMPTED PREPARATION OF $[Ru(BIPY)_2(334)](PF_6)_2$ (354)

A number of attempts were made for the preparation of the mono-nuclear rutheniumbis(bipyridyl) complex **(354)** of the trimer, diacetyldiazinedihydrazone **(334)** according to scheme [4.2].



(348) **(334)** **(354)**

Scheme [4.2]

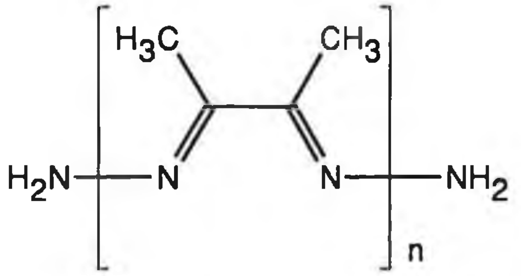
Following the reaction by HPLC indicated that a large number of products were formed during the course of the reaction. Two major products were isolated using semipreparative HPLC. The first eluting product was identified as the $[Ru(bipy)_2(dimer)]^{2+}$, rutheniumbis(bipyridyl)diacetylazinedihydrazone complex, which had identical spectral characteristics with **(353)**. A second eluting product was tentatively assigned as the $[Ru(bipy)_2(trimer)]^{2+}$, $[\text{rutheniumbis(bipyridyl)diacetyldiazinedihydrazone}]^{2+}$ **(354)**. However, difficulties were encountered during its purification as the complex was unstable and readily converted into $[Ru(bipy)_2(dimer)]^{2+}$ **(353)** together with other unidentified products.

A UV/Vis. spectrum (280-600 nm) was obtained for the complex **(354)** and the lowest energy maximum appears at 425 nm. This band was assigned to the metal-to-ligand charge transfer. No evidence for emission was found for the complex, both at room temperature and at low temperature.

4.3 CATALYTIC COUPLING REACTION OF LIGANDS BY TRANSITION METALS

Some attempts to prepare zinc complexes of the ligands using very dilute reactant solutions led to the discovery of a coupling reaction of the ligands with zinc catalysis, producing a mixture of poly-diacetylazinedihydrazones.

For example on mixing a dilute solution of the trimer, diacetyldiazinedihydrazone **(334)** with a solution of zincdichloride, a yellow product precipitated. Elemental composition analysis of this product shows no metal incorporation and that the product was completely organic. Analysis of the product by HPLC using a C_{18} column, (mobile phase; methanol/water 80/20), as depicted in figure [4.2], revealed that the original single peak (Rt. = 3 min. for the trimer) was replaced by a number of peaks. These peaks gave elution times corresponding to the dimer **(247)**, trimer **(334)**, tetramer **(335)**, pentamer **(336)**, and larger oligomers.



(247) n = 2
(334) n = 3
(335) n = 4
(336) n = 5

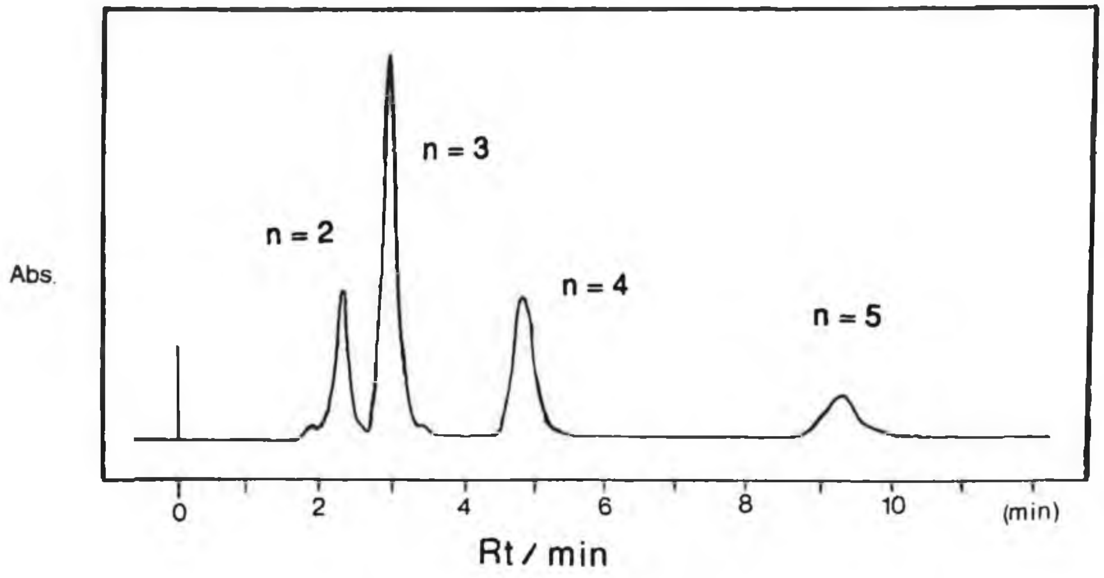


Figure [4.2] **HPLC chromatogram for reaction between trimer (334) and $ZnCl_2$**

Analysis of the peaks using PDA detection showed that the peaks gave identical spectra to the corresponding pure hydrazones. When samples of each of the dihydrazones prepared separately **(247)**, **(334)**, **(335)**, and **(336)**, were refluxed in aqueous ethanol for thirty minutes without the presence of the transition metal, followed by HPLC analysis, the results indicated that very little decomposition had occurred. This suggests that a metal-catalysed coupling of the ligands is occurring. This causes the trimer dihydrazone **(334)** to both disproportionate to produce the dimer **(247)**, and also to oligomerise, to produce the tetramer **(335)**, pentamer **(336)**, etc.

In order to confirm that it was in fact a catalytic reaction, a series of reactions with different ligand to $ZnCl_2$ molar ratios were carried out in methanol. It was found that a zincdichloride-to-ligand ratio of 1:100, was sufficient to promote the coupling reaction. To investigate whether the catalytic reaction was selective to $ZnCl_2$, a series of reactions were carried out which involved the addition of a number of different transition metals, and different counter ions to a standard stock methanolic solution of the dihydrazone trimer **(334)**. Each of the reaction mixtures was refluxed for ten minutes, and immediately analysed by HPLC. It was found that the coupling reaction was catalysed by many of the transition metals. Some of the metals used displayed greater catalytic activity than others. Strongly coordinating metals such as chromium(III), iron(III), nickel(II), cobalt(II) and copper(II) caused the coupling reaction to proceed rapidly, whereas poor coordinating metals such as manganese(II) and titanium(IV) possessed much lesser catalytic activity. Table [4.1] shows the different metals used, with their relative catalytic abilities listed.

Table [4.1] Relative catalytic properties of transition metals

Metal	Response
$ZnCl_2$	++
$Zn(AcO)_2$	+
$CrCl_3$	++++
$CrNO_3$	++++
$FeCl_3$	++++
$MnSO_4$	+
$MnCl_2$	++
$NiCl_2$	+++
$CoCl_2$	+++
$CuCl_2$	+++
$TiCl_4$	+

The reaction was carried out on a series of stirring methanol solutions of the dimer, trimer, tetramer and pentamer with 1% molar equivalent of $CuCl_2$ added to each solution. The solutions were stirred at room temperature and analysed by HPLC, using a C_{18} column. It was found that each reaction mixture reaches an equilibrium stage independent of starting materials used where the amount of each product is broadly similar, as depicted in figures [4.2] to [4.5].

From the reaction products, it was clear that a solution of the trimer dihydrazone **(334)** in the presence of a catalytic amount of transition metal, causes the formation of a number of products including the dimer **(247)**, trimer **(334)** tetramer **(335)** and pentamer **(336)** dihydrazones. A proposed mechanism for the reaction is described; when one of the diimine groups of an oligomer dihydrazone binds to a metal ion in solution, there is an electron density transfer from the imine nitrogen to the metal ion. This decrease in electron density around the imine nitrogens bound to the metal causes the imine carbons to become more electron deficient. These carbons are thus made vulnerable to nucleophilic attack by neighbouring hydrazone groups, either intramolecular from the chain or intermolecular from solution, as depicted in scheme [4.3].

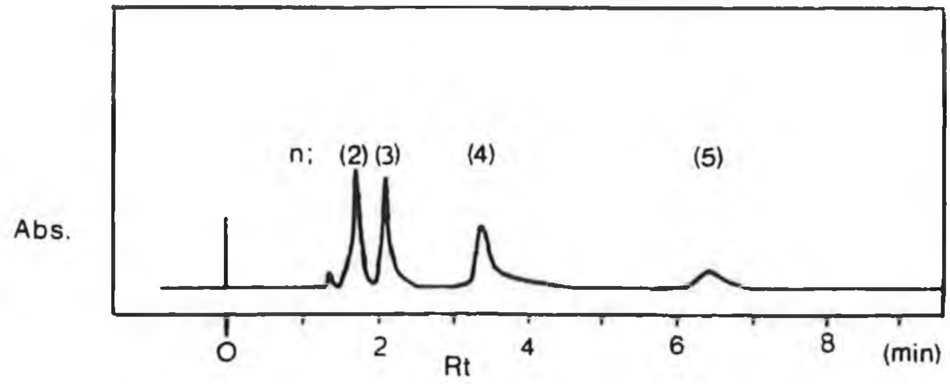


Figure [4.3] HPLC chromatogram for reaction between dimer (247) and $ZnCl_2$

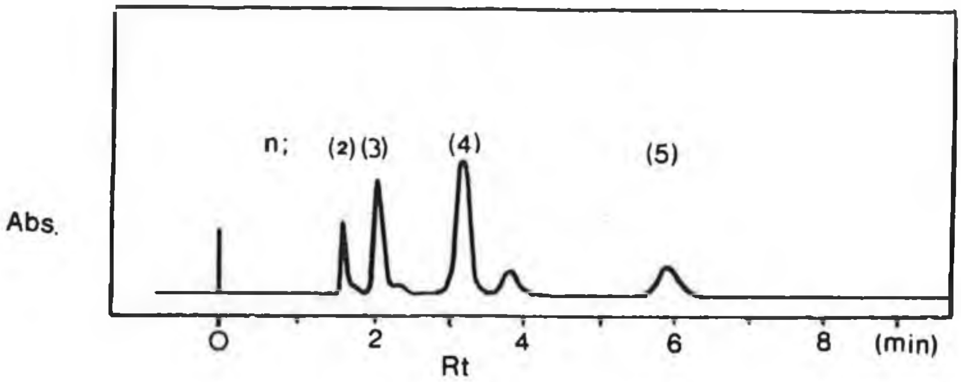


Figure [4.4] HPLC chromatogram for reaction between tetramer (335) and $ZnCl_2$

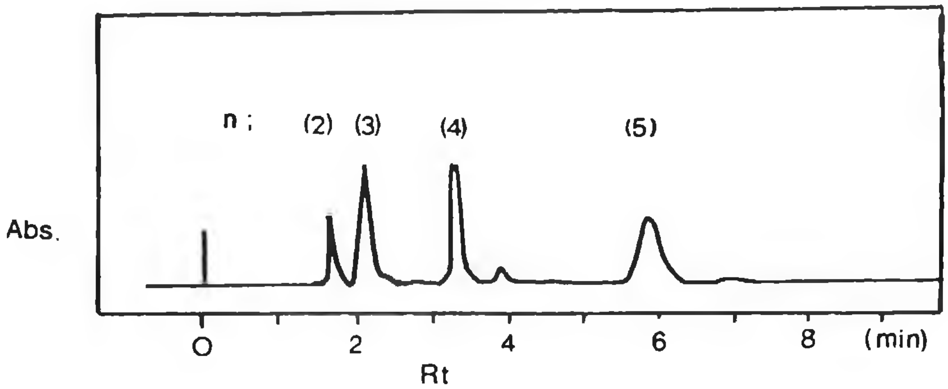
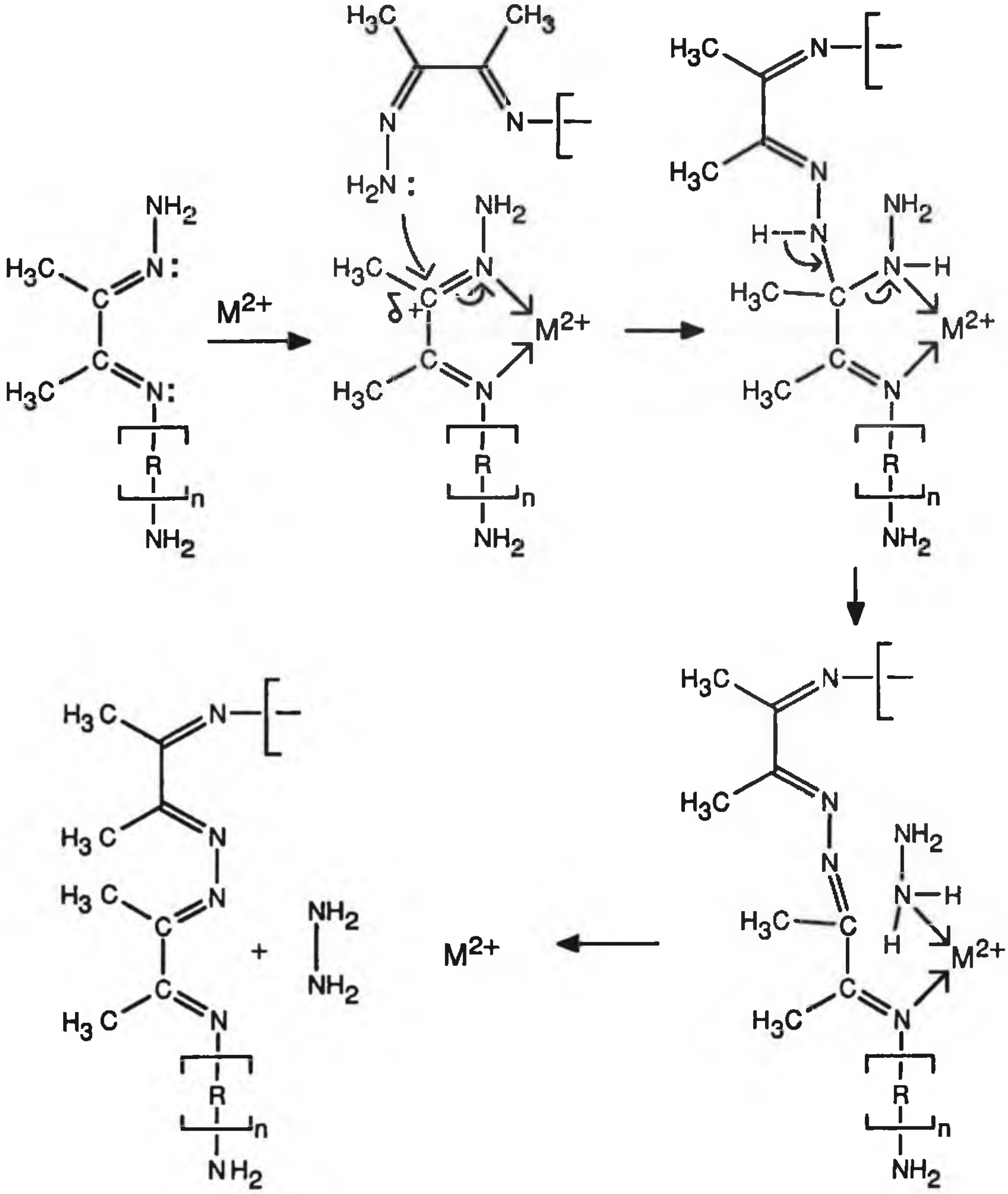


Figure [4.5] HPLC chromatogram for reaction between pentamer (336) and $ZnCl_2$



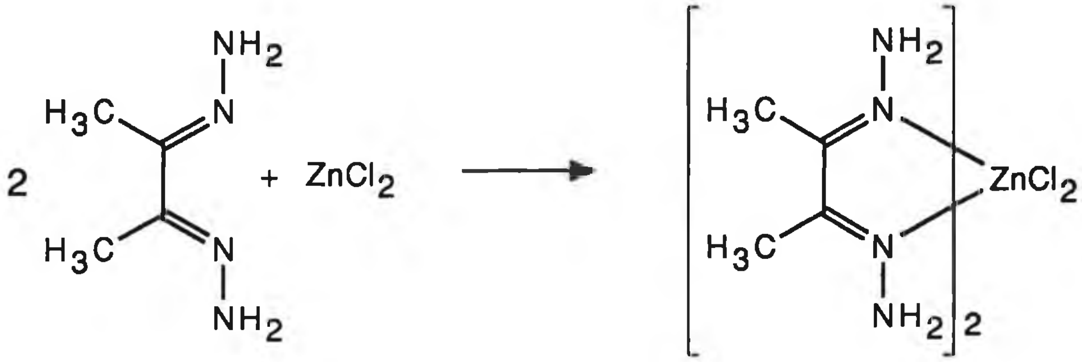
Scheme [4.3]

The reaction mechanism involves nucleophilic attack on an electron deficient carbon by a terminal amino group, with a simultaneous aminolysis of the C=N bond. The result of these reactions lead to the formation of different sized oligomers being formed.

