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THE PREPARATION AND INVESTIGATION OF SOME COORDINATION  
COMPOUNDS OF THE FIRST ROW TRANSITION METALS WITH  
THE LIGANDS, CYANOACETATE ANION, CYANOACETAMIDE,  
CYANOACETOHYDRAZIDE AND N-METHYL-2-PYROLIDINONE

by  
WILLIAM D. COURRIER

A Thesis  
Submitted to the Faculty of Graduate Studies through the  
Department of Chemistry in Partial Fulfillment of  
the Requirements for the Degree of Master of  
Science at the University of Windsor

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1965

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## ABSTRACT

Coordination compounds of some first row transition elements with various ligands, containing both oxygen and nitrogen donor atoms, have been prepared in this laboratory. This investigation concerns complexes made with cyanoacetate anion, cyanoacetamide and cyanoacetohydrazide as ligands. In addition, some complexes have been made with the cyclic amide N-methyl-2-pyrrolidinone (N-methyl- $\gamma$ -butyrolactam) as ligand.

The compounds isolated have been characterized by various means--infrared and ultraviolet and visible spectroscopy, conductance studies, and quantitative analyses. The analyses and conductance studies have been used in conjunction with the spectra to establish stoichiometries. The infrared spectra have been used to determine the type of metal-ligand bonding involved. Bonding through the carbonyl oxygen and through the nitrile nitrogen has been observed.

Several of the complexes prepared have been further characterized by partial ultraviolet and visible spectra and these latter interpreted in terms of crystal field theory.

## ACKNOWLEDGMENTS

I must express my deepest appreciation of the guidance, friendship, and advice of Dr. R. J. Niedzielski during the course of this work.

To the University of Windsor, for a laboratory assistantship and to the Ontario Department of University Affairs for a Graduate Fellowship, I express my heartfelt thanks.

I would like to thank Mr. David Hill for his efforts in obtaining the infrared spectra used in this work. Moreover, I am indebted to the staff of the university and my fellow students who have helped me in many ways.

I would be remiss in my duties if I did not give special thanks to my parents for their help and guidance over the years, and especially to my mother for typing this thesis.

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## CHAPTER I

### INTRODUCTION

#### A General Considerations

One of the characteristics of the transition elements is that these metals, in addition to possessing primary or ionic valences, also possess secondary valences, sometimes referred to as coordination numbers. These secondary valences may be satisfied by other atoms which have a pair of electrons available to form the two electron bond. Molecules which contain such atoms capable of satisfying the secondary valences of a metal are called ligands and the atoms themselves donor atoms or simply donors.

If a ligand contains one donor atom it is called a monodentate ligand. In the case that more than one donor atom is present, the ligand is said to be potentially polydentate; specifically it may be bidentate, tridentate or under proper conditions only monodentate. Polydentate ligands yield ring compounds in which several atoms of the ligand and the metal ion or atom form the ring. These ring compounds are called chelates because of a fancied resemblance of the ligand, particularly a bidentate ligand, to a crab claw.

For each metal, the secondary valences are specifically directed in space, that is, each coordination number has a definite geometry associated with it. Where several geometries are possible, the nature of the metal and surrounding ligands will determine which geometry will exist. For example, the coordination number four admits of

two possible geometries, square planar or tetrahedral. If the metal is zinc, tetrahedral geometry is the more likely. On the other hand, a square planar configuration is possible with copper. Octahedral or distorted octahedral (long axial bonds) configurations are found for coordination number six. These two coordination numbers, four or six, are exhibited by members of the first row transition metal series. Some of these metal elements, such as manganese (II), iron (III), cobalt (II), nickel (II) and copper (II), exhibit coordination numbers of both four and six. Chromium (III) has a coordination number of six only, while zinc (II) has a coordination number of four. The six coordinate species are all octahedral, though some may be distorted. Of the four coordinate species, complexes of manganese (II) and zinc (II) and sometimes cobalt (II) and nickel (II) possess tetrahedral geometries, while copper (II) and usually cobalt (II) and nickel (II) complexes possess square planar geometries.

The geometrical arrangement of ligands around a central metal ion is referred to as the coordination sphere, to distinguish the components as those involved in coordinate rather than some other type of bonding.

A myriad of coordination compounds of transition metal elements with ligands, having oxygen and/or nitrogen as donors, have been prepared. These works are surveyed in books on coordination chemistry such as those by Bailar,<sup>1</sup> Jørgensen,<sup>2</sup> Jones<sup>3</sup> and others. Generalizations have been made about the donor abilities of oxygen and nitrogen atoms, in ligands containing both, to the various transition metals. Oxygen-metal bonds seem to be formed in preference to nitrogen-metal bonds in iron (III), cobalt (II), and manganese (II) complexes. Nitrogen-metal bonds have preference over oxygen-metal bonds in copper (II) and

nickel (II) complexes.<sup>3</sup>

In order to avoid the complication of coordination by the anion of the metal salt starting material, metal perchlorates and metal nitrates are used. This is not to say, however, that these species are never involved in the coordination sphere of complexes. On the contrary, nitratopentammine cobalt (II) salts<sup>4</sup> have been known for some time and more recently, coordination of perchlorate anion has been reported by Wickenden and Krause.<sup>5</sup> Under normal conditions, however, the donor abilities of these anions are less than those of most ligands.

Three of the ligands used, cyanoacetate anion, cyanoacetamide and cyanoacetohydrazide are potentially bidentate; they contain both oxygen and nitrogen atoms which are capable of acting as donors. It was therefore anticipated that in at least some cases chelates would be formed. Chelation is considered to increase the stability of a complex relative to that of a non chelated complex. The chelate rings formed would be either five or six membered rings, which are considered to be the most stable ring sizes for chelates.

The remaining ligand, N-methyl-2-pyrrolidinone, is a cyclic amide. The ligand characteristics of amides have been studied extensively and the investigations related to this one are those by Drago and co-workers<sup>6,7</sup> and Madan and co-workers.<sup>8</sup> Madan's group used caprolactam, a cyclic amide having one more carbon in the ring than N-methyl-2-pyrrolidinone.

A series of metal perchlorate complexes with N-methyl-2-pyrrolidinone have been prepared in this laboratory by Brother Gerard Znider.<sup>9</sup>

The present work involved the preparation of two other compounds as the perchlorates and several as the chlorides

of N-methyl-2-pyrrolidinone-metal ion complexes. Some compounds of this type have been recorded in both English<sup>10</sup> and German<sup>11</sup> patents.

## B Oxygen and Nitrogen Donors

### i) Carbonyl Oxygen

The four ligands used have one common feature-- the presence of a carbonyl oxygen as a potential donor. In cyanoacetamide, cyanoacetohydrazide and 1-methyl-2-pyrrolidinone the carbonyl group is associated with an amide type linkage, whereas in the cyanoacetate anion, it is associated with a carboxy anion.

