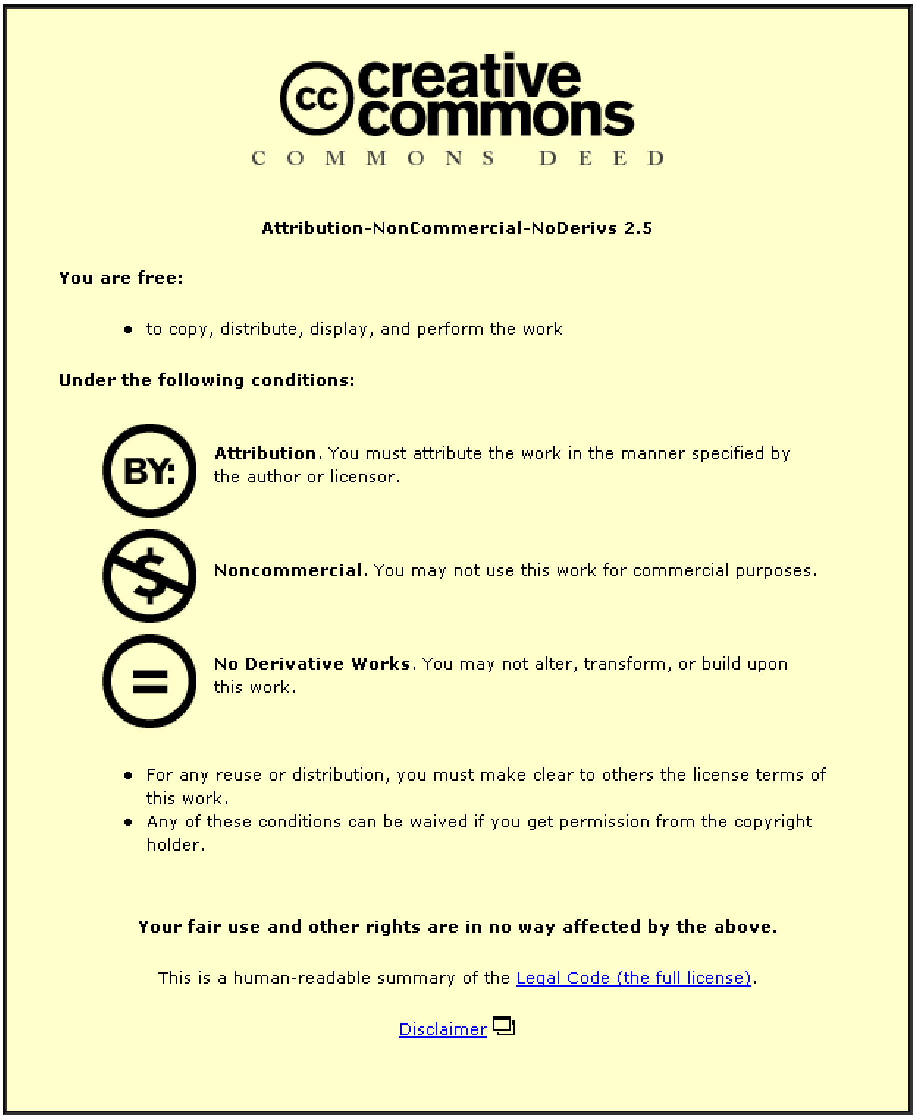

REACTIONS OF SOME METAL IONS WITH CERTAIN SCHIFF BASES AND THEIR PRECURSORS

By

ABDU SALIM SALAMEH

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Supervisors:Dr. B.C. Uff
Dr. H.A. Tayim
Department of Chemistry

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I would like to extend my sincere thanks and gratitude to Dr. Hassan A. Tayim and Dr. Barrie C. Uff for their advice, guidance, encouragement and help throughout this study.

I also extend my thanks to Dr. Alan G. Massey for his helpful suggestions during this work.

Summary

Schiff base complexes with two or three nitrogen donor atoms have recently attracted interest in virtue of their biological activity. 2,6-Pyridinedicarboxaldehyde lends itself to the formation of a host of such Schiff bases. The present work has therefore been devoted to the investigation of the synthesis and reactions of Schiff bases derived from 2,6-pyridinedicarboxaldehyde.

The reaction of 2,6-pyridinedicarboxaldehyde with several transition metal ions was studied. Pd(II), Pt(II) and Ni(II) reacted with two molecules of the dialdehyde whereas Cu(II) and UO_2^{++} reacted with one only. Zn(II), Co(II), Mn(II) and Co(III) failed to react.

2,6-Pyridinedicarboxaldehyde was reacted with Pd(II) and Cu(II) in methanol. Complexes of the diacetal 2,6-bis(dimethoxy-methyl)pyridine were formed. The same respective complexes were obtained as a result of the reaction of the Pd(II) and Cu(II) complexes of 2,6-pyridinedicarboxaldehyde with methanol, and upon the reaction of 2,6-bis(dimethoxy-methyl)pyridine with Pd(II) and Cu(II). The diacetal itself was prepared by the reaction of 2,6-pyridinedicarboxaldehyde with trimethyl-orthoformate in methanol using concentrated hydrochloric acid as a catalyst, and from the decomposition of Pd(II) complex with aqueous cyanide. Similar procedures were followed for the preparation of the diacetal 2,6-bis-

(diethoxy-methyl)pyridine of which a Pd(II) and a Cu(II) complex were formed. The reaction of 2,6-bis(dimethoxy-methyl)pyridine with Pt(II) in an aqueous solution gave dichlorobis(2-dimethoxymethyl-6-pyridinecarboxaldehyde)-platinum(II). Dichloro-2,6-bis(dimethoxy-methyl)pyridine. palladium(II) was reacted with 2,6-diaminopyridine to form dichlorobis(2,6-diaminopyridine)palladium(II).

The reaction of 2,6-diaminopyridine with several transition metal ions was studied. Cu(II), Ag(I), Rh(III) and Ru(III) reacted with one molecule of the diamine whereas Pt(II) in an acidic medium reacted with two. With Pd(II) two different complexes were obtained; one involving a single molecule of the ligand and the other, two. In a neutral medium Pt(II) gave a product with indefinite composition. Ni(II), Fe(III), UO_2^{++} and Zn(II) failed to react with 2,6-diaminopyridine. The decomposition of the Pd(II) complex involving two ligands with aqueous cyanide and that of the Ag(I) complex with concentrated ammonium hydroxide produced the ligand 2,6-diaminopyridine.

The reaction of 2,2'-dithiodianiline with several metal ions was also examined. Ni(II) nitrate and Ni(II) perchlorate gave bis(2-aminothiophenolato)nickel(II). Cu(II) perchlorate reacted with three molecules of the ligand whereas Cu(II) chloride and Cu(II) nitrate yielded complexes including 2,2'-dithiodianiline and its parent precursor, the 2-aminothiophenolate anion. Pd(II) produced a dimer of chloro(aminothiophenolato)palladium(II). Ag(I), Rh(III) and Ru(III) with 2,2'-dithiodianiline gave compounds with indefinite compositions.

2,6-Pyridinedicarboxaldehyde was condensed with 2-aminothiophenol: 2,6-(dibenzothiazol-2-yl)pyridine was formed and its reaction with several transition metal ions was studied. Cu(II) chloride, Cu(II) bromide, Hg(II) chloride, Hg(II) bromide, Zn(II), Co(II), Ag(I), Ru(III) and Rh(III) reacted with one molecule of the dibenzothiazol ligand whereas Ni(II) and Fe(III) reacted with two. Pd(II) gave a dimer involving one molecule of the ligand. Pt(II) reacted with 2,6-(dibenzothiazol-2-yl)pyridine in the ratio of four atoms of the metal to three molecules of the ligand. UO_2^{++}, Cr(III), Th(IV), Y(III), Sn(II), Ir(III), Mo(0) and W(0) failed to react with 2,6-dibenzothiazol-2-yl)pyridine.

The reaction of a mixture of 2,6-pyridinedicarboxaldehyde and 2-aminothiophenol in a basic medium with several transition metal ions was also studied. It was successful with Cu(II), Pd(II), Zn(II) and Ru(III) whereas Fe(III), Ni(II), UO_2^{++} and Pt(II) gave compounds with indefinite compositions. A compound with indefinite composition was also obtained from the reaction of 2,6-pyridinedicarboxaldehyde with 2-aminothiophenol but upon treatment of the product with concentrated hydrochloric acid 2-aminothiophenol hydrochloride was formed which upon its reaction with Pd(II) yielded bis(2-aminothiophenolato)palladium(II).

A Schiff base was prepared by the condensation of 2,6-pyridinedicarboxaldehyde with 2,2'-dithiodianiline. Its reaction with Pd(II) in different solvents produced compounds with indefinite compositions.

The reaction of a mixture of 2,6-pyridinedicarboxaldehyde and 8-aminoquinoline with several transition metal ions was examined. Monomeric complexes of the expected Schiff base were formed with Cu(II) perchlorate, Ag(I) and Co(II) and trimeric complexes with Cu(II) chloride, Pt(II), Zn(II), Ru(III) and Rh(III). No molecular formulas could be assigned for the compounds obtained with Pd(II), UO_2^{++}, Hg(II) and Fe(III).

The reaction of 2,6-diaminopyridine with the Cu(II), Pt(II), UO_2^{+2}, Pd(II) and Ni(II) complexes of 2,6-pyridinedicarboxaldehyde was also examined. The Cu(II) dialdehyde complex was the only complex to give an identifiable condensation product.

The reaction of 2,6-pyridinedicarboxaldehyde with 2,6-diaminopyridine gave a polymeric Schiff base and the reaction of a mixture of the dialdehyde with the diamine with Ni(II) using molar ratios of 2:2:1 and 1:1:1 (dialdehyde:diamine:metal ion) produced an open chain and a macrocyclic Schiff base metal complex respectively. The decomposition of the Ni(II) complexes with aqueous potassium cyanide was unsuccessful.

The reaction of a mixture of 2,6-pyridinedicarboxaldehyde and 2,6-diaminopyridine with Cu(II), Pt(II) and

Zn(II) gave compounds of indefinite compositions.

With the conclusion of the present work the behaviour of 2,6-pyridinedicarboxaldehyde and 2,6-diaminopyridine in their reactions with several transition metal ions is well understood. Optimum conditions for the formation of Schiff bases derived from 2,6-pyridinedicarboxaldehyde and their complexes have been set forth. The way is paved for the investigation of biological activities and other practical applications of the complexes herein reported.

Contents

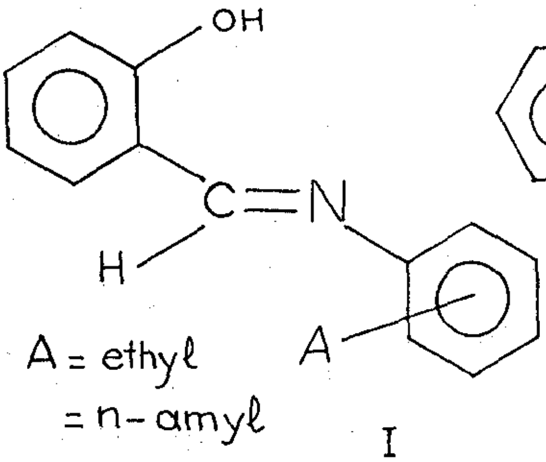
List of Tables

1. Introduction

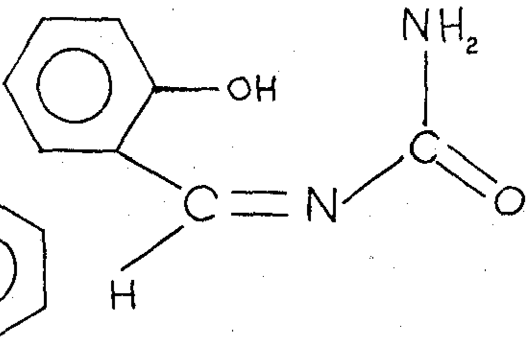
1. Introduction

1. Historical

Polydentate ligands derived from the condensation of aldehydes or ketones with amines are referred to as Schiff bases after H. Schiff[1,2] who was the first to report a systematic method for the preparation and identification of several complexes with the Schiff bases I and II, derived from the condensation of salicylaldehyde with substituted anilines and urea respectively.

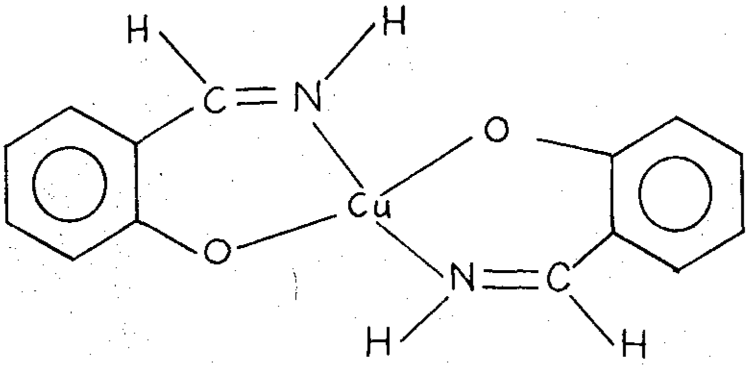


I



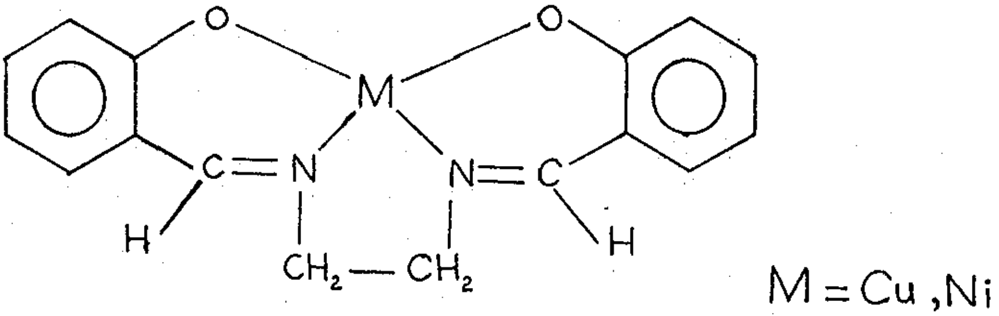
II

Before Schiff, Ettling[3] (1840) prepared the first Schiff base complex from the reaction of cupric acetate, salicylaldehyde and aqueous ammonia but did not identify the reaction product which is known now to be bis(salicylaldiminato)copper(II) III.



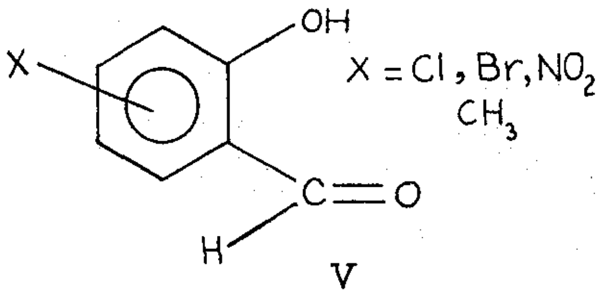
III

After Schiff, and up to 1931, the only important advance in the chemistry of Schiff bases was the work of Dubsky and Sokol[4] who prepared the complex IV.

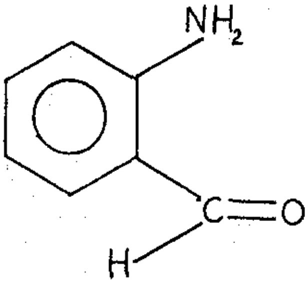


IV

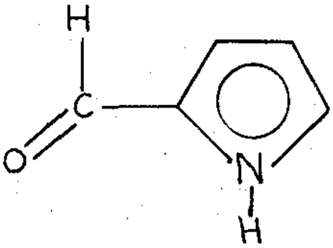
Between 1931 and 1942 the chemistry of Schiff bases complexes progressed very rapidly through the work of Pfeiffer and his co-workers[5-16]. They prepared several new Schiff bases from the condensation of the aldehydes V, VI and VII with several primary amines such as VIII, IX, X and XI. The reactions of these Schiff bases with copper(II), nickel(II), zinc(II), uranium(VI), vanadium(III), iron(III) and cobalt(II) were investigated. The chemistry of the Schiff base metal complexes was also studied.



V



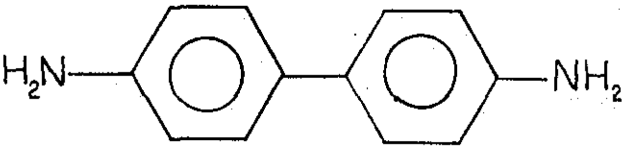
VI



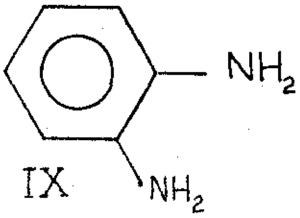
VII

$NH_2(CH_2)_nNH_2$

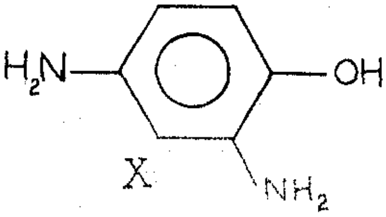
XI $n = 3,4,5$



VIII



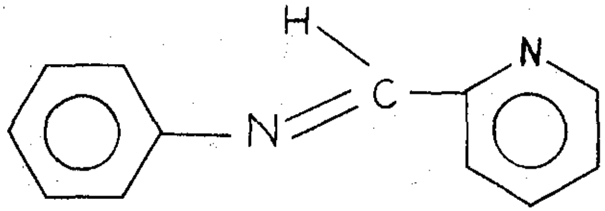
IX



X

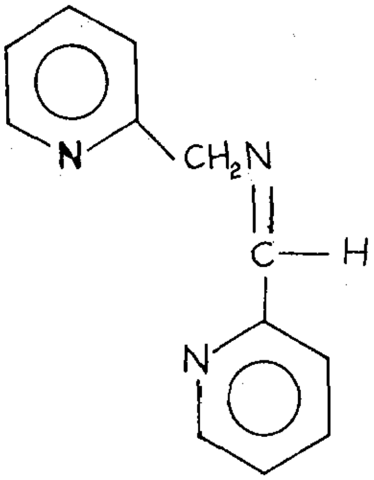
It was in the mid-fifties when the investigation of metal complexes of Schiff bases derived from 2-substituted and 2,6-disubstituted pyridines had virtually started.

Bahr and Thauntz[17] isolated the condensation products of 2-pyridinecarboxaldehyde and some aryl amines. They were particularly interested in the complexes formed by the reaction of XII with zinc(II), copper(II), nickel(II) and iron(II). The metal-to-ligand ratio was determined to be 1:2 for copper, nickel and iron, and 1:1 for zinc.

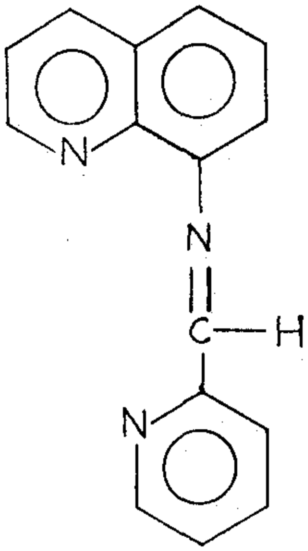


XII

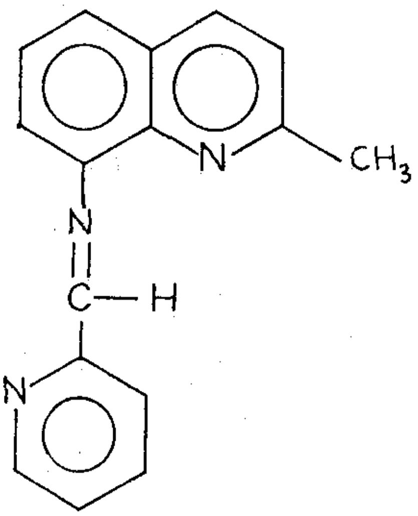
The preparation of iron(II) and cobalt(II) complexes of the Schiff base 2-(α-pyridylmethylene-aminomethyl)-pyridine XIII derived from the condensation of 2-pyridine-carboxaldehyde and 2-aminomethylpyridine was reported by Lions and Martin[18]. They also reported the synthesis of a cobalt(II) complex of the Schiff base 8-(α-pyridylmethylene-amino)quinoline XIV derived from the condensation of 2-pyridine-carboxaldehyde and 8-aminoquinoline and an iron(II) complex of the Schiff base 8-(α-pyridylmethylene-amino)quinoline XV derived from 2-pyridinecarboxaldehyde and 8-aminoquinaldine. Metal complexes of 8-aminoquinoline itself have been reported[19-21]. In addition to their work, Lions and Martin[18]



XIII

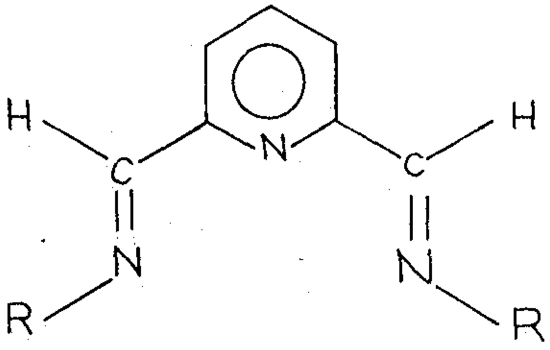


XIV



XV

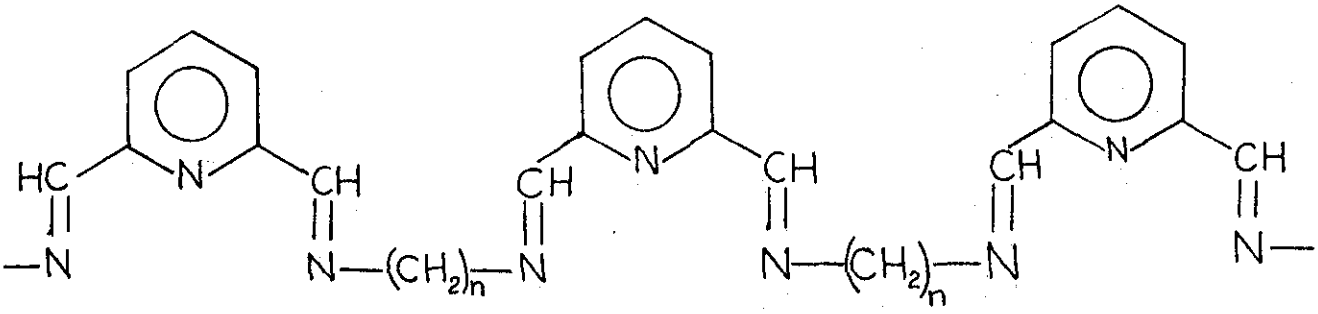
reported some Schiff bases XVI-A and XVI-B prepared from 2,6-pyridinedicarboxaldehyde and primary amines. Schiff bases XVI-A are oily compounds but XVI-B are crystalline solids. The reactions of XVI-B with iron(II) perchlorate, iron(II) bromide, cobalt(II) chloride and cobalt(II) iodide were studied. The condensation of 2,6-pyridinedicarboxaldehyde with ethylenediamine, 1,6-diaminohexane or benzidine gave linear polymers XVII



A:R = methyl, ethyl
B:R = phenyl, benzyl

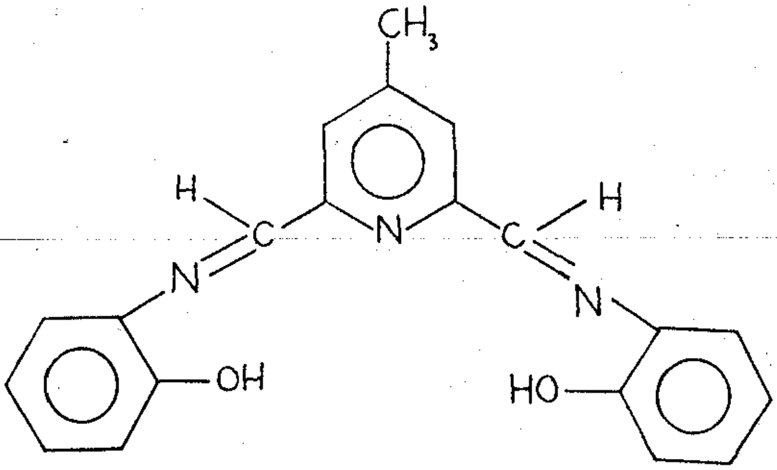
XVI

with potential tridentate repeating units. The polymers obtained from ethylenediamine and 1,6-diaminohexane readily combined with salts such as iron(II) sulfate.



XVII

Uranium(VI) complexes of the Schiff base XVIII derived from the condensation of 4-methyl-2,6-pyridinedicarboxaldehyde and 2-aminophenol were prepared by Seyhan and Fernelius[22].



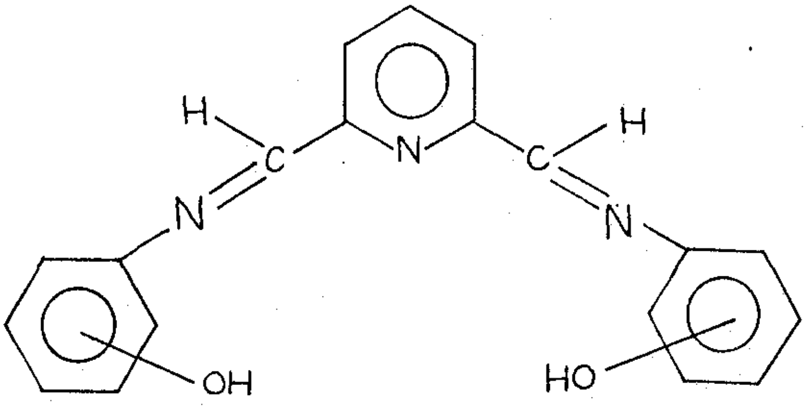
XVIII

Hartkamp[23] investigated the use of 2,6-pyridinedialdoxime or 2,6-pyridinediacetoxime as analytical reagents for the determination of manganese(II). Iron(II), cobalt(II) and nickel(II) were found to interfere by producing coloured chelates.

Busch[24,25] prepared and characterized complexes of 2,6-pyridinedialdbis(methylimine) with iron(II), cobalt(II) and nickel(II). It has also been reported that "the lack" of a suitable preparative method for the dialdehyde has curtailed these studies. He also reported unusual magnetic properties of the six coordinate cobalt(II) complex, bis-(2,6-pyridinedialdihydrazone)cobalt(II)iodide[26].

Using spectrophotometric and potentiometric methods, Bag[27] studied the acid dissociation and the formation constants of copper(II), nickel(II), zinc(II) and manganese(II) complexes of 2,6-pyridinedialdoxime. The metal-to-ligand ratio was 1:1.

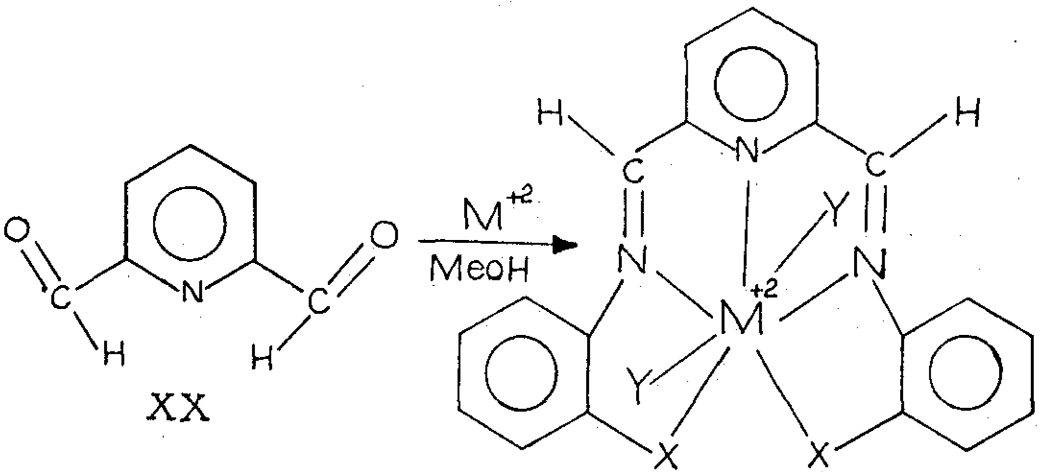
A new method for the differentiation of the o-, m- and p-isomers of aminophenol by adding cadmium(II) to a basic solution of the Schiff base XIX formed by the condensation of 2,6-pyridinedicarboxaldehyde with the aminophenol was reported by Thabet and Hagopian[28]. No precipitate was formed with the m-isomer whereas an intense red color soluble in chloroform was formed by the o-isomer. The red colour of the p-isomer was not soluble in chloroform.



XIX

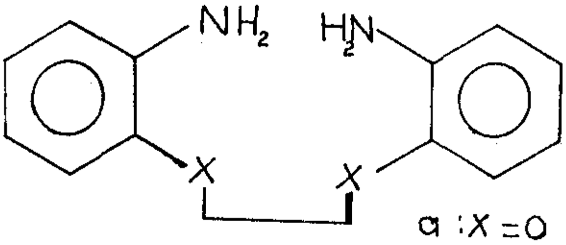
Later, the yellow Schiff base 2,2'-[2,6-pyridinediyl-bis(methylidynenitrilo)] diphenol derived from 2,6-pyridinedicarboxaldehyde and 2-aminophenol was found by Thabet, Adrouni and Tayim[29] to be a highly selective reagent for the detection of uranium(VI), antimony(III) and bismuth(III). The reactions of the same Schiff base with some transition and post-transition metal ions[30] and with some heavier and inner transition[31] metal ions were investigated.

Metal complexes of pentadentate macrocyclic ligands have been isolated from the condensation of 2,6-pyridinedicarboxaldehyde XX with a series of α,ω-diamines XXI in methanol in the presence of manganese(II) and zinc(II) perchlorates or nitrates[32]. X-ray structure analysis of XXII ($Y = ClO_4$) has shown that the donor atoms in the macrocycle define the five vertices of a distorted pentagonal bipyramid.