The coupling reaction is only observed for dilute solutions of ligand and is prevented at high concentrations of ligand and metal by the formation of insoluble complexes.

4.4 PREPARATION OF ZINC(II)BIS(DIACETYLDIHYDRAZONE)DICHLORIDE (355)

In a procedure described by Gonzalez Garmendia in 1982[71], the $ZnCl_2$ complex **(355)** of the ligand diacetyldihydrazone **(5)** was prepared by the addition of a warm solution of zinc dichloride to a solution containing a two molar equivalent of diacetyldihydrazone, according to scheme [4.4]. The structure was assigned on the basis of IR, and X-ray crystal structure. A satisfactory elemental composition was obtained for **(355)**.



(5) **(355)**

Scheme [4.4]

The white product precipitates from solution at 50°C. Studies indicated that the complex was not stable in solution over a period of a few days and decomposes to an unidentified yellow compound. To obtain crystals suitable for X-ray crystallography studies, the product was recrystallised overnight from a hot saturated methanol solution.

IR analysis indicates a number of absorptions in the region of 3200 - 3400 cm^{-1} of the spectrum, as in figure [4.6]. The sharp peaks at 3379 cm^{-1}, 3350 cm^{-1} ($\upsilon_{(free\ ligand)}$ = 3325 cm^{-1}) were assigned to the symmetric NH stretching vibrations. The bands at 3298, 3263 and 3216 cm^{-1} were assigned to the NH asymmetric stretching frequencies of the complex ($\upsilon_{(free\ ligand)}$ = 3182 cm^{-1}). The published values were 3380, 3350, 3295, 3260 and 3207 cm^{-1} for the NH absorptions[71]. This would suggest the *cis* coordination of the ligands to the metal, as a *trans* conformation, being more symmetric, would be expected to have less NH stretching frequencies. It was not possible to assign metal-ligand stretching vibration frequencies in the region 400 - 200 cm^{-1} as only relatively weak absorptions were observed in this region.

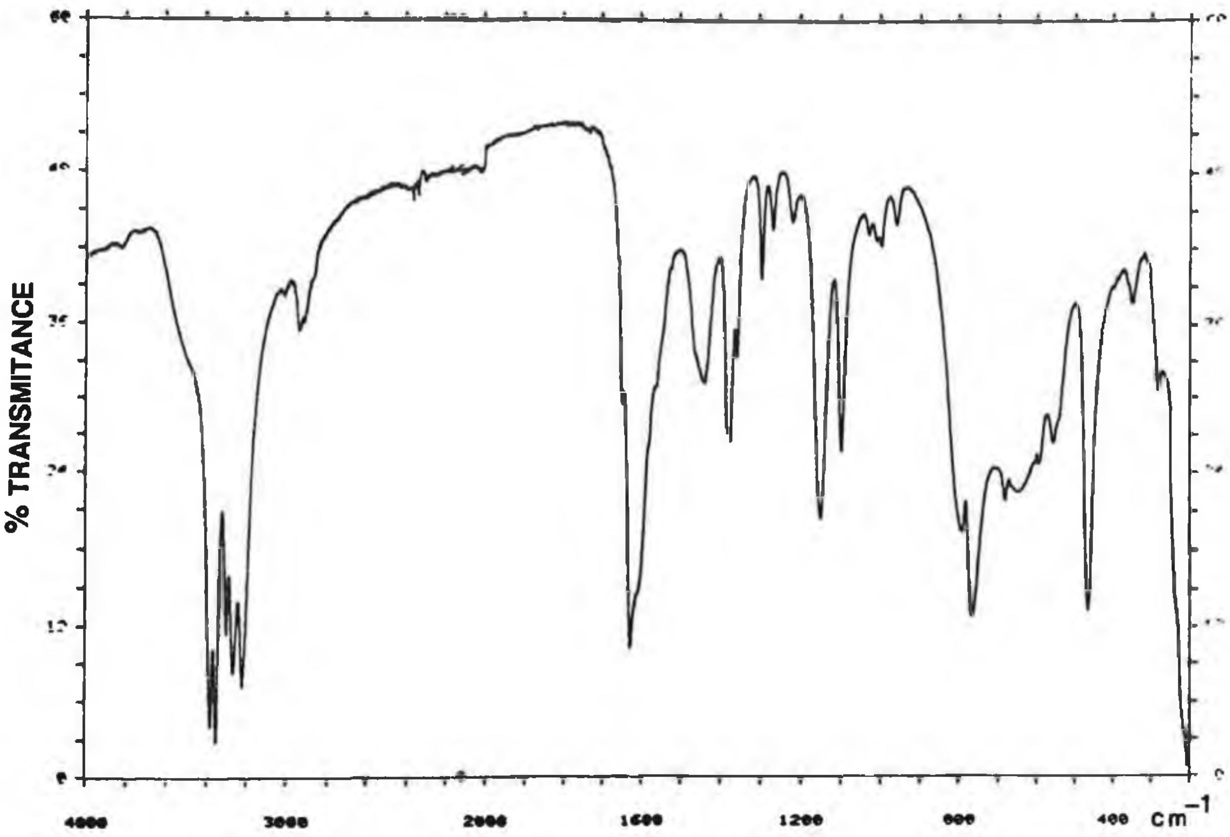


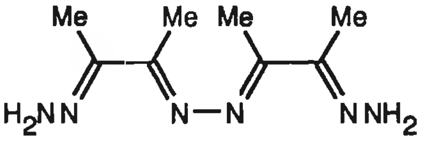
Figure [4.6] **Infrared Spectrum of $Zn(II)(ddh)_2Cl_2$ (355) from 4000 to 200 cm^{-1}**

A strong peak at 1627 cm^{-1} is assigned to the C=N stretching frequency which compares to 1570 cm^{-1} for the $\upsilon_{C=N}$ for the free ligand. This increase in frequency on complexing was explained in terms of the ligand altering its conformation from *trans* to *cis* on complexing.

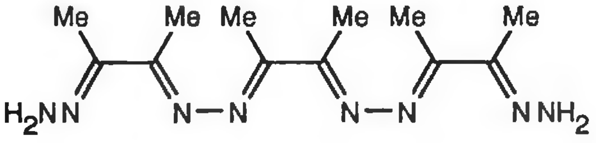
The ^{1}H NMR spectrum of the complex **(355)** was very similar to the spectrum of the ligand. The protons of the four methyl groups appear as a singlet at 2.0 ppm, ($\delta_{(free\ ligand)}$ = 1.8 ppm), and the four terminal amino groups appear as a singlet at a chemical shift of 5.3 ppm, ($\delta_{(free\ ligand)}$ = 5.3 ppm).

4.5 POLYNUCLEAR COMPLEXES OF NICKEL(II) AND ZINC(II) WITH DIACETYLAZINEDIHYDRAZONE AND DIACETYLDIAZINEDIHYDRAZONE

In recent years, there has been considerable attention focused on polydentate ligands which can coordinate to two or more metal ions. Amongst them, diacetylazinedihydrazone **(247)**, has been complexed to Ni(II), Co(II), Cu(II) and Fe(II) by Sahoo in 1982(126). In a further study of this particular area, the synthesis of nickel(II) and zinc(II) complexes of the ligands diacetylazinedihydrazone **(247)** and diacetyldiazinedihydrazone **(334)** is described.



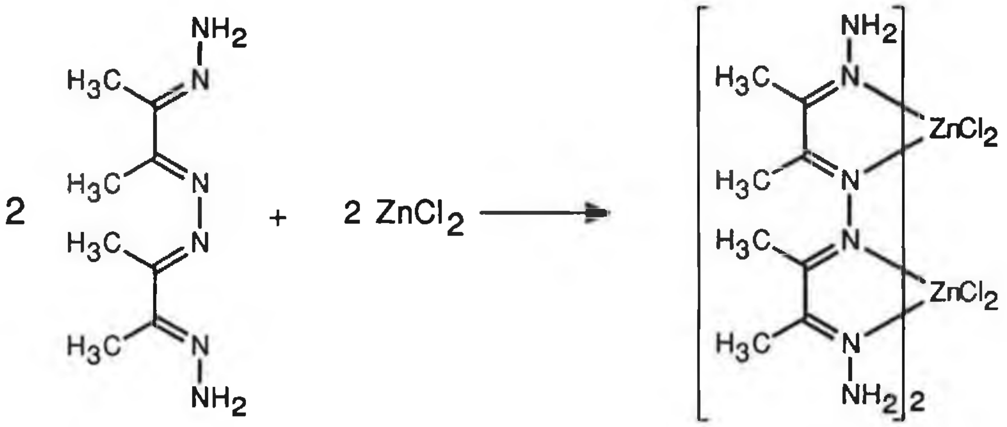
(247)



(334)

4.5.1 Preparation of Zinc(II)diacetylazinedihydrazonedichloride (356)

Using a variation of the method described by Sahoo(126), addition of a solution of zinc(II) to a suspension of the ligand, diacetylazinedihydrazone **(247)** results in the formation of the new complex zinc(II)diacetylazine dihydrazone **(356)** according to scheme [4.5].



(247) **(356)**

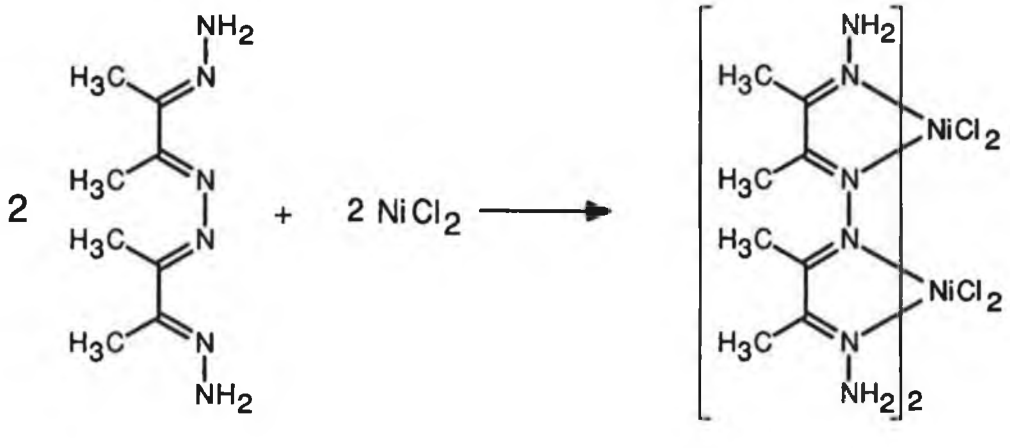
Scheme [4.5]

The yellow coloured complex gave satisfactory elemental analysis. Attempts to recrystallise the complex indicate that the complex is not stable in methanol solution.

Only two N-H stretching frequencies were observed in the IR spectrum, displayed in figure [4.7]. A strong absorption peak at 3386 cm^{-1} was assigned to N-H asymmetric stretching mode, ($\upsilon_{\text{(free ligand)}}$ = 3346 cm^{-1}), and a strong peak 3266 cm^{-1} was assigned to the N-H symmetric stretching frequency, ($\upsilon_{\text{(free ligand)}}$ = 3204 cm^{-1}). The fact that there are only two N-H vibrational modes in the IR spectrum suggests that ligands may be coordinated to the metal in a *trans* configuration. A *cis* configuration might be expected to display a greater number of NH absorption frequencies based on the IR data for the zincdi(diacetyldihydrazone)dichloride **(355)**. The peak at 1605 cm^{-1} was assigned the C=N stretching mode. We were unable to identify metal-chloride absorptions in the 400 - 200 cm^{-1} range. The complex **(356)** was not stable in a range of solvents. All attempts of obtaining NMR spectra gave only the ligand spectrum. The absence of any solution chemistry is attributed to the relatively weak complexing ability of Zn^{2+}.

4.5.2 Preparation of Nickel(II)diacetylazinedihydrazonedichloride (357)

Using a similar method to the procedure used for the dinuclear zinc(II) complex **(356)**, the nickel(II) complex **(357)** of the ligand diacetylazinedihydrazone **(247)** was prepared by the addition of an ethanolic solution of $NiCl_2$ to a suspension of the ligand according to the scheme [4.6].



(247) **(357)**

Scheme [4.6]

Satisfactory elemental analysis of the complex was obtained. The IR spectrum reveals a number of absorptions in the region of 3200 - 3400 cm^{-1} of the spectrum, as depicted in figure [4.8].