Drago and co-workers<sup>6,12,13</sup> and Madan and Denk<sup>8</sup> have studied a series of N-substituted straight chain and cyclic amides as ligands. Coordination through the carbonyl oxygen has been observed with a concomitant lowering of the carbonyl stretching frequency. This behaviour of the carbonyl stretching frequency has also been observed by Jain and Rivest,<sup>14,15</sup> who used ethylcyanoacetate as ligand and observed a decrease of up to  $90 \text{ cm.}^{-1}$  in the carbonyl stretching frequency. Moreover, Hay<sup>16</sup> observed a similar decrease in carbonyl stretching frequency of metal chelates of diethyl oxaloacetate.

### ii) Nitrile Nitrogen

The nitrogen atoms in organic nitriles have fairly strong donor properties, especially toward the heavier metals. Coerver and Curan<sup>17</sup> have observed the nitrile frequency to increase up to  $111 \text{ cm.}^{-1}$  upon coordination. Furthermore, Jain and Rivest<sup>15</sup> observed an increase of 30 to  $50 \text{ cm.}^{-1}$  in the nitrile frequency of metal-halide chelates with ethylcyanoacetate.

The  $\text{C}\equiv\text{N}$  stretching frequencies of some substituted benzonitriles have been observed by Drago, Wayland and Carlson<sup>18</sup> to increase upon coordination to the Lewis acid

stannic chloride. This phenomenon has been explained by Brown and Kubata<sup>19</sup> who proposed that there is little drain at  $\pi$  electron density from the  $C\equiv N$  group and consequently little decrease in this force constant. The coupling effect is more important, and the vibrational frequency increases.<sup>20</sup>

### C Characterization of Coordination Compounds

#### i) Infrared Spectra

That frequency shifts of functional groups on ligands, when these coordinate with a metal ion, are observed has been mentioned previously. The presence of a shift in a group frequency in the spectrum of a complex species is a good indication that bonding occurs through one of the atoms in that group. Care must be taken in interpreting the spectra, however, as the presence of water in a sample can cause what appear to be band frequency shifts and even band splitting.<sup>21</sup>

#### ii) Electrical Conductivity Measurements

Measurements of electrical conductance are used to determine the charge types of complexes in solution. Predictions of the molar conductances for given charge types have been made and measurements are interpreted in terms of these predictions. For aqueous solutions the range of values for a few different charge types is given in Table I.<sup>3</sup>

TABLE I

#### Molar Conductance Values for Aqueous Solutions

Charge Type	Concentration	Molar Conductance Range
1:1 (2 ions)	.001 M	96-115 ohm <sup>-1</sup>
2:1 (3 ions)	.001 M	225-270 ohm <sup>-1</sup>
3:1 (4 ions)	.001 M	380-432 ohm <sup>-1</sup>
4:1 (5 ions)	.001 M	about 520 ohm <sup>-1</sup>

These values will, of course, vary with different solvents. Sutton<sup>22</sup> obtained values of 18-22 ohm<sup>-1</sup> for the molar conductances of some 1:1 electrolytes formed by dissolution of titanium (III) and titanium (IV) complexes in nitromethane. Moreover, some values characteristic of 1:1, 2:1 and 3:1 electrolytes in nitromethane as determined by Gill and Nyholm<sup>23</sup> are given in Table II.

TABLE II

## Molar Conductance Values for Nitromethane Solutions

Charge Type	Concentration	Molar Conductance
1:1	.0005 M	97 ohm <sup>-1</sup>
2:1	.0005 M	177 ohm <sup>-1</sup>
3:1	.0005 M	262 ohm <sup>-1</sup>

It has been observed that when complexes are easily dissociated, the conductivities of the resultant solutions are not characteristic of the charge type.<sup>24</sup>

## iii) Visible and Ultraviolet Spectra

The five d orbitals of a gaseous metal ion are degenerate and hence any d-d electronic transitions are forbidden. In the presence of ligands, however, a crystal field is set up which splits these degenerate orbitals into two levels, the  $t_{2g}$  and the  $e_g$ , the latter being of higher energy. The difference between these two energy levels is defined to be  $10Dq$ . With the degeneracy removed, d-d transitions between these levels are weakly allowed. These transitions give rise to absorption bands in the ultraviolet, visible and near infrared regions of the spectrum.

The nature of the removal of the d orbital degeneracy, or crystal field splitting as it is called, is determined by the number and spatial arrangement of the ligands in the crystal field. Orgel<sup>25,26</sup> has interpreted diagrammatically the increase in the energy levels of the metal atom which result from an increase in field strength (Figure I and II).

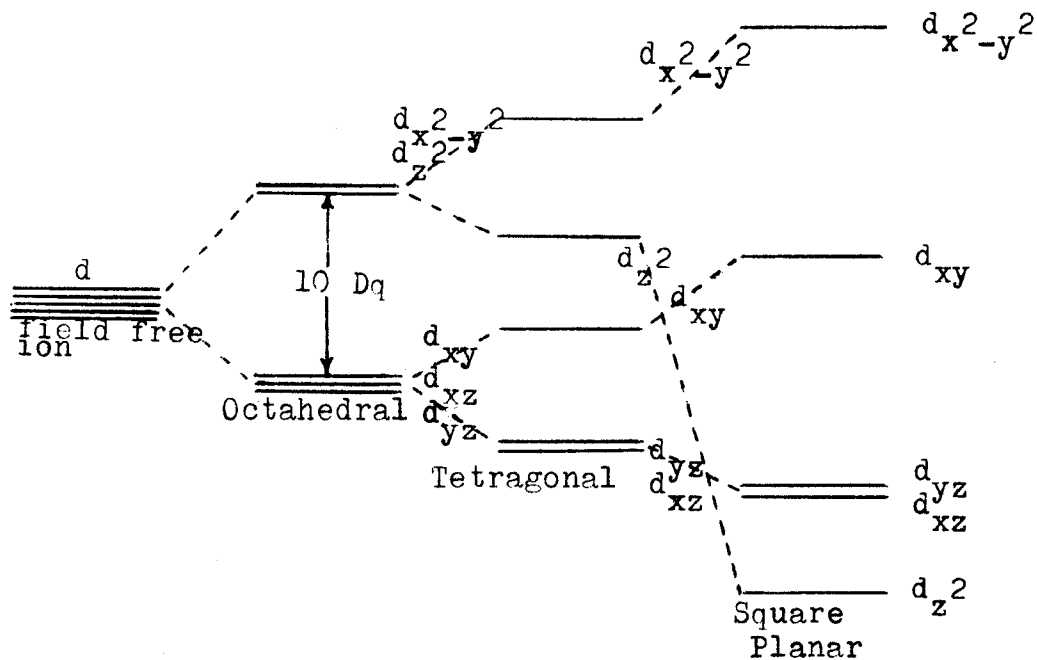


Figure I Energy level schemes for various coordination geometries.