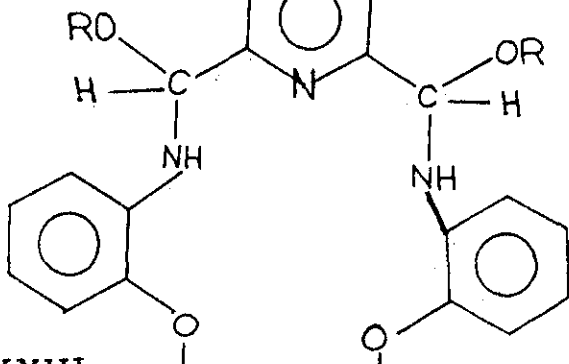
XX

XXII a,b,c



XXI

a : X = O
b : X = NH
c : X = S

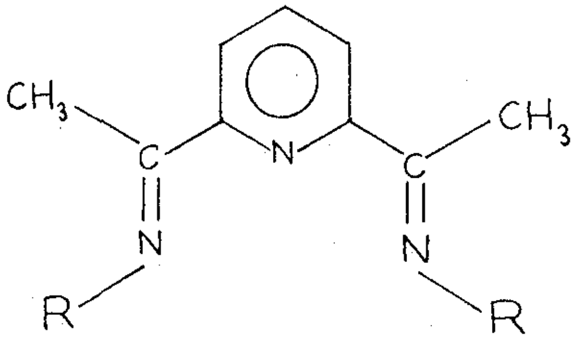


a. R = Et
b. R = Me
c. R = n-Bu

XXIII

The above reaction was re-investigated[32] by attempting to introduce magnesium(II) as the templating cation in view of the success with related reactions of XX with α,ω-polyfunctional diamines. When manganese(II) chloride in methanol was used with XXIa in addition to $\left[(\mathrm{XXIIa})\mathrm{Mn}(\mathrm{H_2O})_2\mathrm{Y}_2\right]$ Y = Cl, XXIIIb was isolated. The reaction of XX with XXIa in ethanol led directly to the crystallization of XXIIIa with no metal required.

Curry and co-workers[33] reported the synthesis and properties of various complexes derived from 2,6-diacetylpyridinebishydrazone XXIV where R = NH_2, $NHCH_3$, NHC_6H_5, $N(CH_3)_2$ and NHC_5H_4N.



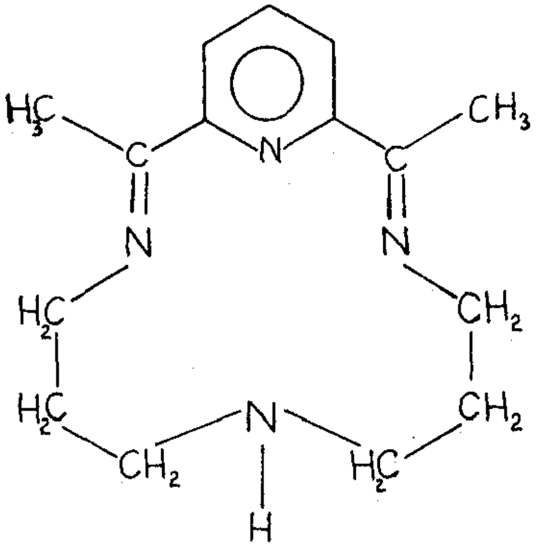
XXIV

A five coordinate structure was suggested for certain 1:1 complexes of cobalt(II) and copper(II) salts having the formula MLX_2 (L = XXIV, R = NMe_2; X = Cl). The authors referred to unpublished work done by Burke on the preparation and characterization of the imine complexes derived from

2,6-diacetylpyridine (XXIV, R = CH_3, CH_2CH_3, $CH_2C_6H_5$, C_6H_5, p-ClC_6H_4, p-FC_6H_4, p-$CH_3C_6H_4$ and p-$OCH_3C_6H_4$) with divalent iron, cobalt and nickel.

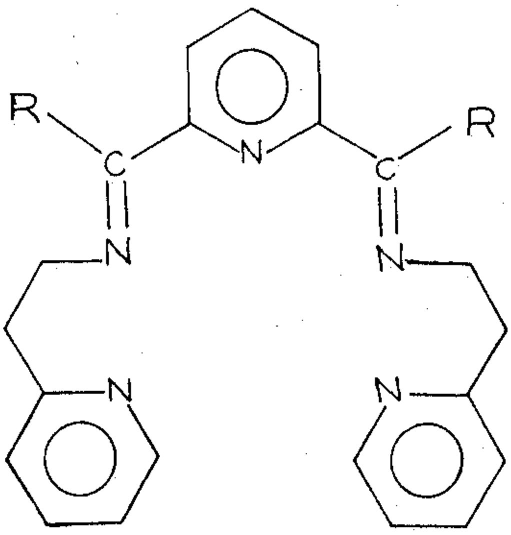
Complexes of 2,6-diacetylpyridine Schiff bases (XXIV, R = Me, Et, n-Pr, i-Pr, sec-Bu and cyclohexyl) with the halides, nitrates and thiocyanates of cobalt(II) and nickel(II) in anhydrous non-solvating solvents were prepared by Sacconi[34]. High spin, five coordinate complexes of the general formula MLX_2 were obtained (L = XXIV, X = Cl, NO_3 or CNS).

Octahedral cobalt(III) complexes of the formula $\left[\text{RCo(III)cypBr}\right]Y$ (R = alkyl or analogous groups, cyp = XXV) were reported by Busch[35].



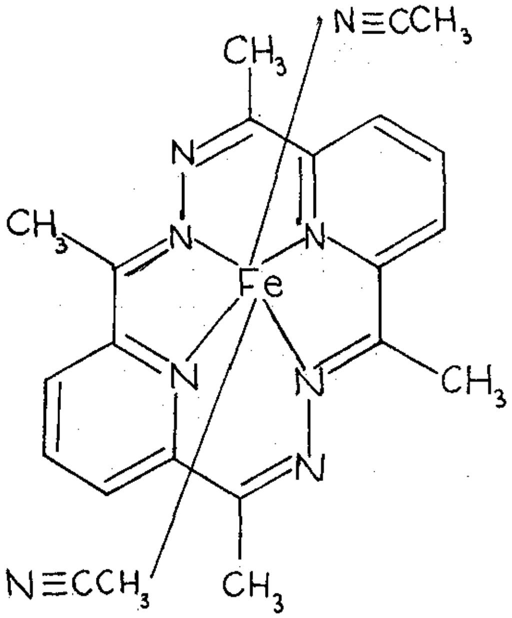
XXV

Bacci and co-workers[36] reported pseudo octahedral complexes of the general formula MLX_2 (M = Co, Ni; X = Br, I, NCS; L = XXVI where R = H) and $ML'I_2.BuOH$ (L' = XXVI where R = Me). It was shown that the magnetic moments of the cobalt(II) iodo complexes were temperature dependent.

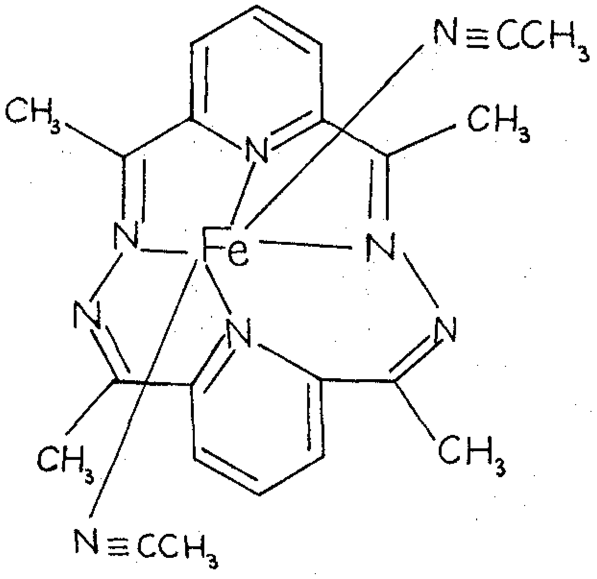


XXVI

The direct formation of the fully conjugated hexaazamacrocyclic complexes of iron(II) XXVII and XXVIII from the template condensation of 2,6-diacetylpyridine with hydrazine and its structural characterization was reported by Goedken[37]. Acetonitrile was used as a solvent.



XXVII



XXVIII

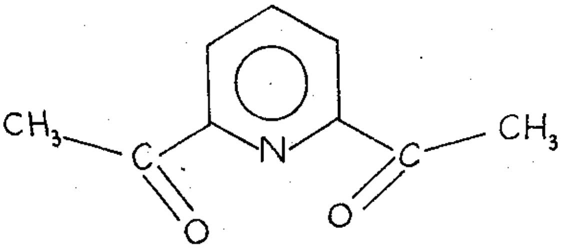
Wester and Palenik[38] reported the synthesis and characterization of cobalt(II) and zinc(II) complexes of neutral and dianionic 2,6-diacetylpyridinebis(2'-pyridylhydrazone) abbreviated as H_2dapp. The complexes were found to have the stoichiometry $[M(H_2dapp)(H_2O)_2]Cl_2$ and the cations to have a pentagonal bipyramidal geometry with H_2dapp forming the equatorial plane and the two water molecules occupying the axial positions. The metal ion exhibits a coordination number of seven which is rare especially with the elements of the first transition series. The Zn(dapp)$CHCl_3.H_2O$ complex formed by deprotonation of the ligand crystallizes with chloroform and water. It is an octahedral dimer. The structures of the complexes were elucidated by x-ray diffraction studies.

Pentagonal bipyramidal complexes resulting from the reactions of chromium(III) and iron(III) with the ligand 2,6-diacetylpyridinebis(semicarbazone) were reported[39].

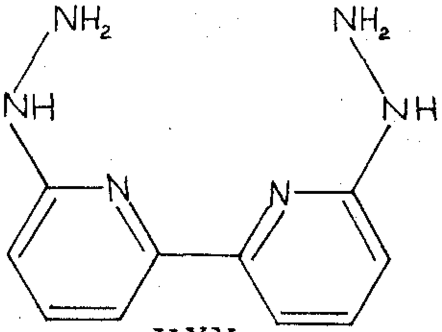
Romanik[40] reported the preparation and characterization of copper(II) complexes of the condensation products of 2,6-diacetylpyridine and 2,6-pyridinedicarboxaldehyde with 1,8-diaminonaphthalene.

In an attempt to prepare complexes with regular coordination polyhedra, synthetic routes were successfully modified to incorporate more donor atoms into fused rings, and thus provide a more rigid and more planar equatorial N_5 donor sets[41]. The condensation of diacetylpyridine XXIX with the dihydrazine XXX in the presence of zinc(II) salts of weakly coordinating anions (e.g. NO_3) resulted in the cationic zinc(II) complex with water molecules occupying axial coordination positions. The complex cation XXXI has a pentagonal bipyramidal coordination geometry. The equatorial 'N_5' donor set of the macrocycle is very nearly planar with no nitrogen deviating by more than 0.001^{o} A from the 'Zn N_5' best (least-squares) plane.

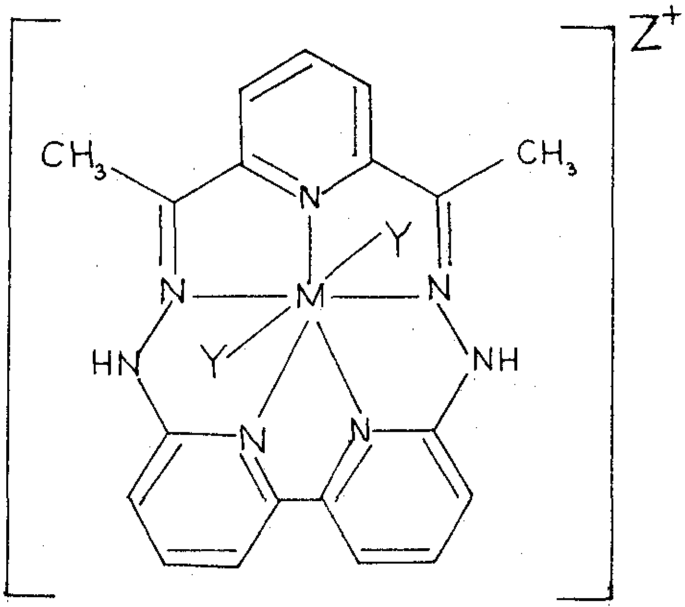
A number of Schiff polybases with a system of conjugated bonds by the reaction of 2,6-diaminopyridine with 1,3-butanedione, benzil, glyoxal, terephthaldehyde, malealdehyde, bis-(acetylphenyl)ether and bis(acetylphenyl)-sulfide was reported by Topchiev and co-workers[42]. The black to grey polymers obtained were found to be soluble in dimethylformamide, acetic acid, formic acid or sulfuric acid.



XXIX



XXX



M = Zn
Y = H$_2$O
Z = 2

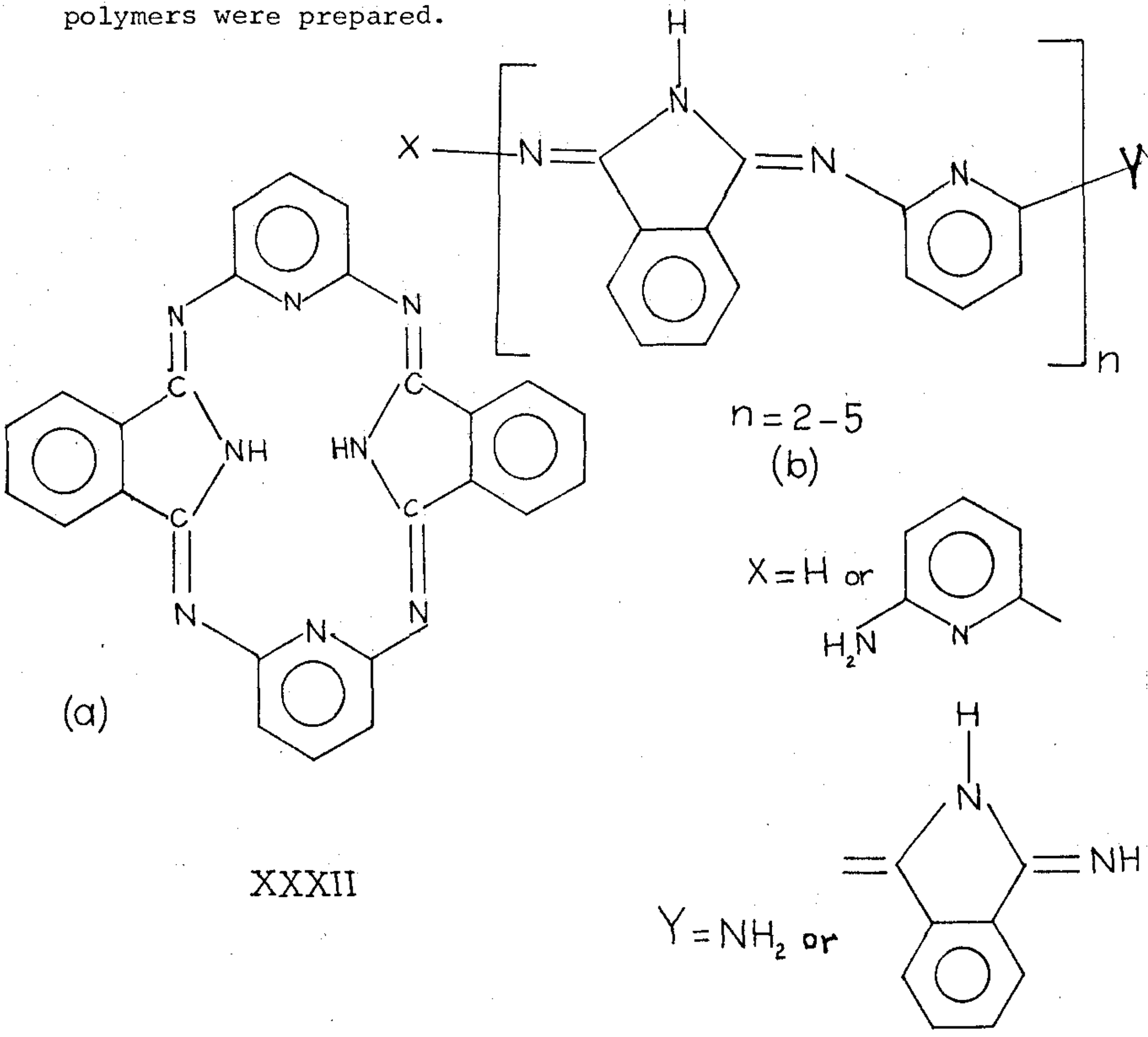
XXXI

Delman[43] synthesized a wide variety of structurally related Schiff base and acid amide compounds and low molecular weight polymers. Among these was the Schiff base prepared from terephthaldehyde and 2,6-diaminopyridine.

Refluxing 2,6-diaminopyridine with tetracyanobenzene in a 2:1 molar ratio in high boiling solvents produced polymers with a hemiporphyrazine structure[44]. Another polymer resulting from Cu-bis(1,2-dicyanoethylene-

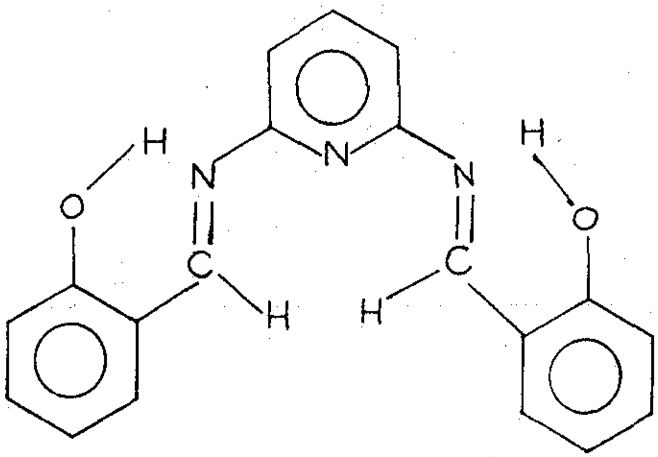
1,2-dithio)cuprate(II) dihydrate and 2,6-diaminopyridine was reported. Similar results were obtained with the last two compounds in the presence of copper-acetylacetonate. A polymer was also prepared from tetracyanothiophene and 2,6-diaminopyridine in the presence of copper(II) chloride.

Pakham and Haydon[45] reported macrocyclic and linear polymers by condensing 2,6-diaminopyridine with phthalonitrile XXXII-a and XXXII-b or pyromellitonitrile in alcohols as solvents under nitrogen atmosphere and with sodium alkoxide as catalyst. Nickel(II) complexes of the polymers were prepared.



XXXII

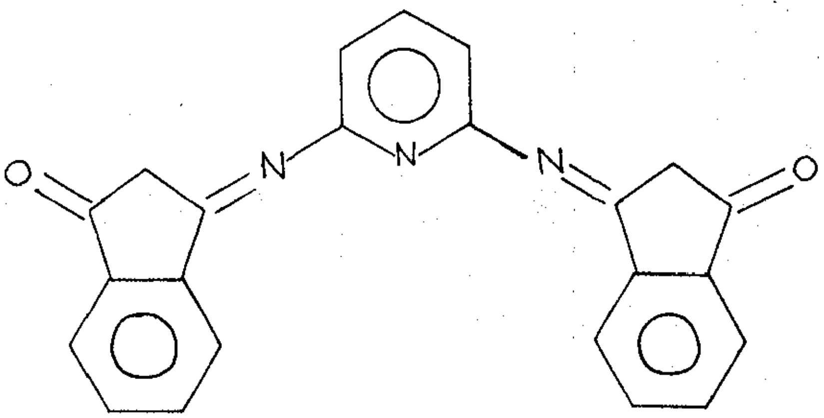
Savich[46] reported the preparation of the Schiff base XXXIII resulting from the condensation of 2,6-diaminopyridine and salicylaldehyde.



XXXIII

The analytical applications of the Schiff base XXXIII for the detection of antimony(III), bismuth(III) and uranium(VI) in the presence of other ions[47] and the specific detection of cadmium(II) in the presence of as many as thirty eight cations[48] with the same Schiff base XXXIII were investigated. The reactions of some transition metal ions with the Schiff base XXXIII which behaved as a neutral monodentate, a monoanionic bidentate or as a dianionic tetradentate ligand were reported[49].

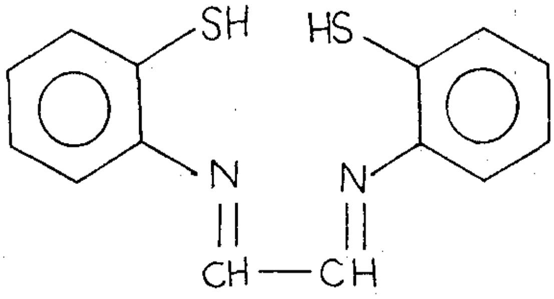
Smirnov and Vorobera[50] reported the preparation of the Schiff base XXXIV by the condensation of 2,6-diaminopyridine with 1,3-indandione. The Schiff base was found to be heat resistant and was also used as a dye for colouring plastics.



XXXIV

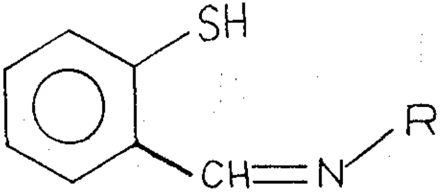
Although complexes of the Schiff bases derived from salicylaldehyde and mono or polyamines are well known, this is not the case with the sulfur analogue of salicylaldehyde, 2-mercaptobenzaldehyde, 2-aminothiophenol or 2,2'-dithiodianiline.

Bayer[51] prepared complexes of zinc(II), copper(II), nickel(II), cobalt(II), manganese(II), cadmium(II) and uranium(VI) with the Schiff bases XXXV derived from 2-aminothiophenol and polycarbonyls. Extensive work has been done on the reactions of 2-aminothiophenol with metal ions[52].

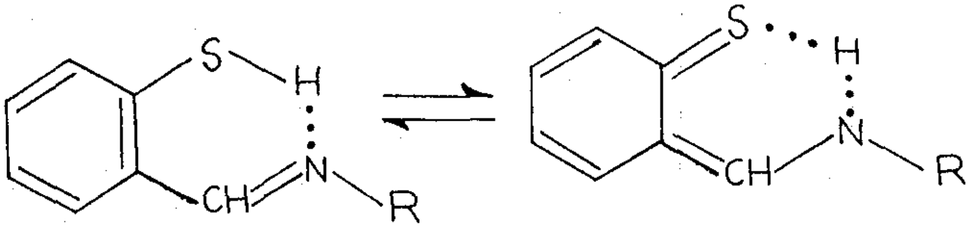


XXXV

A number of N-aryl and N-alkyl imines of 2-mercaptobenzaldehyde XXXVI R = C_6H_5, p-$C_6H_4OCH_3$, p-$C_6H_4N(CH_3)_2$, o-C_6H_4OH and n-$(CH_2)_3CH_3$ has been reported[53]. The presence of a tautomeric benzoid-quinoid XXXVII - XXXVIII equilibrium in solutions of these imines has been established from their electronic and vibrational spectra.

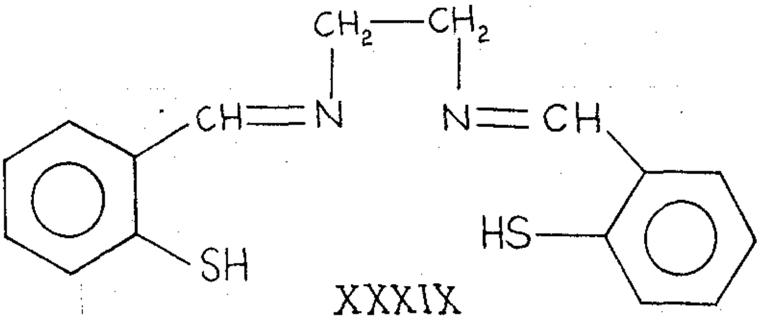


XXXVI

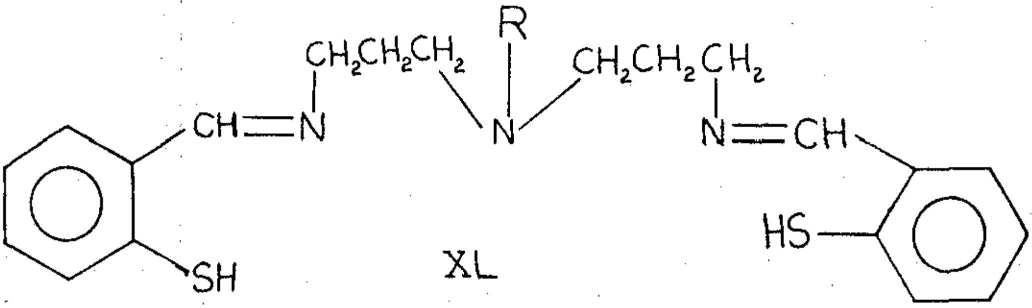


XXXVII XXXVIII

Some nickel(II) and cobalt(II) complexes with the o-mercaptobenzaldiminates XXXVI (R = Me, Et, i-Pr, sec-Bu and tert-Bu) XXXIX and XL were reported by Bertini[54].

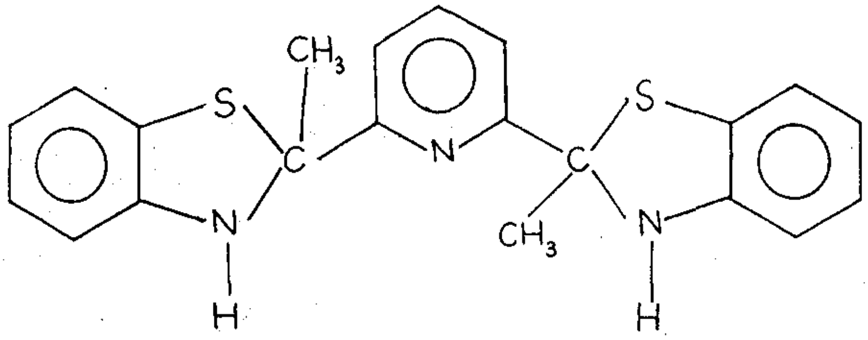


XXXIX

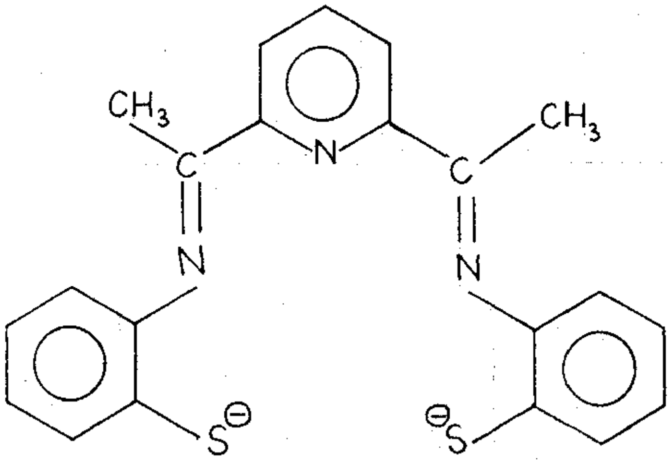


XL

2-Aminothiophenol was condensed with 2,6-diacetylpyridine in a 2:1 molar ratio to give 2,6-bis(2-methyl-2-benzothiazolinyl)pyridine[55] XLI. However, in the presence of zinc(II) and cadmium(II) ions XLI rearranged to give five coordinate complexes of the Schiff base XLII.

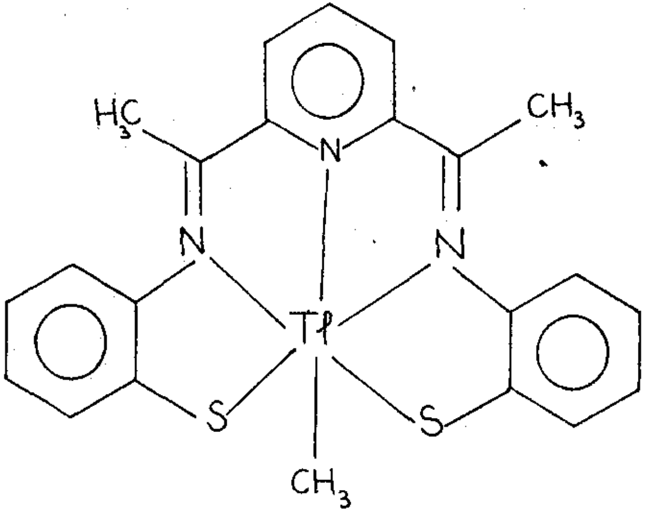


XLI



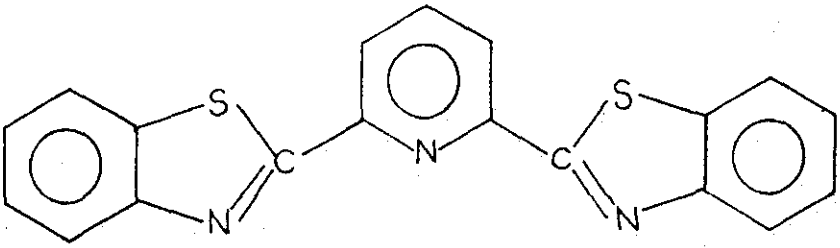
XLII

The preparation and crystal structure of {2,6-bis-[1-methyl-2-(2-thiolophenyl)2-azaethene]pyridine}-methylthallium(III) XLIII was reported by Henrick[56]. The complex was obtained by rearrangement and deprotonation of XLI upon its reaction with an equimolar amount of diacetatomethylthallium(III).