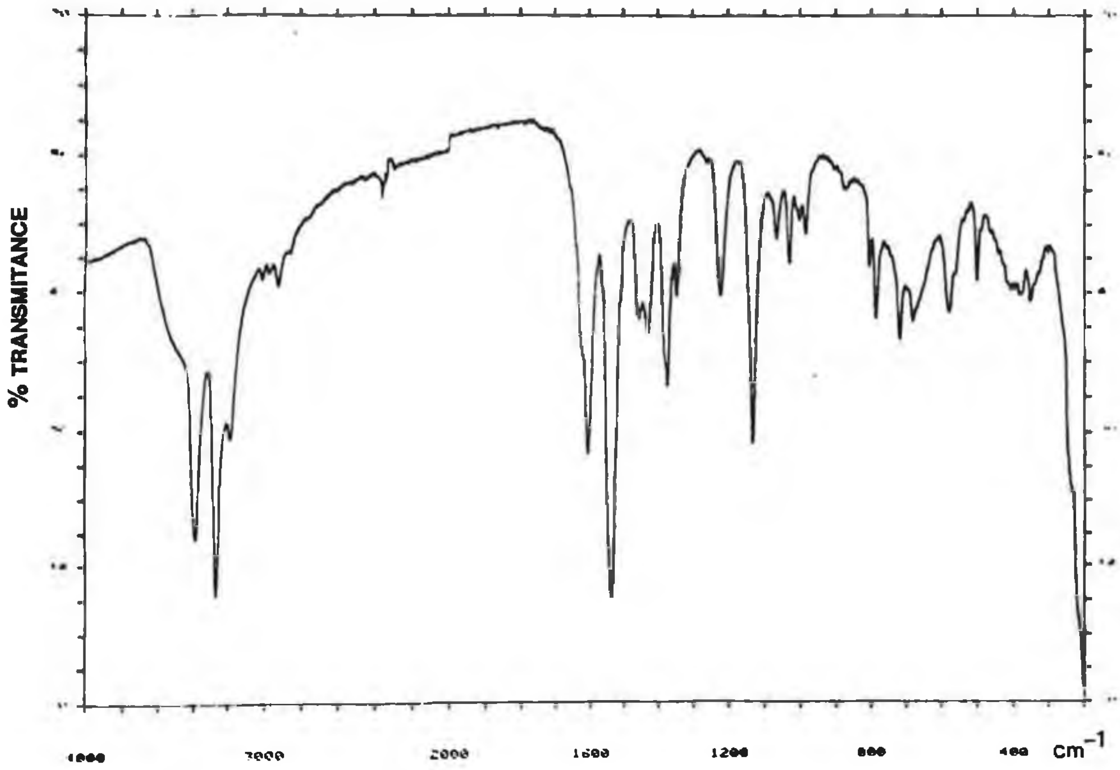


Figure [4.7] IR Spectrum (4000 - 200 cm^{-1}) of (356) in KBr

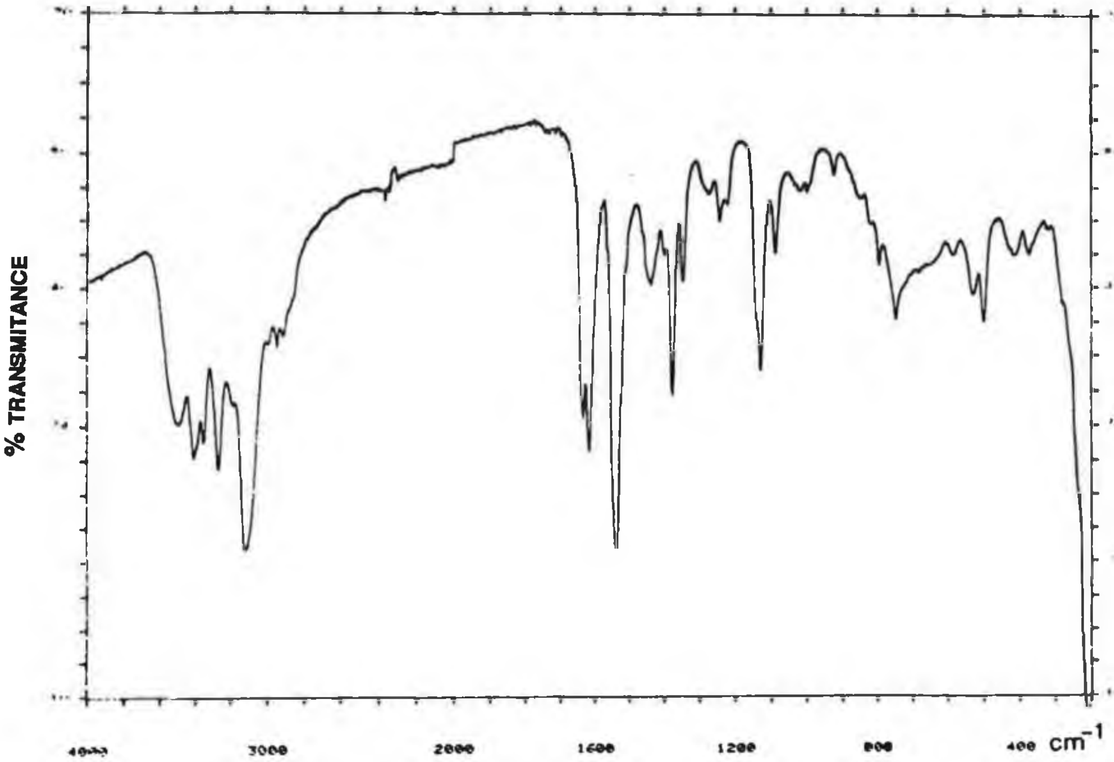
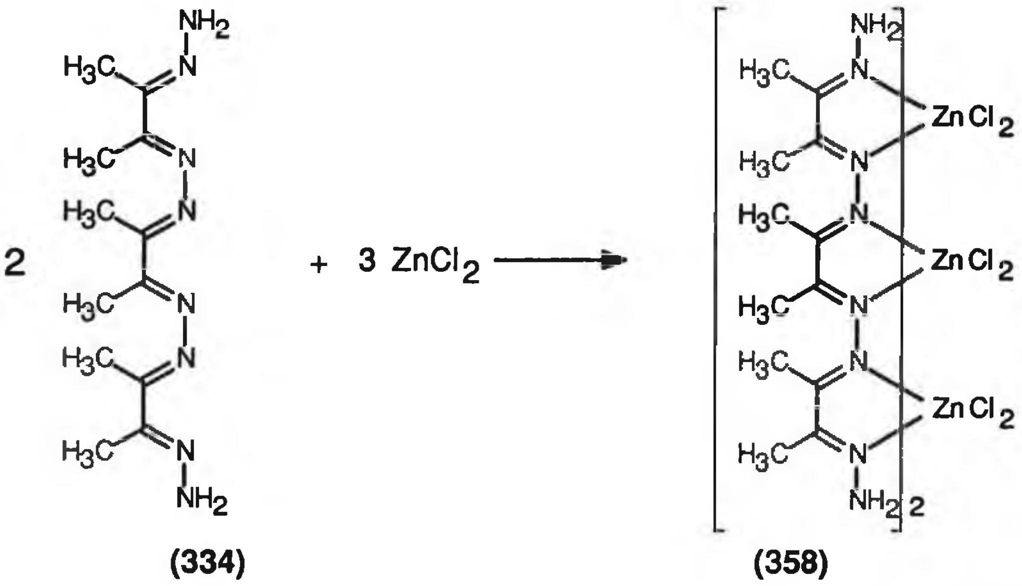


Figure [4.8] IR Spectrum (4000 - 200 cm^{-1}) of complex (357)

Three sharp peaks at 3494 cm^{-1}, 3408 cm^{-1} and 3351 cm^{-1} were assigned to N-H asymmetric stretching frequencies of the complex, ($\upsilon_{(free\ ligand)}$ = 3346 cm^{-1}), and the peaks 3270 cm^{-1} and 3117 cm^{-1} were assigned to the symmetric stretching mode, ($\upsilon_{(free\ ligand)}$ = 3204 cm^{-1}). The large number of N-H absorption bands suggests the formation of the *cis* coordination of the ligands to the metal. The peaks at 1633 cm^{-1} and 1614 cm^{-1} were assigned to C=N stretching vibrations, ($\upsilon_{(free\ ligand)}$ = 1600 cm^{-1}). No metal-ligand stretching vibrations were identified from the IR spectrum.

4.5.3 Preparation of Zinc(II)diacetyldiazinedihydrazonedichloride (358)

The zinc(II)chloride complex **(358)** was synthesised by addition of an ethanolic solution of $ZnCl_2$ to a suspension of the trimer ligand **(334)**, diacetyldiazinedihydrazone in ethanol, according to the scheme [4.7].

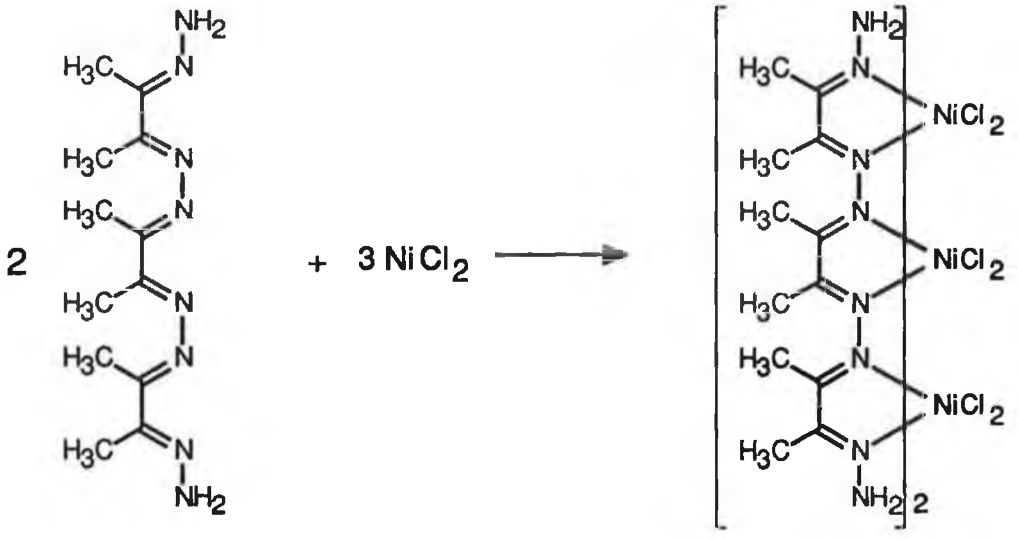


Scheme [4.7]

Two very distinct N-H stretching frequencies are observed in the IR spectrum as depicted in figure [4.9]; a strong absorption peak at 3383 cm^{-1} is assigned to the N-H asymmetric stretching mode, ($\upsilon_{(free\ ligand)}$ = 3346 cm^{-1}), and a strong peak 3267 cm^{-1} is assigned to the N-H symmetric stretching frequency, ($\upsilon_{(free\ ligand)}$ = 3204 cm^{-1}). Because there is only two N-H stretching modes, (the asymmetric and the symmetric), in the IR spectrum suggests that the complex has *trans* configuration. The peak at 1605 cm^{-1} was assigned to N-H rocking, ($\upsilon_{(free\ ligand)}$ = 1633 cm^{-1}), and the C=N stretching mode occurs at 1536 cm^{-1}, ($\upsilon_{(free\ ligand)}$ = 1588 cm^{-1}).

4.5.4 Preparation of Nickeldiacetyldiazinedihydrazonedichloride (359)

The nickel(II) complex **(359)** of the ligand diacetyldiazinedihydrazone was prepared by the addition of an ethanolic solution of $NiCl_2$ to a suspension of the trimer ligand **(334)** in ethanol, according to the scheme [4.8].



(334) **(359)**

Scheme [4.8]

A very broad band in the IR spectrum, illustrated in figure [4.10], with a number of shoulders present ranging from 3200-3400 cm^{-1} was assigned to N-H asymmetric and symmetric stretching frequencies of the complex, ($\upsilon_{(free\ ligand)}$ = 3361 cm^{-1}, 3221 cm^{-1} respectively). This broad peak results from a number of band overlapping and suggests that the ligands take up a *cis* orientation around the nickel(II) metal centre of the complex. The sharp peak at 1611 cm^{-1} was assigned to the C=N stretching mode, ($\upsilon_{(free\ ligand)}$ = 1588 cm^{-1}).

4.5.5 Preparation of Diphenylhydrazone trimer $ZnCl_2$ complex (360)

Under certain reaction conditions, addition of a metal to the ligands causes changes in the ligand composition. To prevent this occurring, a series of oligomers **(337)** - **(339)** were prepared which were similar to the azine dihydrazone ligands except that the terminal amino groups were replaced by a NH-phenyl group.

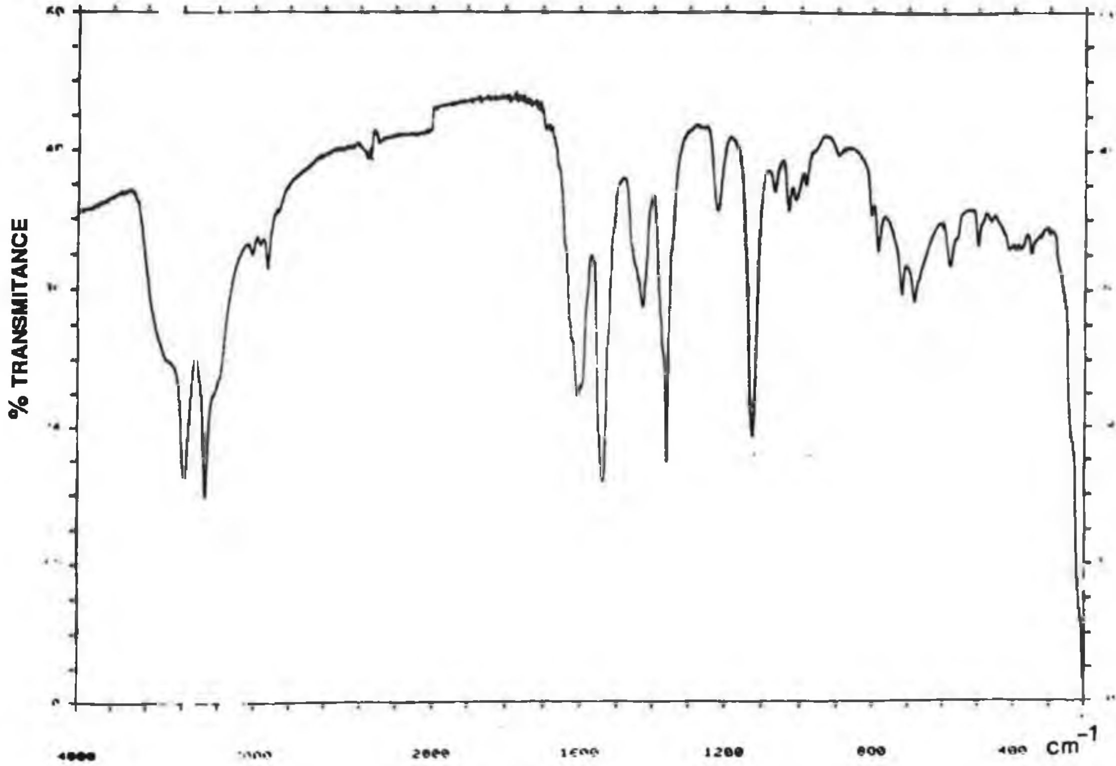


Figure [4.9] IR Spectrum (4000 - 200 cm^{-1}) of Complex (358)

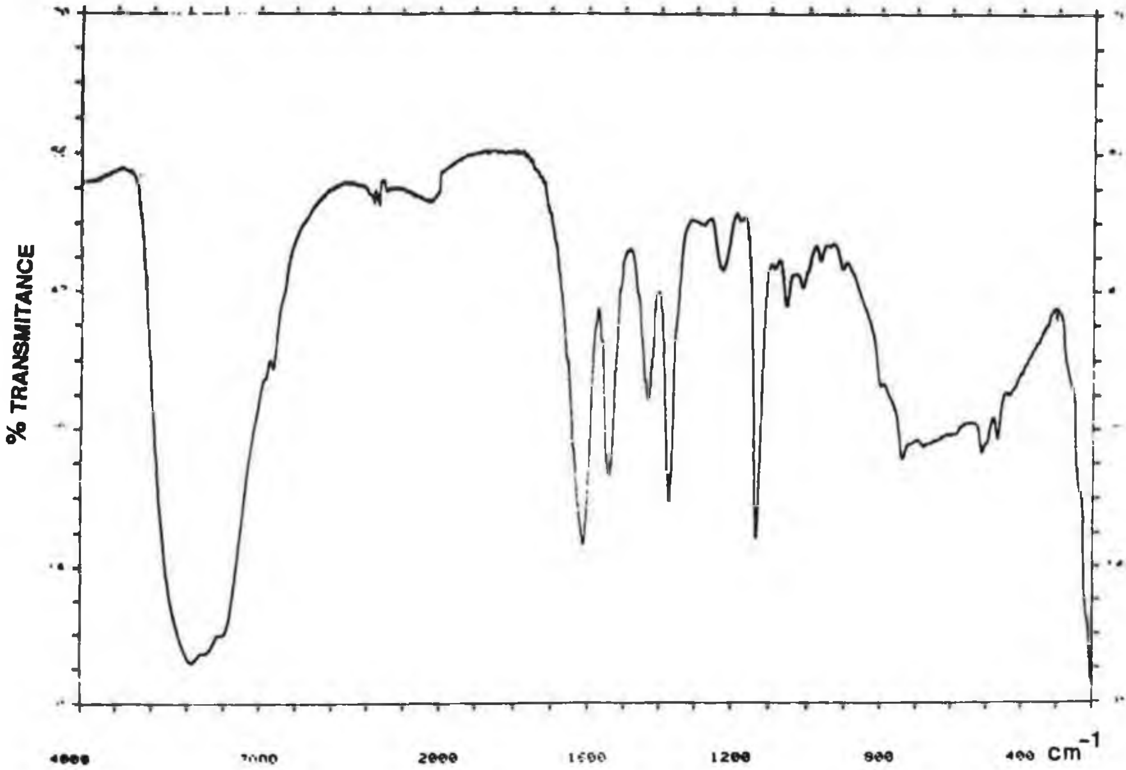
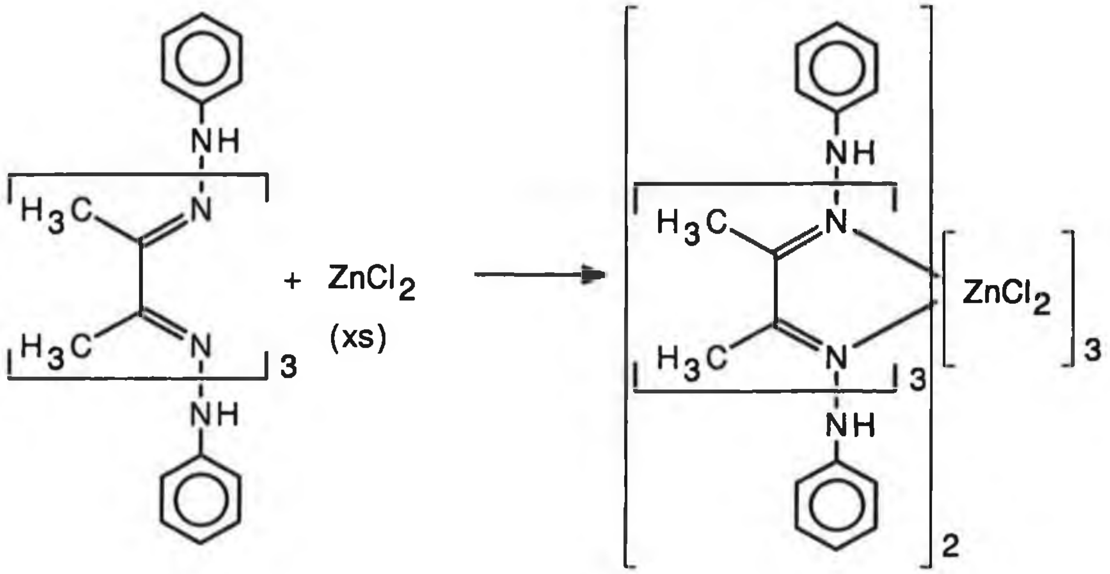


Figure [4.10] IR Spectrum (4000 - 200 cm^{-1}) of Complex (359)

Reacting a solution of diacetyldiazinediphenylhydrazone **(338)** in methanol with a solution containing an excess of zincdichloride at room temperature, produces a green microcrystalline product, according to scheme [4.9].