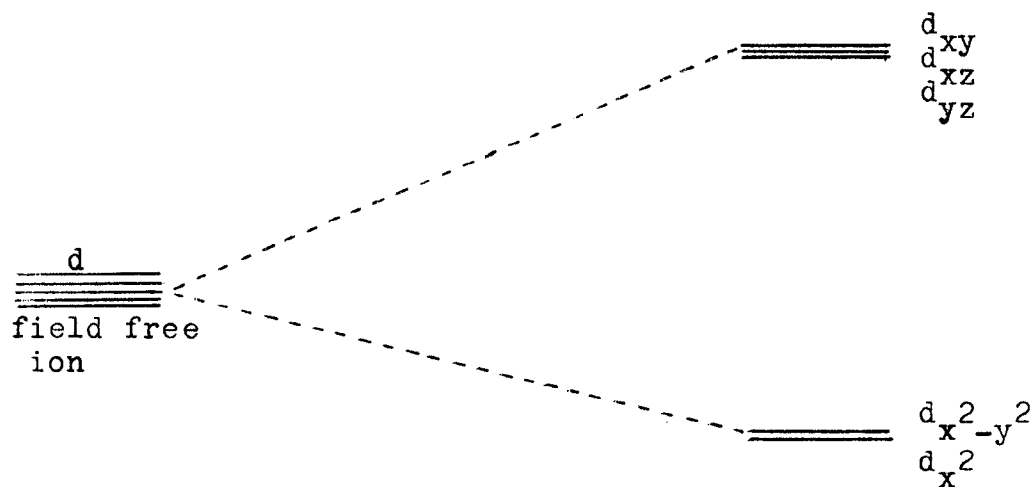


Figure II Energy level scheme for tetrahedral coordination geometry.



Depending on the nature of the ligands, the crystal field may be weakly or more strongly strengthened by the presence of the ligands and hence the general terms weak and strong field complexes. The designations high and low spin are also used and they refer to the degree of pairing of the electrons in the  $t_{2g}$  and  $e_g$  orbitals. Thus, an octahedral species with three unpaired electrons in the  $t_{2g}$  level and one electron in the  $e_g$  level would be termed high spin; whereas a species with two paired and two unpaired electrons in the lower level would be termed low spin.

For an octahedral environment, the molecular orbital energy levels would be as shown in Figure III. If now only the 3d orbitals be considered, for the  $d^9$ , copper (II), case the energy level diagram is rather simple (Figure IV).

Whenever there are more than one or less than nine d electrons, the energy level diagrams are more complicated, as there are a number of different energy states corresponding to the various d electron configurations of the free ion. Quantum mechanical calculations are required to obtain the details of these diagrams (Figures V and VI).

For the nickel (II) ion, that is a  $d^8$  case, the ground state of the free ion is the  $^3F$  and the excited states are the  $^3P$ ,  $^1G$ ,  $^1D$  and  $^1S$  (Figure V). In the ground state and in the  $^3P$  state there are two unpaired electrons; in other states, the  $^1G$ ,  $^1D$  and  $^1S$ , all the electrons are paired.

If the crystal field energy is large, the energy states will be arranged according to the occupancy of the  $t_{2g}$  and  $e_g$  orbitals. Thus, there will be a set of  $(t_{2g})^6(e_g)^2$  states, a set of  $(t_{2g})^5(e_g)^3$  states and a set of  $(t_{2g})^4(e_g)^4$  states. The ground state of the free ion  $^3F$

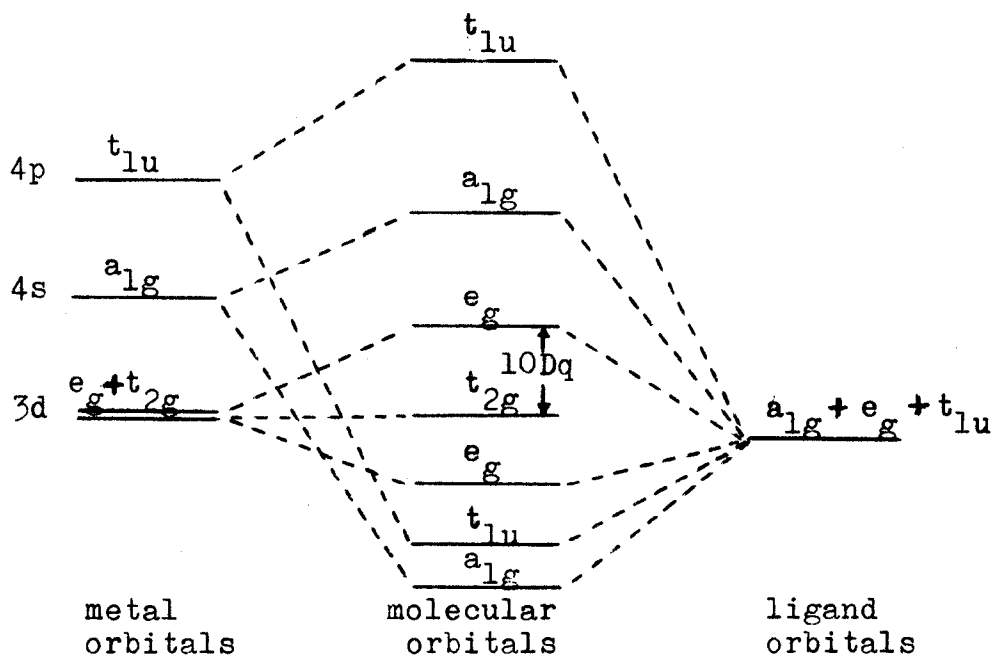


Figure III The molecular-orbital energy level diagram for an octahedral complex.