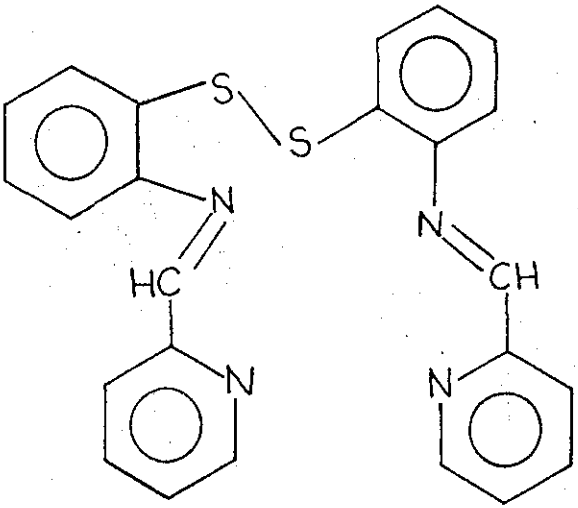
XLIII

Livingstone and Nolan[57] reported the preparation and properties of the manganese(II), iron(II), cobalt(II) and nickel(II) complexes of the α, α', α''-tri-imine Schiff base 2,6-(dibenzothiazol-2-yl)pyridine XLIV obtained by the condensation of 2-aminothiophenol with 2,6-pyridinedicarboxaldehyde. The dialdehyde was prepared and used in situ by the oxidation of 2,6-lutidine with iodine-dimethylsulfoxide complex.



XLIV

In another article, Livingstone and Nolan[52] reported the preparation of manganese(II) and the nickel(II) complexes of the Schiff base α , α'-[dithiobis(o-phenylenenitrilo)] di-2-picoline XLV obtained by the condensation of 2,2'-dithiodianiline with 2-pyridinecarboxaldehyde. The nickel(II) chloride and bromide complexes of 2,2'-dithiodianiline are also reported.



XLV

2. Scope and purpose of the work

The above review of the literature shows that very little work has been done on Schiff bases derived from 2,6-pyridinedicarboxaldehyde. The little work done on the related compounds suggests that the improvement of the solubility of the complexes would make possible the investigation of the structures of the complexes and possibly their reactions by different physicochemical methods. Moreover, the recent discovery* that some complexes of 2,6-diaminopyridine have antitumor activity justifies the investigation of the Schiff bases derived from substituted pyridine. This is because it is well established now that potential anti-tumour complexes should include relatively non-dissociable ligands containing N donor atoms.

Since the synthesis of Schiff-base-transition metal complexes is sometimes carried out by reacting the metal

* H. A. Tayim Private communication.

ions with a mixture of the aldehyde and amine that constitute the Schiff base, the investigation of the individual aldehydes and amines themselves with metal ions should be carried out. The purpose of the present work is therefore:

a) The investigation of the reactions of 2,6-pyridinedicarboxaldehyde, 2,6-diaminopyridine and related ligands with some transition metal ions.

b) The introduction of substituents on one or the other of the components of the Schiff base in order to improve the solubility of its complexes either in polar or non-polar solvents.

c) The synthesis of Schiff bases derived from 2,6-pyridinedicarboxaldehyde and suitable amines.

d) The investigation of the reactions of the Schiff bases, thus prepared with some transition metal ions.

e) The investigation of the reactions of a mixture of the components of the Schiff bases with metal ions, with the intention of understanding the role, if any, of the metal ion in the formulation of the Schiff base.

f) The characterization of the structures of the compounds obtained.

g) Although the investigation of the biological activity of the complexes will not be attempted; we hope that this work will constitute a step towards that end.

2. Experimental and Results

2. Experimental and Results

In discussing this and the following section, reference is made to the table of abbreviations (Table 1), for the names of the ligands.

Table 1

List of Abbreviations

DIAL	2,6-Pyridinedicarboxaldehyde
DAP	2,6-Diaminopyridine
DMMP	2,6-Bis(dimethoxy-methyl)pyridine
DEMP	2,6-Bis(diethoxy-methyl)pyridine
DTDA	2,2'-Dithiodianiline
ATPH	2-Aminothiophenol
ATP	2-Aminothiophenolate
DBTP	2,6-(Dibenzothiazol-2-yl)pyridine
AMQ	8-Aminoquinoline
AQAL	Schiff base derived from 2,6-pyridinedicarboxaldehyde and 8-aminoquinoline
DTDAL	Schiff base derived from 2,6-pyridinedicarboxaldehyde and 2,2'-dithiodianiline
DMPAL	2 -Dimethoxy-methyl-6-pyridinecarboxaldehyde
ATPALH$_2$	Schiff base expected from condensation of 2,6-pyridinedicarboxaldehyde and 2-aminothiophenol
DAPAL	Schiff base derived from 2,6-pyridinedicarboxaldehyde and 2,6-diaminopyridine

2.1 Materials

The solvents used were analytical reagent grade and were used as purchased.

Copper(II) nitrate trihydrate, $Cu(NO_3)_2.3H_2O$; iron(III) chloride hexahydrate, $FeCl_3.6H_2O$; copper(II) bromide, $CuBr_2$; mercury(II) chloride, $HgCl_2$; mercury(II) bromide $HgBr_2$; tin(II) chloride dihydrate, $SnCl_2.2H_2O$; hexachloroplatinic acid hexahydrate, $H_2PtCl_6.6H_2O$; iodine, I_2; phenol, C_6H_5OH; and copper(II) chloride dihydrate, $CuCl_2.2H_2O$, were purchased from Mallinckrodt Chemical Works, New York, U.S.A.

Potassium permanganate, $KMnO_4$; sodium borohydride, $NaBH_4$; phosphorus pentachloride, PCl_5; uranyl acetate dihydrate, $UO_2(CH_3COO)_2.2H_2O$; potassium cyanide, KCN; zinc(II) nitrate hexahydrate, $Zn(NO_3)_2.6H_2O$; phosphorus pentoxide, P_2O_5; cobalt(II) acetate tetrahydrate, $Co(CH_3COO)_2.4H_2O$; manganese(II) chloride tetrahydrate, $MnCl_2.4H_2O$; were purchased from E. Merck A.G., Darmstadt, Germany.

Lithium aluminium hydride, $LiAlH_4$; rhodium(III) chloride trihydrate, $RhCl_3.3H_2O$; copper(II) perchlorate hexahydrate, $Cu(ClO_4)_2.6H_2O$; cobalt(II) iodide dihydrate, $CoI_2.2H_2O$; iridium(III) chloride trihydrate, $IrCl_3.3H_2O$; molybdenum hexacarbonyl, $Mo(CO)_6$; and tungsten hexacarbonyl, $W(CO)_6$, were purchased from Alfa Inorganics Inc. (Vetron), Beverly, Massachusetts, U.S.A.

2-Aminothiophenol, 2-$NH_2.C_6H_4SH$; ruthenium(III) chloride trihydrate, $RuCl_3.3H_2O$; thorium(IV) nitrate tetrahydrate, $Th(NO_3)_4.4H_2O$; yttrium(III) nitrate tetrahydrate, $Y(NO_3)_3.4H_2O$; cobalt(II) perchlorate hexahydrate, $Co(ClO_4)_2.6H_2O$; and palladium(II) chloride, $PdCl_2$, were purchased from Fluka A.G., Buchs, Switzerland.

Manganese(II) sulfate monohydrate, $MnSO_4.H_2O$; silver(I) acetate, $Ag(CH_3COO)$; and chromium(III) nitrate nonahydrate, $Cr(NO_3)_3.9H_2O$ were purchased from J.J. Baker Chemical Company, Phillipsburg, New Jersey, U.S.A.

2,6-Pyridinedimethanol, 2,6-$(CH_2OH)_2C_5H_3N$; cheledamic acid, nickel(II) acetylacetonate monohydrate, $Ni(acac)_2.H_2O$; and cobalt(III) acetylacetonate, $Co(acac)_3$, were purchased from Aldrich Chemical Co., Inc., Milwaukee, Wisconsin, U.S.A.

2,6-Lutidine, 2-6$(CH_3)_2C_5H_3N$ and benzonitrile, C_6H_5CN, were purchased from Eastman Organic Chemicals, Rochester, N.Y.

Silver perchlorate, $Ag(ClO_4)$ and rhodium(III) chloride trihydrate, $RhCl_3.3H_2O$, were purchased from Organic/Inorganic Chemicals Corp., Sun Valley, Calif. U.S.A.

Zinc(II) chloride, $ZnCl_2$ and nickel(II) nitrate hexahydrate, $Ni(NO_3)_2.6H_2O$, were purchased from Fisher Scientific Company, Fair Lawn, N.J., U.S.A.

Nickel(II) perchlorate hexahydrate, $Ni(ClO_4)_2.6H_2O$, was purchased from K and K Laboratories, Inc., Plainview, New York, Hollywood, California, U.S.A.

Cis-dichlorobis(benzonitrile)palladium(II), $PdCl_2(C_6H_5CN)_2$, was prepared by the method described by Kharash[58].

Potassium tetrachloroplatinate(II), K_2PtCl_4, was prepared from hexachloroplatinic acid, H_2PtCl_6, by the method originally introduced by Cooley and Busch[59] and later improved by Tayim[60].

8-Aminoquinoline was prepared by the method of Fieser and Hershberg[61].

2.2 Instrumental

Elemental analyses for carbon, hydrogen, nitrogen, halogens and sulfur were run by Mikroanalytisches Laboratorium, Bonn, Germany. Some of the elemental analyses were run at Manchester University, England.

The infrared spectra were recorded using a Perkin-Elmer 621 Grating Spectrophotometer. Potassium bromide pellets were used.

The ultraviolet spectra were recorded using a Perkin-Elmer 202 Spectrophotometer. Solutions of about 10^{-4} - 10^{-5} M were studied. Rectangular silica cells of 10 mm path-length were used.

The nuclear magnetic resonance spectra were recorded using a Varian 60 A Spectrometer.

Melting and decomposition points (uncorrected) were taken using a Mel-Temp apparatus.

The magnetic moment measurements were carried out on a Gouy balance.

The conductivity measurements were carried out on a Fisher Scientific Conductivity Bridge Model RC 16 B2 at room temperature.

Thermogravimetric analyses were attempted using a TG-750 Standard Redcroft instrument.

2.3 Preparation and purification of ligands

2.3.1. 2,6-Pyridinedicarboxaldehyde (DIAL)

2,6-Pyridinedicarboxaldehyde was prepared by the oxidation of 2,6-pyridinedimethanol with freshly prepared manganese(IV) oxide.

i) Preparation of manganese(IV) oxide, MnO_2[62]

A solution of manganese(II) sulfate monohydrate (96 g, 0.60 mole) in water (250 ml) was placed in a two-liter, three necked flask, equipped with a thermometer and a mechanical stirrer. The solution was heated to 75°C. A solution of potassium permanganate was prepared from the salt (106 g, 0.74 mole) and hot water (600 ml) at 80°C. To the continuously stirred solution of $MnSO_4.H_2O$, the permanganate solution was added in portions of 50 ml at five-minute intervals. The last portion was added after 15 minutes of the one before it, and the stirring was continued for another 40 minutes, after which the supernatant liquid became colourless. The temperature during the whole procedure was maintained within the range 80 - 95°C.

The reaction mixture was filtered while hot, and the solid was washed with three 250-ml portions of hot water, then dried for 24 hours in an oven at 110 - 120°.

The dry dark brown product (123 g) was powdered before use.

ii) Oxidation of 2,6-pyridinedimethanol[63]

A mixture of 2,6-pyridinedimethanol (10 g, 0.08 mole) and chloroform (600 ml) was refluxed until the solid had dissolved. Freshly prepared manganese(IV) oxide (107 g, 1.24 mole) was then added. The mixture was refluxed with stirring for five hours and filtered while hot. The solid was washed with five 100-ml portions of ether. The combined filtrate and washings were evaporated to dryness under reduced pressure, and the residue was extracted with a 1:1 naphtha-light-petroleum-ether mixture (250 ml). The resulting solution was cooled in an ice-bath. After the first crop had been collected, the mother liquor was concentrated and a second crop was obtained.

The resulting compound was white with a very faint yellow tint. It has a melting point of 123° (Lit. 123°)[63]. The yield was 5.0 g (50%).

The manganese(IV) oxide which remained from the reaction was washed three times with 200-ml portions of hot methanol and twice with 100-ml portions of hot chloroform. These were combined and the solvent was evaporated to dryness under reduced pressure. The yellow solid that remained was unreacted 2,6-pyridinedimethanol.

The used MnO_2 was oxidized to $KMnO_4$ which was further converted to fresh MnO_2.

2.3.2. 2,6-Bis(dimethoxy-methyl)pyridine (DMMP)

A mixture of 2,6-pyridinedicarboxaldehyde (DIAL) (2.70 g, 20 mmole), trimethylorthoformate (16 ml), anhydrous methanol (20 ml) and two drops of concentrated hydrochloric acid was refluxed for six hours. The resulting solution, after being neutralized with methanolic potassium hydroxide, was evaporated under reduced pressure. The residue left was extracted with two portions of 30-ml petroleum ether. The petroleum ether solution was dried over anhydrous magnesium sulfate. After the elimination of the solvent by evaporation the residue was distilled under reduced pressure to yield 3.2 g (71%) of 2,6-bis-(dimethoxy-methyl)pyridine (DMMP) as a pale yellow oil. Boiling point: 120° at 5 mmHg. Refractive index: 1.4852 at 20°. Molecular weight 227 gm/mole.

The elemental analysis of DMMP: calculated for $C_{11}H_{17}NO_4$: %C 58.13; %H 7.54; %N 6.16. Found: %C 57.95; %H 7.50; %N 6.23.

The major infrared bands of DMMP with their respective assignments[75-77] are shown in Table II. The ultraviolet spectrum of DMMP in chloroform displays a band at 258 mu ($\epsilon = 0.34 \times 10^4$).

Table II

Infrared Spectrum of DMMP[a]

Assignment	DMMP
C-H stretching	2990(w), 2940(sb), 2840(s)
Ring skeletal vibrations	1600(s), 1460(sb)
C-C and C-N stretching	1350(sb)
C-O stretching	1195(s), 1090(vsb)
In-plane and out-of-plane C-H deformation	990(s), 820(s), 765(m)

The NMR spectrum of DMMP shows a multiplet at 7.6 δ due to the pyridine protons, a singlet at 5.4 δ due to the protons of the carbons directly attached to the ring and a singlet at 3.4 δ due to the methoxy protons in the ratio of 3:2:12.

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[a] Symbols used throughout this section: s = strong; m-s = medium to strong; m = medium; b = broad; w = weak; v = very; sh = shoulder.

2.3.3. 2,6-Bis(diethoxy-methyl)pyridine[78] (DEMP)

A mixture of DIAL (1.35 g, 10 mmole) triethylorthoformate (4 ml), anhydrous ethanol (4 ml) and a drop of concentrated hydrochloric acid was heated at 100° for three hours. The resulting solution, after being neutralized with ethanolic potassium hydroxide, was evaporated under reduced pressure. The residue left was extracted with two portions of 15-ml petroleum ether. The petroleum ether solution was dried over anhydrous magnesium sulfate. After the elimination of the solvent by evaporation the residue was distilled under reduced pressure to yield 2.4 g (86%) of 2,6-bis(diethoxy-methyl)pyridine (DEMP). Boiling point: 136° at 3 mmHg. Refractive index 1.471 at 25°. (Lit. b.p. 136/3 mmHg, n_D^{25} 1.470)[78].

2.3.4. 2,2'-Dithiodianiline[64] (DTDA)

Dimethylsulfoxide (3.90 g, 0.05 mole) was added to 2-aminothiophenol (6.25 g, 0.05 mole) and the mixture was stirred at room temperature for 24 hours, then poured over crushed ice (100 g) with stirring. A yellow precipitate separated out. It was filtered off and recrystallized from an ethanol-water mixture. Yield: 4.40 g (71%). Melting point 92-93° (Lit. 93°)[52].

2.3.5. 2,6-Diaminopyridine (DAP)

2,6-Diaminopyridine (DAP) purchased from City Chemical Corporation, New York, U.S.A. was purified by a hitherto unknown method:

Crude 2,6-diaminopyridine was dissolved in the minimum amount of chloroform. Activated charcoal was added and the mixture was stirred for a few minutes then filtered by gravity. The addition of n-heptane to the filtrate precipitated 2,6-diaminopyridine as a white solid in an almost quantitative yield. M.P. 120-121° (Lit. 121.5)[65].

2.3.6. Substituted 2,6-pyridinedicarboxaldehyde

The following attempted preparations were carried out with the intention of effecting ring substitution on 2,6-pyridinedicarboxaldehyde.

i) 4-Chloro-2,6-pyridinedicarboxaldehyde

4-Chloro-2,6-pyridinedicarboxaldehyde is expected to be obtainable by the oxidation of 4-chloro-2,6-pyridinedimethanol with freshly prepared manganese(IV) oxide, according to the procedure followed for the oxidation of 2,6-pyridinedimethanol to DIAL[63].

In attempts to prepare 4-chloro-2,6-pyridinedimethanol, the reduction of diethyl-4-chloropyridine-2,6-dicarboxylate[66] with the following reagents was tried:

a) Sodium borohydride in ether[67].

b) Sodium borohydride and anhydrous calcium chloride in ethanol[68].

c) Lithium aluminium hydride in ether[69].

In all three cases, the yield of the reaction product was very low, not exceeding 5%.

An attempt was made to reduce dimethyl-4-chloro-2,6-dicarboxylate directly to the corresponding dialdehyde with lithium aluminium hydride in tetrahydrofuran at -70°[70]. The starting material was recovered unchanged at the end of the experiment.

An attempt to isolate 2,6-pyridinedicarboxaldehyde as the oxidation product of 2,6-lutidine with iodine-dimethylsulfoxide[71] failed. That was an illustrative step for the preparation of 4-chloro-2,6-pyridinedicarboxaldehyde from 4-chloro-2,6-lutidine using the same method.

The reduction of tertiary amides to aldehydes is known[72]. An attempt to prepare a 2,6-pyridinebis(diethylamide) by the reaction of chelidamic acid with phosphorus pentachloride[66] followed by the addition of diethylamine failed.

ii) <u>4-Phenoxy-2,6-pyridinedicarboxaldehyde</u>

The attempt to prepare 4-phenoxy-2,6-pyridinedicarboxaldehyde by the formation of diethyl-4-phenoxypyridine-2,6-dicarboxylate and its subsequent reduction, was unsuccessful due to:

a) The yield of the product of the reaction of diethyl-4-chloropyridine-2,6-dicarboxylate with sodium phenoxide[73] was very low, not exceeding 4%.

b) Nonfeasibility of the reduction reactions of the 2,6-dicarboxylate esters.

2.4.1 Reactions of 2,6-pyridinedicarboxaldehyde (DIAL) with metal ions

i) Cis-dichlorobis(benzonitrile)palladium(II)

To a filtered solution of cis-dichlorobis(benzonitrile)palladium(II) (0.384 g, 1 mmole) in benzene (20 ml) a solution of DIAL (0.270 g, 2 mmole) in benzene (16 ml) was added. The pale yellow product which crystallized out immediately was filtered off, washed thoroughly with benzene and dried in vacuo. Yield: 0.210 g (47%). Melting point: 200-204° with decomposition.

ii) Copper(II) chloride dihydrate

A solution of DIAL (0.270 g, 2 mmole) in acetone (10 ml) was added to a solution of copper(II) chloride dihydrate (0.340 g, 2 mmole) in acetone (30 ml). A yellowish-brown solid began to form. The mixture was stirred for one hour. The solid produced was collected by filtration, washed with acetone and dried in vacuo. Yield: 0.352 g (63%). Melting point: 221-222° with decomposition.

iii) Uranyl acetate dihydrate

A solution of DIAL (0.270 g, 2 mmoles) in methanol (10 ml) was added to a stirred solution of uranyl acetate dihydrate (0.441 g, 1 mmole) in methanol (10 ml). After stirring for three minutes, precipitation started. The mixture was then stirred for two hours. The yellow product obtained was filtered off, washed with methanol and dried in vacuo. Yield: 0.40 g (72%).

The compound obtained started darkening at around 270° and did not melt up to 360°.

iv) Potassium tetrachloroplatinate(II)

A filtered solution of potassium tetrachloroplatinate(II) (0.421 g, 1 mmole) in water (14 ml) was added dropwise over a period of 15 minutes to a solution of DIAL (0.270 g, 2 mmole) in water (24 ml). The mixture was cooled in a refrigerator overnight, then stirred at room temperature for three hours to produce an olive green solid. The solid was filtered off, washed thoroughly with water and dried in vacuo over P_2O_5. Yield: 0.260 g (46%). Melting point: 204-206° with decomposition.

v) Nickel(II) acetylacetonate monohydrate

A solution of DIAL (0.270 g, 2 mmole) in toluene (10 ml) was added to a warm solution of nickel(II) acetylacetonate monohydrate (0.275 g, 1 mmole) in toluene

(20 ml). The mixture was refluxed with stirring for 5 1/2 hours. The yellowish-green solid formed was filtered off, washed thoroughly with hot toluene, then with ether and dried in vacuo. Yield: 0.214 g (78%).

The compound obtained did not melt up to 360°.

The elemental analyses for the DIAL complexes are shown in Table III, their solubilities in Table IV and their major infrared bands along with their respective assignments in Table V. Table VI lists the observed ultraviolet bands for DIAL and its complexes.

Table III

Results of the Elemental Analyses of Some Complexes of DIAL

Compound		%C	%H	%N	%Cl	% Metal
Pd(DIAL)$_2$Cl$_2$	Calc:	37.57	2.25	6.26	15.84	
	Found:	37.81	2.35	6.10	15.77	
Cu(DIAL)Cl$_2$	Calc:	31.19	1.87	5.20	26.30	23.57
	Found:	31.35	2.18	5.13	25.82	23.15
UO$_2$(DIAL)(CH$_3$COO)$_2$	Calc:	23.62	2.70	2.51		
.2H$_2$O	Found:	22.69	2.60	2.96		
Pt(DIAL)$_2$Cl$_2$.2H$_2$O	Calc:	29.38	2.47	4.90	12.40	
	Found:	29.92	2.57	4.99	12.45	
Ni(DIAL)$_2$(acac)$_2$*	Calc:	52.87	4.81	5.14		10.73
.H$_2$O	Found:	52.60	4.40	4.95		10.83

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* acac is acetylacetonate.

Table IV

Solubilities of the Complexes of DIAL[b]

Compound	H_2O	MeOH	EtOH	Me_2CO	Et_2O	C_6H_6	Diox.	CH_2Cl_2	$CHCl_3$	DMF	DMSO
$Pd(DIAL)_2Cl_2$	-	-	-	±	-	-	+	-	-	+	+
$Cu(DIAL)Cl_2$	+	+	+	-	-	-	-	-	-	+	+
$UO_2(DIAL)(CH_3COO)_2 \cdot 2H_2O$	-	-	-	-	-	-	-	-	-	-	-
$Pt(DIAL)Cl_2 \cdot 2H_2O$	-	-	-	-	-	-	-	-	-	+	+
$Ni(DIAL)_2(acac)_2 \cdot H_2O$	-	-	-	-	-	-	-	-	-	+	+

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[b] Symbols used throughout this report: + = soluble; - = insoluble, ± slightly soluble.

Diox: dioxane; *DMF: dimethylformamide; DMSO:* dimethyl sulfoxide; Pet. ether: petroleum ether.

Table V

Infrared Spectra of DIAL and its Complexes

Assignment	DIAL	$Pd(DIAL)_2Cl_2$	$Cu(DIAL)Cl_2$
C-H in py-ring	3020(w)	3080(w)	3065(w), 3030(w)
C-H in CHO	2850(w)	2870(m)	2895(w)
C=O stretching	1705(vs)	1700(vs)	1700(vs)
C=C and C=N stretching	1585(w)	1590(m-s), 1425(mb)	1592(m-s), 1568(m-s), 1460(m)
C-C stretching	1370(s), 1255(s), 1200(s)	1345(s), 1242(s), 1195(s)	1388(m-s), 1278(m), 1235(m)
Py-ring vibrations	1310(m), 1170(m), 1085(m-s), 990(s)	1365(vw), 1144(s), 1092(s), 1025(s)	1155(s), 1097(m), 1025(m)
C-H out-of-plane in CHO bending	912(vs)	890(vs)	1005(s)
C-H out-of-plane bending	805(vs), 785(vs), 725(m)	790(vs), 720(m)	817(s)
M-Cl stretching		335(m)	255(m)

Table V continued

Assignment	$UO_2(DIAL).(CH_3COO)_2.2H_2O$	$Pt(DIAL)_2Cl_2.2H_2O$	$Ni(DIAL)_2(acac)_2.H_2O$
O-H stretching	3420 (b)	3532 (m-s), 3410 (sb)	3400 (b)
C-H in py-ring	3090 (vw)	3070 (vw)	3050 (vw)
Alkyl C-H st.	2930 (vw)		
C-H in -CHO	2832 (w)	2938 (w)	2900 (w)
C=O stretching	1705 (m)	1700 (s)	1700 (s)
O-H deformation	1650 (b)	1640 (s)	1650 (w)
C=C and C=N st.	1540 (s), 1445 (m)	1470 (s)	1505 (s)
C-C stretching	1355 (vs), 1345 (vw)	1380 (m), 1282 (s), 1182 (s)	1385 (mb), 1253 (m)
Py-ring vibrations	1365 (vw), 1162 (m) 1019 (w)	1400 (w), 1182 (s), 1142 (s), 1080 (m)	1440 (w), 1170 (w), 1070 (m)
C-H out-of-plane in CHO bending	915 (vs)	995 (s), 910 (m-s)	1005 (m-s), 912 (m-s)
C-H out-of-plane bending	808 (m-s), 725 (m-s)	830 (s), 782 (s), 762 (s)	790 (w), 765 (m)
C=O stretching of acetate	1603 (w)		
C-O stretching	1162 (m), 1094 (w)		
C=O of acac			1580 (vsb)
M-Cl stretching		310 (m)	

Table VI

Ultraviolet Spectra of DIAL and its Complexes in DMF

Compound	mμ	ϵ^{*} x 10^4
DIAL	263	0.70
$Pd(DIAL)_2Cl_2$	267	1.00
$Cu(DIAL)Cl_2$	270	0.44
$Pt(DIAL)_2Cl_2.2H_2O$	270	1.05
$Ni(DIAL)_2(acac)_2.H_2O$	272(b)	0.48

2.4.2. Decomposition of DIAL complexes with aqueous potassium cyanide

$Pd(DIAL)_2Cl_2$ and $Pt(DIAL)_2Cl_2.2H_2O$ were decomposed by aqueous potassium cyanide according to the following method:

The DIAL complex (100 mg) was added to an aqueous solution (35%) of potassium cyanide (100 ml); the mixture was stirred at room temperature for one hour and then extracted with two 10-ml portions of ether. After drying the ethereal solution over anhydrous magnesium sulfate, it was evaporated to dryness to produce DIAL as evidenced by its melting point, its infrared spectrum and by thin layer chromatography.

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* is the extinction coefficient.

2.4.3. Reactions of 2,6-pyridinedicarboxaldehyde (DIAL) with metal ions in methanol

i) Cis-dichlorobis(benzonitrile)palladium(II)

A solution of DIAL (0.360 g, 2.64 mmole) in methanol (20 ml) was added to a filtered solution of cis-dichlorobis(benzonitrile)palladium(II) (0.512 g, 1.32 mmole) in methanol (30 ml). The mixture was refluxed with stirring for 18 hours. The solid obtained was filtered off by suction. It was then dissolved in dichloromethane and upon the addition of diethyl ether, a yellow compound precipitated. The precipitate was filtered off, washed with ether and dried in vacuo. Yield: 0.540 g (65%). Melting point: 220-222° with decomposition.

ii) Copper(II) chloride dihydrate

A solution of DIAL (0.135 g, 1 mmole) in methanol (10 ml) was added to a solution of copper(II) chloride dihydrate (0.170 g, 1 mmole) in methanol (5 ml). The mixture was refluxed with stirring for 18 hours with no solid formed. The solution was evaporated to dryness under reduced pressure. The residue was extracted with dichloromethane (15 ml) and the extract was treated with diethyl ether. The pinkish solid which precipitated was filtered off, washed with ether and dried in vacuo. Yield: 0.257 g (71%). Melting point: 175-182° with decomposition.

The elemental analyses for the Pd(II) and Cu(II) complexes of DMMP are listed in Table VII. More evidence for the assigned formulas of the complexes was obtained from molecular weight measurements.

Table VII

Elemental Analyses of Reaction Products of DIAL With Metal Ions in Methanol

Compound		%C	%H	%N	%Cl	% Metal	Molecular weight gm/mole
$Pd(DMMP)_2Cl_2$	Calc.	41.82	5.42	4.43	11.22		631.8
	Found	42.12	5.22	4.48	12.00		633.2
$Cu(DMMP)Cl_2$	Calc.	36.52	4.73	3.87	19.60	17.57	361.7
	Found	35.89	4.66	3.84	20.30	17.94	359.5

$Pd(DMMP)_2Cl_2$ is soluble in dichloromethane, chloroform and carbon tetrachloride; and insoluble in methanol, acetone and ether; whereas $Cu(DMMP)Cl_2$ is soluble in dichloromethane, chloroform, carbon tetrachloride, methanol, acetone, dioxane and benzene; and insoluble in ether.

The major infrared bands of $Pd(DMMP)_2Cl_2$ and $Cu(DMMP)Cl_2$ along with their respective assignments are shown in Table VIII.

The ultraviolet spectrum of Pd(DMMP)$_2$Cl$_2$ shows a band at 246 mμ ($\epsilon = 2.12 \times 10^4$) and that of Cu(DMMP)Cl$_2$ shows two bands at 260 mμ ($\epsilon = 0.30 \times 10^4$) and 285 mμ ($\epsilon = 0.53 \times 10^4$). Chloroform was used as a solvent.

Table VIII

Infrared Spectra of the Reaction Products of DIAL With Metal Ions in Methanol

Assignment	Pd(DMMP)$_2$Cl$_2$	Cu(DMMP)Cl$_2$
C-H stretching in py-ring	3070(w), 2970(w)	3080(m), 2970(w)
Alkyl C-H stretching	2940(m), 2840(s)	2930(m), 2840(s)
Ring skeletal vibrations	1605(s), 1460(s)	1600(s), 1460(m), 1450(s)
C-C and C-N stretching	1360(vs)	1345(s)
C-O stretching	1190(s), 1110(vs), 1065(vs)	1200(s), 1160(m), 1100(b), 1050(b)
In-plane and out-of-plane -CH deformation	990(s), 900(s), 810(vs), 765(s)	985(b), 900(s), 820(s), 770(s)
M-Cl stretching	335(m)	260(m)

The proton NMR spectrum of Pd(DMMP)$_2$Cl$_2$ in CDCl$_3$ showed 2 singlets at 7.8 δ and 3.6 δ with areas in the ratio of 5:12.