(338) **(360)**

Scheme [4.9]

The infrared spectrum displays an NH stretching frequency at 3283 cm^{-1}, compared with 3360 cm^{-1} for the free ligand. Because there is only one NH stretching frequency, leads to the suggestion that the ligands are coordinated around the zinc in a *trans* configuration as a *cis* configuration would produce multiple NH stretching frequencies. The C=N frequency band appears at 1604 cm^{-1}. There is a weak band at 328 cm^{-1} which was assigned to the metal-chloride stretching mode.

Analysis of the complex by NMR produced a spectrum which was identical to the NMR spectrum of the ligand. This was due to dissociation of the labile diacetyldiazinediphenylhydrazone zinc chloride complex **(360)** in solution, where excess zincdichloride is not present. This was supported by TLC and recrystallisation studies. A UV/Vis. spectrum of the trimer ligand **(338)** in chloroform and of its zinc complex **(360)** in chloroform, (200 - 500 nm), was obtained, (illustrated in figure [4.11], (a) and (b)). There was a large overlap in the two spectra at 320 nm, suggesting that the complex was dissociating. To investigate this theory, an excess of zinc chloride was added to the complex solution, and the UV/Vis. spectrum of this solution was obtained, (see figure [4.11], part (c)). $ZnCl_2$ is used in excess to push the equilibrium in the direction of the complex.

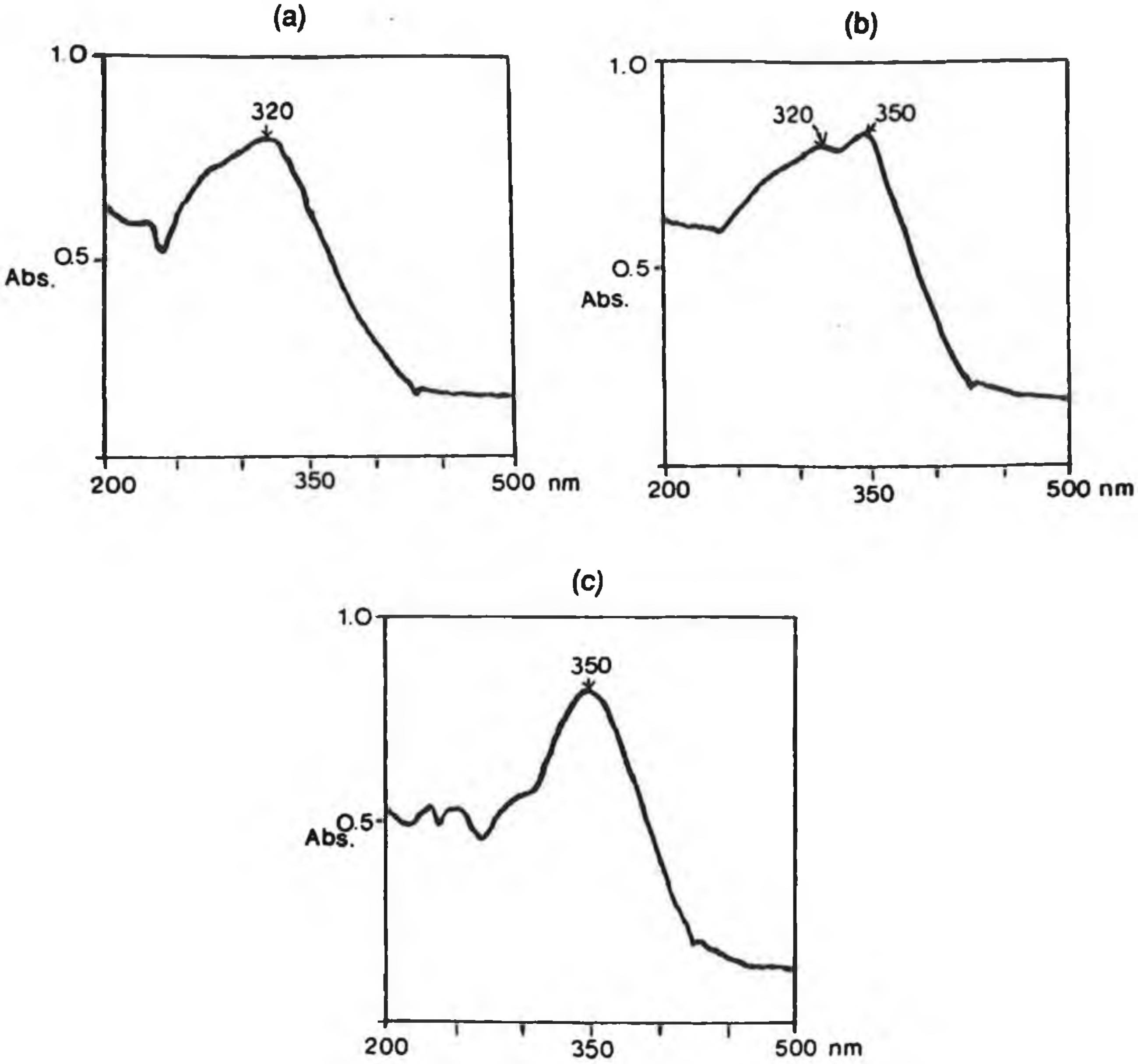


Figure [4.11] (a) UV/Vis. spectrum of trimer (338) in chloroform

(b) UV/Vis. spectrum of complex (360) in chloroform

(c) UV/Vis. spectrum of complex (360) and excess $ZnCl_2$

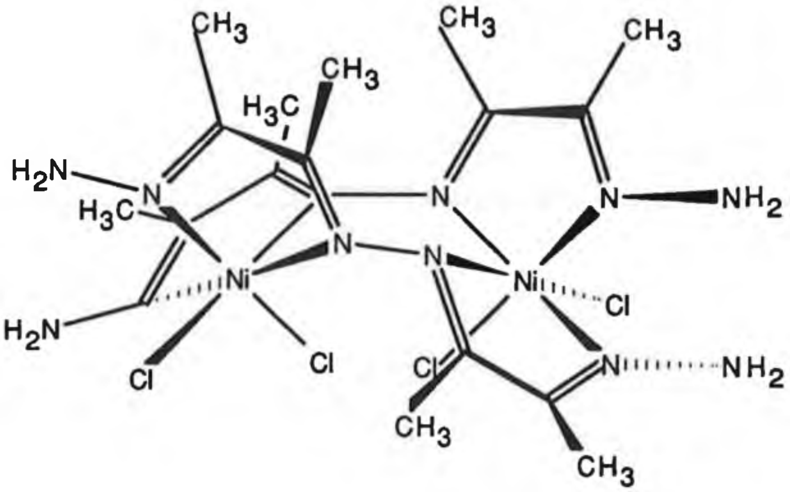
As observed in figure [4.11] part (c), there is a 30 nm shift in the maximum absorption band of the complex **(360)** compared to its ligand **(338)**. C,H,N analysis of the complex **(360)** indicates that the ligand-to-metal ratio was 2:3.

4.6 GENERAL DISCUSSION

The main objective of this section was to investigate the nature of complexation of polyazines of diacetyl to metals. Infrared and elemental analysis proved to be the most useful techniques in elucidating the structures of the complexes.

Initially, complexation of the monomer, diacetyldihydrazone **(5)** to transition metals was examined. Diacetyldihydrazone **(5)** reacts with zincdichloride in a 2:1 ligand to metal ratio, to produce the white complex zincdi(diacetyldihydrazone)dichloride **(355)**. The complex **(355)** was first reported by Gonzalez Garmendia in 1982(71), without a proposed structure. IR data indicate a variety of N-H stretching modes suggesting that the chlorines are bound to the zinc in a *cis* configuration, whereas a *trans* configuration would be expected to have only two N-H stretching modes, symmetric and asymmetric. A strong band at 1627 cm^{-1} was assigned to the C=N stretching frequency which compares to 1570 cm^{-1} for the $\upsilon_{C=N}$ for the free ligand. Variation in the C=N stretching frequency between the free ligand and complexes can be caused by two main features. The *cis* conformation of the diacetyldihydrazone as a bidentate ligand in complexes has higher $\upsilon_{C=N}$ frequency than the *trans* form of the free ligand, because of its higher degree of conjugation. In the opposite trend, the back donation from metal d orbitals to the π^* (antibonding) orbitals of C=N group of ligands, shifts the $\upsilon_{C=N}$ frequency to lower values(71). Our results indicate that the ligand **(5)** is coordinated to the metal in a bidentate manner since the $\upsilon_{C=N}$ increases on complexation of the ligand, confirming a transition of the ligand from *trans* to *cis*. The proposed *cis* configuration of the zinc(II) complex **(355)** was confirmed by an X-ray crystal structure determination.

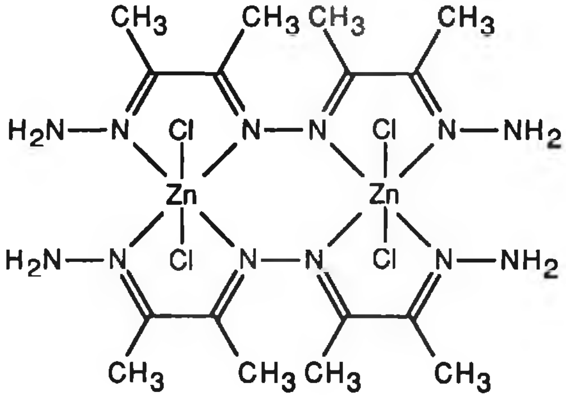
The next stage was to investigate what type of complex, the dimer, diacetylazinedihydrazone **(247)**, forms with transition metals. Sahoo(128) describes the preparation of tri(diacetylazinedihydrazone)dinickeltetrachloride, $[Ni_2(C_8H_{16}N)_3]Cl_4NiCl_2.6H_2O$ **(255)**. Using this procedure, a green complex was isolated which is believed to be the di(nickel)di(diacetylazinedihydrazone)-tetrachloride $[Ni_2(C_8H_{16}N_6)_2Cl_4]$ **(357)**, which has the same metal-to-ligand ratio (1:1) as the above reported complex **(255)**. The IR data of complex **(357)** suggests that the ligands of the complex **(357)** are bound to the metal centres in a *cis* configuration. There is a relatively large number of N-H bands in the IR spectrum, symmetric and asymmetric stretching which indicates that all of the N-H's of the complex are not equivalent. This would suggest that the complex has its ligands bound to the metals in a *cis* orientation giving the molecule a double helical type structure, illustrated below.



(357)

Proposed *cis* configuration of dimer ligands around nickel atoms

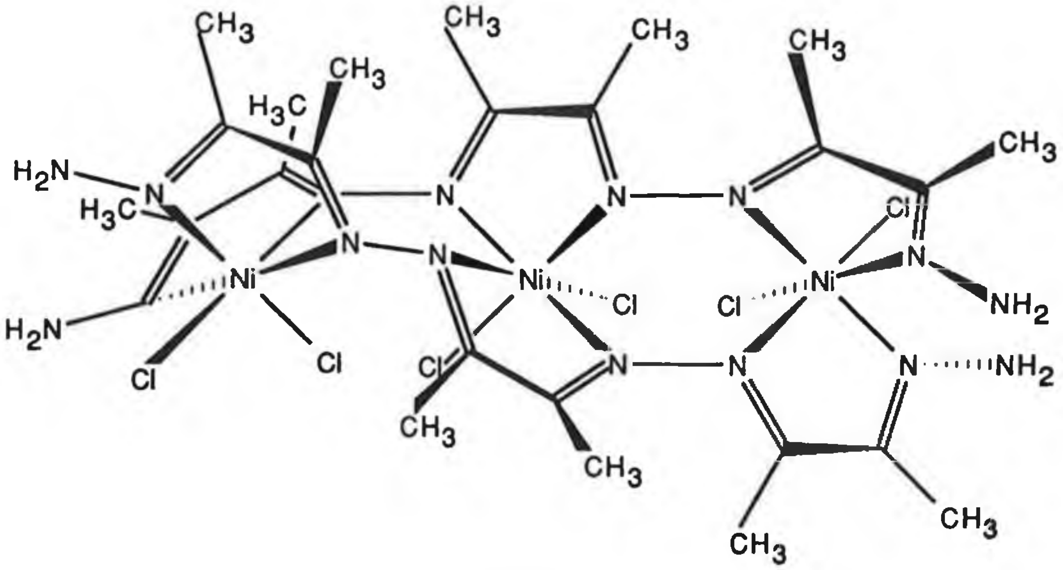
The zincdichloride derivative of the ligand diacetylazinedihydrazone **(247)** was also prepared in a similar manner. The product was of the type di(zinc)di(diacetylazine-dihydrazone)tetrachloride, **(356)**. Based on infrared data, the zinc complex of the dimer ligand, **(356)** is thought to have a *trans* configuration, as there are only two N-H stretching frequencies in the IR spectrum. A *trans* configuration of the ligands around the metals would cause the N-H's to be equivalent and therefore only a single symmetric and a single asymmetric band would be observed in the IR spectrum. The proposed structure, illustrated below, displays the two azine ligands *trans* coordinated to the metal centres occupying the same plane.