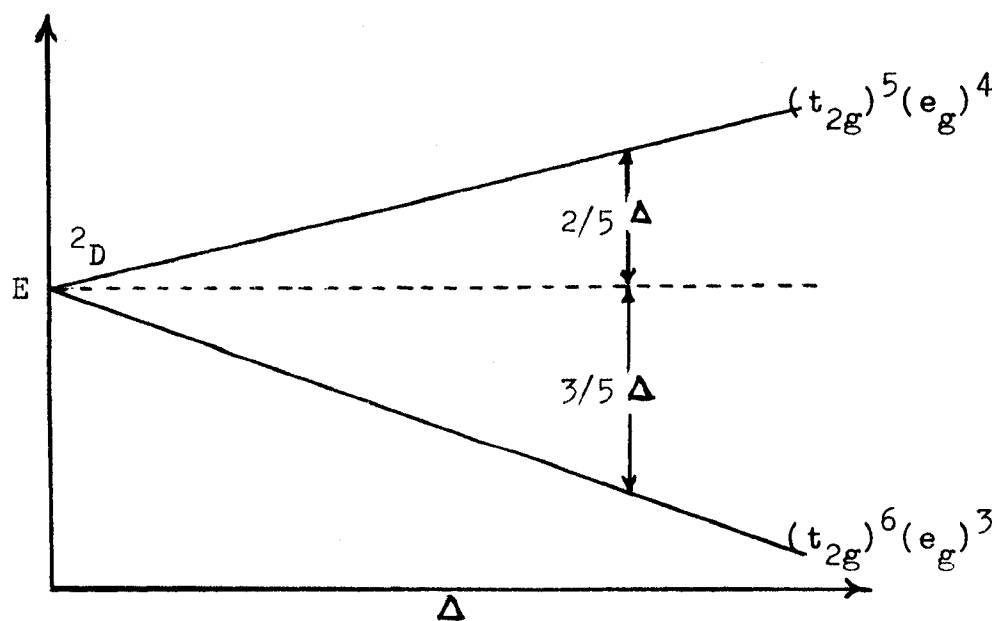


Figure IV Energy level diagram for a  $d^9$  ion.

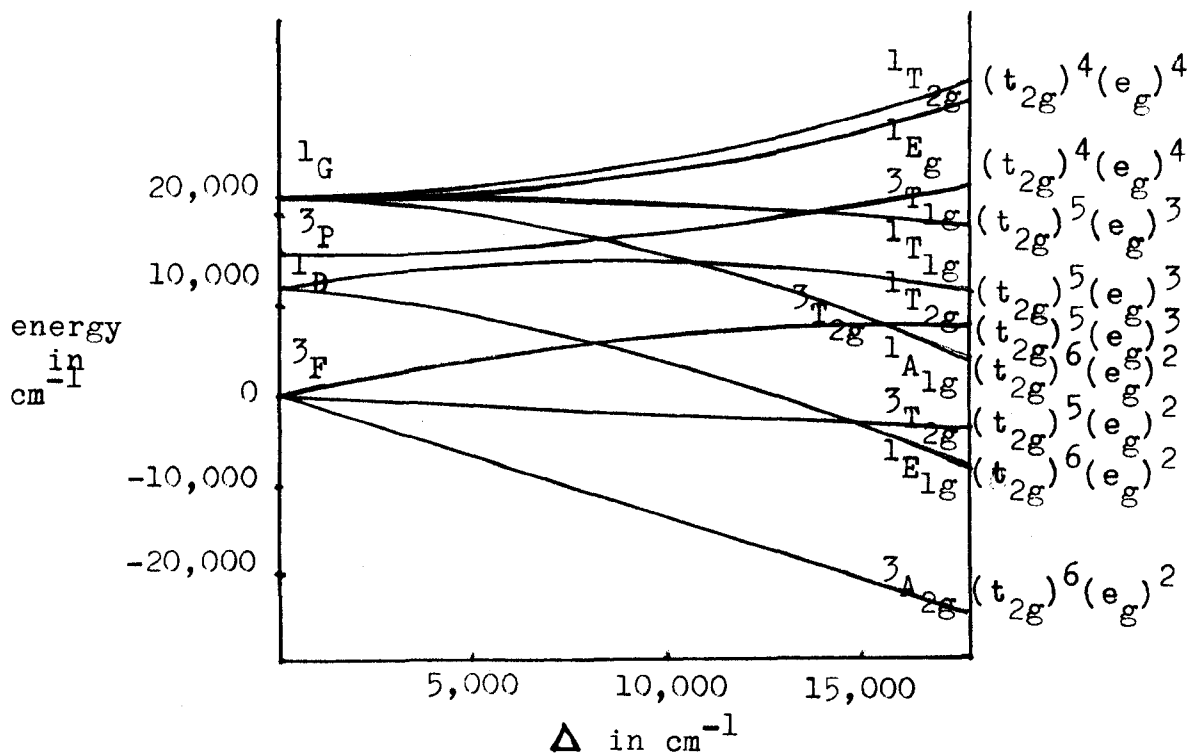


Figure V Energy level diagram for a  $d^8$  ion.

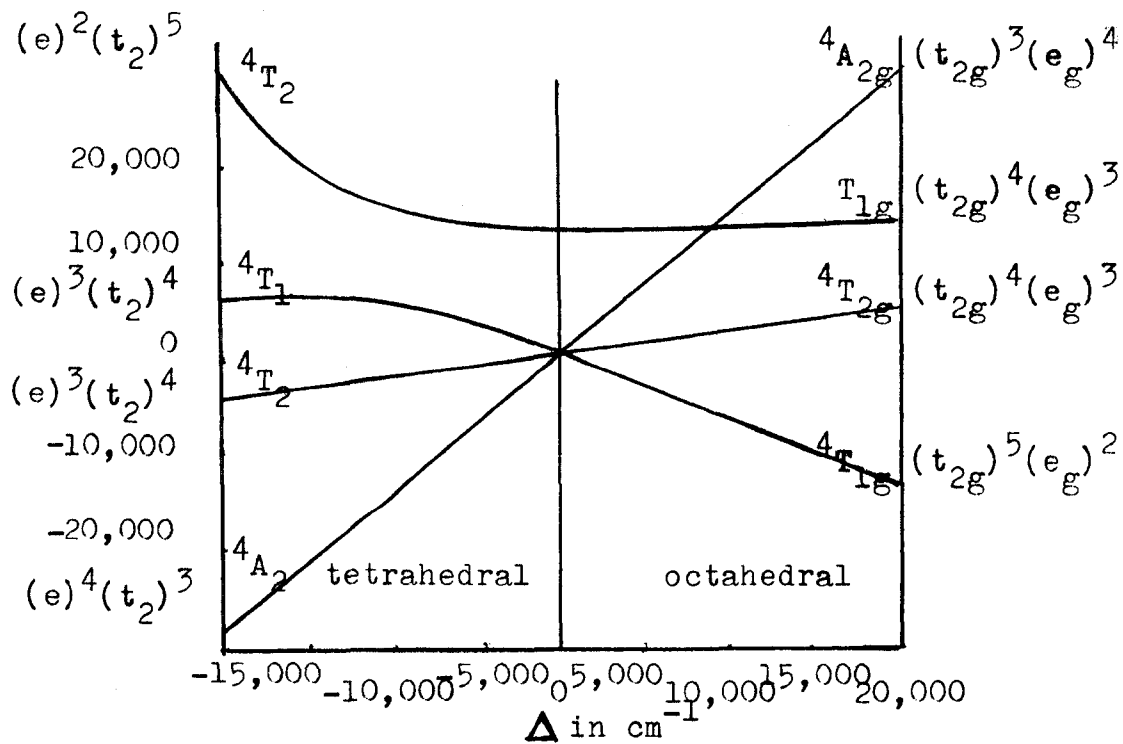


Figure VI Energy level diagram for a  $d^7$  ion.