Zinc(II) acetate dihydrate and cobalt(II) acetate tetrahydrate in methanol; manganese(II) chloride in acetone, and tris(acetylacetonate)cobalt(III) in benzene failed to react with DIAL.

2.4.4. Reactions of 2,6-pyridinedicarboxaldehyde-metal complexes with methanol

i) Dichlorobis(2,6-pyridinedicarboxaldehyde)-palladium(II) $Pd(DIAL)_2Cl_2$

A mixture of $Pd(DIAL)_2Cl_2$ (0.158 g, 0.35 mmole) and methanol (30 ml) was refluxed with stirring for 18 hours. The solid obtained was filtered off. It was dissolved in dichloromethane (15 ml) and upon the addition of diethyl ether, a yellow solid crystallized out. The solid was filtered off, washed with ether and dried in vacuo. Yield: 0.080 g (36%). Melting point: 220-222^{o} with decomposition.

ii) Dichloro(2,6-pyridinedicarboxaldehyde)-copper(II) $Cu(DIAL)Cl_2$

A mixture of $Cu(DIAL)Cl_2$ (0.135 g, 0.5 mmole) and methanol (15 ml) was refluxed with stirring for 18 hours with no solid formed. The solution was evaporated to dryness under reduced pressure. The residue was extracted with dichloromethane (15 ml) and upon the addition of diethyl ether a pinkish solid precipitated.

The solid was filtered off, washed with ether and dried in vacuo. Yield: 0.100 g (55%). Melting point: 175-182^{o} with decomposition.

Pd(DMMP)$_2$Cl$_2$ and Cu(DMMP)Cl$_2$ were the products of reactions i) and ii) above, respectively. That was evidenced by their melting points, mixed melting points and infrared spectra as compared with authentic samples prepared by the reaction of DMMP with the respective metal salts.

2.5.1. Reactions of 2,6-bis(dimethoxy-methyl)pyridine (DMMP) with metal ions

i) Cis-dichlorobis(benzonitrile)palladium(II)

The addition of a filtered solution of cis-dichlorobis(benzonitrile)palladium(II) (0.192 g, 0.5 mmole) in methanol (12 ml) to a solution of DMMP (0.227 g, 1 mmole) in methanol (5 ml) produced an immediate yellow precipitate identical to that obtained from reaction 2.4.3.i) as evidenced by its melting point, mixture melting point with the known compound, and comparison of its infrared and nuclear magnetic resonance spectra with those of the known compound. Yield (66%).

ii) Copper(II) chloride dihydrate

A solution of DMMP (0.227 g, 1 mmole) in methanol (5 ml) was added to a solution of copper(II) chloride dihydrate (0.170 g, 1 mmole) in methanol (5 ml) and the mixture was refluxed with stirring for two hours. The solution was evaporated to dryness under reduced pressure. The residue was extracted with dichloromethane (15 ml) and the extract treated with diethyl ether. The pinkish solid which precipitated, was filtered off, washed with ether and dried in vacuo. It was identical to the compound produced from reaction 2.4.3.ii) as evidenced by its melting point, mixed melting point and infrared spectrum in comparison with an authentic sample of the compound. Yield: (60%).

iii) Potassium tetrachloroplatinate(II)

A solution of DMMP (0.218 g, 0.96 mmole) in acetone (4 ml) was added to a filtered solution of potassium tetrachloroplatinate(II) (0.200 g, 0.48 mmole) in water (10 ml). The solution was stirred in a water bath at 40-45^o for two hours. The pale yellow precipitate formed was filtered off, washed with water and dried in vacuo over P_2O_5. Yield: 0.060 g (20%). Melting point: 232-237^o with decomposition.

The complex obtained is formulated as $Pt(DMPAL)_2Cl_2$ (dichlorobis(2-dimethoxy-methyl-6-pyridinecarboxaldehyde)platinum(II). Elemental analysis: calculated for $PtC_{18}H_{22}N_2Cl_2$: %C 34.40; %H 3.53; %N 4.46; %Cl 11.28. Found: %C 34.66; %H 3.61; %N 4.38; %Cl 11.47.

Its major infrared bands with their respective assignments are shown in Table IX.

Table IX

Infrared Spectrum of $Pt(DMPAL)_2Cl_2$

Assignment	
C-H stretching	3070(w), 1300(sh), 2950(w), 2930(w), 2900(sh), 2830(ms)
C=O stretching	1705(vs)
Ring skeletal vibrations	1605(s), 1460(sb)
C-C and C-N stretching	1350(s), 1300(m), 1250(m)
C-O stretching	1190(s), 1162(m), 1115(vs), 1065(vs)
In-plane and out-of-plane C-H deformation	1000(s), 850(s), 805(s)
Pt-Cl stretching	310(m)

2.6.1. Reactions of 2,6-bis(diethoxy-methyl)pyridine (DEMP) With Metal Ions

DEMP was reacted with cis-dichlorobis(benzonitrile)palladium(II) and copper(II) chloride dihydrate in ethanol following procedures 2.5.1.i) and 2.5.1.ii) respectively. The formulas assigned for the complexes obtained were $Pd(DEMP)_2Cl_2$ and $Cu(DEMP)Cl_2$ based on the similarity in spectroscopic properties with the corresponding

DMMP complexes, on their molecular weights, and their elemental analyses listed in Table X.

Table X

Elemental Analyses of DEMP Complexes

Compound		%C	%H	%N	%Cl	% Metal	Molecular Weight gm/mole
$Pd(DEMP)_2Cl_2$	Calc.	48.43	6.77	3.77	9.53		744.1
	Found	48.32	6.73	3.81	9.70		747.3
$Cu(DEMP)Cl_2$	Calc.	43.12	6.03	3.35	16.97	15.20	417.9
	Found	42.67	5.93	3.44	16.77	15.11	416.4

The pale yellow $Pd(DEMP)_2Cl_2$ complex melted at 193-195° with decomposition whereas the pinkish $Cu(DEMP)Cl_2$ melted at 130-133° with decomposition too.

2.6.2. Decomposition of $Pd(DMMP)_2Cl_2$ and $Pd(DEMP)_2Cl_2$ with aqueous potassium cyanide

The following procedure was carried out for the decomposition of the Pd(II) complexes with aqueous cyanide:

A mixture of the Pd(II) complex (1.27 mmole) and 35% potassium cyanide (25 ml) was refluxed for 30 minutes. After being cooled to room temperature, the mixture was extracted with two 15-ml portions of low boiling petroleum ether. The solvent was removed by evaporation and the residue was distilled under reduced pressure to produce the diacetal in 74% yield. DMMP was recovered from $Pd(DMMP)_2Cl_2$ and DEMP from $Pd(DEMP)_2Cl_2$. Both acetals were identified by their b.p.'s, IR's and NMR's in comparison with the authentic compounds.

2.6.3. Reaction of $Pd(DMMP)_2Cl_2$ with 2,6-diaminopyridine

2,6-Diaminopyridine (0.462 g, 4.2 mmole) was added to a stirred solution of $Pd(DMMP)_2Cl_2$ (0.632 g, 1 mmole) in chloroform (25 ml) and the mixture was refluxed for three hours. An orange precipitate of $Pd(DAP)_2Cl_2$ was obtained, collected by suction filtration, washed with chloroform and dried in vacuo. Yield: 0.280 g (70%). $Pd(DAP)_2Cl_2$ was identified by its melting point, mixed melting point, IR and elemental analysis (Tables XI and XIII).

In an attempt to test if the transformation of aldehydes to acetals could be made catalytic, benzaldehyde, 2-pyridinecarboxaldehyde and 2,6-pyridinedicarboxaldehyde were separately mixed with methanol in the presence of $CuCl_2, 2H_2O$ and the mixtures were refluxed for 18 hours. With benzaldehyde and 2-pyridinecarboxaldehyde, no reaction took place. The starting material was recovered unchanged, whereas with 2,6-pyridinedicarboxaldehyde partial conversion to the acetal took place as evidenced by IR and by the amount of the dialdehyde recovered at the end of the experiment. This work should be further investigated.

2.7.1. Reactions of 2,6-diaminopyridine (DAP) with metal ions

i) Copper(II) chloride dihydrate

A solution of DAP (0.218 g, 2 mmole) in methanol (10 ml) was added dropwise to a stirred solution of copper(II) chloride dihydrate (0.171 g, 1 mmole) in methanol (14 ml). A purple-black solid started to form. The mixture was stirred for one hour and the precipitate was filtered off on a glass sintered funnel, washed thoroughly with methanol and dried in vacuo. Yield: 0.160 g (66%).

The product obtained did not melt up to 360°.

ii) Silver acetate

Silver acetate (0.167 g, 1 mmole) was added to a solution of DAP (0.109 g, 1 mmole) in methanol (10 ml) and the mixture was stirred overnight. A pink precipitate was formed, filtered off, washed with methanol and dried in vacuo. Yield: 0.160 g (58%). Melting point 154-155° with decomposition.

iii) Rhodium(III) chloride trihydrate

A solution of DAP (0.218 g, 2 mmole) in ethanol (20 ml) was added dropwise to a stirred solution of rhodium(III) chloride trihydrate (0.260 g, 1 mmole) in ethanol (30 ml). The formation of a dark brown solid was observed. The mixture was stirred for one hour and the precipitate was filtered off on a glass sintered funnel, washed thoroughly with ethanol, then with ether, and dried in vacuo. Yield: 0.280 g (78%).

The compound obtained did not melt up to 360°.

iv) Ruthenium(III) chloride trihydrate

A solution of DAP (0.218 g, 2 mmole) in ethanol (20 ml) was added dropwise to a solution of ruthenium(III) chloride trihydrate (0.261 g, 1 mmole) in ethanol (30 ml). The formation of a black solid was observed. The mixture was stirred for one hour and the precipitate was filtered off on a glass sintered funnel, washed thoroughly with ethanol, then with ether, and dried in vacuo. Yield: 0.20 g (59%).

The compound obtained did not melt up to 360°.

v) Cis-dichlorobis(benzonitrile)palladium(II)

A solution of DAP (0.218 g, 2 mmole) in chloroform (15 ml) was added to a filtered solution of cis-dichlorobis(benzonitrile)palladium(II) (0.384 g, 1 mmole) in chloroform (50 ml). An orange solid was formed immediately. The mixture was stirred for one hour and the precipitate was filtered off, washed thoroughly with chloroform and dried in vacuo. Yield: 0.244 g (62%). Melting point: 272-275° with decomposition.

vi) Cis-dichlorobis(benzonitrile)palladium(II) in 1:1 molar ratio

A solution of DAP (0.109 g, 1 mmole) in methanol (10 ml) was added to a filtered solution of cis-dichlorobis(benzonitrile)palladium(II) (0.384 g, 1 mmole) in methanol (15 ml). The mixture was stirred for one hour. An orange brown precipitate was formed, filtered off, washed thoroughly with methanol, and dried in vacuo. Yield: 0.185 g (61%). Melting point 262-265° with decomposition.

vii) Potassium tetrachloroplatinate(II) in presence of HCl

A solution of DAP (0.218 g, 2 mmole) in water (12 ml) acidified with two drops of concentrated hydrochloric acid, was added dropwise to a filtered solution of potassium tetrachloroplatinate(II) (0.420 g, 1 mmole) in water (12 ml). A pink precipitate started to form. After stirring for additional 15 minutes, the solid was filtered off, washed with ethanol, and dried in vacuo over P_2O_5. Yield: 0.150 g (27%). The compound melted at 231-234° with decomposition.

viii) Potassium tetrachloroplatinate(II)

A solution of DAP (0.109 g, 1 mmole) in water (10 ml) was added to a filtered solution of potassium tetrachloroplatinate(II) (0.210 g, 0.5 mmole) in water (5 ml) and the mixture was stirred overnight. A green precipitate was formed, filtered off, and dried in vacuo over P_2O_5. Yield: 0.150 g.

The compound obtained started darkening around 200°. It was black at 310° and did not melt up to 360°.

The elemental analyses for the complexes of DAP are shown in Table XI, their solubilities in Table XII and their major infrared bands along with their respective assignments in Table XIII. Table XIV lists the observed ultraviolet bands for DAP and its complexes.

Table XI

Results of the Elemental Analyses of the Complexes of DAP

Compound		%C	%H	%N	%Cl	% Metal
$Cu(DAP)Cl_2$	Calc.	24.65	2.89	17.25	29.11	26.10
	Found	24.70	2.45	16.90	28.83	25.73
$Ag(DAP)(CH_3COO)$	Calc.	30.45	3.65	15.22		39.08
	Found	30.45	3.68	15.07		39.85
$Rh(DAP)Cl_3.2H_2O$	Calc.	16.93	3.10	11.85	30.05	
	Found	16.31	2.70	12.33	29.77	
$Ru(DAP)Cl_3.\frac{1}{2}C_2H_5OH$	Calc.	21.22	2.97	12.37	31.32	
	Found	21.20	2.80	13.30	32.11	
		21.06	2.92	13.38		
$Pd(DAP)Cl_2.H_2O$	Calc.	19.85	3.01	13.90	23.44	
	Found	20.23	3.02	13.30	23.15	
$Pd(DAP)_2Cl_2$	Calc.	30.36	3.57	21.25	17.93	
	Found	30.52	3.71	20.89	18.09	
$Pt(DAP)_2Cl_2.2HCl$	Calc.	21.62	2.88	15.14	25.58	
	Found	21.76	3.02	15.10	24.79	

Table XII

Solubility of the Complexes of DAP

Compound	H_2O	MeOH	EtOH	Me_2CO	Et_2O	C_6H_6	Diox.	Pet. Eth.	CH_2Cl_2	$CHCl_3$	CCl_4	DMF	DMSO
$Cu(DAP)Cl_2$	−	−	−	−	−	−	−	−	−	−	−	−	−
$Ag(DAP)CH_3COO$	−	−	−	−	−	−	−	−	−	−	−	−	±
$Rh(DAP)Cl_3 \cdot 2H_2O$	−	−	−	−	−	−	−	−	−	−	−	±	+
$Ru(DAP)Cl_3 \cdot \frac{1}{2}C_2H_5OH$	−	−	−	−	−	−	−	−	−	−	−	−	−
$Pd(DAP)Cl_2 \cdot H_2O$	±	±	−	−	−	−	−	−	−	−	−	±	+
$Pd(DAP)_2Cl_2$	−	−	−	±	−	−	−	−	−	−	−	+	+
$Pt(DAP)_2Cl_2 \cdot 2HCl$	±	−	−	±	−	−	−	−	−	−	−	±	+

Table XIII

Infrared Spectra of DAP and its Complexes

Assignment	DAP	Cu(DAP)Cl_2	Ag(DAP)CH_3COO
O-H stretching			
NH_2 stretching	3440(s), 3370(w) 3330(m), 3190(m)	3410(w), 3300(w)	3380(w), 3290(w)
Aromatic C-H st.	3060(sh)	3080(sh)	3100(sh)
O-H deformation			
Ring skeletal vibrations	1580(sb), 1460(sb) 1445(sb)	1600(sb), 1505(w) 1430(mb)	1560(vsb), 1450(s) 1400(m-s)
In-plane and out-of-plane C-H deformation	780(s), 720(s) 1110(s), 1050(s)	1155(m), 775(s)	1175(mb), 775(s)
Alkyl C-H st.			2940(sh), 2900(sh)
C=O of CH_3COO			1650(vs), 1630(vw)
C-O stretching			1150(vw), 1100(w)

Table XIII continued

Assignment	$Rh(DAP)Cl_3.2H_2O$	$Ru(DAP)Cl_3.\frac{1}{2}C_2H_5OH$	$Pd(DAP)Cl_2.H_2O$
O-H stretching	3560 (b)	3410 (shb)	3600 (b)
NH_2 stretching	3430 (w), 3320 (w) 3180 (w)	3300 (w), 3180 (w)	3430 (m), 3310 (m) 3125 (m), 3160 (m)
Aromatic C-H st.	3080 (sh)	3080 (sh)	3080 (w)
Alkyl C-H st		2890 (sh), 2870 (sh)	
O-H deformation	1640 (s)	1620 (sb)	1640 (s)
Ring skeletal vibrations	1570 (m), 1490 (s) 1450 (s)	1560 (w), 1480 (m)	1600 (m), 1560 (s) 1490 (s), 1450 (s)
In-plane and out-of-plane C-H def.	1120 (b), 790 (s)	1060 (sh), 775 (mvb)	1120 (m), 1030 (m) 790 (s), 725 (s)
C-O stretching		1160 (w)	
M-Cl			335 (m), 330 (w)

Assignment	$Pd(DAP)_2Cl_2$	$Pt(DAP)_2Cl_2.2HCl$
O-H stretching		
NH_2 stretching	3415 (s), 3315 (s)	3395 (s), 3310 (s), 3210 (s)
Aromatic C-H st.	3080 (sh), 3020 (sh)	3080 (sh), 2990 (w)
Ring skeletal vibrations	1605 (sb), 1580 (w) 1470 (s), 1370 (w)	1630 (s), 1480 (w), 1390 (sh)
In-plane and out-of-plane C-H def.	1120 (s), 785 (s)	1170 (s), 1115 (w), 775 (s), 700 (s)
M-Cl stretching	335 (m)	310 (m)

Table XIV

Ultraviolet Spectra of DAP and its Complexes in DMSO

Compound	mμ	$\epsilon \times 10^4$
DAP	332	1.72
$Ag(DAP)(CH_3COO)$	328	1.24
$Rh(DAP)Cl_3.2H_2O$	275(b)	0.92
$Pd(DAP)_2Cl_2$	330	3.03
$Pt(DAP)_2Cl_2.2HCl$	330	2.51

2.7.2. Decomposition of $Pd(DAP)_2Cl_2$ with aqueous potassium cyanide

$Pd(DAP)_2Cl_2$ (0.200 g) was added to aqueous potassium cyanide (35%, 15 ml) and the mixture was refluxed for 30 minutes. After cooling, the mixture was extracted with two 10-ml portions of chloroform. The extract was dried over anhydrous magnesium sulfate and filtered. The solvent was evaporated to leave 2,6-diaminopyridine as the residue in 72% yield. DAP was identified by its melting point, mixed melting point and its IR spectrum in comparison with the authentic compound.

2.7.3. Decomposition of Ag(DAP)CH_3COO with aqueous ammonia

Ag(DAP)(CH_3COO) (0.200 g) was added to concentrated ammonium hydroxide (15 ml) and the mixture was stirred at room temperature for three hours. After extraction with two 10-ml portions of chloroform and drying the extract over anhydrous magnesium sulfate, the solution was evaporated to leave a residue of 2,6-diaminopyridine in 45% yield. DAP was identified in comparison with the authentic compound.

Potassium tetrachloroplatinate(II) was reacted with DAP in a neutral aqueous medium. No molecular formula could be assigned for the product obtained based on its elemental analysis shown below:

%C 21.63; %H 2.67; %N 14.77; %Cl 12.85.

The following metal salts failed to react with DAP: nickel(II) perchlorate hexahydrate, iron(III) chloride hexahydrate, uranyl acetate dihydrate, and zinc(II) chloride.

2.8 Reactions of 2,2'-dithiodianiline (DTDA) with metal ions

The reactions of DTDA with different metal salts were carried out by the following general procedure: A solution of DTDA (1 mmole) in hot ethanol (15 ml) was added to a solution of the metal salt (1 mmole) in hot ethanol (15 ml). Immediate crystallization occurred.

The solids obtained were filtered off on a glass sintered funnel, washed with hot ethanol, then with ether and dried in vacuo over P_2O_5. In the cases of nickel(II) perchlorate hexahydrate and nickel(II) nitrate hexahydrate the reaction mixtures were refluxed for one hour and for forty eight hours respectively.

The colours, melting points and the yields of the reaction products are listed in Table XV.

Table XV[c]

Reactions of DTDA With Metal Ions

Metal Salt	Colour of Product	M.P. °C	% Yield
$Ni(ClO_4)_2.6H_2O$	Green	360 d	65
$Ni(NO_3)_2.6H_2O$	Green	360 d	63
$Cu(ClO_4)_2.6H_2O$	Black	>360	18
$Cu(NO_3)_2.3H_2O$	Black	>360	21
$CuCl_2.2H_2O$	Black	>360	17
$Pd(C_6H_5CN)_2Cl_2$	Greenish-Brown	110 sd	80
$RuCl_3.3H_2O$	Black	150 sd	--
$RhCl_3.3H_2O$	Grayish-Green	>360	--
$AgClO_4$	Violet	180-210 d	--

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[c] Symbols used throughout this section: d = decomposition; sd = started darkening but did not melt up to 360°; -- = no % yield reported due to the fact that no molecular formula could be assigned to the product based on its elemental analysis.

The elemental analyses of the products obtained from the reactions of 2,2'-dithiodianiline DTDA with the compounds: nickel(II) perchlorate hexahydrate, nickel(II) nitrate hexahydrate, copper(II) perchlorate hexahydrate, copper(II) chloride dihydrate, copper(II) nitrate trihydrate and cis-dichlorobis(benzonitrile)-palladium(II) are shown in Table XVI, their solubilities in Table XVII and their major infrared bands along with their respective assignments in Table XVIII. Table XIX shows the ultraviolet bands of DTDA and its soluble complexes.

Table XVI

Results of the Elemental Analyses of the Reaction Products of DTDA

Compound		%C	%H	%N	%Cl	%S	% Metal
$Ni(ATP)_2^*$	Calc.	46.93	3.94	9.12	-----	20.88	19.12
	Found	47.15	3.86	9.06	-----	20.29	19.00
		47.68	4.09	9.03	-----	20.32	19.54
$Cu(DTDA)_3(ClO_4)_2 \cdot H_2O$	Calc.	35.05	3.10	6.81	5.75	15.60	5.15
	Found	34.04	2.79	6.63	5.99	15.11	5.13
$Cu_2(DTDA)(ATP)_2Cl_2$	Calc.	37.89	3.18	7.36	12.43	16.86	22.28
	Found	37.76	2.64	6.94	12.02	16.12	21.75
$Cu_3(DTDA)(ATP)_2NO_3$	Calc.	34.58	2.90	8.96	-----	15.38	30.50
	Found	35.26	2.82	8.71	-----	15.35	29.22
$Pd(ATP)Cl$	Calc.	27.08	2.27	5.27	13.33	12.05	
	Found	26.64	2.48	5.29	13.19	12.82	

---

[*] $Ni(ATP)_2$ was obtained from the reactions of DTDA with $Ni(ClO_4)_2 \cdot 6H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$.

Table XVII

Solubilities of Reaction Products of DTDA With Metal Ions

Compound	H_2O	MeOH	EtOH	Me_2CO	Et_2O	Diox.	C_6H_6	Pet. Eth.	CH_2Cl_2	$CHCl_3$	CCl_4	DMF	DMSO
$Ni(ATP)_2$	-	-	-	-	-	-	-	-	-	-	-	-	±
$Cu(DTDA)_3.(ClO_4)_2.H_2O$	-	-	-	-	-	-	-	-	-	-	-	-	-
$Cu_2(DTDA).(ATP)_2Cl_2$	-	-	-	-	-	-	-	-	-	-	-	-	+
$Cu_3(DTDA).(ATP)_2NO_3$	-	-	-	-	-	-	-	-	-	-	-	-	-
Pd(ATP)Cl	-	-	-	-	-	-	-	-	-	-	-	-	-

Table XVIII

Infrared Spectra of Reaction Products of DTDA With Metal Ions

Assignment	DTDA	$Ni(ATP)_2$	$Cu(DTDA)_3(ClO_4)_2.H_2O$
O-H stretching	-----	-----	3500 (mb)
N-H stretching	3365 (m), 3280 (m)	3390 (wb), 3190 (w)	3200 (mb)
Aromatic C-H st.	3050 (vs), 3010 (sh) 3000 (sh)	3040 (wb), 3000 (sh)	3040 (sh), 3030 (sh) 3000 (sh)
Ring skeletal vibrations	1600 (sb), 1465 (s) 1440 (s)	1580 (s), 1455 (s)	1580 (sb), 1465 (s)
C-N stretching	1290 (s), 1240 (m-s)	1290 (m), 1240 (w)	1290 (mb), 1240 (sh)
In-plane and out-of-plane C-H def.	745 (s)	745 (vs)	745 (s)
In-plane and out-of-plane O-H def.	-----	-----	1650 (w)
ClO_4^- absorption	-----	-----	1080 (vsb)

Table XVIII continued

Assignment	$Cu_2(DTDA)(ATP)_2Cl_2$	$Cu_3(DTDA)(ATP)_2NO_3$	Pd(ATP)Cl
O-H stretching	-----	-----	-----
N-H stretching	3100(mb)	3100(mb)	3190(sh), 3100(mb)
Aromatic C-H st.	3000(sh)	3000(sh)	3000(sh)
Ring skeletal vibrations	1580(sb), 1465(sb)	1590(sb), 1465(s)	1580(sb), 1460(s)
C-N stretching	1290(m), 1240(sh)	1370(vs), 1300(sh)	1275(mb), 1240(sh)
In-plane and out-of-plane C-H deformation	745(s)	745(s)	745(s)
M-Cl stretching	260(m)	-----	265(m)
NO_3 absorption	-----	1380(s)	-----

Silver perchlorate, rhodium(III) chloride and ruthenium(III) chloride trihydrate were reacted with DTDA. No molecular formulas could be assigned for the products on the basis of their found analyses which are listed below:

Metal Salt	%C	%H	%N	%S	%Cl
$Ag(ClO_4)$	27.30	2.27	5.23	11.97	4.80
$RhCl_3.3H_2O$	24.37	3.00	5.75	10.14	25.34
$RuCl_3.3H_2O$	27.30	2.95	5.29	11.69	22.74

Table XIX

Ultraviolet Spectra of DTDA and its Soluble Complexes in DMSO

Compound	mμ	$\epsilon \times 10^4$
DTDA	244(b), 340	0.60, 0.47
Pd(ATP)Cl	268	2.04
$Cu_2(DTDA)(ATP)_2Cl_2$	272	1.52

Cobalt(II) perchlorate hexahydrate, mercury(II) bromide, zinc(II) chloride, zinc(II) nitrate hexahydrate, iron(III) chloride hexahydrate and iron(II) perchlorate hexahydrate failed to react with DTDA.

2.9 Reactions of Schiff bases derived from 2,6-pyridinedicarboxaldehyde with metal ions

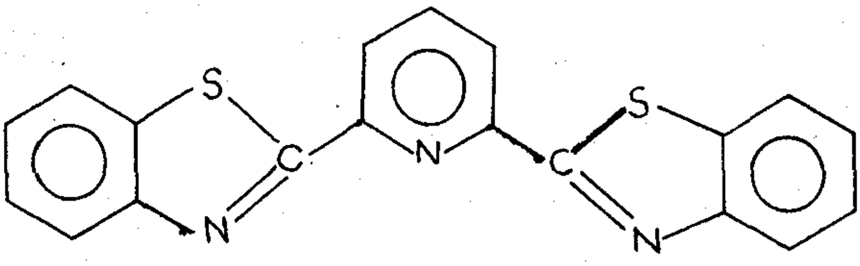
2.9.1. Preparation and reactions of 2,6-(dibenzothiazol-2-yl)pyridine (DBTP)

(a) Preparation of 2,6-(dibenzothiazol-2-yl)pyridine (DBTP)[57]

Iodine (171 g, 0.65 mole) was added in small portions and with stirring to 2,6-lutidine (36 g, 0.37 mole) contained in a 400-ml beaker. The reaction mixture became quite warm. The iodine-lutidine complex, which solidified after the mixture had been cooled and the container scratched with a glass rod, was then added slowly, with stirring, to dimethylsulfoxide (300 ml) at 130°. The mixture was stirred and heated at 150° for 15 minutes, then cooled to 20°. 2-Aminothiophenol (25 g, 0.2 mole) was then added to the mixture and a vigorous reaction ensued. The mixture was cooled and the crystalline product was filtered off, washed with ethanol, then with acetone, and recrystallized from chloroform to give pale yellow crystals melting at 274-276° (Lit. 273-275°)[57]. The yield was 3.0 g (9%).

2,6-(Dibenzothiazol-2-yl)pyridine was also prepared by the following method:

To a solution of 2,6-pyridinedicarboxaldehyde (1 g, 7.4 mmole) in ethanol (12 ml), 2-aminothiophenol (4.35 g, 35 mmole) was added. The mixture was refluxed for 2½ hours then left to stand overnight at room temperature. A pale yellow precipitate was formed. It was recrystallized from chloroform. Yield: 1.6 g, (49%). Melting point: 275-277°.



DBTP

(b) Reactions of 2,6-(dibenzothiazol-2-yl) pyridine (DBTP) with metal ions

Except with potassium tetrachloroplatinate(II) and ruthenium(III) chloride trihydrate the reactions of DBTP with different metal salts were carried out by the following general procedure:

A solution of DBTP (0.230 g, 0.67 mmole) in hot chloroform (40 ml) was added to a stirred solution of the metal salt (0.8 mmole) in hot ethanol (10-15 ml). The complex which crystallized immediately, was filtered off, washed with hot chloroform, then with hot ethanol, followed by ether, and dried in vacuo over P_2O_5.

The reaction of DBTP with potassium tetrachloroplatinate(II) was carried out by the addition of a solution of DBTP (0.230 g, 0.67 mmole) in hot dioxane (60 ml) to a filtered solution of the Pt(II) salt (0.336 g, 0.8 mmole) in water (30 ml) and the mixture was heated with stirring on a steam bath for three hours. The brown solid obtained, was filtered off, washed with water, then with hot dioxane, followed by ether, and dried in vacuo over P_2O_5.

In the case of ruthenium(III) chloride trihydrate, a solution of DBTP (0.230 g, 0.67 mmole) in hot dioxane (60 ml) was added to a solution of the metal salt (0.210 g, 0.8 mmole) in hot ethanol (20 ml) and the reaction mixture was refluxed with stirring for two hours.