(356)

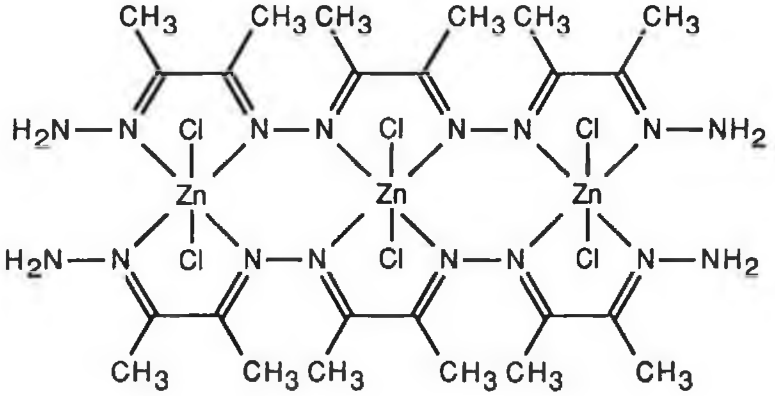
Proposed *trans* configuration of dimer ligands around zinc metal centres

New nickel(II) **(359)** and zinc(II) **(358)** complexes of the trimer ligand, diacetyldiazinedihydrazone **(334)** were prepared from corresponding ethanolic solutions of nickel(II)chloride and zinc(II)chloride. Elemental analysis revealed that the complexes contained a ligand to metal ratio of 2:3, suggesting the formation of the complexes, tri(nickel)di(diacetyldiazinedihydrazone)-hexachloride, $[Ni_3(C_{12}H_{22}N_8)_2Cl_6]$ **(359)**, and tri(zinc)di(diacetyldiazine-dihydrazone)-hexachloride, $[Zn_3(C_{12}H_{22}N_8)_2Cl_6]$ **(358)**. IR data of the nickel(trimer ligand) complex **(359)** indicated that the ligands and chlorines of the complex are coordinated to the metal centres in a *cis* configuration, similar to the structure of the nickel(dimer ligand) complex **(357)**. Two sharp N-H stretching bands in the infrared spectrum of the zinc(trimer ligand) complex **(358)** suggests a *trans* configuration of the complex.



(359)

Proposed configuration of trimer ligands around nickel metal centres

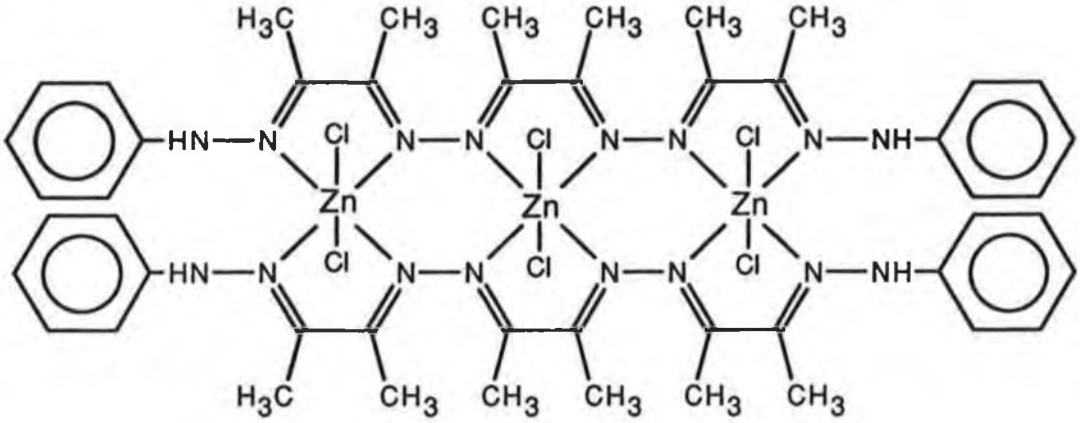


(358)

Proposed *trans* configuration of trimer ligands around zinc metal centres

The breakdown of the dihydrazone oligomers in the preparation of their metal complexes prompted us to examine the phenylhydrazone analogues. A series of oligomers, **(337) - (339)** was prepared which were in effect the diphenyl hydrazone derivatives of the diacetylazinedihydrazone ligands **(5)**, **(247)**, **(334) - (336)**. Replacing the terminal amino groups of the dihydrazones with an N-H phenyl group produces ligands which do not undergo disproportionation in the presence of metal catalysts.

The zinc chloride complex **(360)** was prepared from the trimer ligand **(335)**, which has a metal to ligand composition of 3:2 with the chloride ions remaining bound to the zinc atoms. $[Zn_3(C_{24}H_{30}N_8)_2Cl_6]$ **(360)**, is thought to have its ligands in a *trans* coordination around the metal centres based on IR data. UV/Vis. analysis of the complex indicates that the complex does not stay intact in solution unless the zinc concentration is high. Based on IR data, the most likely orientation of the ligands around the zinc metal centres, is where the ligands are coordinated in *trans* configuration.



(360)

Proposed *trans* configuration of dimer ligands around zinc metal centres

4.7 X-ray Structure of ZINC(II)DIACETYLDIHYDRAZONEDICHLORIDE (355)

An X-ray crystal structure of the complex was obtained verifying the proposed structure, as depicted in figure [4.12]. The crystal used for the analysis of the complex was obtained by hot recrystallisation of the complex from methanol.

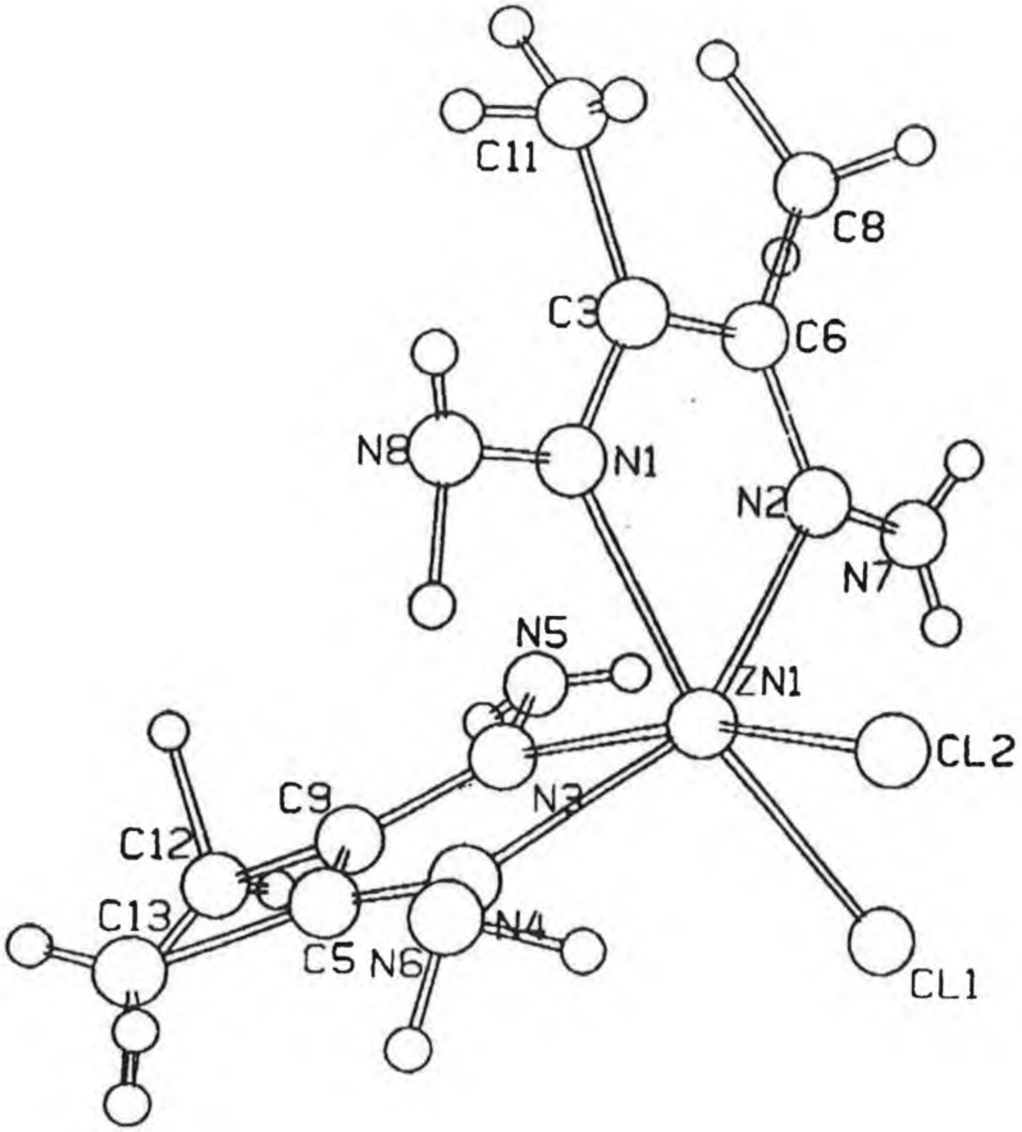


Figure [4.12] **X-ray Crystal Structure of Complex $Zn(C_4H_{10}N_4)_2Cl_2$ (355)**

The complex has octahedral geometry, with a zinc(II) metal centre cation bound to two diacetyldihydrazone (5) ligands and two chlorine anion ligands. The ligands are bound to the metal in a *cis* orientation. The structure was solved to an R factor less than 3%.

Preliminary results indicate that there is good deal of hydrogen bonding between the complexes and the crystal structure packing is depicted in figure [1.13]

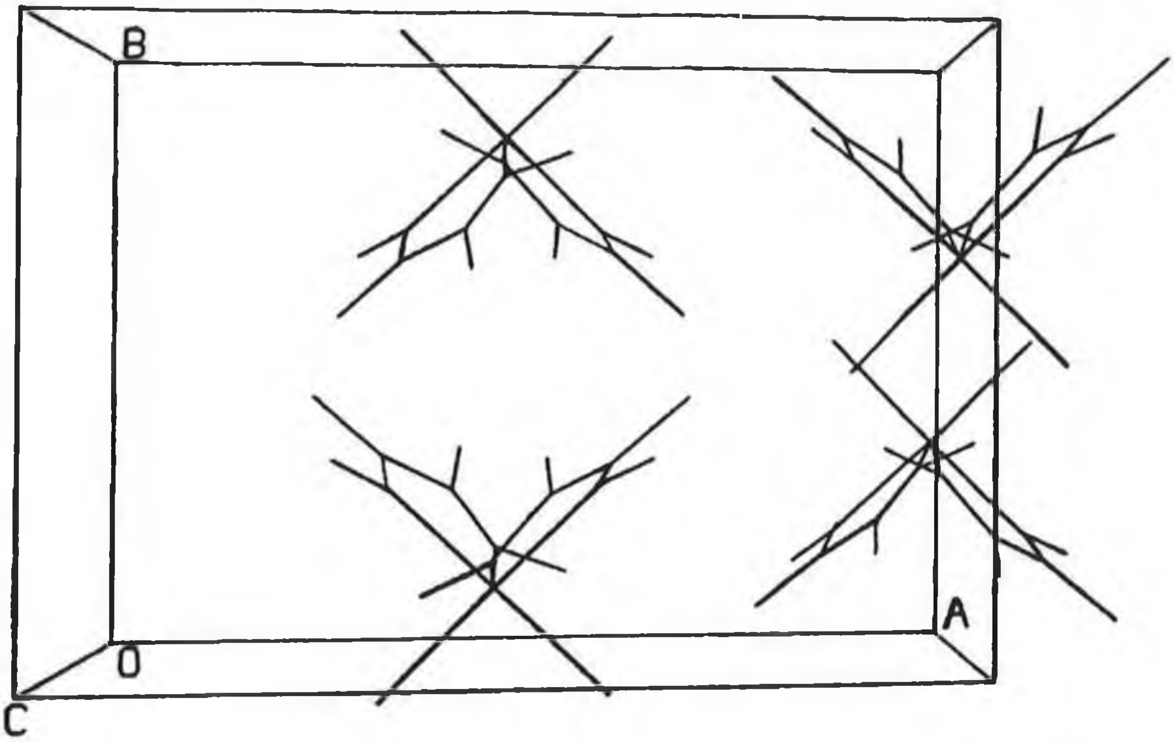


Figure [1.13] **Crystal Structure Packing of Complex $Zn(C_4H_{10}N_4)_2Cl_2$ (355)**

The crystal structure was determined by Professor C.A.McAuliffe at the University of Manchester, Institute for Science and Technology (UMIST), P.O.Box 88, Manchester M60 1QD.

4.8 Experimental

INSTRUMENTATION & TECHNIQUES

Infrared, ^{1}H NMR, UV/Vis. Spectra were obtained using the same instrumentation as described in Chapter II.

Analytical HPLC experiments were performed using a Waters 501 HPLC pump, a Waters 990 Photodiode Array HPLC system with a NEC PAC III computer and a 20 μL injector loop. A μ Partisil SCX radial PAK cation cartridge was used for the analytical separation of the ruthenium complexes, the detection wavelength was 280 nm and the mobile phase acetonitrile/water (80/20 v/v), containing 0.08 M $LiClO_4$ at a flow rate of 2.5 ml/min. A standard C_{18} column was used for the separation of the dihydrazone oligomer mixtures using a mobile phase methanol/water (80/20 v/v) and (60/40 v/v).

$[Ru(bipy)_2(diacetylazinedihydrazone)](PF_6)_2$ (353)

To a solution of 200 mg (0.38 mmol) of $[Ru(bipy)_2Cl_2].(H_2O)_2$ in 40 ml water, 200 mg (1.02 mmol) of diacetylazinedihydrazone **(247)** in 40 ml ethanol was added. The reaction mixture was refluxed for 5 days. The solvent was removed at 90°C. The residue was washed well with diethylether, redissolved into 10 ml acetone/water (50:50 v/v), and added dropwise to a solution of 100 mg of NH_4PF_6 in 20 ml water. Using cation exchange semipreparative HPLC the product was purified, the mobile phase removed by rotary evaporation at 40°C and precipitated as the PF_6 complex: yield, 105 mg, (0.114 mmol) 30%. IR(KBr); 3634, 3400, 3388, 3314, 556 cm^{-1}. UV(mlct max) 425 nm. ^{1}H NMR-2DCOSY (400MHz, DMSO-d_6) hydrazone ligand; δ 1.08(s,3H), 2.55(s,3H), 2.55(s,3H), 2.71(s,3H), 7.18(s,2H), 7.21(s,2H). 2,2'-bipyridine ligands; δ 7.47(t,1$H^{5''}$), 7.50(t,1$H^{5'}$), 7.84(d,1$H^{6''}$), 7.91(d,1$H^{6'}$), 7.93(t,1$H^{4''''}$), 7.95(t,1$H^{4'''}$), 8.07(t,1$H^{4''}$), 8.14(t,1$H^{4'}$), 8.36(t,1$H^{5'''}$,1$H^{5''''}$), 8.66(d,1$H^{3''}$), 8.74(d,1$H^{3'}$), 8.80(d,1$H^{6''''}$), 8.84(d,$H^{3''''}$,$H^{3'''}$), 8.90(d,1$H^{6'''}$).

Attempted Preparation of $[Ru(bipy)_2(334)](PF_6)_2$ (354)

To a solution of 200 mg (0.38 mmol) of $[Ru(bipy)_2Cl_2].(H_2O)_2$ in 40 ml water, 400 mg (0.0014 mol) of diacetyldiazinedihydrazone **(334)** in 40 ml ethanol was added. The reaction mixture was refluxed for 2 h. The solvent was removed at 35°C by rotary evaporation. The residue was washed with chloroform, filtered, redissolved into 10 ml acetone/water (50:50 v/v), and precipitated into a solution of 100 mg of NH_4PF_6 in 20 ml water. Using cation exchange semipreparative HPLC the product was purified [(i) mobile phase = 80/20 acetonitrile/water 0.1M KNO_3, (ii) 50/50 acetonitrile/water 0.1M KNO_3], the mobile phase removed by rotary evaporation at 40°C and precipitated as the PF_6 complex: yield, 50 mg, (0.114 mmol) 16%. IR(KBr); 3421, 3125, 559cm^{-1}. UV/Vis.(mlct max) 425 nm. ^{1}H NMR (270 MHz, DMSO-d_6) hydrazone ligand; δ 0.97(s,3H), 1.64(s,3H), 1.78(s,3H), 1.93(s,3H), 2.36(s,3H), 2.50(s,3H), 7.2(s,4H). 2,2'-bipyridine ligands; δ 7.46(t,1H^5), 7.50(t,1H^5), 7.54(m,1H$^{5'}$,1H^6), 7.63(d,1H$^{5'}$), 7.96(d,1H^4), 8.07(d,1H$^{6'}$), 8.18(t,1H$^{5'}$), 8.40(m,1H^3,1H$^{4'}$), 8.53(d,1H^3), 8.61(d,1H$^{3''}$), 8.72(d,1H$^{3'}$), 8.82(d,1H$^{6'}$), 8.92(t,2H$^{4''}$).