whose energy diverges linearly for even small values of  $\Delta$  gives a pure configuration of the type  $(t_{2g})^n(e_g)^m$  even for weak crystal fields; whereas, the  $^3P$  state, whose energy varies nonlinearly for small values of  $\Delta$ , gives a mixed strong field configuration--that is, a mixture of  $(t_{2g})^6(e_g)^2$  and  $(t_{2g})^5(e_g)^3$  configurations for a weak crystal field. As the strength of the crystal field increases, however, a pure strong field configuration  $(t_{2g})^5(e_g)^3$  is obtained.

For the  $d^7$  case, the energy of even the ground state does not vary linearly with  $\Delta$ . Therefore the first state or ground state in even a strong crystal field is not a pure  $(t_{2g})^5(e_g)^2$ , (Figure VI). However, for octahedral cobalt (II) complexes the crystal field is usually strong enough that the deviations from a pure  $(t_{2g})^5(e_g)^2$  configuration are small enough to be neglected.

The absorption bands observed in the ultraviolet, visible and near infrared regions of the spectrum for transition metal complexes are the result of either charge transfer or the now weakly allowed d-d transitions. These d-d transitions may be explained if the environment of the ion lacks a centre of symmetry. In such a case, the d and p orbitals of the free ion become mixed to a certain extent. Therefore, an electronic transition which in the free ion would involve electron transfer from one d orbital to a second d orbital, and hence be forbidden, would in the complex, involve a small amount of transfer from a d orbital to a p orbital and thereby be weakly allowed.

The intensity with which these transitions occur should be roughly proportional to the extent of the mixing of the d and p orbitals. The observed values of  $\epsilon_{\max}$ , the maximum extinction coefficient, for bands arising from such transitions are usually smaller than 50, whereas charge

transfer bands have extinction coefficients in the  $10^4$ - $10^5$  range.

The value of  $10Dq$  is the wave number in reciprocal centimetres of the first spin allowed absorption band. This usually occurs in the near infrared or visible region of the spectrum. For cobalt (II) values around  $8,000 \text{ cm.}^{-1}$  have been obtained;  $10Dq$  values for nickel (II) have been found to be in the same range. Other assignments have been made by Dunn<sup>27</sup> and those for nickel (II) and cobalt (II) are given in Tables III and IV.

TABLE III

Electronic Transitions and Frequencies for  
Nickel (II) Complexes

$3A_{2g} \longrightarrow$	$3T_{2g}$ (F)	$8,600 \text{ cm.}^{-1}$
$\longrightarrow$	$3T_{1g}$ (F)	$13,500 \text{ cm.}^{-1}$
$\longrightarrow$	$1E_g$ (D)?	$15,400 \text{ cm.}^{-1}$
$\longrightarrow$	$1A_{1g}$ (G)?	$18,500 \text{ cm.}^{-1}$
$\longrightarrow$	$3T_{1g}$ (P)	$25,500 \text{ cm.}^{-1}$

TABLE IV

Electronic Transitions and Frequencies for  
Cobalt (II) Complexes

$4T_{1g} \longrightarrow$	$4T_{2g}$ (F)	$8-9,000 \text{ cm.}^{-1}$
$\longrightarrow$	$2E_g$	$11,000 \text{ cm.}^{-1}$
$\longrightarrow$	$4A_{2g}$ (F)	$16-18,000 \text{ cm.}^{-1}$
$\longrightarrow$	$4T_{1g}$ (P)	$20-21,000 \text{ cm.}^{-1}$

The magnitude of  $10Dq$ , that is, the magnitude of the

splitting between the lower  $t_{2g}$  and the upper  $e_g$  orbitals is a reflection of the coordinating ability of the ligands. The spectrochemical series or Fajans-Tsuchida<sup>28</sup> series is an arrangement of ligands in order of magnitude of the  $10 Dq$  values. Another series, the nephelauxetic series,<sup>29</sup> is an arrangement of ligands in order of increasing co-valent nature of bonding to the central metal ion.

## CHAPTER II

### EXPERIMENTAL METHODS

#### A Solvents and Reagents

##### i) Solvents

Fisher Laboratory reagent grade methanol and ethanol were dried by refluxing over magnesium turnings and then distilling the resulting mixture. The benzene and acetone were Fisher Certified A.C.S. reagents and were used without further purification or drying, as was the Fisher reagent ether (anhydrous). The 2,2-dimethoxypropane used was Eastman practical grade and it was not subjected to further purification.

##### ii) Reagents

The hydrated metal chlorides were obtained from the Fisher Scientific Company, and the perchlorates were obtained from the G. F. Smith Chemical Company. Of the ligands, cyanoacetic acid, cyanoacetamide and 1-methyl-2-pyrrolidinone, all were from Eastman Chemical Company and only the last was purified by distillation under vacuum. The fraction boiling at 58°C under 2 m.m. pressure was used. The cyanoacetohydrazide used was obtained from Aldrich Chemical Company and was not further purified. Fisher Laboratory reagent grade sodium metholate was used.

#### B Apparatus

##### i) Infrared Spectra

In the early stages of the work a Beckman model I.R. 5 spectrophotometer was used. Later, access to a Beckman model I.R. 10 spectrophotometer was obtained. In both cases the samples were made into potassium bromide pellets, the sample concentration of which was about .3%.

## ii) Ultraviolet and Visible Spectra

A Bausch and Lomb Spectronic 505 recording spectrometer was used to record spectra in the region 305 millimicrons to 750 millimicrons. Matched silica cuvettes one centimetre square were used with Fisher Certified 99.9 Mol.% pure methanol as solvent. Solutions of .04 M. concentrations were run against a pure methanol standard.

## iii) Conductivity Measurements

Conductivities were measured using a cell having platinized electrodes 1 centimetre apart. The cell was placed in a thermostated bath at 25.0°C for one hour after being filled with a solution of .001 M concentration which had been sitting in the bath over night. The conductivity bridge used was an Industrial Instruments Model R.C. 1B Conductivity Bridge which was phase balanced with a Heathkit Model DC-1 Decade Condenser. Solvents used were distilled water and Fisher Certified Reagent grade nitromethane.