The brownish-black precipitate formed, was filtered off, washed with hot dioxane, then hot ethanol, followed by ether and dried in vacuo over P_2O_5.

The elemental analyses for the complexes of DBTP are shown in table XXI, their solubilities in Table XXII and their major infrared bands along with their respective assignments in Table XXIII. Table XXIV lists the observed ultraviolet bands of DBTP and its soluble complexes.

Table XX

Reactions of DBTP With Metal Ions

Metal Salt	Colour of Product	Melting Point °C	% Yield
$CuCl_2.2H_2O$	Yellow	245-248 d	71
$CuBr_2$	Yellow	>360	63
$FeCl_3.6H_2O$	Orange	283-285 d	62
$Ni(ClO_4)_2.6H_2O$	Pale-Yellow	253-257 d	92
$Pd(C_6H_5CN)_2Cl_2$	Brown	>360	78
$ZnCl_2$	Pale-Yellow	>360	81
K_2PtCl_4	Brown	>360	40
$RuCl_3.3H_2O$	Brownish-Black	>360	70
$HgBr_2$	Pale-Yellow	322-324 d	74
$HgCl_2$	Pale-Yellow	326-331 d	69
$CoI_2.2H_2O$	Brown	>360	72
$RhCl_3.3H_2O$	Yellow	>360	77
$AgClO_4$	Pale-Yellow	311-313 d	73

Table XXI

Results of the Elemental Analyses of the Complexes of DBTP

Compound		%C	%H	%N	%S	%X	% Metal
Cu(DBTP)$Cl_2.H_2O$	Calc.	45.80	2.63	8.44	12.88	14.24	12.76
	Found	45.6	2.5	8.0	13.0	13.6	12.7
Cu(DBTP)Br_2	Calc.	40.12	1.95	7.39	11.27	28.15	11.17
	Found	39.8	1.9	7.4	11.8	27.8	10.8
Fe(DBTP)$_2Cl_3.H_2O$	Calc.	52.40	2.81	9.60	14.70	12.21	6.41
	Found	52.5	2.6	9.5	13.7	12.6	6.6
Ni(DBTP)$_2(ClO_4)_2.2H_2O$	Calc.	46.35	2.66	8.54	13.00	7.20	5.96
	Found	45.8	2.5	8.0	12.9	6.9	6.4
Zn(DBTP)Cl_2	Calc.	47.37	2.30	8.72	13.31	14.72	13.57
	Found	47.0	2.2	8.4	13.3	15.0	13.2
Hg(DBTP)Cl_2	Calc.	36.99	1.80	6.81	10.39	11.49	
	Found	37.07	1.80	6.94	9.96	11.49	
Hg(DBTP)Br_2	Calc.	32.33	1.57	5.95	9.08	22.64	
	Found	32.32	1.56	6.00	8.88	22.01	
Co(DBTP)I_2	Calc.	34.67	1.68	6.39	9.74	38.56	
	Found	34.72	1.73	6.37	9.74	37.96	

Table XXI continued

Compound		%C	%H	%N	%S	%X	% Metal
$Ag(DBTP)ClO_4$	Calc.	41.28	2.00	7.60	11.60	6.41	19.52
	Found	41.38	2.07	7.60	11.33	7.32	19.89
$Pd_2(DBTP)Cl_4$	Calc.	32.60	1.58	6.00	9.16	20.26	
	Found	33.2	1.6	6.0	9.4	19.98	
$Pt_4(DBTP)_3Cl_8.2H_2O$	Calc.	31.5	1.90	5.80	8.86	13.06	
	Found	30.4	1.6	5.7	9.0	13.4	
$Ru(DBTP)Cl_3.C_2H_5OH$	Calc.	42.11	2.86	7.02	10.55	17.76	
	Found	42.4	2.8	6.8	11.6	17.9	
$Rh(DBTP)Cl_3.2H_2O$	Calc.	38.63	2.56	7.11	10.85	18.01	
	Found	37.76	2.28	7.20	10.26	17.47	

Table XXII

Solubilities of Complexes of DBTP

Compound	H_2O	MeOH	EtOH	Acetone	Ether	Diox.	Benzene	Pet. Eth.	CH_2Cl_2	$CHCl_3$	CCl_4	DMF	DMSO
$Cu(DBTP)Cl_2.H_2O$	-	-	-	-	-	-	-	-	-	-	-	+	-
$Cu(DBTP)Br_2$	-	-	-	-	-	-	-	-	-	-	-	±	-
$Fe(DBTP)_2Cl_3.H_2O$	-	-	-	-	-	-	-	-	-	-	-	+	±
$Ni(DBTP)_2(ClO_4)_2.2H_2O$	-	-	-	-	-	-	-	-	-	-	-	+	+
$Zn(DBTP)Cl_2$	-	-	-	-	-	-	-	-	-	-	-	±	±
$Hg(DBTP)Cl_2$	-	-	-	-	-	-	-	-	-	-	-	-	-
$Hg(DBTP)Br_2$	-	-	-	-	-	-	-	-	-	-	-	-	-
$Co(DBTP)I_2$	-	-	-	-	-	-	-	-	-	-	-	+	+
$Ag(DBTP)ClO_4$	-	-	-	-	-	-	-	-	-	-	-	-	-
$Pd_2(DBTP)Cl_4$	-	-	-	-	-	-	-	-	-	-	-	-	-
$Pt_4(DBTP)_3Cl_4.2H_2O$	-	-	-	-	-	-	-	-	-	-	-	-	±
$Ru(DBTP)Cl_3.C_2H_5OH$	-	-	-	±	-	-	-	-	±	±	±	+	+
$Rh(DBTP)Cl_3.2H_2O$	-	-	-	-	-	-	-	-	-	-	-	±	±

Table XXIII

Infrared Spectra of DBTP and its Complexes

Assignment	DBTP	$Cu(DBTP)Cl_2.H_2O$	$Cu(DBTP)Br_2$
O-H stretching	----	3440 (b)	----
C-H stretching	3035 (w)	3060 (w), 3030 (sh) 3000 (sh)	3050 (m), 3020 (sh)
O-H deformation		1650 (wb)	
C=N and C=C st.	1565 (s), 1560 (s)	1595 (m), 1580 (m)	1595 (s), 1580 (m)
Aromatic skeletal vibrations	1445 (m), 1430 (mb)	1490 (vs), 1455 (m)	1490 (vs), 1455 (m)
C-N stretching	1320 (s), 1275 (m) 1150 (m-s)	1320 (s), 1265 (m) 1245 (s), 1180 (vs)	1315 (s), 1260 (s) 1175 (vs)
C-C stretching	1080 (m), 1010 (w)	1080 (m), 1015 (m)	1080 (s), 1020 (m)
In-plane and out-of-plane deform.	975 (s), 890 (m)	900 (s), 765 (vs)	895 (s), 770 (vs)
M-X stretching		260 (m), 255 (w)	260 (m), 255 (w)

Table XXIII continued

Assignment	$Fe(DBTP)_2Cl_3.H_2O$	$Ni(DBTP)_2(ClO_4)_2.2H_2O$	$Zn(DBTP)Cl_2$
O-H stretching	3400(b)	3400(b)	----
C-H stretching	3050(w), 3020(sh)	3080(mb), 3000(sh)	3050(m), 3020(sh)
O-H deformation	1640(w)	1650(w)	----
C=C and C=N st.	1595(m), 1580(m) 1560(m)	1605(m), 1585(w) 1555(m)	1595(s), 1580(m) 1560(m)
Aromatic skeletal vibrations	1490(s), 1445(m)	1500(vs), 1455(m)	1495(vs), 1455(m) 1425(m)
C-N stretching	1325(s), 1270(m) 1180(s), 1255(m)	1320(s), 1280(m) 1260(m), 1250(m) 1200(s)	1315(s), 1270(m) 1240(s), 1175(s)
C-C stretching	1090(w), 1015(m)	1145(m), 1020(m)	1130(s), 1015(m)
In-plane and out-of-plane deform.	890(m-s), 755(vs) 715(s)	895(s), 765(vs) 740(m)	885(s), 770(vs) 750(s), 720(s)
ClO_4^- absorption		1090(vsb)	

Table XXIII continued

Assignment	$Hg(DBTP)Cl_2$*	$Co(DBTP)I_2$	$Ag(DBTP)ClO_4$
C-H stretching	3050 (m), 3020 (sh)	3050 (m), 3020 (sh)	3040 (sh), 3020 (sh)
C=C and C=N st.	1560 (mb), 1540 (w)	1580 (mb), 1540 (w)	1590 (w), 1580 (mb)
Aromatic skeletal vibrations	1480 (sb), 1420 (w)	1480 (s), 1410 (mb)	1485 (sb), 1420 (s)
C-N stretching	1300 (sb), 1260 (m) 1225 (s)	1305 (s), 1235 (s)	1315 (vs), 1290 (s) 1260 (s), 1220 (s) 1170 (s)
C-C stretching	1170 (s), 1125 (s) 1000 (mb)	1165 (s), 1130 (s)	1150 (m), 1110 (w) 1010 (w)
In-plane and out-of-plane deform.	870 (sb), 790 (m) 760 (s)	785 (m), 760 (s) 720 (m)	885 (s), 765 (vs) 720 (s)
ClO_4^- absorption			1080 (vsb)

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* The IR spectrum of $Hg(DBTP)Br_2$ is identical to that of $Hg(DBTP)Cl_2$.

Table XXIII continued

Assignment	$Pd_2(DBTP)Cl_4$	$Pt_4(DBTP)_3Cl_4.2H_2O$	$Ru(DBTP)Cl_3.C_2H_5OH$
O-H stretching	----	3440(b)	3440(mb)
C-H stretching	1595(m), 1545(w)	3090(w), 3060(w) 3010(w)	3070(m), 3000(w) 2960(w)
C=N and C=C st.	1595(m), 1545(w)	1600(m), 1555(m)	1595(m), 1560(m)
Aromatic skeletal vibrations	1490(s), 1445(w) 1435(w)	1490(s), 1450(m)	1515(s), 1440(mb)
C-N stretching	1320(s), 1265(s) 1235(s), 1190(s)	1325(s), 1270(s) 1240(s), 1195(s)	1320(s), 1270(m) 1250(m), 1185(s)
C-C stretching	1125(m), 1090(m)	1100(w), 1015(w)	1075(m), 1010(m)
In-plane and out-of-plane deform.	895(m-s), 755(s) 715(s)	905(m-s), 755(vs) 720(s)	890(m), 765(vs) 725(s)
Alkyl C-H st.			2860(w)
C-O stretching			1160(m-s), 1115(s)
O-H deformation		1640(b)	1125(m)
M-Cl stretching	335(m), 260(m)	310(m)	330(m)

Table XXIII continued

Assignment	$Rh(DBTP)Cl_3.2H_2O$
O-H stretching	3400(b)
C-H stretching	3050(mb), 3000(sh)
C=C and C=N st.	1580(mb), 1540(sh)
Aromatic skeletal vibrations	1485(s)
C-N stretching	1315(s), 1265(s), 1235(m)
C-C stretching	1180(s), 1150(w), 1120(w)
In-plane and out-of-plane deformation	755(s)
M-Cl stretching	325(m)

Table XXIV

Ultraviolet Spectra of DBTP and its Soluble Complexes in DMF

Compound	mμ	$\epsilon \times 10^5$
DBTP	300(b)	0.74
$Cu(DBTP)Cl_2.H_2O$	300(vb)	0.20
$Ni(DBTP)_2(ClO_4)_2.2H_2O$	300(vb)	4.05
$Co(DBTP)I_2$	300(vb)	2.10
$Ru(DBTP)Cl_3.C_2H_5OH$	264	3.00
$Rh(DBTP)Cl_3.2H_2O$	264	3.00

(c) Miscellaneous

Procedure (b) was followed in an attempt to investigate the reactions of DBTP with the below-mentioned metal salts. In all cases no complex formation was observed and unreacted DBTP was recovered.

A chloroform solution of DBTP was used with an ethanolic solution of each of the following metal salts: uranyl acetate dihydrate, chromium(III) nitrate nonahydrate, iridium(III) trichloride trihydrate. On the other hand, a dioxane solution of DBTP was used with a methanolic solution of the following metal salts: uranyl acetate dihydrate, thorium(IV) nitrate tetrahydrate, tin(II) chloride dihydrate, yttrium(III) nitrate tetrahydrate and chromium(III) nitrate nonahydrate. With molybdenum hexacarbonyl and tungsten hexacarbonyl a chloroform solution of DBTP was added to a benzene solution of the carbonyl.

2.9.2. The System: 2,6-Pyridinedicarboxaldehyde and 2-aminothiophenol in a basic medium

(A) The reaction of DIAL with ATPH in a basic medium

An aqueous solution of 4 N sodium hydroxide (2.4 ml) was added to a solution of DIAL (0.240 g, 1.76 mmole) in hot ethanol (28 ml). ATPH (1.10 g, 8.8 mmole) was added and the mixture was stirred for seven minutes.

An orange coloration was observed. Diethyl ether (100 ml) was added and a pale yellow solid precipitated. The precipitate was filtered off, washed with ether and dried in vacuo. It was dissolved in ethanol, and upon the addition of ether a white solid precipitated, which turned pale yellow on the filter paper. Yield: 1.50 g. The compound obtained started darkening at 240° and melted at 353-357° with decomposition. No molecular formula could be assigned for the product based on its analysis: %C 37.27; %H 4.46; %N 6.56; %S 14.42.

(B) <u>The reaction of product from (A) with HCl</u>

To a solution of the product from (A) (0.81 g) in ethanol (60 ml), concentrated HCl (3 ml) was added. A white precipitate was formed and removed by filtration. The filtrate was concentrated at reduced pressure, and upon the addition of ether, 2-aminothiophenol hydrochloride ATPH·HCl precipitated. It was filtered off, washed with ether and dried in vacuo. Yield: 0.40 g. Melting point: 215-217° with decomposition. (Lit. 217° dec)[74]. Elemental analysis: calculated for C_6H_8NClS: %C 44.58; %H 4.99; %N 8.67; %Cl 21.94; %S 19.79; Found: %C 44.27; %H 5.19; %N 8.59; %Cl 21.75; %S 18.11.

(C) The reaction of ATPH.HCl with cis-dichlorobis(benzonitrile)palladium(II)

Cis-dichlorobis(benzonitrile)palladium(II) (0.202 g, 0.52 mole) in ethanol (30 ml) was added to a solution of ATPH.HCl (0.360 g, 1.04 mmole) in ethanol (30 ml). The mixture was heated with stirring for five minutes. A brown solid of bis(2-aminothiophenolato)-palladium(II) dihydrochloride $Pd(ATP)_2.2HCl$ crystallized out. It was filtered off, washed thoroughly with ethanol, and dried in vacuo. Yield: 0.170 g (77%).

$Pd(ATP)_2.2HCl$ started darkening at 330° and did not melt up to 360°. It is insoluble in common organic solvents. Its elemental analysis: Calculated for $PdC_{12}H_{14}N_2Cl_2S_2$: %C 33.70; %H 3.30; %N 6.55; %Cl 16.58; %S 14.99; Found: %C 33.57; %H 3.12; %N 6.52; %Cl 16.32; %S 15.08. Its major infrared bands along with their respective assignments are listed in Table XXV.

Table XXV

Infrared Spectrum of $Pd(ATP)_2.2HCl$

Assignment	
N-H stretching	3350(wb)
C-H stretching	3000(wb)
C=C and C=N stretching	1590(s), 1545(s)
Aromatic skeletal vibrations	1465(s)
C-C and C-N stretching	1290(w), 1260(w), 1200(w)
In-plane and out-of-plane C-H deformation	750(vs)

(D) Reactions of a mixture of DIAL and ATPH with metal ions in a basic medium

The reactions of a mixture of DIAL and ATPH with different metal salts in a basic medium were carried out by the following general procedure:

An aqueous solution of 4 N sodium hydroxide (2.4 ml) was added to a solution of DIAL (0.240 g, 1.76 mmole) in hot ethanol (25-30 ml). To the mixture, ATPH (1.10 g, 8.8 mmole) was added, followed directly by the addition of a solution of the metal salt (0.88 mmole) in ethanol (10 ml). The precipitate formed was filtered off on a glass sintered funnel, washed with ethanol, then with ether and dried in vacuo.

In the case of potassium tetrachloroplatinate(II), the platinum salt was dissolved in a 1:1 ethanol-water mixture (25 ml) and the reaction mixture was stirred for thirty minutes at room temperature.

The colours, melting points and yields of the reaction products of the mixture of DIAL and ATPH in a basic medium with the different metal salts are shown in Table XXVI.

Table XXVI

Reactions of a Mixture of DIAL and ATPH With Metal Ions in a Basic Medium

Metal Salt	Colour of Product	Melting Point °C	% Yield
$CuCl_2.2H_2O$	Reddish-Brown	260-265 d	80
$Pd(C_6H_5CN)_2Cl_2$	Gray	330-333 d	70
$ZnCl_2$	Pale Yellow	280-284 d	26
$RuCl_3.3H_2O$	Black	$>$360	63
K_2PtCl_4	Green	105 sd	--
$FeCl_3.6H_2O$	Brown	$>$360	--
$Ni(ClO_4)_2.6H_2O$	Black	332-338 d	--
$UO_2(CH_3COO)_2.2H_2O$	Brown	230 sd	--

The reactions of a mixture of DIAL and ATPH in a basic medium with metal ions gave identifiable products with copper(II) chloride dihydrate, cis-dichlorobis(benzonitrile)palladium(II), zinc(II) chloride and ruthenium(III) chloride trihydrate. The elemental analyses for such products are listed in Table XXVII, their solubilities in Table XXIII and their major infrared bands along with their respective assignments in Table XXIX.

Iron(III) chloride hexahydrate, nickel(II) perchlorate hexahydrate, uranyl acetate dihydrate and potassium tetrachloroplatinate(II) were reacted with a mixture of DIAL and ATPH in a basic medium but no molecular formulas could be assigned for the reaction products on the basis of their found analyses which are listed below:

Metal Salt	%C	%H	%N	%S
$FeCl_3.6H_2O$	16.46	2.12	2.54	0.2
$Ni(ClO_4)_2.6H_2O$	53.23	3.03	9.55	14.47
$UO_2(CH_3COO)_2.2H_2O$	12.32	1.89	1.94	1.91
K_2PtCl_4	57.38	4.02	10.43	17.64

Bis(2-aminothiophenolato)palladium(II) $Pd(ATP)_2$ was treated with concentrated hydrochloric acid. The compound bis(2-aminothiophenolato)palladium(II) dihydrochloride $Pd(ATP)_2.2HCl$ was obtained, identical to the reaction product of ATPH.HCl with cis-dichlorobis-(benzonitrile)palladium(II) (p. 100(C)).

Table XXVII

Results of the Elemental Analyses of the Reaction Products of a Mixture of DIAL With ATPH in a Basic Medium With Metal Ions

Compound		%C	%H	%N	%Cl	%S	% Metal
Cu(ATPAL)*.2HCl.H$_2$O	Calc.	45.46	3.41	8.37	14.13	12.78	12.62
	Found	46.33	3.15	8.36	14.63	12.60	12.20
Pd(ATP)$_2$	Calc.	40.62	3.41	7.90	-----	18.08	-----
	Found	40.43	3.36	7.69	-----	17.60	-----
DBTP	Calc.	66.06	3.21	12.16	-----	18.50	-----
	Found	65.03	3.29	11.91	-----	17.89	-----
Ru(ATPALH$_2$)Cl$_3$.½C$_2$H$_5$OH	Calc.	41.42	3.13	7.25	18.34	11.06	-----
	Found	41.80	3.20	7.45	17.96	11.96	-----

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* ATPAL is

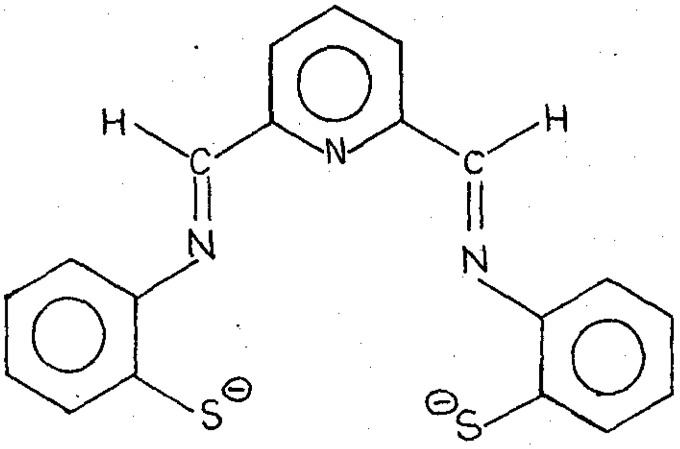


Table XXVIII

Solubilities of the Reaction Products of a Mixture of DIAL With ATPH in a Basic Medium With Metal Ions

Compound	H_2O	MeOH	EtOH	Acetone	Ether	Diox.	Benzene	Pet. Eth.	CH_2Cl_2	$CHCl_3$	CCl_4	DMF	DMSO
Cu(ATPAL) $\cdot 2HCl \cdot H_2O$	–	–	–	–	–	–	–	–	–	–	–	±	+
$Pd(ATP)_2$	–	–	–	–	–	–	–	–	–	–	–	–	–
$Ru(ATPALH_2) \cdot Cl_3 \cdot \frac{1}{2}C_2H_5OH$	–	–	–	–	–	–	–	–	±	±	±	+	+

Table XXIX

Infrared Spectra of the Products of the Reactions of a Mixture of DIAL and ATPH in a Basic Medium With Metal Ions

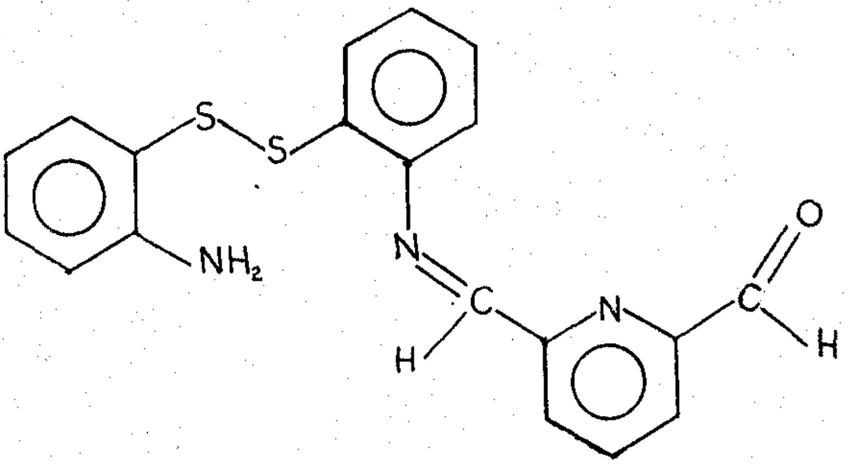
Assignment	$Cu(ATPAL).2HCl.H_2O$	$Pd(ATP)_2$	$Ru(ATPALH_2)Cl_3.\frac{1}{2}C_2H_5O$
O-H stretching	3400 (b)		3400 (b)
N-H stretching		3175 (w), 3220 (sh)	
Aromatic C-H st.	3050 (w), 3000 (sh)	3050 (sh), 3020 (sh)	3040 (w), 3020 (sh)
Alkyl C-H st.			2940 (sh)
S-H stretching			2610 (sh)
O-H deformation	1650 (wb)		
C=C and C=N st	1610 (mb), 1575 (s)	1580 (s), 1540 (m) 1525 (m)	1580 (sb)
Aromatic skeletal vibrations	1460 (sb)	1460 (s), 1425 (m-s)	1450 (sb)
C-N stretching	1375 (wb), 1260 (mb)	1285 (s), 1255 (s)	1365 (wb), 1310 (w) 1260 (w)
C-O stretching			1150 (w), 1115 (wb)
C-C stretching	1155 (m-s), 1055 (m) 1035 (m)	1190 (m-s), 1145 (m) 1050 (m)	1050 (m), 1015 (mb)
In-plane and out-of-plane C-H def.	950 (wb), 750 (s) 730 (w)	925 (s), 725 (vsb)	900 (sh), 750 (s) 720 (w)

2.9.3. 2,6-Pyridinedicarboxaldehyde (DIAL) and 2,2'-dithiodianiline (DTDA)

i) Reaction of DIAL with DTDA

DIAL (0.135 g, 1 mmole) in ethanol (15 ml) was added to a solution of DTDA (0.248 g, 1 mmole) in ethanol (10 ml). The mixture was heated with stirring in a water bath at 70° for 15 minutes. A yellow solid was deposited. The mixture was cooled to room temperature and the solid was filtered off, and recrystallized from dioxane-water mixture. Yield: 0.247 g (68%). Melting point: 192-200° with decomposition.

The Schiff base DTDAL produced is soluble in benzene, dichloromethane, chloroform and dioxane, and insoluble in methanol, ethanol and water.



DTDAL

Analysis of DTDAL: Calculated for $C_{19}H_{15}N_3OS_2$: %C 62.44; %H 4.14; %N 11.50; %S 17.54. Found: %C 63.27; %H 4.31; %N 11.17; %S 17.12.

The major infrared absorption bands of DTDAL and their respective assignments are listed in Table XXX.

Table XXX

Infrared Spectrum of DTDAL

Assignment	
N-H stretching	3410(w), 3340(w)
C-H stretching	3040(w), 2950(w), 2840(sh)
C=O stretching	1700(s)
Ring skeletal vibrations	1610(s), 1575(s), 1555(m), 1485(m), 1450(m-s)
C-C and C-N stretching	1325(m), 1300(s), 1260(mb)
In-plane and out-of-plane C-H deformation	1040(s), 980(m), 840(s), 790(sb), 730(vsb)

ii) Reaction of a mixture of DIAL and DTDA with cis-dichlorobis(benzonitrile)palladium(II)

a) In ethanol

To a filtered stirred solution of cis-dichlorobis(benzonitrile)palladium(II) (0.192 g, 0.5 mmole) in ethanol (15 ml), DIAL (0.068 g, 0.5 mmole) was added, followed by the addition of DTDA (0.124 g, 0.5 mmole). The yellowish brown solid which crystallized immediately was filtered off on a glass sintered funnel, washed with ethanol, then ether and dried in vacuo. Yield: 0.22 g.

The compound obtained started darkening at 276° and melted at 309-315° with decomposition.

b) In benzene

Procedure (a) was followed using benzene (20 ml) in place of ethanol and refluxing the mixture for four hours. The dark brown solid formed, was filtered off on a glass sintered funnel, washed with benzene, then with ether and dried in vacuo. Yield: 0.21 g.

The compound obtained decomposed at 318°.

No molecular formulas could be assigned for the products obtained from reactions (a) and (b) on the basis of their found analyses which are listed below:

Solvent	%C	%H	%N	%Cl	%S
Ethanol	41.60	3.02	7.58	10.01	12.76
Benzene	40.33	2.60	7.38	10.60	11.47

2.9.4. 2,6-Pyridinedicarboxaldehyde (DIAL) and 8-aminoquinoline (AMQ)

The reactions of a mixture of DIAL and AMQ with different metal salts were carried out by the following general procedure:

To a stirred hot solution of AMQ (0.288 g, 2 mmole) in acetone (20 ml), DIAL (0.135 g, 1 mmole) was added, followed directly by the addition of a solution of the metal salt (1 mmole) in an appropriate solvent (10-15 ml) (Table XXXI). The reaction mixture was refluxed for a period of time as shown in Table XXXI too. The product formed was filtered off, washed with the solvents used and dried in vacuo.

Table XXXI

Reactions of DIAL and AMQ with Metal Ions

Metal Salt	Solvent Used	Reflux Period (hr)
$Cu(ClO_4)_2.6H_2O$	Acetone	3
$CuCl_2.2H_2O$	Acetone	1
$AgClO_4$	Ethanol	3
$Co(ClO_4)_2.6H_2O$	Acetone	3
$ZnCl_2$	Ethanol	1
K_2PtCl_4	Water	...[a]
$RhCl_3.3H_2O$	Ethanol	3
$RuCl_3.3H_2O$	Ethanol	3
$Pd(C_6H_5CN)_2Cl_2$	Toluene	1
$UO_2(CH_3COO)_2.2H_2O$	Methanol	3
$HgCl_2$	Ethanol	3
$FeCl_3.6H_2O$	Ethanol	3

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[a] The reaction mixture was stirred at 40-45°C for two hours.

The colours, melting points and yields of the reaction products of the mixture of DIAL and AMQ with the different metal salts are shown in Table XXXII.

Table XXXII

Reactions of DIAL and AMQ with Metal Ions

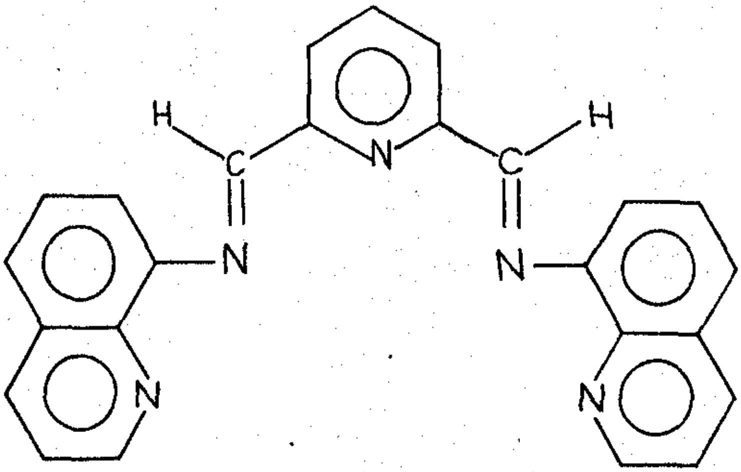
Metal Salt	Colour of Product	Melting Point °C	% Yield
$Cu(ClO_4)_2.6H_2O$	Grayish-Brown	210-215 d	64
$CuCl_2.2H_2O$	Greenish-Brown	165 sd	79
$AgClO_4$	Yellow	250-255 d	68
$Co(ClO_4)_2.6H_2O$	Greenish-Brown	265-268 d	44
$ZnCl_2$	Yellow	255-259 d	66
K_2PtCl_4	Brown	>360	90
$RhCl_3.3H_2O$	Grayish-Brown	290-293 d	93
$RuCl_3.3H_2O$	Black	>360	93
$Pd(C_6H_5CN)_2Cl_2$	Grayish-Brown	205 sd	--
$UO_2(CH_3COO)_2.2H_2O$	Yellow	310-316 d	--
$HgCl_2$	Brown	205 sd	--
$FeCl_3.6H_2O$	Brown	273-278 d	--

The reactions of the mixture of DIAL and AMQ with metal ions gave identifiable products with copper(II) perchlorate hexahydrate, copper(II) chloride dihydrate, silver perchlorate, cobalt(II) perchlorate hexahydrate, zinc(II) chloride, potassium tetrachloroplatinate(II), rhodium(III) chloride trihydrate and ruthenium(III) chloride trihydrate. The elemental analyses for the complexes obtained are shown in Table XXXIII, their solubilities in Table XXXIV, and their major infrared bands along with their respective assignments in Table XXXV. Table XXXVI shows the observed ultraviolet bands of AMQ and the soluble AQAL complexes.