Diacetyldihydrazone complex of $ZnCl_2$ $[Zn(C_4H_{10}N_4)_2Cl_2]$ (355)

A heated solution of 2.0 g (0.0144 mol) of $ZnCl_2$ in 30 ml of methanol was added to a heated (50°C) solution of 3.3 g (0.03 mol) of diacetyldihydrazone **(5)** in 150 ml of methanol. The stirring solution was heated at 50°C for 15 min. On cooling, the white precipitate was filtered, washed with methanol, and dried under vacuum. The product was recrystallised from hot methanol to obtain crystals suitable for crystal structure: yield, 4.2 g (0.0115 mol), 80%; mp = 219 - 222°C, (Lit. mp = 220°C). IR(KBr); 3379, 3350, 3298, 3263, 3216, 1646, 1626 cm^{-1}. ^{1}H NMR (DMSO-d_6) δ 2.0(s,12H), 5.3(s,8H). Anal. Calcd. for $[Zn(C_8H_{20}N_8)Cl_2]$: C,26.33; H,5.48; N,30.72. Found: C,26.18; H,5.50; N,30.97.

Diacetylazinedihydrazone complex of $ZnCl_2$ $[(Zn_2(C_8H_{16}N_6)_2Cl_4]$ (356)

To a suspension of 1.00 g (0.0051 mol) of diacetylazinedihydrazone **(247)** in 100 ml ethanol, 1.00 g (0.0055 mol) of $ZnCl_2$ dissolved in 50 ml of ethanol was added. The reaction mixture was stirred at room temperature for 24 h. The yellow precipitate was filtered, washed with ethanol, and dried at 50°C under vacuum: yield, 1.2 g (0.0037 mol), 72%; IR(KBr); 3386, 2266, 1605, 1536 cm^{-1}. Anal. Calcd. for $[(Zn_2(C_8H_{16}N_6)_2Cl_4]$: C,28.88; H,4.81; N,25.27. Found: C,28.54; H,4.85; N,24.72.

Diacetylazinedihydrazone complex of $NiCl_2$ $[Ni_2(C_8H_{16}N_6)_2Cl_4]$ (357)

A variation of the method by Sahoo(126) was used. To a suspension of 1.00 g (0.0051 mol) of diacetylazinedihydrazone **(247)** in 100 ml ethanol, 1.00 g (0.0055 mol) of $NiCl_2$ dissolved in 50 ml of ethanol was added. An immediate colour change from yellow to dark brown was observed. The reaction mixture was stirred at room temperature for 24 h. The green/brown precipitate was filtered, washed with ethanol, and dried at 50°C under vacuum: yield, 1.1 g (0.0037 mol), 66%; IR(KBr); 3494, 3408, 3351, 3270, 3117, 1633, 1614 cm^{-1}. Anal. Calcd. for $[Ni_2(C_8H_{16}N_6)_2Cl_4]$: C,29.47; H,4.91; N,25.79. Found: C,28.79; H,5.01; N,25.34.

Diacetyldiazinedihydrazone complex of $ZnCl_2$ $[Zn_3(C_{12}H_{22}N_8)_2Cl_6]$ (358)

To a stirring suspension of 1.00 g (0.0036 mol) of diacetyldiazinedihydrazone **(334)** in 25 ml ethanol, 1.5 g (0.011 mol) of $ZnCl_2$ dissolved in 25 ml of ethanol was added. The reaction mixture was stirred at room temperature for 24 h, filtered, washed with ethanol, pet. ether and dried at 40°C under vacuum: yield, 0.8 g (0.00083 mol), 46%; IR(KBr); 3386, 2266, 1605, 1536 cm^{-1}. Anal. Calcd. for $[Zn_3(C_{12}H_{22}N_8)_2Cl_6]$: C,29.84; H,4.56; N,23.21. Found: C,33.56; H,5.27; N,24.72.

Diacetyldiazinedihydrazone complex of $NiCl_2$ $[Ni_3(C_{12}H_{22}N_8)_2Cl_6]$ (359)

To a stirring suspension of 0.80 g (0.003 mol) of diacetyldiazinedihydrazone **(334)** in 25 ml ethanol, 1.38 g (0.0058 mol) of $NiCl_2$ dissolved in 25 ml of ethanol was added. The colour of the solution was observed to change from yellow to brown. The reaction mixture was stirred at room temperature for 24 h. The product was filtered, washed with ethanol, pet. ether and dried at 40°C under vacuum: yield, 1.3 g (0.0014 mol), 91%; IR(KBr); 3200-3400(v.broad), 1611, 1539 cm^{-1}. Anal. Calcd. for $[Ni_3(C_{12}H_{22}N_8)_2Cl_6]$: C,30.47; H,4.66; N,23.75. Found: C,28.57; H,5.48; N,21.37.

Diacetyldiazinediphenylhydrazone complex $[Zn_3(C_{48}H_{60}N_{16})_2Cl_6]$ (360)

To a solution of 200 mg (0.0465 mmol) of diacetyldiazinediphenylhydrazone **(338)** in 75 ml of methanol, (heated to dissolve), 20 g of $ZnCl_2$ was added as a solid. A red colour was observed at the surface of the solid $ZnCl_2$. After 10 min., the zincdichloride dissolved. The solution was stirred, and a green microcrystalline product precipitated. The product was filtered and washed with a small amount of methanol, and dried under vacuum: yield, 260 mg (0.41 mmol), 86%; mp = 320°C. IR(KBr); 3286, 1604, 328 cm^{-1}. UV/Vis. (λmax = 350 nm). Anal. Calcd. for $[Zn_3(C_{48}H_{60}N_{16})_2Cl_6]$: C,43.57; H,4.99; N,16.94. Found: C,43.90; H,5.06; N,16.33.

4.9 Summary

In chapter III, the rutheniumdi(bipyridyl) derivative of the monomer ligand **(5)**, $[Ru(bipy)_2(ddh)](PF_6)_2$ **(346)** was prepared and characterised. In a continuation of this series of $[Ru(bipy)_2]$ derivatives of oligomeric dihydrazones of diacetyl, we report the preparation of ruthenium bipyridyl complexes of the dimer **(247)** and trimer **(334)** dihydrazone ligands. Their zinc and nickel complexes **(356)** - **(359)** were also prepared and the geometry of the ligands around the metal centres was proposed based on IR data.

These results indicate that it is possible to bind metal to these oligomers and future research in this area could include binding of $[Ru(bipy)_2]$ to similar oligomers which have been " end-capped " to prevent degradation of the product. Future work could also include the reaction of the dihydrazone complexes **(356)** - **(359)** with formaldehyde, (or diacetyl) to form large macrocycles of definite sizes. The metal centres should act as templates to orientate terminal NH_2 groups close together to be linked to produce template condensation products.

An unusual catalytic reaction was discovered, when a very dilute ethanolic solution of the trimer dihydrazone **(334)** was added to a solution of zinc(II)chloride. Analysis of the yellow precipitate indicated that it was composed of a mixture of oligomeric azine **(247)**, **(334)** - **(336)**. The reaction was found not to be selective to the trimer **(334)**, and the action of zincdichloride on the various individual dihydrazone oligomers, produced a product which contained a mixture of oligomeric dihydrazones. The dihydrazone oligomers were found to be quite stable in refluxing aqueous ethanol in the absence of any metals.

The coupling reaction was found to be catalytic, and a 1% molar equivalent of zinc chloride was sufficient to catalyse the reaction. Various other transition metals were examined for their catalytic value for this reaction, Cr(III), Fe(III), Ni(II), Co(II) and Cu(II) being very effective.

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APPENDICES

APPENDIX I

Crystal Structure Data for $[Ru(bipy)_2(dbph)](PF_6)_2$ (342)

Tables for Deposition at Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW.

Table A **Crystal Data for $[Ru(bipy)_2(dbph)](PF_6)_2$ (342)**

Crystal Size (mm)	0.3 x 0.35 x 0.28
Formula	$[C_{36}H_{34}N_8Ru][PF_6]_2.[C_7H_8]$
M (a.m.u.)	1061.858
Monoclinic Space Group	C2/c
a (Å)	25.895 (3)
b (Å)	10.505 (1)
c (Å)	17.431 (2)
B (°)	106.03 (2)Å
U ($Å^3$)	4557
Z	4
D_c g cm^{-3}	1.55
μ cm^{-1}	4.31
F000	1952
Radiation Mo - Kα	
Graphite Monochromator	$\lambda = 0.7093$ Å
Diffractometer	Enraf-Nonius CAD4F
Orienting Reflections, Range	25, $13 < \Theta < 20^{o}$
Temperature (°C)	22
Scan Method	ω-2Θ
Data Collection Range	$2 < 2\Theta < 72^{o}$
No. unique data	6328
Total $I > 3 \sigma I$	3944
No. of Parameters fitted	307
R^a, R_w^b	4.63%, 5.27%
Quality-of-fit indicator [c]	1.9
Largest Shift/esd,final cycle	< 0.001
Largest positive peak ($e/Å^3$)	0.25
Largest negative peak ($e/Å^3$)	-0.14

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[a] $R = [\Sigma \,|\, |F_o| - |F_c| \,|] / \Sigma |F_o|$

[b] $R_w = [[\Sigma w\,(|F_o - F_c|)^2] / \Sigma w\,(|F_o|)^2]]^{1/2}$; $w = 1.59/[(\sigma F_o)^2 - 0.0014 * F_o^2]$

[c] Quality-of-fit = $[\Sigma w(|F_o| - |F_c|)^2/(N_{obs}-N_{parameters})]^{1/2}$

Table B **Fractional Atomic Coordinates for (342)**

	x	y	z
Ru(1)	0.00000	0.77960(4)	0.75000
N(1)	0.0412(1)	0.9307(3)	0.8068(1)
N(2)	0.0885(1)	0.9235(3)	0.8739(2)
N(3)	-0.0533(1)	0.7617(3)	0.8180(2)
N(4)	-0.0502(1)	0.6349(3)	0.6906(2)
C(1)	0.0248(1)	1.0447(3)	0.7839(2)
C(2)	0.0503(2)	1.1663(4)	0.8191(2)
C(11)	0.1367(1)	0.8946(3)	0.8514(2)
C(12)	0.1481(1)	0.9533(4)	0.7876(2)
C(13)	0.1962(2)	0.9305(6)	0.7715(3)
C(14)	0.2325(2)	0.8477(7)	0.8186(4)
C(15)	0.2213(2)	0.7887(6)	0.8829(4)
C(16)	0.1732(2)	0.8124(4)	0.8992(2)
C(22)	-0.0872(1)	0.5963(3)	0.7248(2)
C(23)	-0.1226(2)	0.4979(4)	0.6913(3)
C(24)	-0.1190(2)	0.4420(4)	0.6234(4)
C(25)	-0.0798(2)	0.4800(4)	0.5874(3)
C(26)	-0.0458(2)	0.5777(4)	0.6234(2)
C(32)	-0.0892(1)	0.6662(4)	0.7964(2)
C(33)	-0.1253(2)	0.6418(5)	0.8409(3)
C(34)	-0.1256(2)	0.7148(6)	0.9051(4)
C(35)	-0.0890(2)	0.8160(6)	0.9259(3)
C(36)	-0.0539(2)	0.8346(4)	0.8813(2)
P(2)	0.59461(5)	0.74223(12)	0.59840(7)
F(1)	0.5618(1)	0.6390(3)	0.6310(2)
F(2)	0.5550(2)	0.8465(4)	0.6093(4)
F(3)	0.5616(2)	0.7182(5)	0.5108(2)
F(4)	0.6314(2)	0.7671(5)	0.6858(2)
F(5)	0.6361(2)	0.6380(4)	0.5896(4)
F(6)	0.6290(1)	0.8459(4)	0.5700(2)
F(11)	0.5386(20)	0.8344(59)	0.5428(31)
F(21)	0.5935(23)	0.8160(45)	0.6736(28)
F(31)	0.6381(17)	0.6530(47)	0.6434(30)
F(41)	0.5944(24)	0.6405(51)	0.5350(33)
C1(a)	0.2691(3)	0.3329(6)	0.0674(4)
C1(b)	0.2598(3)	0.2298(6)	0.1123(4)
C1(c)	0.2401(3)	0.1157(6)	0.0745(4)
C1(d)	0.2297(3)	0.1046(6)	-0.0081(4)
C1(e)	0.2390(3)	0.2077(6)	-0.0530(4)
C1(f)	0.2587(3)	0.3219(6)	-0.0152(4)
C1(g)	0.2761(9)	0.4328(15)	-0.0547(12)

Table C **Bond Lengths (Angstroms) for (342)**

Bond	Length / Å	Bond	Length / Å
Ru(1) --N(1)	2.013(3)	Ru(1) --N(3)	2.060(3)
Ru(1) --N(4)	2.081(3)	N(1) --N(2)	1.444(3)
N(1) --C(1)	1.296(5)	N(2) --C(11)	1.439(5)
N(3) --C(32)	1.349(5)	N(3) --C(36)	1.347(5)
N(4) --C(22)	1.323(5)	N(4) --C(26)	1.350(5)
C(1) --C(2)	1.490(5)	C(1) --C(1)	1.487(6)
C(11) --C(12)	1.374(5)	C(11) --C(16)	1.378(5)
C(12) --C(13)	1.371(6)	C(13) --C(14)	1.374(8)
C(14) --C(15)	1.380(9)	C(15) --C(16)	1.376(7)
C(22) --C(23)	1.398(6)	C(22) --C(32)	1.461(6)
C(23) --C(24)	1.348(8)	C(24) --C(25)	1.390(8)
C(25) --C(26)	1.385(6)	C(32) --C(33)	1.393(6)
C(33) --C(34)	1.359(7)	C(34) --C(35)	1.403(8)
C(35) --C(36)	1.363(6)	P(2) --F(1)	1.577(3)
P(2) --F(2)	1.547(4)	P(2) --F(3)	1.550(3)
P(2) --F(4)	1.579(4)	P(2) --F(5)	1.577(4)
P(2) --F(6)	1.571(3)	P(2) --F(11)	1.79(5)
P(2) --F(21)	1.53(4)	P(2) --F(31)	1.51(4)
P(2) --F(41)	1.53(5)	F(2) --F(11)	1.13(5)
F(2) --F(21)	1.32(5)	F(3) --F(11)	1.53(5)
F(3) --F(41)	1.17(6)	F(4) --F(21)	1.08(5)
F(4) --F(31)	1.44(5)	F(5) --F(31)	0.94(5)
F(5) --F(41)	1.23(6)	C1(a) --C1(b)	1.395(1)
C1(a) --C1(f)	1.395(1)	C1(b) --C1(c)	1.395(1)
C1(c) --C1(d)	1.395(1)	C1(d) --C1(e)	1.395(1)
C1(e) --C1(f)	1.395(1)	C1(e) --C1(e)	1.99(1)
C1(f) --C1(g)	1.485(9)	C1(f) --C1(f)	1.70(1)

Table D Bond Angles (Degrees) for (342)