## C Preparative Methods

### i) Sodium Cyanoacetate

Sodium metal (7.78 grams) was added to 300 millilitres of ethanol. After the sodium had been consumed, 21.27 grams of cyanoacetic acid, dissolved in a minimum amount of ethanol, were added very slowly whilst the solution was stirred with a magnetic stirrer. A fine white precipitate formed as the acid was added. Ten millilitres of 2,2-dimethoxypropane were added, and the mixture stirred for one hour. The pearlescent appearing precipitate was filtered and washed with several portions of diethyl ether and then dried in vacuo over phosphorus pentoxide. A fine creamy-white powder was obtained which melted at 179°C.

Alternatively, equimolar amounts of cyanoacetic

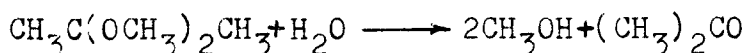


acid dissolved in methanol and sodium metholate suspended in methanol were mixed, the former being added to the latter. As the acid was added, the sodium metholate disappeared and a clear yellowish solution was obtained. The addition of about 25 millilitres of diethyl ether was sufficient to cause the precipitation of the sodium salt.

A solution of sodium cyanoacetate in methanol and 2,2-dimethoxypropane was prepared by dissolving .24 moles of the sodium salt in 500 millilitres of methanol to which 125 millilitres of 2,2-dimethoxypropane were then added and the volume made up to 1 litre with methanol.

#### ii) Cyanoacetate Anion Complexes

Fifteen millimoles of the hydrated metal perchlorate salt were dehydrated with a forty mole percent excess of 2,2-dimethoxypropane by stirring for at least two hours at room temperature.<sup>30</sup> The reaction--



goes 96% to completion with equimolar amounts of reactants.

In the case of zinc (II) and iron (III) perchlorates, the 2,2-dimethoxypropane solution turned a deep maroon colour, presumably due to the polymerization of 2-methoxy-1-propene,<sup>31</sup> a contaminant in the practical grade 2,2-dimethoxypropane. Distillation of the 2,2-dimethoxypropane under vacuum (b.p. 34° C at 130 m.m.) made no noticeable difference. For these two metal salts, the dehydration period was shortened to that length of time after which the solution had darkened noticeably.

A 2:1 mole ratio of the ligand to the metal ion was used, except for the iron (III) and chromium (III) complexes when a 3:1 mole ratio was used. The ligand was added as the methanol and 2,2-dimethoxypropane solution, described previously, or as a suspension in methanol. The former method proved more successful. The mixture was

stirred vigorously as the ligand was added and in all cases a change in colour of the metal ion solution was observed.

The complexes were precipitated with a ten-fold excess of diethyl ether. The iron (III), chromium (III), zinc (II) and manganese complexes formed oils which were crystallized by further treatment with diethyl ether. The crystalline complexes were powdered by stirring with several glass beads in successive portions of 2,2-dimethoxypropane and diethyl ether. After filtering, the complexes were dried in a drying pistol under vacuum over phosphorus pentoxide at the temperature of refluxing methanol.

Furthermore, variations of this procedure with respect to ligand to metal ion ratios were attempted, but these proved insignificant. In the case of copper (II), however, a complex was prepared using copper (II) chloride as starting material. Moreover, a copper (II) complex could be prepared in an aqueous medium using the perchlorate salt.

The nickel (II), cobalt (II), iron (III) and chromium (III) complexes were not prepared in a pure form. It was found that the reactions between the ligand and salts of these metals did not go to completion, and sodium cyanoacetate was precipitated with the complexes. No method was found to separate the mixtures as the solubilities of the complexes and sodium cyanoacetate are quite similar.

TABLE V

## Analyses of cyanoacetate anion complexes

Complex	Found			Calculated		
	C	H	N	C	H	N
$\text{Cu}(\text{L}^-)_2$	30.97	2.00	11.71	31.11	1.74	12.09
$\text{Mn}(\text{L}^-)_2 \cdot \text{H}_2\text{O}$	28.48	2.23	10.95	29.89	2.51	11.62
$\text{Zn}(\text{L}^-)_2 \cdot \text{H}_2\text{O}$	28.83	2.31	11.15	28.65	2.41	11.14
$\text{Na}_2[\text{Cu}(\text{L}^-)_2\text{Cl}_2]$	21.02	1.47	7.88	20.67	1.16	8.04
$\text{Ni}(\text{L}^-)_2 \cdot 2\text{H}_2\text{O}$	27.35	2.37	10.23	27.41	3.06	10.66
$\text{Co}(\text{L}^-)_2 \cdot 2\text{H}_2\text{O}$	27.48	2.31	9.26	27.39	3.06	10.65
$\text{Fe}(\text{L}^-)_3 \cdot 3\text{H}_2\text{O}$	26.11	3.68	6.84	29.85	3.34	11.61
$\text{Cr}(\text{L}^-)_3 \cdot 3\text{H}_2\text{O}$	28.42	2.40	9.50	30.17	3.38	11.73

Note - Cyanoacetate anion is represented by the symbol  $\text{L}^-$ .

## iii) Cyanoacetamide Complexes

Two methods of preparation were used to make the complexes with cyanoacetamide. The first method was very similar to that employed in making the cyanoacetate anion complexes. The ligand to metal ion ratio used was three to one and the cyanoacetamide was dissolved in a minimum amount of hot methanol before being added to the 2,2-dimethoxypropane solution of the metal ion (methanol and acetone from the dehydration reaction were also present). The treatment of the crystalline complexes and the methods used to crystallize any oils formed were the same as for the cyanoacetate anion complexes.

Better results were obtained when a method similar to that used by Madan and Denk<sup>8</sup> for making iron (III) and chromium (III) amide complexes was employed. The perchlorate salt, (0.075 moles), was dissolved in a minimum amount of acetone in a 500 millilitre round bottom flask.

The cyanoacetamide, (0.450 moles), was added slowly with stirring and the mixture heated gently until a clear solution was obtained. Two hundred fifty millilitres of benzene were then added, which caused the formation of a semi-solid. The solid was scraped from the sides of the flask and pulverized with a stirring rod. The flask was then fitted with a trap and condenser, as shown in Figure VII. Refluxing was continued until no more water droplets came down into the trap. The mixture was stirred while it cooled, then the precipitate was filtered off and powdered by stirring with several glass beads in diethyl ether. The complexes were dried in vacuo over phosphorus pentoxide in a drying pistol at the temperature of refluxing methanol.

Complexes were made with copper (II), nickel (II), cobalt (II), manganese (II), but very little product could be crystallized in the case of chromium (III). A crystalline product of unknown composition could be made with iron (III).