On the basis of their found analyses which are listed below, no molecular formulas could be assigned for the reaction products of the mixture of DIAL and AMQ with cis-dichlorobis(benzonitrile)palladium(II), uranyl acetate dihydrate, mercury(II) chloride and iron(III) chloride hexahydrate.

The nickel salts: perchlorate hexahydrate, nitrate hexahydrate and chloride dihydrate failed to react with the mixture of DIAL and AMQ.

Metal Salt	%C	%H	%N	%Cl
$Pd(C_6H_5CN)_2Cl_2$	57.62	3.65	13.66	7.68
$UO_2(CH_3COO)_2 \cdot 2H_2O$	32.04	2.60	7.42	----
$HgCl_2$	41.57	2.88	7.79	9.27
$FeCl_3 \cdot 6H_2O$	53.23	3.68	8.85	14.42



AQAL

Table XXXIII

Results of the Elemental Analyses of the Reaction Products of a Mixture of DIAL and AMQ With Metal Salts

Compound		%C	%H	%N	%Cl	% Metal
$Cu(AQAL)(ClO_4)_2 \cdot 4H_2O$	Calc.	41.59	3.49	9.70	9.82	8.80
	Found	41.71	3.28	10.05	8.75	8.62
$Cu_3(AQAL)_2Cl_6 \cdot 2H_2O$	Calc.	46.68	3.60	10.89	16.54	14.83
	Found	45.64	3.38	10.15	16.80	14.91
$Ag(AQAL)ClO_4 \cdot 3H_2O$	Calc.	46.28	3.55	10.79	5.47	16.63
	Found	45.31	2.95	10.62	6.20	16.42
$Co(AQAL)(ClO_4)_2 \cdot 2H_2O$	Calc.	44.06	3.10	10.28	10.41	
	Found	43.69	2.87	10.11	10.06	
$Pt_3(AQAL)_2Cl_6 \cdot H_2O$	Calc.	36.92	2.46	8.61	13.07	
	Found	37.99	2.78	8.79	12.07	
$Zn_3(AQAL)_2Cl_6 \cdot 2H_2O$	Calc.	46.48	3.59	10.84	16.47	15.18
	Found	45.89	3.37	10.23	17.24	14.96
$Rh_3(AQAL)_2Cl_9 \cdot 3H_2O$	Calc.	38.38	3.35	8.95	20.40	
	Found	37.67	3.56	9.21	19.93	
$Ru_3(AQAL)_2Cl_9 \cdot 2H_2O$	Calc.	39.89	3.08	9.30	21.20	
	Found	40.55	3.33	9.00	20.24	

Table XXXIV

Solubilities of AQAL Complexes

Compound	H_2O	MeOH	EtOH	Acetone	Ether	Diox.	Benzene	Pet. Eth.	CH_2Cl_2	$CHCl_3$	CCl_4	DMF	DMSO
$Cu(AQAL)\cdot(ClO_4)_2\cdot 4H_2O$	-	-	-	-	-	-	-	-	-	-	-	+	+
$Cu_3(AQAL)_2\cdot Cl_6\cdot 2H_2O$	-	-	-	-	-	-	-	-	-	-	-	±	+
$Ag(AQAL)ClO_4\cdot 3H_2O$	-	-	-	-	-	-	-	-	-	-	-	+	+
$Co(AQAL)\cdot(ClO_4)_2\cdot 2H_2O$	-	-	-	-	-	-	-	-	-	-	-	+	+
$Pt_3(AQAL)_2\cdot Cl_6\cdot H_2O$	-	-	-	-	-	-	-	-	-	-	-	±	±
$Zn_3(AQAL)_2\cdot Cl_6\cdot 2H_2O$	±	-	-	-	-	-	-	-	-	-	-	±	+
$Rh_3(AQAL)_2\cdot Cl_9\cdot 3H_2O$	-	-	-	-	-	-	-	-	-	-	-	±	+
$Ru_3(AQAL)_2\cdot Cl_9\cdot 2H_2O$	-	-	-	-	-	-	-	-	-	-	-	+	+

Table XXXV

Infrared Spectra of AQAL Complexes

Assignment	Cu(AQAL)$(ClO_4)_2 \cdot 4H_2O$	Cu_3(AQAL)$_2Cl_6 \cdot 2H_2O$	Ag(AQAL)$ClO_4 \cdot 3H_2O$
O-H stretching	3400(b)	3420(b)	3400(b)
Aromatic C-H st.	3110(vw), 3030(sh)	3040(w), 3000(sh)	3040(w), 3000(sh)
O-H deformation	1625(m)	1620(w)	1625(m)
Ring skeletal vibrations	1580(sb), 1510(s), 1480(m), 1405(s)	1590(mb), 1505(m-s) 1465(wb)	1575(sb), 1500(s) 1460(m)
C-C and C-N st.	1380(m), 1325(s)	1380(s), 1320(m)	1380(sb), 1320(m)
	1250(m), 1225(m)	1240(w)	1270(s), 1210(m)
In-plane and out-of-plane C-H def.	915(m), 835(vs) 785(vs), 735(s)	1075(m), 1015(w) 840(s), 785(sb)	835(s), 795(s) 765(s)
ClO_4^- absorption	1100(vsb)		1085(vs)
M-Cl stretching		265(m)	

Table XXXV continued

Assignment	Co(AQAL)$(ClO_4)_2 \cdot 2H_2O$	Pt_3(AQAL)$_2Cl_6 \cdot H_2O$	Zn_3(AQAL)$_2Cl_6 \cdot 2H_2O$
O-H stretching	3400(b)	3450(b)	3460(b)
Aromatic C-H st.	3040(mb)	3050(mb)	3050(wb)
O-H deformation	1650(w)	1650(w)	1680(w), 1620(s)
Ring skeletal vibrations	1580(s), 1495(s) 1465(wb)	1585(sb), 1515(s) 1470(wb)	1585(s), 1495(s)
C-C and C-N st.	1385(m), 1310(m-s) 1275(s)	1380(m), 1325(w) 1230(m)	1390(m), 1320(w)
In-plane and out-of-plane deform.	950(w), 825(vs) 780(vs)	1080(wb), 840(s) 785(s)	1080(m), 825(s) 780(s), 755(m-s)
ClO_4^- absorption	1080(vsb)		

Table XXXV continued

Assignment	$Rh_3(AQAL)_2Cl_9 \cdot 3H_2O$	$Ru_3(AQAL)_2Cl_9 \cdot 2H_2O$
O-H stretching	3420(b)	3420(b)
Aromatic C-H st.	3060(sh), 3000(sh)	3050(wb)
O-H deformation	1630(mb)	1650(w), 1620(wb)
Ring skeletal vibrations	1580(mb), 1510(m) 1460(w)	1595(m), 1525(w) 1495(m), 1450(mb)
C-C and C-N st.	1375(mb), 1320(w) 1220(w)	1375(m), 1315(w) 1210(w)
In-plane and out-of-plane deform.	1150(mb), 1075(w) 840(s), 780(s)	1160(w), 1130(w) 825(s), 770(s)
m-Cl stretching	330(m)	335(m)

Table XXXVI

Ultraviolet Spectra of AMQ and AQAL Complexes in DMSO

Compound	mµ	$\epsilon \times 10^4$
AMQ	260, 340(b)	2.46, 0.32
$Cu(AQAL)(ClO_4)_2 \cdot 4H_2O$	261	2.30
$Cu_3(AQAL)_2Cl_6 \cdot 2H_2O$	263	1.42
$Ag(AQAL)_2ClO_4 \cdot 3H_2O$	263	1.23
$Co(AQAL)(ClO_4)_2 \cdot 2H_2O$	260	1.81
$Pt_3(AQAL)_2Cl_6 \cdot H_2O$	262	1.90
$Zn_3(AQAL)_2Cl_6 \cdot 2H_2O$	259	2.12
$Rh_3(AQAL)_2Cl_9 \cdot 3H_2O$	263	1.91
$Ru_3(AQAL)_2Cl_9 \cdot 2H_2O$	264	1.40

2.9.5. 2,6-Pyridinedicarboxaldehyde-2,6-diaminopyridine system

a) Reactions of 2,6-pyridinedicarboxaldehyde (DIAL) metal complexes with 2,6-diaminopyridine (DAP)

i) Dichloro-2,6-pyridinedicarboxaldehyde copper(II) (Cu(DIAL)Cl_2)

To a stirred solution of Cu(DIAL)Cl_2 (0.081 g, 0.3 mmole) in methanol (30 ml), DAP (0.131 g, 1.2 mmole) was added and the mixture was refluxed for two hours. A brown solid was formed. It was filtered off, washed with methanol, and dried in vacuo. Yield: 0.246 g (81%).

The compound obtained did not melt up to 360°.

ii) Dichlorobis(2,6-pyridinedicarboxaldehyde)-platinum(II) dihydrate (Pt(DIAL)$_2Cl_2.2H_2O$)

A solution of DAP (0.218 g, 2 mmole) in tetrahydrofuran (10 ml) was added to a suspension of Pt(DIAL)$_2Cl_2.2H_2O$ (0.230 g, 0.4 mmole) in tetrahydrofuran (20 ml). The reaction mixture was refluxed with stirring for four hours. A brown precipitate was formed. It was filtered off, washed with tetrahydrofuran, and dried in vacuo. Yield: 0.280 g.

The compound obtained did not melt up to 360°.

iii) Dichlorobis(2,6-pyridinedicarboxaldehyde)-palladium(II) (Pd(DIAL)$_2$Cl$_2$)

A solution of DAP (0.109 g, 1 mmole) in tetrahydrofuran (5 ml) was added to a stirred hot solution of Pd(DIAL)$_2$Cl$_2$ ().149 g, 0.33 mmole) in tetrahydrofuran (15 ml) and the reaction mixture was refluxed for one hour. The orange brown solid formed, was filtered off, washed with tetrahydrofuran and dried in vacuo. Yield: 0.164 g.

The compound obtained started darkening around 200°. It was black at 280° and did not melt up to 360°.

iv) Diacetato-2,6-pyridinedicarboxaldehyde uranyl(II) dihydrate $UO_2(DIAL)(CH_3COO)_2.2H_2O$

DAP (0.115 g, 1.05 mmole) was added to a suspension of $UO_2(DIAL)(CH_3COO)_2.2H_2O$ (0.195 g, 0.35 mmole) in tetrahydrofuran (15 ml) and the mixture was refluxed with stirring for five hours. A mustard yellow solid was formed. It was filtered off, washed with tetrahydrofuran and dried in vacuo. Yield: 0.180 g.

The compound obtained did not melt up to 360°.

v) Diacetylacetatobis(2,6-pyridinedicarboxaldehyde)nickel(II) monohydrate $Ni(DIAL)_2(acac)_2.H_2O$

DAP (0.109 g, 1 mmole) was added to a suspension of $Ni(DIAL)_2(acac)_2.H_2O$ (0.164 g, 0.30 mmole) in tetrahydrofuran (30 ml) and the mixture was refluxed with stirring for five hours. The mustard yellow solid formed, was filtered off, washed with tetrahydrofuran and dried in vacuo. Yield: 0.220 g.

The compound obtained did not melt up to 360°.

Of the DIAL complexes, only $Cu(DIAL)Cl_2$ gave a condensation product for which a molecular formula could be assigned. Table XXXVII shows the elemental analyses results of the reaction products of DIAL metal complexes with DAP.

Table XXXVII

Elemental Analyses Results of the Reaction Products of DIAL Metal Complexes With DAP

Compound or metal ion		%C	%H	%N	%Cl	% Metal
Cu(APALAP)*$Cl_2.3H_2O$	Calc.	40.36	4.18	19.39	14.02	12.56
	Found	40.71	3.96	18.80	13.21	12.51
Pt(II)	Found	40.80	3.50	18.20	7.00	
Pd(II)	Found	45.69	5.03	15.68	9.15	
UO_2^{++}	Found	24.82	2.80	6.55		
Ni(II)	Found	47.61	5.14	6.87		

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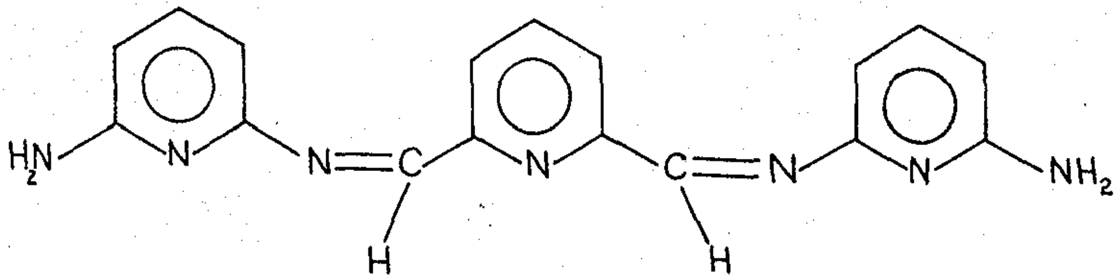
* APALAP is



$Cu(APALAP)Cl_2.3H_2O$ is insoluble in common organic solvents. It is soluble in concentrated nitric and sulfuric acids. It displays infrared bands at 3400 cm^{-1} and 1650 cm^{-1} due to O-H stretching and O-H deformation respectively, 3305, 3195 cm^{-1} due to N-H stretching and 1600 cm^{-1}, 1445 cm^{-1} due to C=C and C=N stretching in pyridine ring. It does not show any absorption in the C=O stretching region.

The attempt to decompose $Cu(APALAP)Cl_2.3H_2O$ with cyanide in order to isolate the free ligand was unsuccessful.

b) Reaction of DIAL with DAP

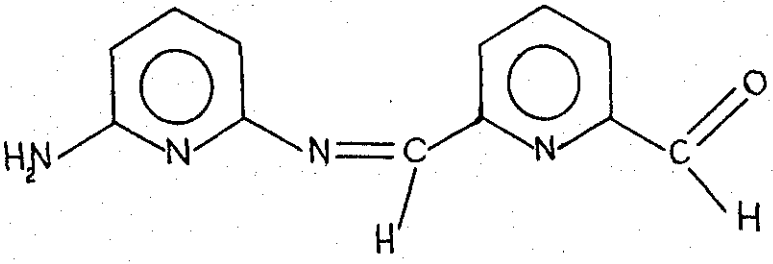
DIAL (0.135 g, 1 mmole) was added to a stirred solution of DAP (0.109 g, 1 mmole) in methanol (15 ml). Stirring was continued and the solution was refluxed. After about three minutes, the colour of the solution turned pale yellow. A yellow precipitate appeared after 15 minutes. The reaction mixture was then refluxed for two hours. The product obtained was filtered off, washed with methanol and dried in vacuo. Yield: 0.187 g, (77%).

The yellow solid obtained started darkening at 270° and did not melt up to 360°.

The Schiff base $DAPAL.H_2O$ obtained from the condensation of DIAL and DAP is insoluble in water, methanol,

ethanol, acetone, ether, dioxane, petroleum ether, dichloromethane, chloroform, carbon tetrachloride, benzene, dimethyl formamide and dimethyl sulfoxide. It is soluble in concentrated nitric acid and sulfuric acid.

Elemental analysis of DAPAL.H_2O: Calculated for $C_{12}H_{12}N_4O_2$: %C 59.00; %H 4.95; %N 22.94. Found: %C 59.60; %H 4.53; %N 23.80.



DAPAL

The infrared absorption bands of DAPAL.H_2O and their respective assignments are listed in Table XXXVIII.

Table XXXVIII

Infrared Spectrum of the Schiff Base DAPAL.H_2O

Assignment	
O-H stretching	3595(sh), 3495(sh)
N-H stretching	3390(m-s), 3228(sh)
C-H stretching	3100(vs), 2858(vw), 2905(vw) 2710(vw)
C=O stretching	1720(s)
O-H deformation	1620(sh)
C=C and C=N stretching	1598(vsb), 1455(s)
C-C and C-N stretching	1358(w), 1240(m-w)
Py-ring vibrations	1290(w), 1152(m), 1130(m), 1075(mb), 997(m), 952(wb)
N-H and C-H out-of-plane bending	782(vsb), 725(wb)

c) Reactions of a mixture of 2,6-pyridinedicarboxaldehyde and 2,6-diaminopyridine with metal ions

i) Nickel(II) perchlorate hexahydrate

(a) To a stirred hot solution of DAP (0.437 g, 4 mmole) in methanol (60 ml), DIAL (0.540 g, 4 mmole) was added, followed directly by the addition of a solution of nickel(II) perchlorate hexahydrate (0.731 g, 2 mmole) in methanol (20 ml). After heating for about three minutes an orange precipitate appeared. The mixture was then refluxed for 90 minutes. The product obtained was filtered off, washed with methanol and dried in vacuo over P_2O_5. Yield: 1.06 g (54%).

The orange solid started darkening at 294°. It was black at 316° and did not melt up to 360°.

(b) Procedure (a) was followed using the molar ratio 1:1:1 of 2,6-pyridinedicarboxaldehyde: 2,6-diaminopyridine : nickel(II) perchlorate hexahydrate. A dark orange solid was obtained in 60% yield and melted at 260° with decomposition.

ii) Copper(II) bromide

To a stirred hot solution of DAP (0.218 g, 2 mmole) in methanol (30 ml), DIAL (0.270 g, 2 mmole) was added, followed directly by the addition of a solution of copper(II) bromide in methanol (40 ml). After heating for about two minutes a brown precipitate appeared. The mixture was then refluxed for two hours. The product obtained was filtered off, washed with methanol, and dried in vacuo over P_2O_5. Yield: 0.75 g.

The brown solid started darkening at 240° and did not melt up to 360°.

iii) Potassium tetrachloroplatinate(II)

To a stirred solution of DAP (0.109 g, 1 mmole) in water (20 ml) at 60°, a solution of DIAL (0.135 g, 1 mmole) in water (20 ml) was added. The warm aqueous solution was stirred for two minutes before a filtered solution of potassium tetrachloroplatinate(II) (0.589 g, 1.4 mmole) in water (20 ml) was added. After stirring for about one minute, a brown precipitate started to form. The reaction mixture was further stirred for an additional 90 minutes. The solid formed was filtered off, washed with hot water and dried in vacuo over P_2O_5. Yield 0.280 g.

The brown solid did not melt up to 360°.

iv) Cis-dichlorobis(benzonitrile)palladium(II)

To a stirred hot solution of DAP (0.109 g, 1 mmole) in methanol (20 ml), DIAL (0.135 g, 1 mmole) was added, followed directly by the addition of a filtered solution of cis-dichlorobis(benzonitrile)palladium(II) (0.544 g, 1.4 mmole) in methanol (40 ml). After stirring for a few seconds an orange brown solid began to form. The reaction mixture was refluxed for two hours and the product obtained was filtered off, washed with methanol and dried in vacuo over P_2O_5. Yield: 0.310 g. Melting point 310-312^o with decomposition.

v) Zinc(II) nitrate hexahydrate

To a stirred hot solution of DAP (0.109 g, 1 mmole) in methanol (20 ml), DIAL (0.135 g, 1 mmole) was added, followed directly by the addition of a solution of zinc(II) nitrate hexahydrate (0.416 g, 1.4 mmole) in methanol (28 ml). Stirring was continued and the solution was refluxed. After five minutes, an orange solid began to form. The reaction mixture was further refluxed for one hour. The product formed was filtered off, washed with methanol and dried in vacuo over P_2O_5. Yield: 0.224 g.

The orange solid did not melt up to 360^o.

When the mixture of DIAL and DAP was reacted with nickel(II) perchlorate hexahydrate using the molar ratio 2:2:1 and 1:1:1 of DIAL:DAP:nickel salt, two different compounds: $Ni(L\text{-}A)(ClO_4)_2.5H_2O$ and $Ni(L\text{-}B)(ClO_4)_2.2H_2O$ insoluble in common organic solvents but soluble in dilute hydrochloric acid were respectively obtained.

The elemental analyses of Ni(L-A)* $(ClO_4)_2 \cdot 5H_2O$ and Ni(L-B)* $(ClO_4)_2 \cdot 2H_2O$ are listed below:

Compound		%C	%H	%N	%Cl	% Metal
Ni(L-A)$(ClO_4)_2 \cdot 5H_2O$	Calc.	43.65	3.66	16.97	7.16	5.93
	Found	43.59	3.57	16.34	7.27	5.77
Ni(L-B)$(ClO_4)_2 \cdot 2H_2O$	Calc.	40.59	2.84	15.78	9.98	8.27
	Found	40.78	3.24	14.98	9.74	8.36

The major infrared bands of Ni(L-A)$(ClO_4)_2 \cdot 5H_2O$ and Ni(L-B)$(ClO_4)_2 \cdot 2H_2O$ along with their respective assignments are shown in Table XXXIX.

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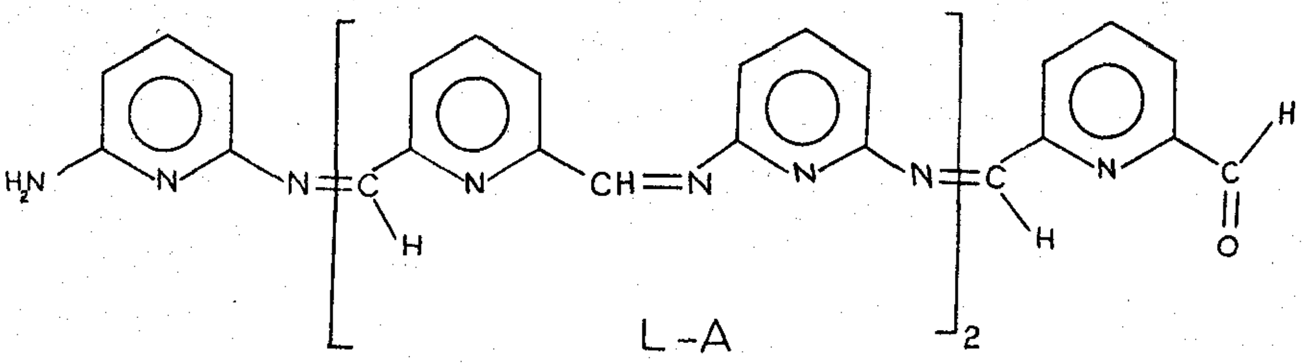
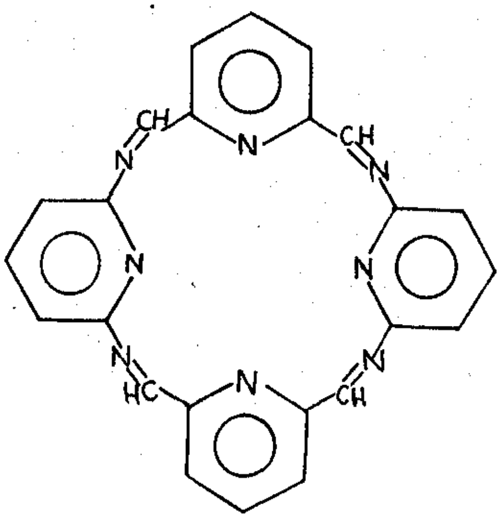


L-A



L-B

Table XXXIX

Infrared Spectra of Ni(L-A)$(ClO_4)_2 \cdot 5H_2O$ and Ni(L-B)$(ClO_4)_2 \cdot 2H_2O$

Assignment	Ni(L-A)$(ClO_4)_2 \cdot 5H_2O$	Ni(L-B)$(ClO_4)_2 \cdot 2H_2O$
O-H stretching	3340(b)	3430(sh), 3335(m)
N-H stretching	3200(sh), 3160(sh)	----
C-H stretching	3000(sh), 2915(sh)	3068(w), 2904(w)
C=O stretching	1700(m-s)	----
O-H deformation	1650(b), 1630(sh)	1640(b)
C=C and C=N stret. in Py ring	1585(vsb), 1450(sb)	1595(s), 1570(sh) 1445(sb)
C-C and C-N stret.	1280(mb), 1225(mb)	1280(w), 1225(w)
Py-ring vibrations	1025(w)	1025(w)
In-plane and out-of-plane in C-H deform.	780(sb), 725(mb)	790(mb), 732(wb)
ClO_4^- absorption	1090(vsb)	1085(vsb)

Copper(II) bromide, potassium tetrachloroplatinate(II), cis-dichlorobis(benzonitrile)palladium(II) and zinc(II) nitrate hexahydrate were reacted with a mixture of DIAL and DAP. No molecular formulas could be assigned for the products obtained on the basis of their analyses shown in Table XL.

Table XL

Elemental Analyses of the Reaction Products of Some Metal Salts With a Mixture of DIAL and DAP

Metal Salt	%C	%H	%N	%Cl	% Metal
$CuBr_2$	15.40	1.41	5.03	-----	24.41
K_2PtCl_4	32.72	2.92	13.20	9.22	-----
$Pd(C_6H_5CN)_2Cl_2$	25.20	2.73	12.06	20.04	-----
$Zn(NO_3)_2 \cdot 6H_2O$	48.97	4.35	20.44	-----	9.02

In an attempt to decompose the complexes and recover the ligands, the complexes $Ni(L\text{-}A)(ClO_4)_2 \cdot 5H_2O$ and $Ni(L\text{-}B)(ClO_4)_2 \cdot 2H_2O$ were reacted with aqueous potassium cyanide (procedure d). No molecular formulas could be assigned for the organic products obtained on the basis of their found analyses which are shown below:

Decomposition product of:

	%C	%H	%N
Ni(L-A)$(ClO_4)_2 \cdot 5H_2O$	58.10	4.02	25.20
Ni(L-B)$(ClO_4)_2 \cdot 2H_2O$	58.17	4.33	25.19

d) Decomposition of Ni(L-A)$(ClO_4)_2 \cdot 5H_2O$ and Ni(L-B)$(ClO_4)_2 \cdot 2H_2O$ with aqueous potassium cyanide

The same procedure was followed with both complexes:

The Ni(II) complex was added in portions to a stirred aqueous solution of potassium cyanide (35%). A brown precipitate was formed. It was filtered off, washed with aqueous cyanide solution, then thoroughly with water and dried in vacuo over P_2O_5. The Ni(L-A)$(ClO_4)_2 \cdot 5H_2O$ decomposition product started darkening at 200° was black at 270°, and did not melt up to 360° whereas that of Ni(L-B)$(ClO_4)_2 \cdot 2H_2O$ started darkening at 190°. It was black at 240° and did not melt up to 360°.

3. Discussion

3. Discussion

The present work deals with the synthesis and the reactions of Schiff bases derived from 2,6-pyridinedicarboxaldehyde. As part of this investigation, it was necessary to study the reactions of the individual components of the Schiff bases with metal ions, namely the aldehyde and the amine.

Reactions of 2,6-pyridinedicarboxaldehyde itself were therefore studied. Reactions of 2,6-diaminopyridine and 2,2'-dithiodianiline were also examined. Those of 8-aminoquinoline, and 2-aminothiophenol are already known and they have been reviewed in the introduction of this work.

The syntheses of Schiff bases were then attempted either by the direct interaction of the aldehyde and the amine or by the reaction of the metal ion with a mixture of the aldehyde and the amine followed by the decomposition of the Schiff base complex thus formed.

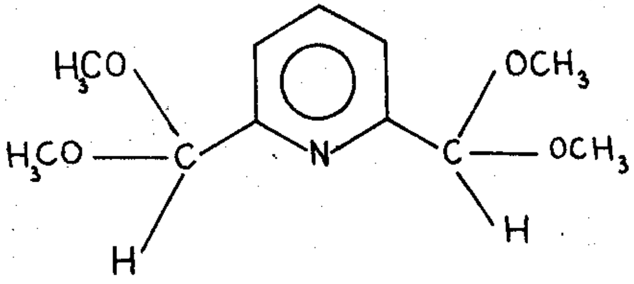
The reactions of each of the respective Schiff bases with several metal ions were then studied. The characterization of the complexes obtained was based on the normal parameters such as elemental analysis, IR, UV, conductivity, magnetic measurements, thermogravimetric analysis and NMR spectrometry.

Many of the structures proposed remain tentative pending more intensive investigations by more decisive methods such as X-ray diffraction.

3.1 The ligands

1. 2,6-Diaminopyridine is normally purified by sublimation. This method is not effecient due to the low recovery of the diamine. The method used in the present work is almost quantitative. It involves the dissolution of the diamine in chloroform and precipitating it by the addition of either n-heptane or petroleum ether.

2. Acetals are known to be prepared by the reaction of aldehydes with alcohols in the presence of a Lewis acid catalyst. A different method involving the reaction of 2,6-pyridinedicarboxaldehyde DIAL with trimethylorthoformate in methanol and in the presence of a catalytic amount of concentrated hydrochloric acid was followed for the preparation of 2,6-bis(dimethoxy-methyl)pyridine DMMP, an acetal which has not hitherto been reported.



DMMP

The diacetal 2,6-bis(diethoxy-methyl)pyridine DEMP which has been previously reported[78] was prepared by a similar method.

The molecular formula of DMMP was assigned on the basis of its elemental analysis, its molecular weight and spectrometry.

The infrared spectrum of DMMP shows the usual aromatic C-H and alkyl C-H stretching in addition to C-O, C=C and C=N stretching frequencies, and frequencies due to pyridine ring vibrations. No C=O or O-H frequencies were observed.