N(3)	--Ru(1)	--N(1)	97.9(1)	N(4)	--Ru(1)	--N(1)	173.7(1)
N(4)	--Ru(1)	--N(3)	78.1(1)	N(2)	--N(1)	--Ru(1)	124.9(2)
C(1)	--N(1)	--Ru(1)	119.5(2)	C(1)	--N(1)	--N(2)	115.5(3)
N(1)	--Ru(1)	--N(1)	75.9(2)	C(11)	--N(2)	--N(1)	113.4(3)
C(32)	--N(3)	--Ru(1)	115.3(3)	C(36)	--N(3)	--Ru(1)	125.5(3)
C(36)	--N(3)	--C(32)	119.2(4)	C(22)	--N(4)	--Ru(1)	115.5(3)
C(26)	--N(4)	--Ru(1)	124.4(3)	C(26)	--N(4)	--C(22)	120.0(3)
N(4)	--Ru(1)	--N(4)	86.1(1)	C(2)	--C(1)	--N(1)	126.6(3)
C(12)	--C(11)	--N(2)	121.5(3)	C(16)	--C(11)	--N(2)	118.0(4)
C(16)	--C(11)	--C(12)	120.4(4)	C(13)	--C(12)	--C(11)	119.9(4)
C(14)	--C(13)	--C(12)	120.0(5)	C(15)	--C(14)	--C(13)	120.4(5)
C(16)	--C(15)	--C(14)	119.5(5)	C(15)	--C(16)	--C(11)	119.9(5)
C(23)	--C(22)	--N(4)	120.8(4)	C(32)	--C(22)	--N(4)	115.5(3)
C(32)	--C(22)	--C(23)	123.7(4)	C(24)	--C(23)	--C(22)	119.4(5)
C(25)	--C(24)	--C(23)	120.5(4)	C(26)	--C(25)	--C(24)	117.4(5)
C(25)	--C(26)	--N(4)	121.8(4)	C(22)	--C(32)	--N(3)	115.3(3)
C(33)	--C(32)	--N(3)	119.9(4)	C(33)	--C(32)	--C(22)	124.8(4)
C(34)	--C(33)	--C(32)	120.9(5)	C(35)	--C(34)	--C(33)	118.8(4)
C(36)	--C(35)	--C(34)	118.1(5)	C(35)	--C(36)	--N(3)	123.2(5)
F(2)	--P(2)	--F(1)	90.1(2)	F(3)	--P(2)	--F(1)	92.2(2)
F(3)	--P(2)	--F(2)	91.9(3)	F(4)	--P(2)	--F(1)	90.4(2)
F(4)	--P(2)	--F(2)	90.5(3)	F(4)	--P(2)	--F(3)	176.5(3)
F(5)	--P(2)	--F(1)	90.4(2)	F(5)	--P(2)	--F(2)	178.3(3)
F(5)	--P(2)	--F(3)	89.8(3)	F(5)	--P(2)	--F(4)	87.9(3)
F(6)	--P(2)	--F(1)	177.3(2)	F(6)	--P(2)	--F(2)	90.0(2)
F(6)	--P(2)	--F(3)	90.5(2)	F(6)	--P(2)	--F(4)	86.9(2)
F(6)	--P(2)	--F(5)	89.4(2)	F(11)	--P(2)	--F(1)	97. (2)
F(11)	--P(2)	--F(2)	39. (2)	F(11)	--P(2)	--F(3)	54. (2)
F(11)	--P(2)	--F(4)	128. (2)	F(11)	--P(2)	--F(5)	143. (2)
F(11)	--P(2)	--F(6)	84. (2)	F(21)	--P(2)	--F(1)	84. (2)
F(21)	--P(2)	--F(2)	51. (2)	F(21)	--P(2)	--F(3)	142. (2)
F(21)	--P(2)	--F(4)	40. (2)	F(21)	--P(2)	--F(5)	128. (2)
F(21)	--P(2)	--F(6)	94. (2)	F(21)	--P(2)	--F(11)	89. (2)
F(31)	--P(2)	--F(1)	78. (2)	F(31)	--P(2)	--F(2)	143. (2)
F(31)	--P(2)	--F(3)	123. (2)	F(31)	--P(2)	--F(4)	56. (2)
F(31)	--P(2)	--F(5)	35. (2)	F(31)	--P(2)	--F(6)	101. (2)
F(31)	--P(2)	--F(11)	174. (3)	F(31)	--P(2)	--F(21)	93. (2)

Table E Fractional Atomic Coordinates for Hydrogen Atoms for (342)

Atom	x	y	z
H2(a)	0.030	1.236	0.791
H2(b)	0.086	1.170	0.815
H2(c)	0.051	1.170	0.874
H(12)	0.123	1.010	0.755
H(13)	0.204	0.972	0.728
H(14)	0.266	0.831	0.807
H(15)	0.247	0.732	0.916
H(16)	0.165	0.772	0.943
H(23)	-0.149	0.471	0.716
H(24)	-0.143	0.376	0.600
H(25)	-0.077	0.441	0.540
H(26)	-0.018	0.605	0.600
H(26)	-0.150	0.573	0.826
H(26)	-0.150	0.698	0.935
H(26)	-0.089	0.870	0.970
H(26)	-0.029	0.902	0.895
H1(a)	0.283	0.411	0.093
H1(b)	0.267	0.237	0.169
H1(c)	0.234	0.045	0.105
H1(d)	0.216	0.027	-0.034
H1(e)	0.232	0.200	-0.109
H1(f)	0.268	0.418	-0.111
H1(g)	0.314	0.444	-0.034
H1(h)	0.258	0.507	-0.045

Table F Anisotropic thermal parameters (Angstroms) for (342)

Atom	U11	U22	U33	U23	U13	U12
Ru(1)	0.042(2)	0.048(2)	0.045(2)	0.001(1)	0.004(1)	0.001(1)
N(1)	0.044(1)	0.058(2)	0.045(1)	0.002(1)	0.008(1)	0.001(1)
N(2)	0.048(1)	0.073(2)	0.048(1)	0.005(1)	0.001(1)	0.001(1)
N(3)	0.049(1)	0.062(2)	0.058(2)	0.016(1)	0.010(1)	0.009(1)
N(4)	0.053(1)	0.048(2)	0.062(2)	0.003(1)	-0.002(1)	0.001(1)
C(1)	0.049(2)	0.060(2)	0.054(2)	-0.004(1)	0.015(1)	0.001(1)
C(2)	0.074(2)	0.056(2)	0.078(2)	-0.013(2)	0.023(2)	-0.008(2)
C(11)	0.049(2)	0.061(2)	0.055(2)	-0.013(1)	0.001(1)	-0.005(1)
C(12)	0.052(2)	0.087(3)	0.063(2)	-0.011(2)	0.009(1)	-0.005(2)
C(13)	0.059(2)	0.137(5)	0.081(3)	-0.022(3)	0.018(2)	-0.011(3)
C(14)	0.064(3)	0.153(6)	0.113(4)	-0.047(4)	0.005(3)	0.021(3)
C(15)	0.069(3)	0.121(5)	0.092(4)	-0.017(3)	-0.008(2)	0.024(3)
C(16)	0.058(2)	0.080(3)	0.073(2)	-0.009(2)	-0.003(2)	-0.009(2)
C(22)	0.050(2)	0.050(2)	0.078(2)	0.016(2)	0.005(2)	0.001(1)
C(23)	0.068(2)	0.064(3)	0.112(4)	0.017(2)	0.009(2)	-0.013(2)
C(24)	0.080(3)	0.056(3)	0.127(4)	-0.007(3)	-0.013(3)	-0.013(2)
C(25)	0.082(3)	0.066(3)	0.090(3)	-0.010(2)	0.001(2)	-0.013(2)
C(26)	0.075(2)	0.063(2)	0.066(2)	-0.006(2)	-.001(2)	-0.011(2)
C(32)	0.053(2)	0.062(2)	0.081(2)	0.031(2)	0.010(2)	0.005(2)
C(33)	0.062(2)	0.088(3)	0.105(3)	0.037(3)	0.028(2)	0.007(2)
C(34)	0.072(2)	0.119(4)	0.102(4)	0.050(3)	0.039(3)	0.023(3)
C(35)	0.087(3)	0.111(4)	0.070(3)	0.026(2)	0.032(2)	0.034(3)
C(36)	0.069(2)	0.079(3)	0.058(2)	0.013(2)	0.020(2)	0.014(2)
P(2)	0.080(1)	0.074(1)	0.065(1)	-0.003(1)	0.023(1)	-0.009(1)
F(1)	0.113(3)	0.97(3)	0.121(3)	0.013(2)	0.053(2)	0.026(2)
F(2)	0.124(3)	0.107(3)	0.230(6)	-0.028(3)	0.069(4)	-0.019(3)
F(3)	0.138(4)	0.170(5)	0.069(2)	-0.015(2)	0.005(2)	-0.009(3)
F(4)	0.123(4)	0.173(4)	0.088(3)	-0.025(2)	0.011(2)	-0.029(3)
F(5)	0.116(3)	0.116(3)	0.162(4)	-0.015(3)	0.054(3)	-0.027(2)
F(6)	0.114(3)	0.116(3)	0.141(3)	0.032(2)	0.036(2)	-0.030(2)

Table G **Isotropic Thermal Parameters for (342)**

F(11)	0.382(39)	F(21)	0.089(19)
F(31)	0.239(27)	F(41)	0.251(32)
C1(a)	0.103(3)	C1(b)	0.100(3)
C1(c)	0.111(4)	C1(d)	0.122(4)
C1(e)	0.106(4)	C1(f)	0.100(3)
C1(g)	0.190(8)		

APPENDIX II

Resonance Raman Spectra of [Ru(bipy)$_2$(apph)](PF$_6$)$_2$ (351)

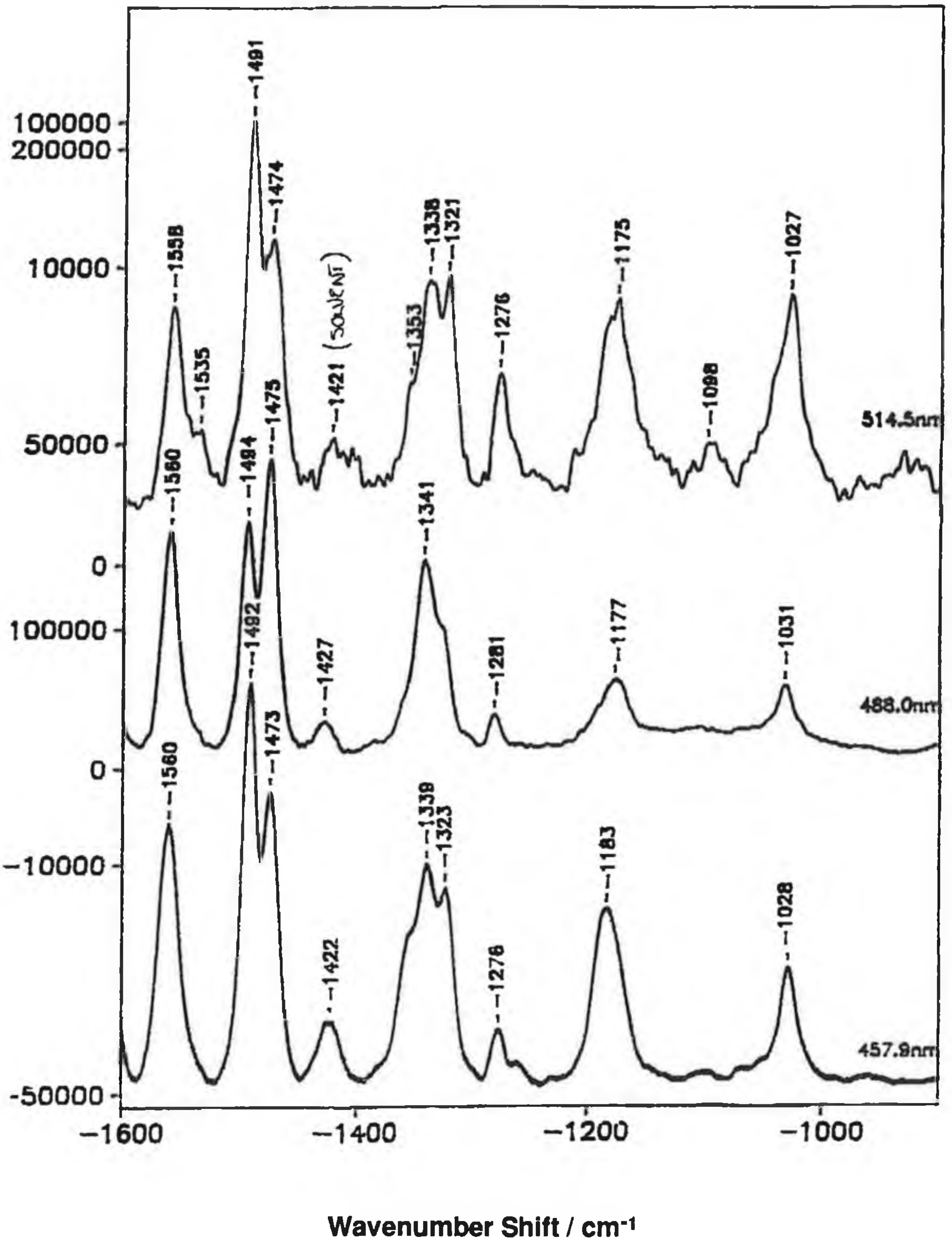

Figure A Resonance Raman Spectra of [Ru(bipy)$_2$(apph)](PF$_6$)$_2$ (351) in Acetone Excited at (i) 457.9 nm, (ii) 488.0 nm, (iii) 514.5 nm.

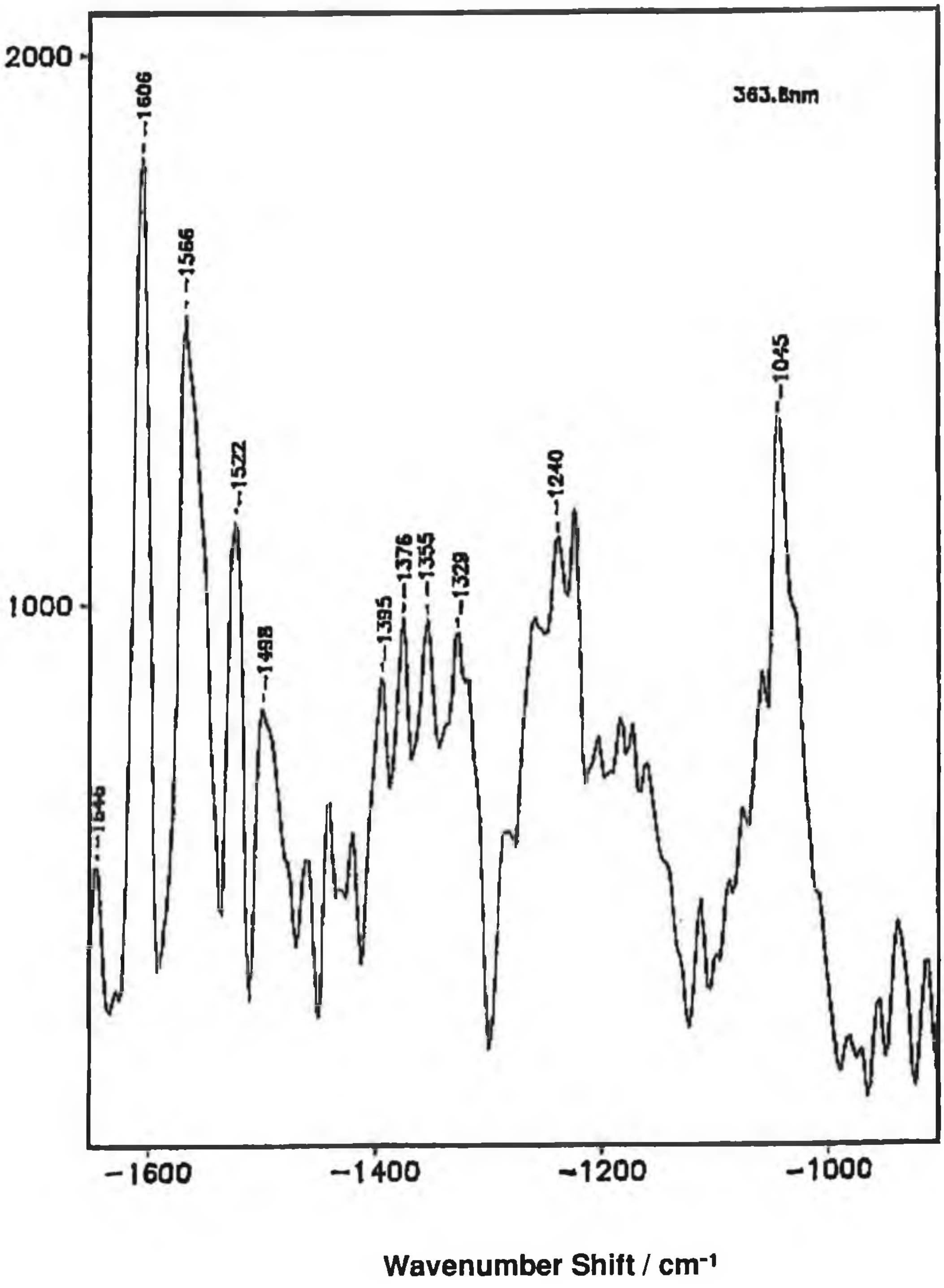

Figure B Resonance Raman Spectra of [Ru(bipy)$_2$(apph)](PF$_6$)$_2$ (351) in Acetone Excited at 363.8 nm.