TABLE VI

Complex	Analyses of cyanoacetamide complexes					
	Found			Calculated		
	C	H	N	C	H	N
$[\text{Ni}(\text{La})_3](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$	20.64	2.70	16.20	20.48	2.67	15.92
$[\text{Co}(\text{La})_2, \text{CH}_3\text{OH}, \text{H}_2\text{O}](\text{ClO}_4)_2$	17.55	2.93	11.82	17.66	2.96	11.77
$[\text{Cu}(\text{La})_2](\text{ClO}_4)_2$	16.66	2.08	12.89	16.73	1.87	13.01
$[\text{Zn}(\text{La})_2, 2\text{CH}_3\text{OH}](\text{ClO}_4)_2$	20.03	3.24	11.24	19.35	3.25	11.28
$[\text{Mn}(\text{La})_2, \text{CH}_3\text{OH}, \text{H}_2\text{O}](\text{ClO}_4)_2$	17.97	2.42	13.61	17.81	2.99	11.87

Note: Cyanoacetamide is represented by the symbol La.

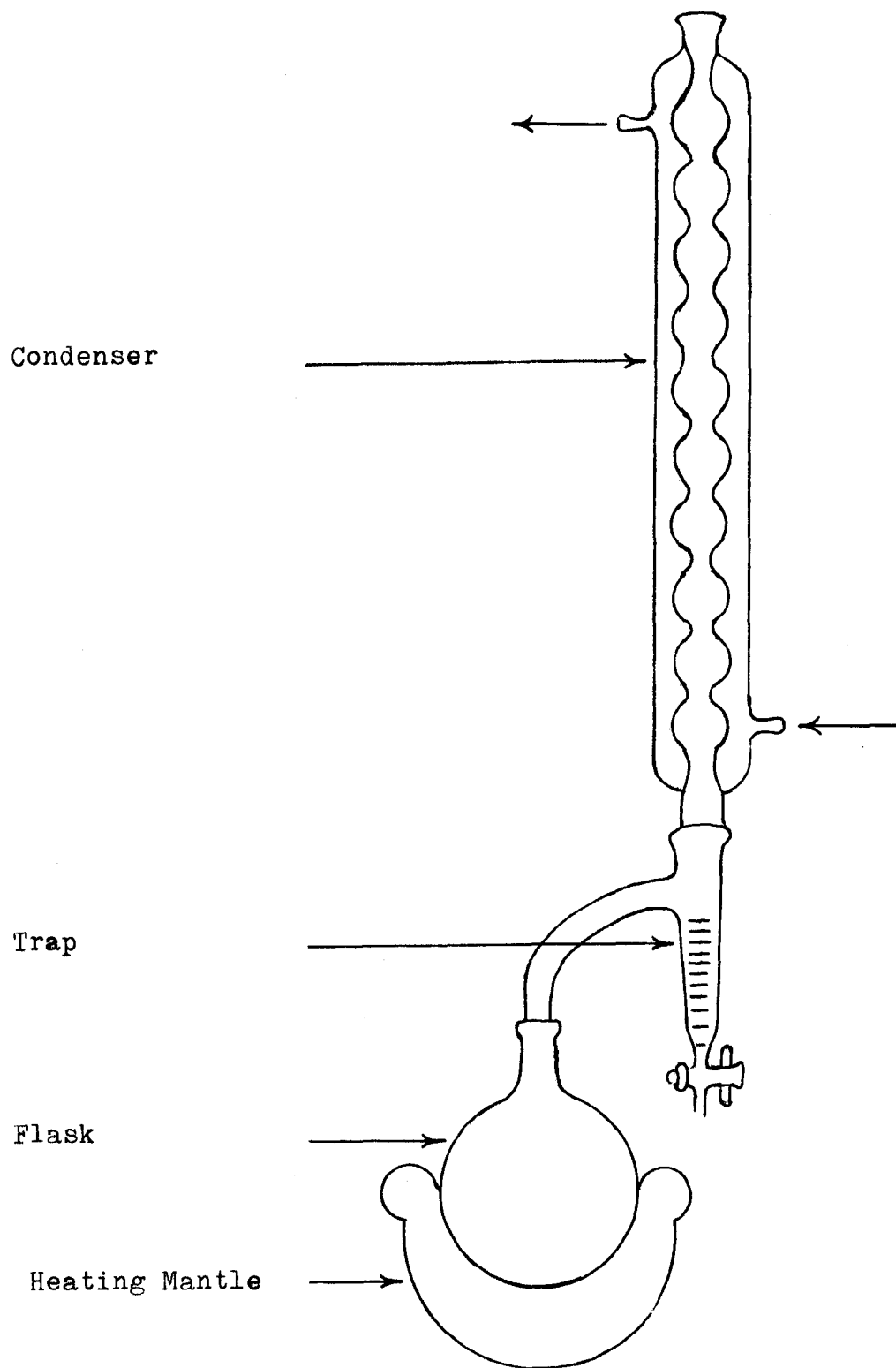


Figure VII Apparatus used for dehydration with benzene

## iv) Cyanoacetohydrazide Complexes

The complexes with cyanoacetohydrazide as ligand were prepared in the same manner that the cyanoacetamide complexes were prepared. The hydrated metal perchlorate salt, (0.0075 moles), was dissolved in about 5 millilitres of acetone and .0225 moles of cyanoacetohydrazide was added slowly. The mixture was heated gently till all the ligand had dissolved and then 250 millilitres of benzene were added. Oils were formed when the benzene was added but after a few minutes of refluxing these turned to semi-solids. Refluxing was continued till no more water droplets came down into the trap. The benzene was decanted off and the complexes were washed with diethyl ether, then powdered and dried as before.

The iron (III) and chromium (III) complexes with cyanoacetohydrazide could not be obtained in a stable crystalline form. Attempts were made to crystallize the oils formed from various solvents and solvent combinations but no success was achieved.

TABLE VII

Analyses of cyanoacetohydrazide complexes

	Found			Calculated		
	C	H	N	C	H	N
$[\text{Ni}(\text{L}_h)_2, 2(\text{CH}_3)_2\text{CO}] (\text{ClO}_4)_2$	25.23	3.96	14.65	25.20	3.88	14.69
$[\text{Co}(\text{L}_h)_2, 2(\text{CH}_3)_2\text{CO}] (\text{ClO}_4)_2$	25.75	4.02	14.89	25.19	3.88	14.69
$[\text{Mn}(\text{L}_h)_2, 2(\text{CH}_3)_2\text{CO}] (\text{ClO}_4)_2$	26.53	3.85	16.35	25.36	3.90	14.79
$[\text{Zn}(\text{L}_h)_2, 2(\text{CH}_3)_2\text{CO}] (\text{ClO}_4)_2$	26.31	4.02	15.32	24.91	3.83	14.53
$[\text{Cu}(\text{L}_h)_2, 2(\text{CH}_3)_2\text{CO}] (\text{ClO}_4)_2$	28.46	3.87	16.50	24.99	3.85	14.57

Note: Cyanoacetohydrazide is represented by the symbol  $\text{L}_h$ .