The NMR spectrum of DMMP shows a multiplet at 7.6 δ due to the pyridine protons a singlet at 5.4 δ due to the protons of the carbons directly attached to the ring and a singlet due to the methoxy protons at 3.4 δ in the ratio of 3:2:12.

DMMP has been prepared by this method to be used as an authentic sample for comparison with ligands that are thought to be acetal arising from the preparation of the complexes of DIAL.

3. The attempts made for effecting ring substitution on DIAL (sect. 2.3.6) were unsuccessful due to the failure of some of the reactions and to the nonfeasibility of others.

A possible method which might lead to the formation of 4-chloro-2,6-pyridinedicarboxaldehyde, involves the bromination of 4-chloro-2,6-lutidine with N-bromosuccinimide followed by hydrolysis to produce 4-chloro-2,6-pyridinedimethanol[79] which might be oxidized to the corresponding dialdehyde. 4-Chloro-2,6-lutidine is prepared by the reaction of 4-nitro-2,6-lutidine-1-oxide with phosphorus oxychloride.[79]

Similarly, the preparation of 4-phenoxy-2,6-pyridinedicarboxaldehyde might be effected by the manganese dioxide oxidation of 4-phenoxy-2,6-pyridinedimethanol prepared from the reaction of 4-chloro-2,6-lutidine with sodium phenoxide[80] followed by its reaction with N-bromosuccinimide then by hydrolysis, but the yield of the substituted dialdehyde (based on the 4-chloro-2,6-lutidine) is expected to be low (in the order of 10%).

4. Very few complexes of 2,2'-dithiodianiline DTDA have been reported[52]. It makes it feasible then, to further extend the reactions of this ligand with other transition metal ions.

3.2 Reactions of DIAL with metal ions

In the reactions of DIAL with metal ions, the nature of the product depended more or less on the solvent used. In solvents other than methanol, the complexes obtained involved DIAL itself as the ligand. When methanol was used as the solvent, the complexes obtained contained co-ordinated DMMP. The identity of the ligand was confirmed by decomposing the diacetal complex with aqueous potassium cyanide and recovering the ligand. The latter was then compared with authentic DIAL and DMMP.

a) Complexes containing co-ordinated DIAL

DIAL was reacted with salts or complexes of Pd(II), Cu(II), UO_2^{++}, Pt(II) and Ni(II) in benzene, acetone, methanol, water and toluene, respectively, as solvents. Compounds of the formula ML_2X_2 were obtained. M = Pd, Pt; X = Cl; M = Ni; X = acac, L = DIAL. With UO_2^{++} and Cu(II), it afforded $UO_2(L)(CH_3COO)_2 \cdot 2H_2O$ and $Cu(L)Cl_2$. In all these complexes the ligand apparently behaves as a monodentate, bonding with the metal through the pyridine nitrogen. This is suggested by the fact that the infrared spectra of all the complexes obtained show only one band in the ν C = O region at 1700 cm^{-1}, unshifted from its position in the free dialdehyde ligand. The identity of the ligand as being DIAL was ascertained in the cases of Pt(II) and Pd(II) by the decomposition of the complex with aqueous potassium cyanide and the identification of the recovered ligand.

The Pd(II) and Pt(II) complexes are presumably square planar. The appearance of only one band in each of the complexes in the M-Cl region of the IR spectra at 335 cm^{-1} (Pd) and 310 cm^{-1} (Pt) suggests that the complexes probably have a trans configuration (Fig. 1).

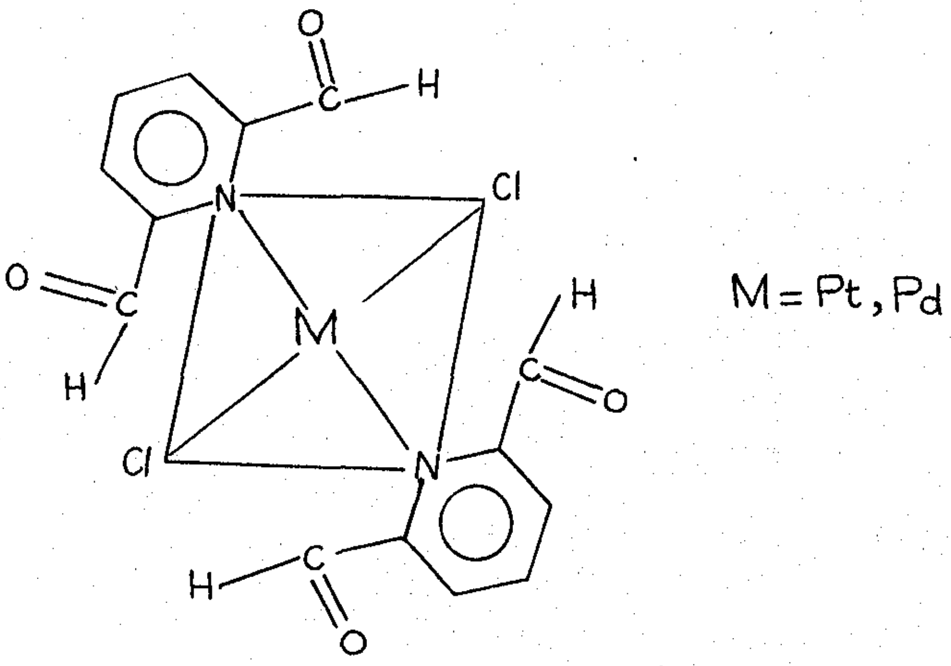


Fig-1

The Ni(II) complex is paramagnetic with a μ(eff) of 3.48 B.M., a value higher than the spin - only moment, as encountered with many Ni(II) high-spin octahedral complexes. The complex is therefore octahedral with the water of hydration not directly bonded to the metal (Fig. 2).

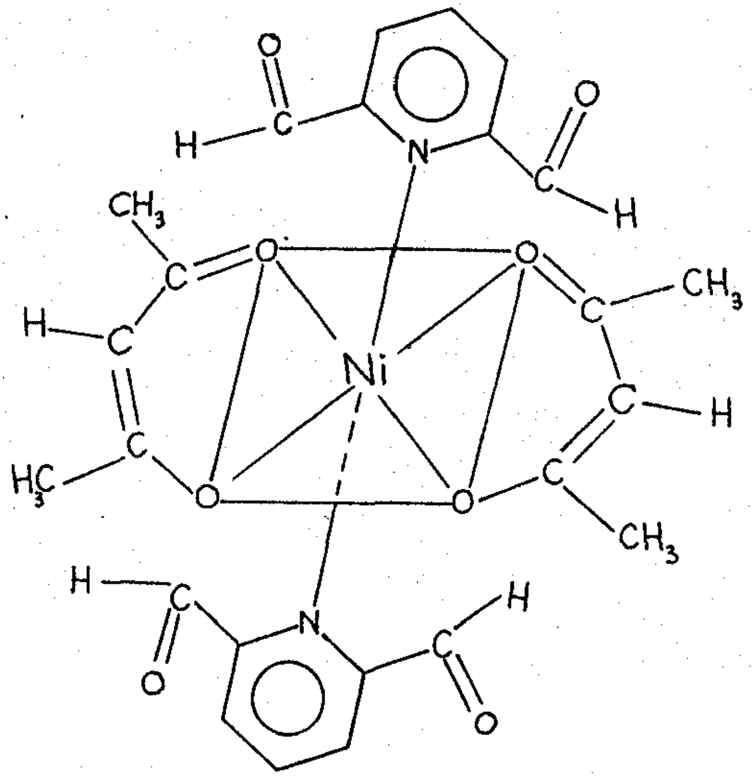


Fig-2

The DIAL complex of Cu(II) has a magnetic moment of 1.84 B.M. thus excluding the occurrence of dimerization via Cu-Cu interaction. It is a monomeric molecule as indicated by its molecular weight (Calc. 269.6; Found 271.4 g/mole).

Although uranyl acetate dihydrate was reacted with DIAL in methanol, the co-ordinated DIAL did not undergo further reaction with methanol. The IR spectrum and elemental analysis suggest that the product is UO_2-(DIAL)$(CH_3COO)_2 \cdot 2H_2O$. The position of ν C = O at 1700 cm^{-1} in the complex suggests that the oxygen atoms of DIAL are not involved in bonding to the metal. To account for the eight-co-ordination typical of U(VI) complexes, one may assume that one of the H_2O molecules is directly bonded to the metal and the other H_2O molecule is encountered as water of hydration. The broad overlapping bands associated with O-H in the complex do not allow the differentiation between the two environments of the two H_2O molecules in the complex.

The presence of water of hydration in the complexes of DIAL is ascertained by IR where an O-H stretching frequency is shown in the region 3400-3600 cm^{-1} and O-H deformation around 1650 cm^{-1}. It is also crudely indicated by a condensate collected at the top of a melting point tube after heating a DIAL complex in such a tube. NMR measurements could not be run on the complexes of DIAL due to their insolubility. Thermogravimetric analysis failed to distinctly detect the water of hydration.

b) Complexes containing co-ordinated DMMP and DEMP

DIAL was reacted with Pd(II) and Cu(II) in methanol and in ethanol to yield complexes containing co-ordinated DMMP and DEMP, respectively, and not dialdehyde. Thus, the complexes $Pd(DMMP)_2Cl_2$, $Cu(DMMP)Cl_2$, $Pd(DEMP)_2Cl_2$ and $Cu(DEMP)Cl_2$ were obtained. The IR spectra of these complexes showed no absorption in the ν C = O region. The proton NMR spectrum of $Pd(DMMP)_2Cl_2$ in $CDCl_3$ showed two singlets at 7.8 δ and 3.6 δ with areas in the ratio of 5:12 assigned to five protons in the aromatic region and 12 due to protons of the methoxy groups. The accidental equivalence of the three pyridine protons and the two protons of the carbons directly attached to the ring may be due to a significant shift of the signal of these latter protons due to their proximity to the metal atom in the complex. Such equivalence was not observed in the free diacetal which was obtained from the decomposition of this acetal complex.

From their molecular weight values (Table VII) $Pd(DMMP)_2Cl_2$ and $Cu(DMMP)Cl_2$ were observed to be monomeric molecules. $Pd(DMMP)_2Cl_2$ is presumably square planar. The appearance of only one band in the ν M-Cl region of its IR spectrum at 335 cm^{-1} suggests that the Pd(II) complex probably has the trans configuration (Fig. 3).

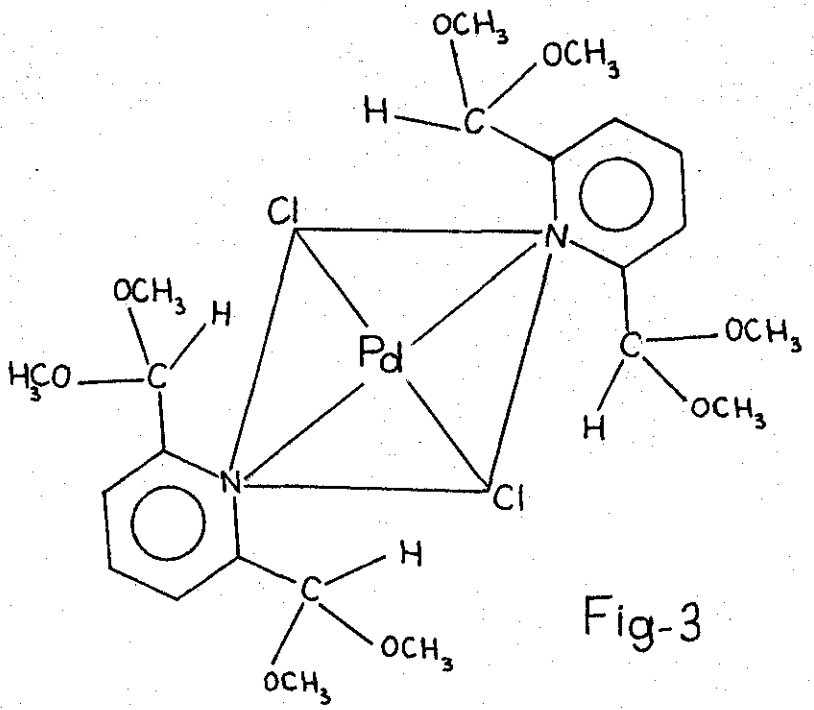


Fig-3

Identical Pd-DMMP and Cu-DMMP and the corresponding DEMP complexes were obtained upon reacting Pd(II) and Cu(II), respectively, with DMMP and DEMP. The Pd(II) and Cu(II) complexes of DMMP and DEMP were also obtained upon refluxing the corresponding DIAL complexes with methanol and ethanol respectively. Attempts to synthesize the Pt(II) complex of DMMP lead to the formation of dichlorobis(2-dimethoxy-methyl-6-pyridinecarboxaldehyde)-platinum(II) Pt(DMPAL)$_2$Cl$_2$ indicating that the co-ordinated ligand had undergone partial elimination of methanol which is the reverse of the reaction of Cu(II) and Pd(II)-DIAL complexes.

Pt(DMPAL)$_2$Cl$_2$ is presumably square planar. The appearance of only one band in the M-Cl region of its IR spectrum at 310 cm^{-1} suggests that the Pt(II) complex has the trans configuration (Fig. 4).

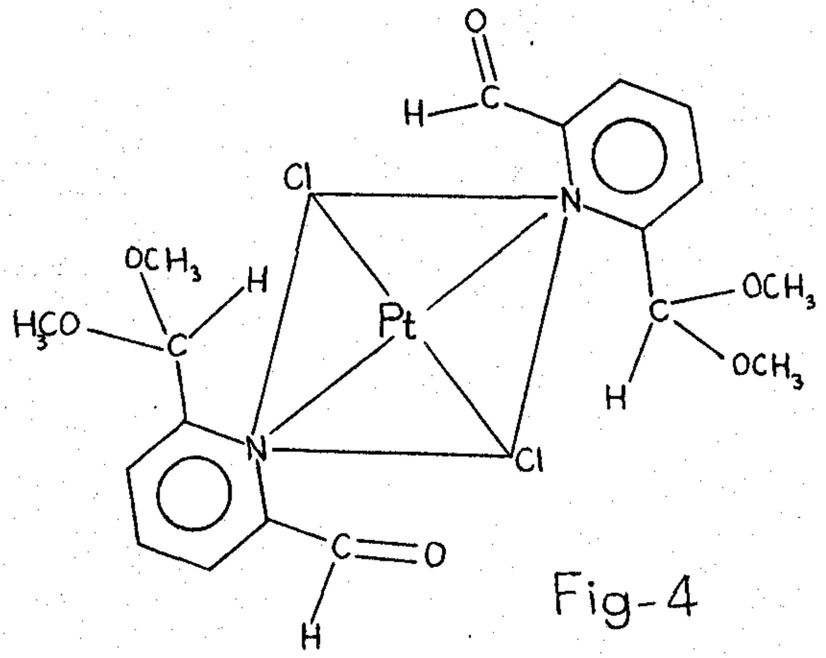


Fig-4

Further work on $Pt(DMPAL)_2Cl_2$ requires the decomposition of the complex with aqueous potassium cyanide to remove the intact DMPAL ligand and to identify it using analysis, mass spectroscopy, NMR, IR and other techniques.

The reactions of Pd(II) and Cu(II) with DIAL leading to the formation of DMMP complexes of the metal ions, made it a point of interest to study the possibility of these metal ions as catalysts in a general method for the preparation of acetals other than the usual one. However, the reaction of benzaldehyde and 2-pyridinecarboxaldehyde with methanol using a catalytic amount of Cu(II) under reflux conditions for eighteen hours failed and the starting materials were recovered quantitatively. The reaction of DIAL with methanol using a catalytic amount of Cu(II) was also examined. It was observed that Cu(II) catalyzed the acetal formation to a certain extent as evidenced by ν alkyl C-H and ν C-O and a much less intense ν C=O band in the IR spectrum of the presumed acetal compound.

3.3 Reactions of DAP with metal ions

DAP was reacted with the metal ions Cu(II), Ag(I), Rh(III), Ru(III), Pd(II) and Pt(II). The following complexes were obtained: $M(DAP)Cl_n$: M = Cu, Pd; n = 2; M = Rh, Ru; n = 3; $Ag(DAP)(CH_3COO)$, $Pd(DAP)_2Cl_2$ and $Pt(DAP)_2Cl_2 \cdot 2HCl$. The identity of the ligand as being DAP was ascertained in the cases of Pd(II) and Ag(I) by the decomposition of the corresponding complexes with aqueous potassium cyanide and aqueous ammonia and the identification of the recovered ligand. The conductivity measurement for $Ag(DAP)(CH_3COO)$ in pyridine at room temperature shows that it is an electrolyte containing two ions. An aqueous solution of $Pt(DAP)_2Cl_2 \cdot 2HCl$ was found to be acidic and its titration against a standard sodium hydroxide solution indicated the presence of two moles of HCl per one of the Pt(II) complex.

DAP can behave as a monodentate ligand bonding to the metal through the pyridine nitrogen and as a bidentate ligand bonding through the pyridine nitrogen and a nitrogen of one of the amino groups. Kingston[81] reported the preparation of Rh(I) complexes of 2-aminopyridine, where the ligand chelates to the metal via the pyridine nitrogen and the amine groups whereas Poddar[82] reported the preparation of Ru(II) complexes of the type RuL_4Cl_2 (L = 2-aminopyridine) where the ligand behaves as monodentate. In either case, the pyridine nitrogen is involved in co-ordination, being the most basic.

DAP behaves as a monodentate ligand in $Pd(DAP)_2Cl_2$ and $Pt(DAP)_2Cl_2 \cdot 2HCl$, being bonded to the metal through the pyridine nitrogen. No shift is observed in the IR of these complexes in the ν N-H region. The appearance of ν N-H at a lower frequency (at 3210 cm^{-1}) in the Pt(II) complex is due to $-\overset{+}{N}H_3$ group; as one $-NH_2$ of each ligand occurs as the hydrochloride. The conductivity measurement for $Pt(DAP)_2Cl_2 \cdot 2HCl$ in water at room temperature shows that it is an electrolyte containing four ions. This is most likely due to the dissociation of the two ammonium salts $-NH_3Cl \rightleftharpoons -NH_3^+ + Cl^-$.

DAP behaves as a bidentate in the other complexes which involve one ligand each. Bonding of DAP most likely occurs through the pyridine nitrogen (being more basic than the other nitrogens) and a nitrogen of one of the amino groups (Fig. 5). This is evidenced by the IR spectra of the complexes which show ν N-H's due to both free and co-ordinated NH_2 groups (a co-ordinated NH_2 group shows a lowering in ν N-H).

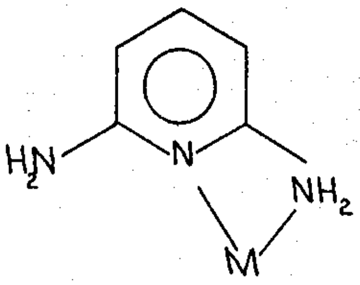


Fig-5

$Pd(DAP)_2Cl_2$ and $Pt(DAP)_2Cl_2.2HCl$ are presumably square planar. The appearance of only one band in each of the complexes in the M-Cl region of the IR spectra suggests that the complexes probably have a trans configuration (Fig. 6). The appearance of two bands in the M-Cl region of the IR spectrum of $Pd(DAP)Cl_2$ suggests that it has the cis configuration (Fig. 6).

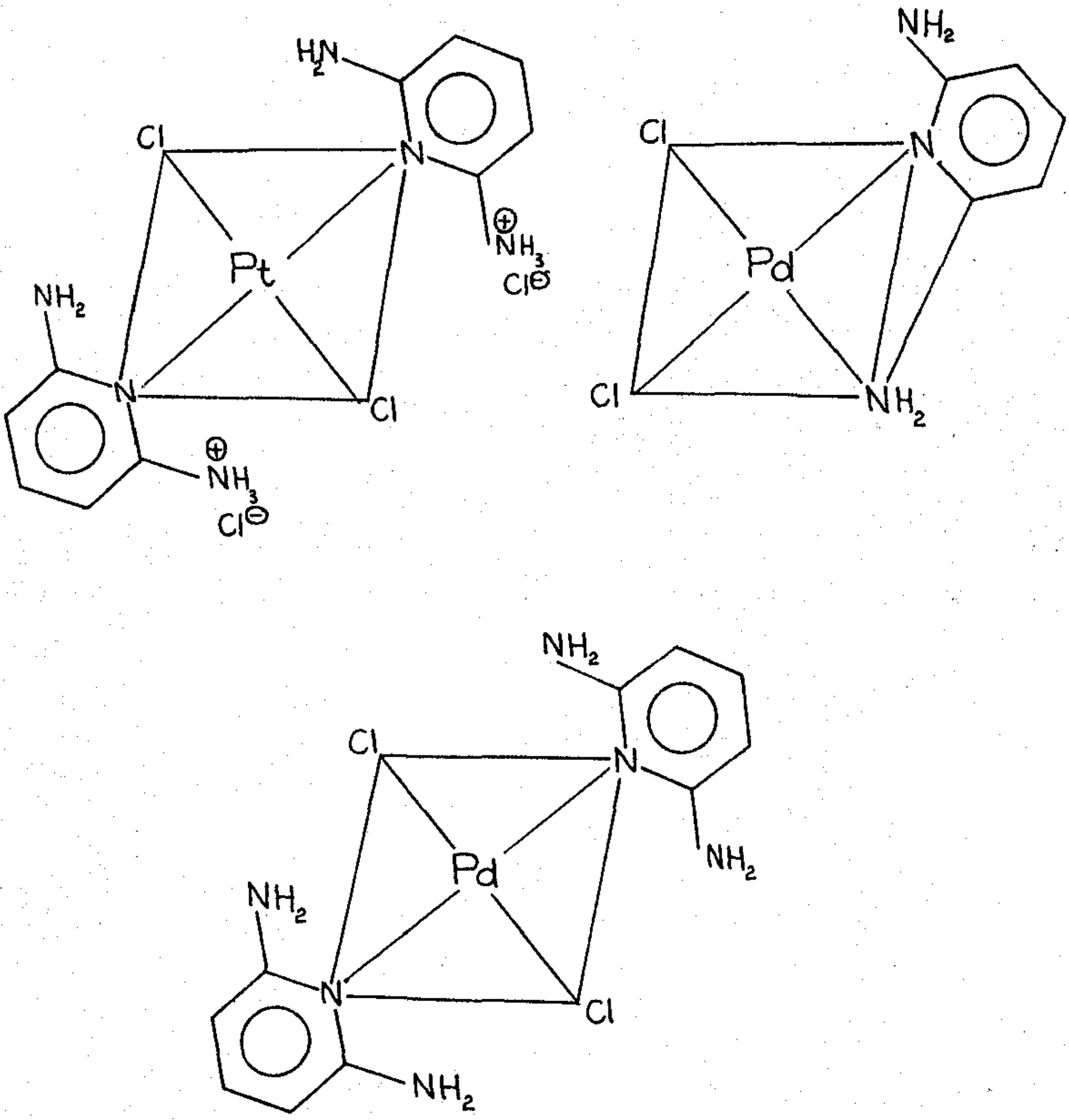


Fig-6

The Rh(III) and Ru(III) complexes of DAP are most likely octahedral with DAP spanning two co-ordination sites. The conductivity measurement for Rh(DAP)$Cl_3.2H_2O$ in dimethylsulfoxide at room temperature shows that it is a nonelectrolyte suggesting that one of the H_2O molecules is directly bonded to the metal and the other

H_2O molecule is encountered as water of hydration. The broad overlapping bands associated with O-H in the complex do not allow the differentiation between the environments of the two H_2O molecules in the complex.

The formula for the Ru(III) complex $Ru(DAP)Cl_3 \cdot \frac{1}{2}C_2H_5OH$ was assigned on the basis of its elemental analysis results. The presence of ethanol incorporated in the complex is ascertained by ν O-H, ν C-O, ν alkyl C-H and σ O-H present in the IR spectrum of the complex. Nuclear magnetic resonance measurements could not be run on the complex due to its insolubility.

Thermogravimetric analysis failed to detect the solvents of crystallization in the Rh(III) and Ru(III) complexes of DAP because of the rapid decomposition of the complexes upon heating.

3.4 Reactions of DTDA with metal ions

DTDA is obtained by the oxidation (formation of S-S linkage) of ATPH. It has four potential donor atoms. However, they are not suitably positioned to make DTDA behave as a tetradentate ligand bonded to one metal atom (Fig. 7).

The reactions of DTDA have not been hitherto well investigated[52]. However, several complexes of its parent precursor, ATPH, have been synthesized and their chemistry is well understood.

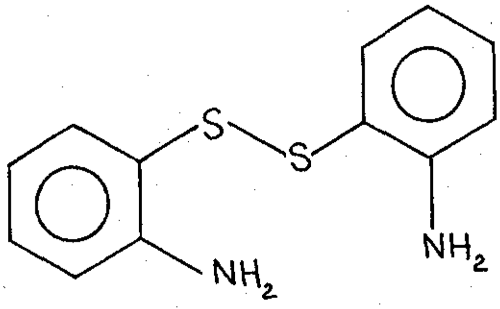


Fig-7

We have observed that DTDA behaves either as a neutral ligand, bonded most likely through its nitrogens, or it may dissociate by the breakage of the S-S bond and the formation of two ATP anions. One or more of these anions are then bonded to the metal as individual ligands.

The reactions of Nickel(II), whether as nitrate or perchlorate with DTDA afforded bis(2-aminothiophenolato)-nickel(II), $Ni(ATP)_2$. This complex has been previously synthesized from the reaction of ATPH and Ni(II)[83].

The reactions of the Cu(II) salts with DTDA afforded the complexes $Cu(DTDA)_3(ClO_4)_2.H_2O$, $Cu_2(DTDA)(ATP)_2Cl_2$ and $Cu_3(DTDA)(ATP)_2NO_3$. The IR spectra of these complexes show ν N-H at 3100-3200 cm^{-1} with no ν S-H at 2400-2600 cm^{-1}. The presence of water of hydration in the complexes is ascertained by ν O-H and σ O-H at 3400-3500 cm^{-1} and around 1650 cm^{-1} respectively.

The reaction of Pd(II) with DTDA afforded the dimeric complex $Pd_2(ATP)_2Cl_2$ (Fig. 8).

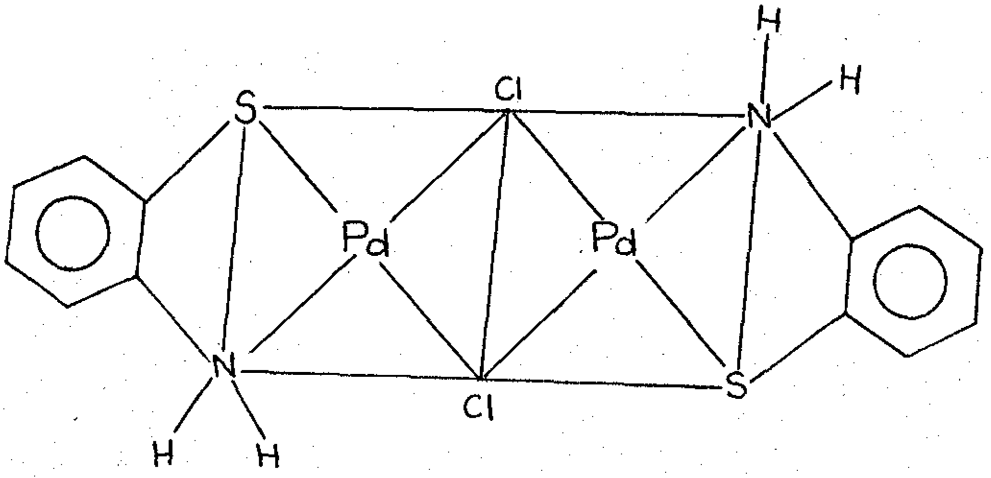


Fig-8

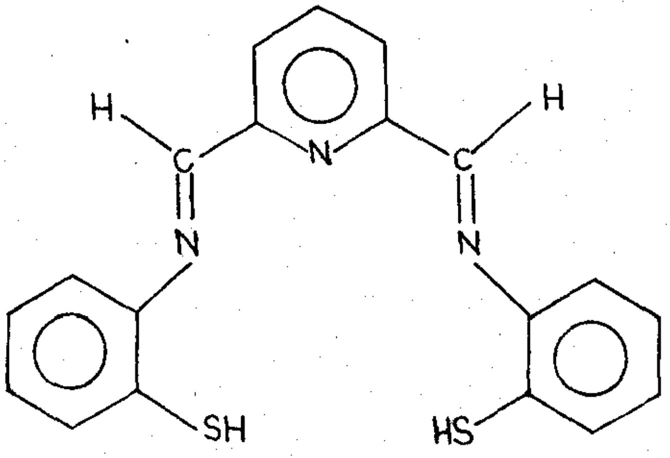
The IR spectrum of the dimeric Pd(II) complex shows absorption in the ν N-H region at 3190 cm^{-1} and in the ν Pd-Cl region at 265 cm^{-1} consistent with bridging chloride[77]. Nuclear magnetic resonance measurement on the complex could not be run due to its insolubility. The decomposition of $Pd_2(ATP)_2Cl_2$ with aqueous potassium cyanide produced ATPH indicating that DTDA was indeed cleaved upon its reaction with Pd(II).