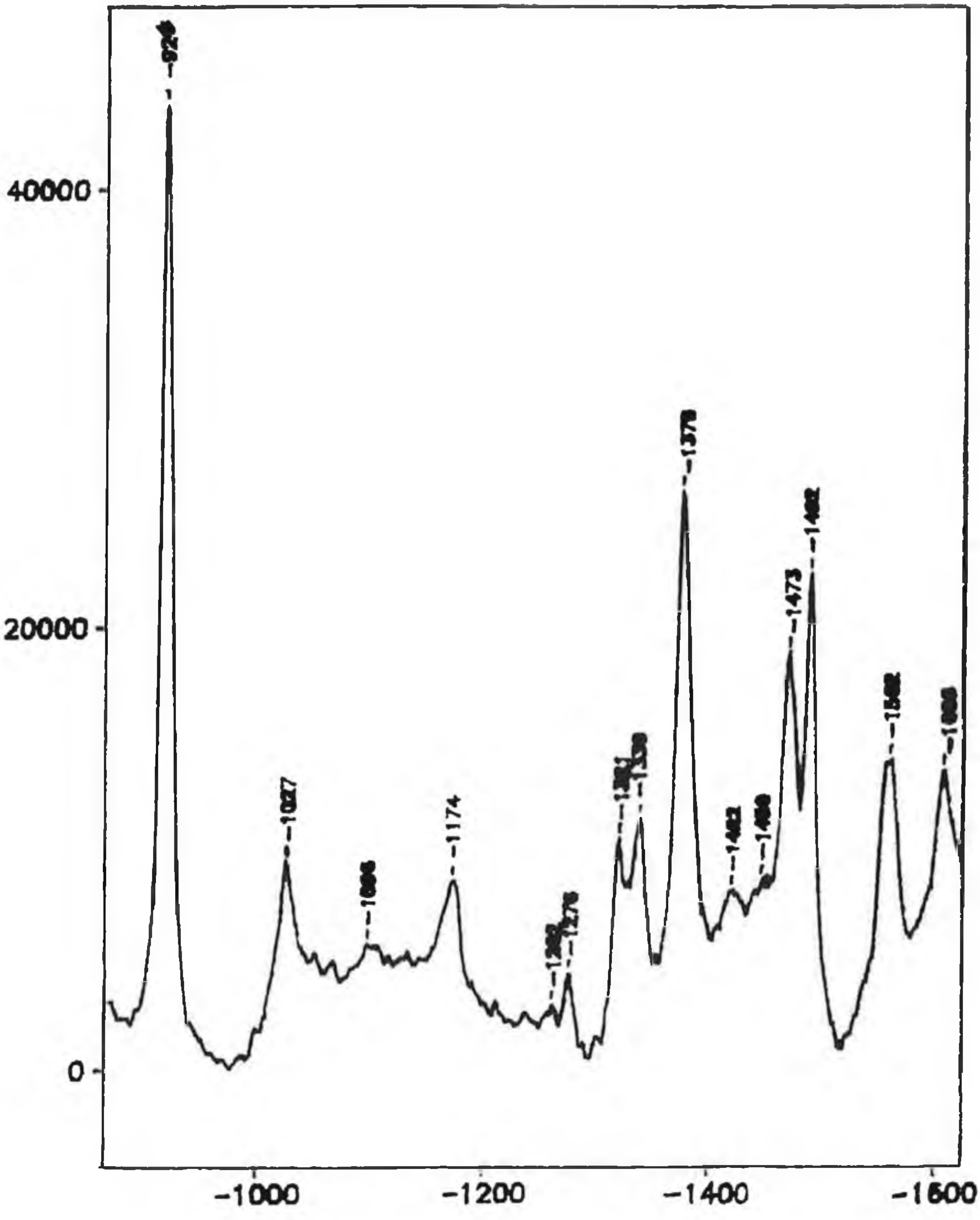

Figure C Resonance Raman Spectra of $[Ru(bipy)_2(apph)](PF_6)_2$ (351) in Acetonitrile Excited at 457.9 nm.

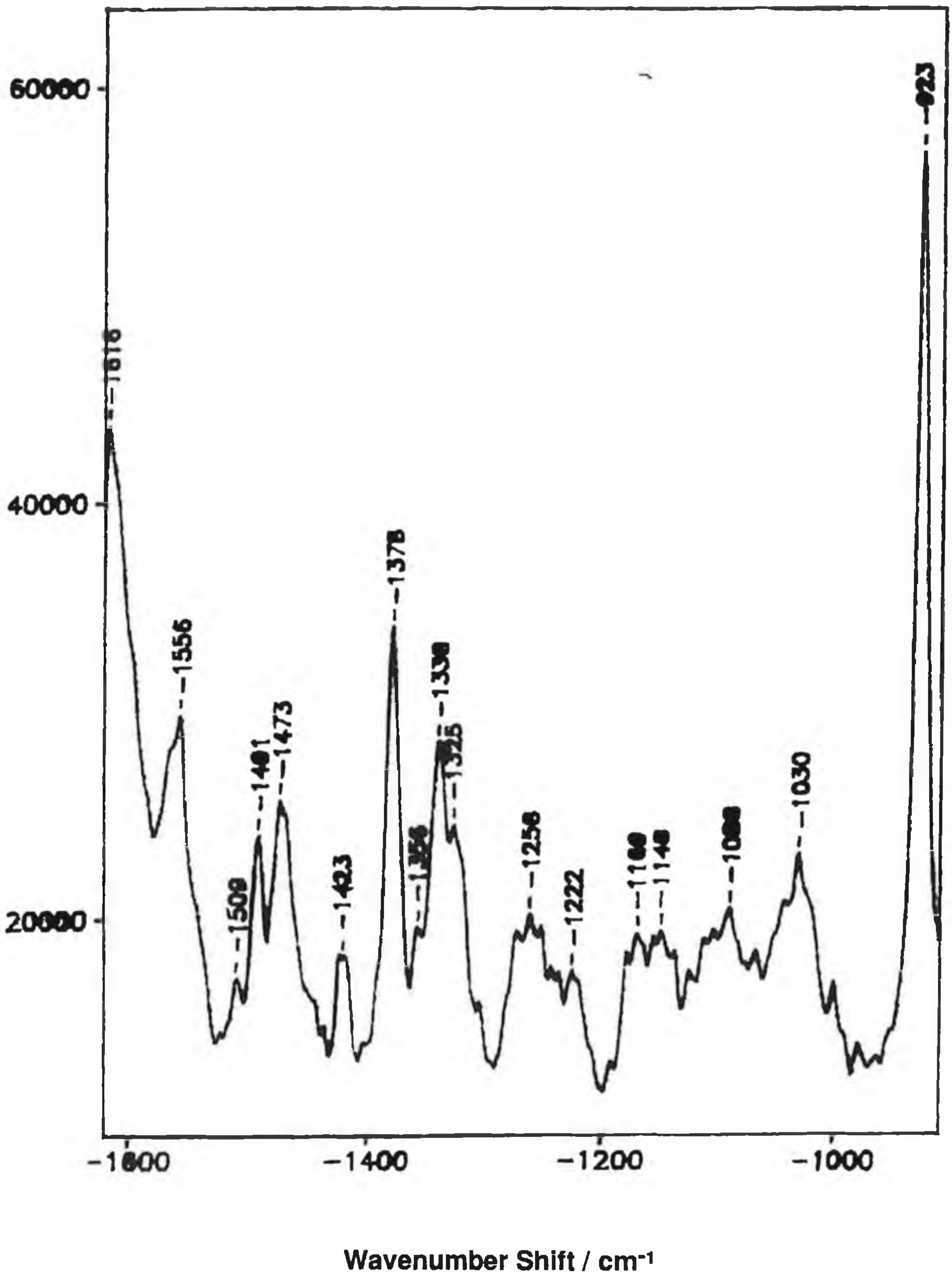

Figure D Resonance Raman Spectra of $[Ru(bipy)_2(apph)](PF_6)_2$ (351) in Acetonitrile Excited at 488.0 nm.

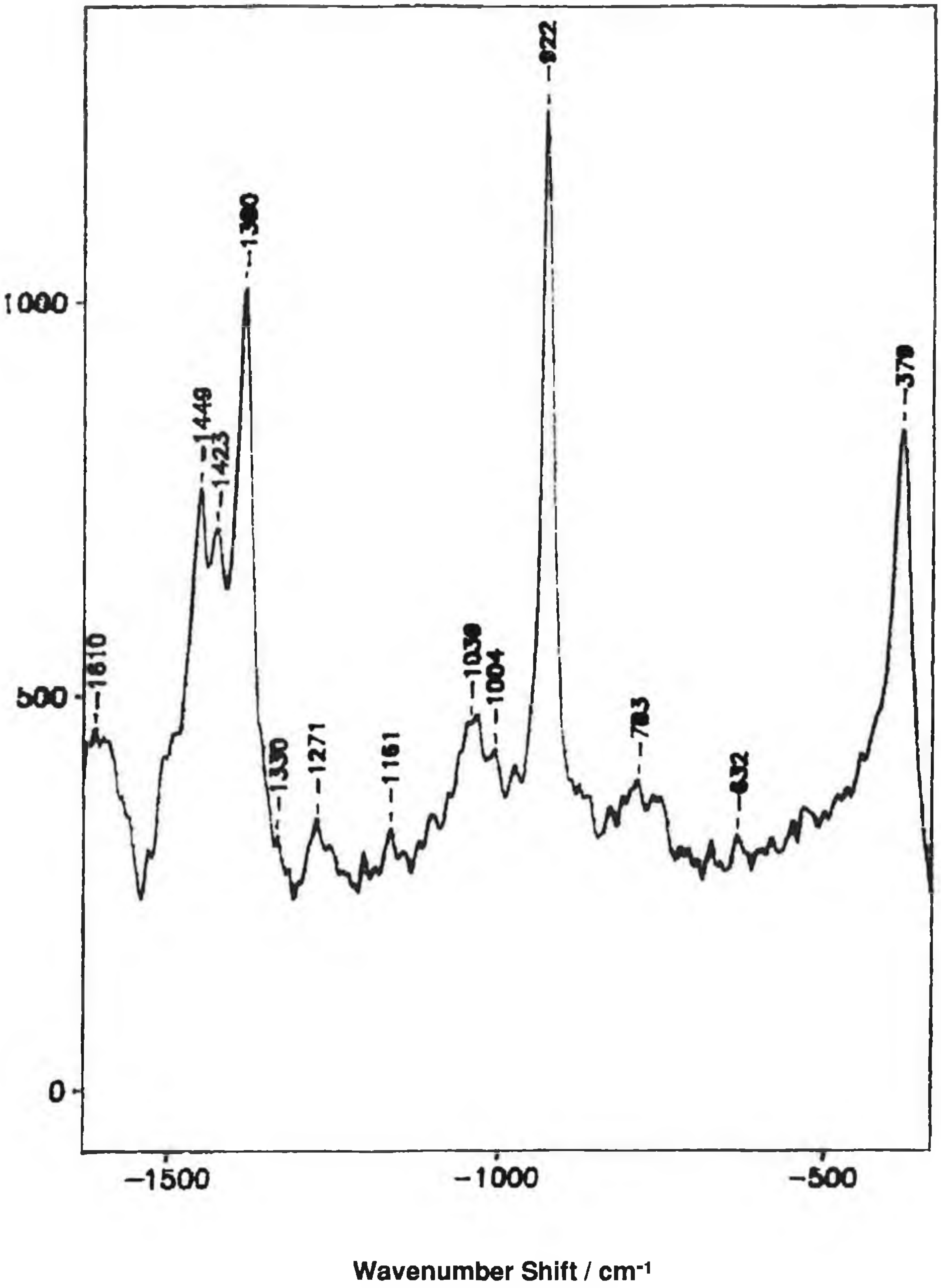

Figure E Resonance Raman Spectra of $[Ru(bipy)_2(apph)](PF_6)_2$ (351) in Acetonitrile Excited at 355.0 nm.

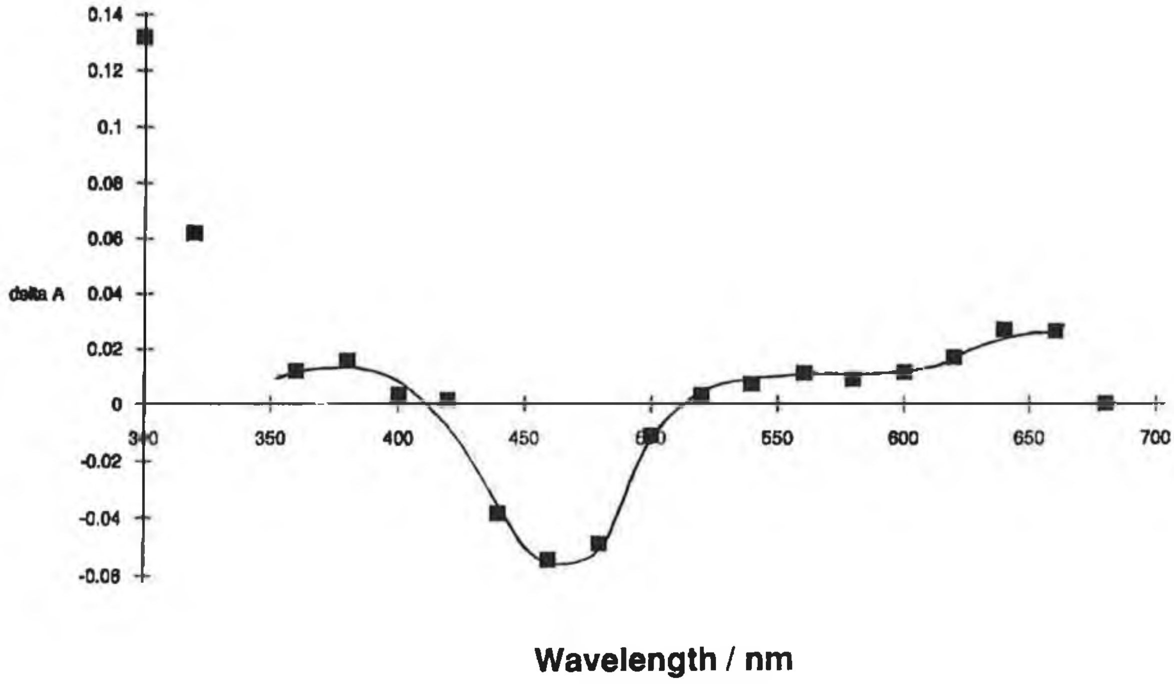

Figure F ΔA Plot for $[Ru(bipy)_2(apph)](PF_6)_2$ (351) in Acetonitrile Excited at 355.0 nm.