3.5 Reactions of Schiff bases derived from DIAL with metal ions

a) DIAL with ATPH

1. In a neutral medium

DIAL was condensed with ATPH in ethanol as a solvent, with the intention of producing the Schiff base $ATPALH_2$. However, the compound obtained was 2,6-(dibenzothiazol-2-yl)pyridine (DBTP). The evidence for such formulation of the product consists of the following:



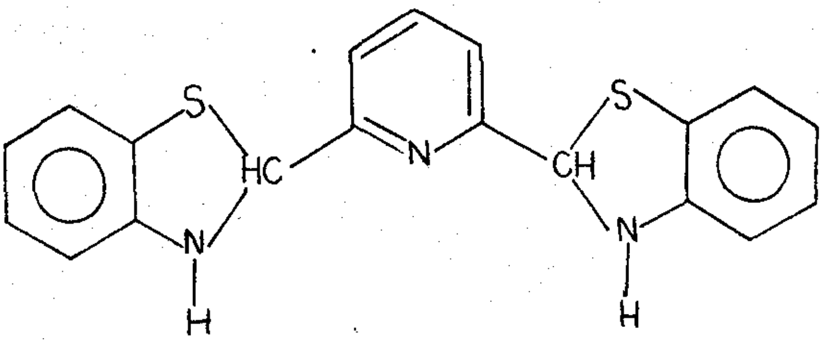
$ATPALH_2$

i) The found elemental analyses of the product are in good agreement with those calculated for the structure DBTP and not with those for $ATPALH_2$ since the hydrogen content of the latter is high.

ii) The absence of ν S-H at 2500-2600 cm^{-1} in the spectrum of the produced compound and the failure of its S-methylation disfavours the formation of ATPALH_2 as the Schiff base.

iii) The behaviour of the Schiff base produced as a neutral ligand in its reactions with metal ions as part of our work, favours the formulation DBTP.

The same product resulting from the condensation of DIAL with ATPH was obtained by a different route[57] consisting of the oxidation of 2,6-lutidine by iodine-dimethylsulfoxide to DIAL which was condensed in situ with ATPH to give DBTP. However, DIAL itself could not be isolated. Had this been possible a most feasible route for the preparation of DIAL would have been at hand. There is no doubt about the identity of the Schiff base DBTP produced, but the mechanism of its formation is not quite clear. In their paper, Livingstone and Nolan[57] proposed the formation of the following bis(benzothiazoline) as the condensation product which



was not isolated but was readily oxidized in situ with iodine-dimethylsulfoxide to produce DBTP. However, our condensation reaction does not involve any oxidation with iodine. It is either that $ATPALH_2$ was the condensation product which might have rearranged with oxidation to DBTP or the bis(benzothiazoline) product which was readily oxidized with atmospheric oxygen[84] in the ethanolic solution to produce DBTP.

2,6-(Dibenzothiazol-2-yl)pyridine DBTP was reacted with some compounds of Cu(II), Fe(III), Ni(II), Zn(II), Hg(II), Co(II), Ag(I), Pd(II), Pt(II), Ru(III) and Rh(III). The following complexes were obtained: $Cu(DBTP)Cl_2.H_2O$, $Cu(DBTP)Br_2$, $Fe(DBTP)_2Cl_3.H_2O$, $Ni(DBTP)_2(ClO_4)_2.2H_2O$, $Zn(DBTP)Cl_2$, $Hg(DBTP)Cl_2$, $Hg(DBTP)Br_2$, $Co(DBTP)I_2$, $Ag(DBTP)ClO_4$, $Pd_2(DBTP)Cl_4$, $Pt_4(DBTP)_3Cl_8.2H_2O$, $Ru(DBTP)Cl_3.C_2H_5OH$ and $Rh(DBTP)Cl_3.2H_2O$.

The molecular formulas of the complexes obtained were assigned on the basis of their found analyses. The complexes are practically insoluble in common organic solvents.

The ligand DBTP may behave as mono-, bi- or tridentate. It is rather difficult to decide which donor atoms are involved in bonding to the metal. Electron spin resonance would help solve this problem with complexes of paramagnetic ions e.g. Cu(II). However, the insolubility of the complexes makes the confirmation of their proposed structures almost impossible. Therefore, the structures proposed here for the complexes are tentative and are based on the known chemistry of the metal ions involved.

The Ni(II) and Fe(III) complexes of DBTP are octahedral. The Ni(II) complex is diamagnetic suggesting that the ligand is rather strong field. Its conductivity measurement in dimethylsulfoxide at room temperature shows that it is a 1:1 electrolyte. The Fe(III) complex is of high spin (μ eff = 5.11 B.M.), a value common for paramagnetic Fe(III) complexes[57] and its conductivity measurement in DMF at room temperature shows that it is a 1:1 electrolyte.

$Cu(DBTP)Cl_2$ and $Cu(DBTP)Br_2$ are presumably square planar since the ligand is rather strong field. The appearance of two bands in each of the complexes in the M-Cl region of the IR spectra suggests that the complexes probably have a cis configuration (Fig. 9).

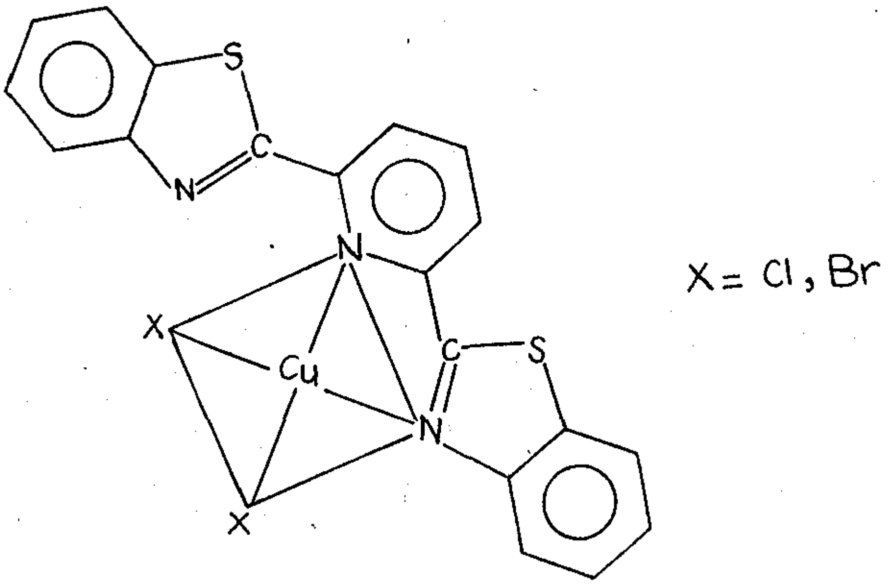


Fig - 9

$Zn(DBTP)Cl_2$, $Hg(DBTP)Cl_2$, $Hg(DBTP)Br_2$ and $Co(DBTP)I_2$ are most likely tetrahedral, involving a bidentate ligand (Fig. 10). The ligand is bonded to these metals through the pyridine nitrogen (the most basic) and one of the exapyridine nitrogens.

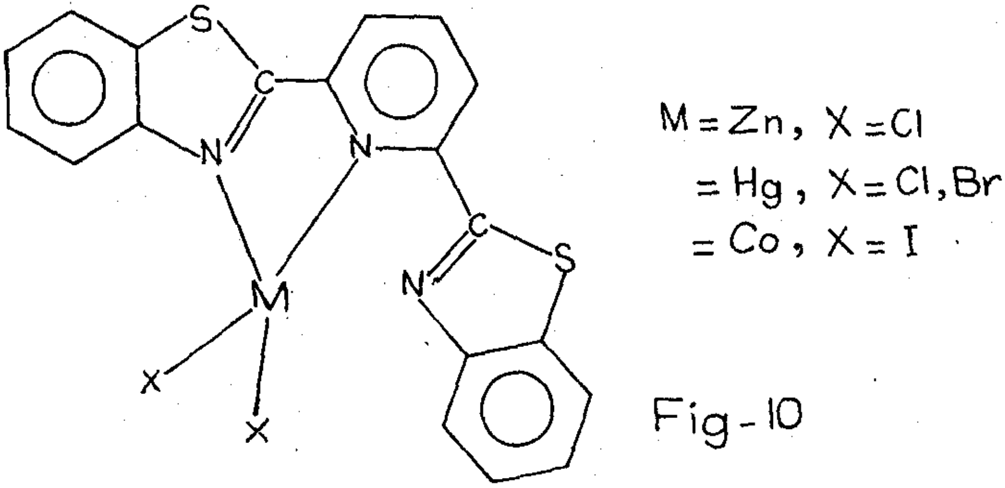


Fig-10

The Pd(II) complex of DBTP is probably dimeric ($Pd_2(DBTP)Cl_4$) with bridging chlorine atoms ν Pd-Cl at 260 cm^{-1} and terminal ν Pd-Cl at 335 cm^{-1} (Fig. 11). Due to its insolubility, the molecular weight of this Pd(II) complex could not be determined.

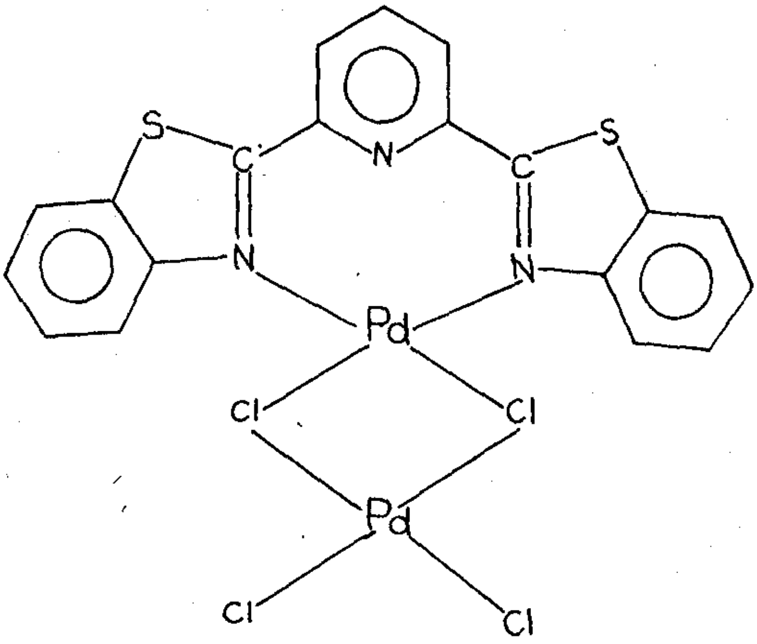


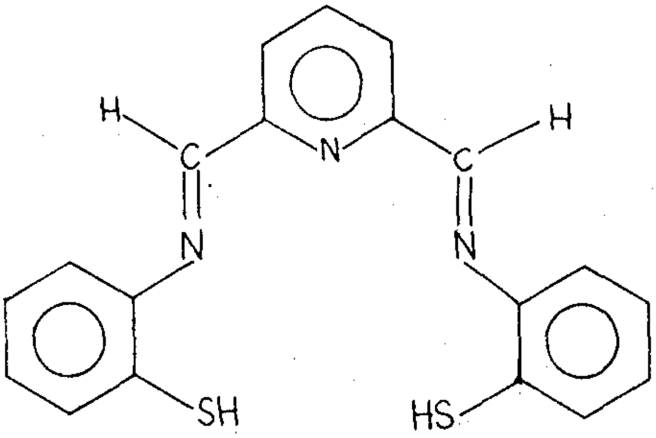
Fig-11

Ru(DBTP)$Cl_3.C_2H_5OH$ and Rh(DBTP)$Cl_3.2H_2O$ are probably octahedral with a bidentate ligand. Hexa-co-ordination is satisfied by solvent molecules. The conductivity measurements of these complexes in dimethylsulfoxide at room temperature show that they are non-electrolytes.

The presence of water of hydration in the complexes of DBTP is ascertained by IR and crudely indicated by a condensate collected at the top of a melting point tube after heating a DBTP complex in such a tube. The presence of ethanol incorporated in the Ru(III) complex was ascertained by IR and NMR spectroscopy. The insolubility of the other complexes did not allow any NMR measurements.

2. <u>In a basic medium</u>

In order to prepare ATPALH_2, the expected

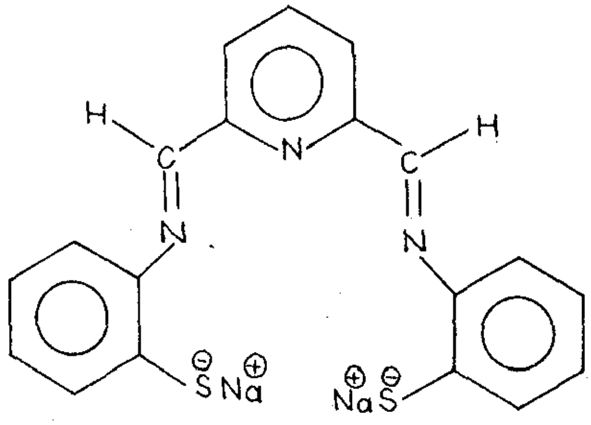


ATPAL H_2

condensation product of DIAL and ATPH, the reaction was carried out in a basic medium. The Schiff base solution (no Schiff base was isolated) was reacted with Cu(II), Pd(II) and Ru(III). Copper(II) afforded the complex Cu(ATPAL).2HCl.H_2O and Ru(III) the complex Ru($ATPALH_2$)Cl_3.½C_2H_5OH. The molecular formulas of the complexes were assigned on the basis of their found analyses (Table XXVII) and IR spectra.

Under the same experimental conditions Pd(II) gave bis(2-aminothiophenolato)palladium(II), Pd$(ATP)_2$ which has been previously reported[83] and which upon treatment with concentrated hydrochloric acid produced bis(2-aminothiophenolato)palladium(II) dihydrochloride, Pd$(ATP)_2$.2HCl (Fig. 12).

The isolation of the Schiff base



was attempted by reacting DIAL with ATPH in a basic medium. The product obtained could not be identified. However, when it was reacted with concentrated HCl, 2-ammonium thiophenol chloride was obtained which upon its reaction with cis-dichlorobis(benzonitrile)-palladium(II) yielded $Pd(ATP)_2.2HCl$.

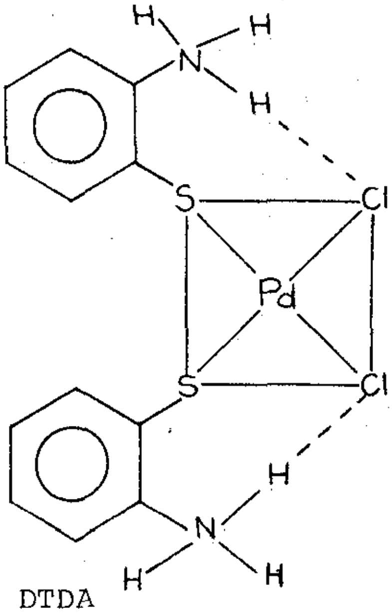
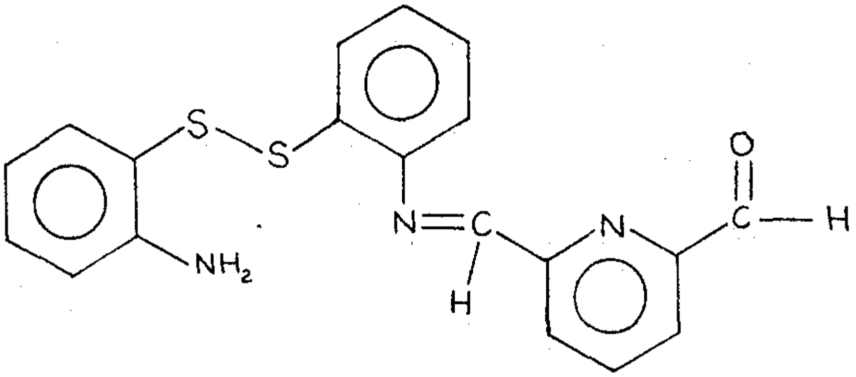


Fig-12

b) DIAL and DTDA

The reaction of DIAL with DTDA yielded the Schiff base DTDAL.

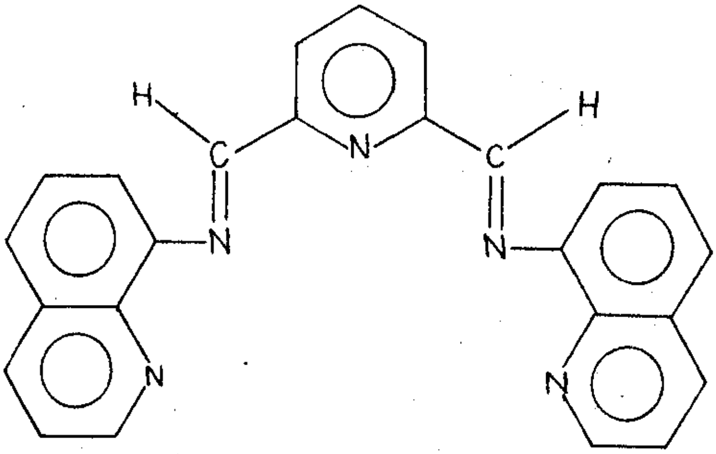


DTDAL

The structure of DTDAL was assigned on the basis of its elemental analysis and IR spectrum which shows ν C=O at 1700 cm^{-1} and ν N-H at 3410 cm^{-1}. Unfortunately, no complexes of this Schiff base could be synthesized neither by direct reaction with metal salts nor by the reaction of metal salts with a mixture of its constituent amine and aldehyde.

c) DIAL and AMQ

A mixture of DIAL and AMQ was reacted with $Cu(ClO_4)_2.6H_2O$, $CuCl_2.2H_2O$, $AgClO_4$, $Co(ClO_4)_2.6H_2O$, $ZnCl_2$, K_2PtCl_4, $RhCl_3.3H_2O$ and $RuCl_3.3H_2O$. Two types of complexes, monomeric and trimeric, of the Schiff base AQAL were obtained.



AQAL

The monomeric complexes of AQAL are $Cu(AQAL)(ClO_4)_2.4H_2O$, $Ag(AQAL)ClO_4$ and $Co(AQAL)(ClO_4)_2.2H_2O$. Speculation as to the geometry of these complexes requires further physiochemical measurements which could not be carried out in the present work due to the insolubility of the complexes. However, the stereochemistry of the ligand, presumably square planar, suggests that only some of the potential N donor atoms are involved in bonding to the metal.

The trimeric complexes obtained are $M_3(AQAL)_2Cl_n$: M = Cu, Pt, Zn; n = 6; M = Rh, Ru; n = 9. Again, feasible geometry of these complexes can be proposed if further physicochemical measurements were possible e.g. molecular weight determinations, ESR and others. Bridging in these complexes should take place through the ligands. Metal-metal bonding is not feasible due to the bulkiness of the ligand. The repeated occurrance of the oligomers as trimers is rather remarkable. It seems that after the ligand has formed a monomeric complex with the metal ion, it is left with bonding ability via the unused N donor atoms on it. The unused capacity in two monomers may be utilized by a third metal ion to form a trimer with a metal: ligand ratio of 3:2.

The molecular formulas of the complexes of AQAL were assigned on the basis of their found analyses. Infrared spectroscopy showed the absence of any absorption bands due to ν C=O and ν N-H suggesting no carbonyl or NH_2 groups. It showed the presence of absorption bands due to C=N and C=C stretching frequencies and bands due to pyridine ring vibrations (Table XXXV). The presence of water of hydration in the complexes was ascertained by IR where an O-H stretching frequency was shown in the region 3400-3600 cm^{-1} and O-H deformation around 1650 cm^{-1}, and it was crudely indicated by a condensate collected at the top of a melting point tube after heating the AQAL complex in such a tube. Nuclear magnetic resonance measurements could not be run on the complexes of AQAL due to their insolubility.

3.6 DIAL and DAP complexes

a) Reactions of DIAL complexes with DAP

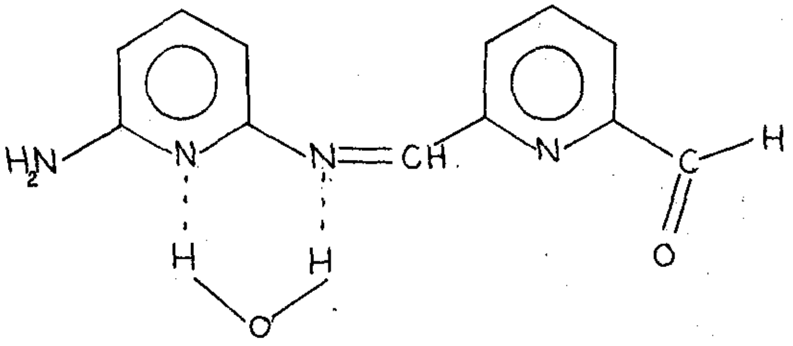
DIAL complexes of Cu(II), Pt(II), Pd(II), UO_2^{++} and Ni(II) were reacted with DAP in an attempt to effect the condensation of DIAL with DAP to form square planar (template) Schiff base. Only Cu(II) afforded a Schiff base complex, $Cu(APALAP)Cl_2.3H_2O$, with meaningful analysis (the structure of the ligand APALAP is shown on p. 123. The Cu(II) complex did not show any IR absorption in the ν C=O region but showed bands at 3305 cm^{-1} due to ν N-H.

The water of hydration in the Cu(II) complex is ascertained by its IR absorption bands at 3400 cm^{-1} and 1650 cm^{-1} due to ν O-H and σ O-H respectively and by the condensate collected at the top of the tube when a sample of the complex was heated. Nuclear magnetic resonance measurements could not be run due to the insolubility of the complex.

The attempt to decompose the complex with aqueous potassium cyanide in order to isolate the ligand APALAP was unsuccessful. It resulted in the hydrolysis of the expected Schiff base into its component DIAL and DAP. This is suggested by the elemental analysis of the decomposition product and by the occurrence of ν C=O and ν N-H in its IR spectrum.

b) Reaction of DIAL with DAP

The condensation of DIAL with DAP produced the yellow Schiff base DAPAL.H_2O which was characterized

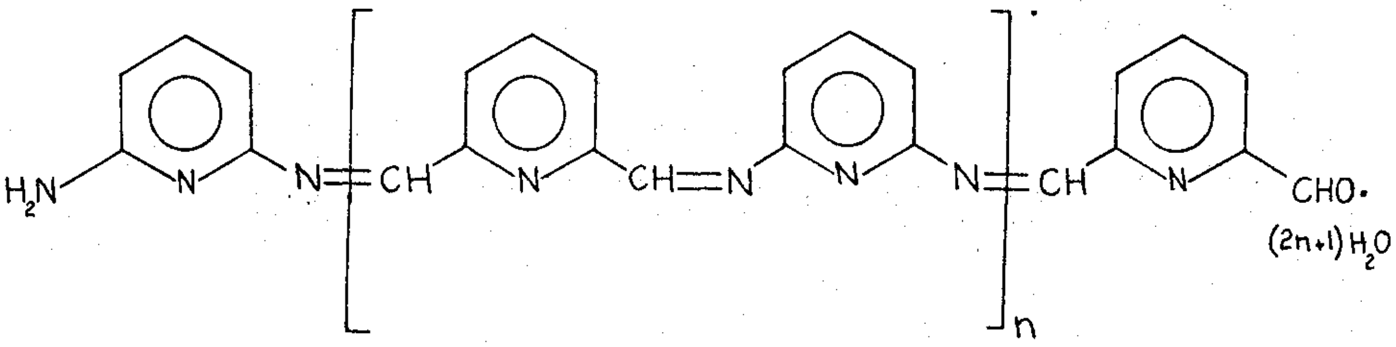


DAPAL·H_2O

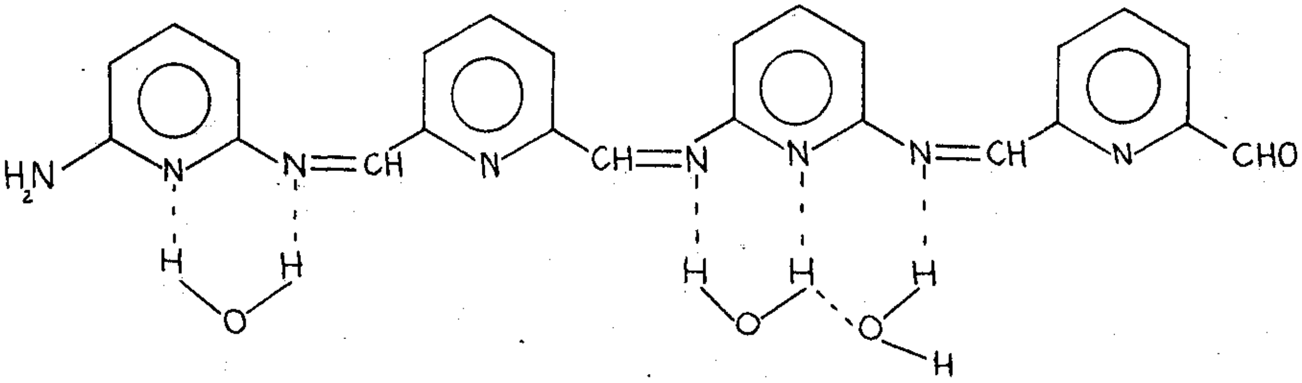
by elemental analysis and IR spectrophotometry. The IR spectrum shows the usual C=O stretching frequency of a carbonyl group and stretching and deformation frequencies of a free NH_2 group. Based on this information, structure DAPAL.H_2O is proposed for the Schiff base.

The molecule of water produced by the condensation reaction is probably hydrogen-bonded to the intracyclic N atom and to the N atom of the azomethine group (C=N) forming a six-membered ring. The involvement of the intracyclic N atom in H-bonding has been previously suggested in free DAP where a hydrogen bond is formed between an amine group of one molecule and an intracyclic N of another molecule[85]. This type of H-bonding probably explains the broadening of the absorption band in the IR spectrum extending from 1520-1380 cm^{-1} where a shoulder and a strong band are observed at 1490 cm^{-1} and 1455 cm^{-1} respectively. The bands in this region are attributed to the C=N and the C=C in the substituted pyridine ring and to the external azomethine stretching frequencies.

A compound such as DAPAL.H_2O with free CHO and NH_2 functional groups and low molecular weight is expected to dissolve in common organic solvents. It's being insoluble, except in concentrated sulfuric and nitric acids, would rather suggest a polymeric structure of the formula:



For n = 2, three molecules of water are expected to be present and these are possibly involved in H-bonding as shown in the following structure:



It seems that each water molecule produced by the condensation reaction does not go very far from the site of the reaction and remains H-bonded to the neighbouring N-atom.

c) Reactions of a mixture of DIAL and DAP with metal ions

$Ni(ClO_4)_2.6H_2O$ was reacted with a mixture of DIAL and DAP in molar ratios of DIAL:DAP:Ni of 2:2:1 and 1:1:1. Two different compounds $Ni(L\text{-}A)(ClO_4)_2.5H_2O$ and $Ni(L\text{-}B)(ClO_4)_2.2H_2O$ were obtained (the structures of the ligands L-A and L-B are shown on p. 130).

$Ni(L\text{-}A)(ClO_4)_2.5H_2O$ is an open chain Schiff base metal complex. Its molecular formula was assigned on the basis of its elemental analysis. Its IR spectrum has the same absorption bands as those of the free ligand DAPAL.H_2O. The similarity between the IR spectrum of the ligand DAPAL.H_2O and that of $Ni(L\text{-}A)(ClO_4)_2.5H_2O$, in addition to their common insolubility, suggest that this Ni(II) complex is probably polymeric with metal ions bonded to the linear polymeric chain of the ligand.

The molecular formula of $Ni(L\text{-}B)(ClO_4)_2.2H_2O$ was assigned on the basis of its elemental analysis. The absence of an absorption band characteristic of C=O absorption and the absence of bands in the ν N-H region provide a strong evidence for a macrocyclic ligand (L-B). The strong broad absorption at 1085 cm^{-1} suggests that the perchlorate ion is not co-ordinated[86].

The presence of water of hydration in the two Ni(II) complexes was ascertained by IR spectroscopy and crudely indicated by the condensate formed at the top of the tube after heating the complexes. No NMR measurements could be run on the complexes due to their insolubilities.

In the complex Ni(L-B)$(ClO_4)_2 \cdot 2H_2O$, the ligand is expected to co-ordinate with the metal ion through the N atoms of the external azomethine group (Fig. 13) rather than the pyridine nitrogens (Fig. 14) because in (Fig. 14) we have seven-membered rings but in (Fig. 13) stable six-membered rings are formed.

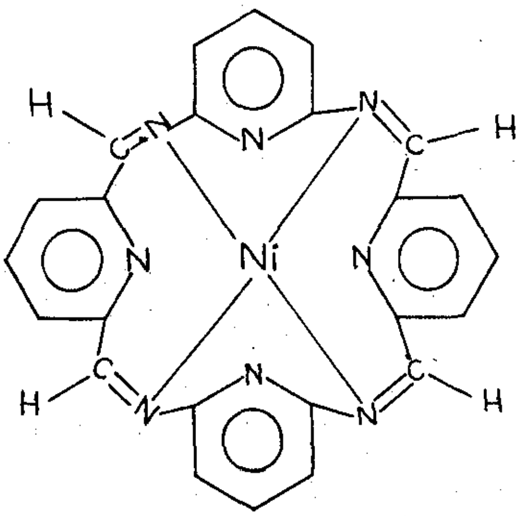


Fig-13

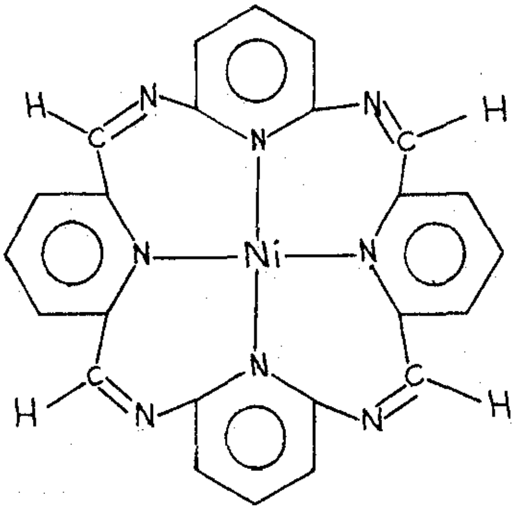


Fig-14

The macrocyclic complex Ni(L-B)$(ClO_4)_2 \cdot 2H_2O$ is diamagnetic. So it is either square planar tetraco-ordinate with water of hydration associated with the perchlorate ions, or low spin hexaco-ordinate octahedral, with two co-ordinated water molecules.

Ni(L-B)$(ClO_4)_2 \cdot 2H_2O$ was decomposed with aqueous potassium cyanide in an attempt to recover the free Schiff base (L-B). No molecular formula could be assigned to the recovered product. This could be due to partial decomposition (hydrolysis) of the Schiff base.

4. Bibliography

4. Bibliography

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