## v) N-methyl-2-pyrrolidinone Complexes

The iron (III) and chromium (III) perchlorate salts were dissolved in a minimum amount of acetone. A 6:1 mole ratio of ligand to metal ion was used, and the benzene, ligand, acetone and metal salt mixture was refluxed as before. Semi-solids were formed after about fifteen minutes refluxing time, but refluxing was continued until no more water droplets came down into the trap. The crystalline complexes were filtered, washed powdered, and dried as before.

The complexes with zinc (II), cobalt (II), copper (II), nickel (II) and manganese (II) chlorides were prepared in the same manner, even though the copper (II) chloride was anhydrous. The cobalt (II) complex could be obtained only in a semi-solid form, and the copper (II) complex was crystallized by dissolving the semi-solid in a benzene and diethyl ether mixture and allowing it to stand undisturbed at room temperature for about three weeks. The iron (III) and chromium (III) chloride complexes were not prepared.

TABLE VIII

Analyses of N-methyl-2-pyrrolidinone complexes

	Found			Calculated		
	C	H	N	C	H	N
$[\text{Fe}(\text{L}_p)_6](\text{ClO}_4)_3$	37.36	5.75	8.23	37.97	5.73	8.86
$[\text{Cr}(\text{L}_p)_6](\text{ClO}_4)_3$	37.37	6.01	8.13	38.12	5.76	8.89
$\text{Mn}(\text{L}_p)\text{Cl}_2$	27.15	4.64	6.26	26.69	4.03	6.23
$\text{Zn}(\text{L}_p)_2\text{Cl}_2$	35.83	5.47	9.63	35.90	5.42	8.38
$\text{Ni}(\text{L}_p)_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$	32.95	6.28		33.00	6.11	

Note: N-methyl-2-pyrrolidinone is represented by the symbol  $\text{L}_p$ .

## CHAPTER III

### RESULTS AND DISCUSSION

#### A Infrared Spectra

##### i) Cyanoacetate Anion Complexes

The carbonyl band frequencies and the nitrile band frequencies for sodium cyanoacetate, cyanoacetic acid and the cyanoacetate anion complexes are given in Table IX.

TABLE IX

Infrared spectral data for cyanoacetate anion complexes

Compound	Carbonyl band frequency	Shift in carbonyl band frequency	Nitrile band frequency	Shift in nitrile band frequency
cyanoacetic acid	1735	--	2260(sh.2245)	--
Na(L <sup>-</sup> )	1595	--	2242(sh.2205)	--
Cu(L <sup>-</sup> ) <sub>2</sub>	1645	50	2275(sh.2250)	33
Na <sub>2</sub> [Cu(L <sup>-</sup> ) <sub>2</sub> Cl <sub>2</sub> ]	1650	55	2280(sh.2250)	38
Mn(L <sup>-</sup> ) <sub>2</sub> ·H <sub>2</sub> O	1630	35	2265(sh.2230)	23
Zn(L <sup>-</sup> ) <sub>2</sub> ·H <sub>2</sub> O	1630	35	2255	13
Ag(I) salt	1600	5	2240	2
Fe(III) complex	1615	20	2260	18
Cr(III) complex	1625	30	2250	8
Ni(II) complex	1615	20	2295-2260(split)	53
Co(II) complex	1605	10	2280-2260(split)	38

If the carbonyl band and nitrile band frequencies for sodium cyanoacetate be taken as references, then shifts in the frequencies of both bands have been observed in all cases except the silver (I) compound. Since no frequency shifts were observed with this compound, it was concluded



that no coordination was involved and that the compound was the simple silver salt.

As was expected, and in keeping with results cited earlier, the nitrile band frequency was observed to increase upon coordination.<sup>16,18</sup> If the magnitude of these frequency shifts be taken as a measure of the coordinating ability of the cyano nitrogen, in cyanoacetate anion, to the various transition metal elements, the order of decreasing donor ability would be: Ni(ii) > Co(II), Cu(II) > Mn(II) > Fe(III) > Zn(II) > Cr(III).

The carbonyl band frequencies observed for the complexes were observed to increase over that observed for sodium cyanoacetate. This is contrary to the observations of other workers<sup>6,8,12,13,14,15,16</sup> that this frequency is decreased upon coordination. If, however, the carbonyl band frequency for cyanoacetic acid were taken as a reference, the frequencies of this band would be said to decrease in the complexes. The difficulty is, of course, that no spectrum of the anion could be recorded. Since no quantitative or detailed interpretation of these frequency shifts has been attempted, this problem was not considered to be critical.

On the basis of the magnitude of the carbonyl frequency shifts for the complexes, the coordinating ability of the carbonyl oxygen in cyanoacetate anion, to the various transition metal elements may be said to decrease in the order Cu(II) > Mn(II), Zn(II) > Cr(III) > Fe(III), Ni(II) > Co(II). With the exception of Cu(II), this order is almost the reverse of that for the coordinating ability of the nitrile nitrogen.

Examination of the spectra in the regions 3550-3200 and 1630-1600  $\text{cm}^{-1}$  for lattice water and the region 800-1000  $\text{cm}^{-1}$  for coordinated water<sup>32</sup> proved inconclusive as

the pellets absorbed water on their surface as the spectra were being recorded. Moreover, two bands in the 800-1000  $\text{cm}^{-1}$  region effectively masked any expectedly weak, broad absorption bands in this region that might arise from coordinated water. No further band assignments were made and the only other bands investigated were those around 1100 and 650  $\text{cm}^{-1}$  to check for the presence of perchlorate anion.

Strict comparisons of band intensities for the various complexes could not be made as the pellets used to obtain the spectra were not all of the same concentration. Nevertheless, several general statements may be permitted. In all cases the intensity of the nitrile absorption band relative to that of the carbonyl absorption band was decreased slightly. This decrease was more apparent in the iron (III), chromium (III) and manganese (II) complexes than in the others. However, in general, the intensities of all the absorption bands were greater for the complexes than for either cyanoacetic acid or sodium cyanoacetate.

The spectra of the copper complexes were, in general, less diffuse than those recorded for the other complexes as shown in Figures VIII and IX. Furthermore, the prominent splitting of the nitrile absorption band in the nickel (II) and cobalt (I) complexes is shown.

Finally, the shifts in the band frequencies for the nitrile and carbonyl groups in the ligand have been considered to give sufficient evidence that chelates have been formed. If this be the case, then a plausible geometry for the complexes (except the copper (II) chloride and the zinc (II) and manganese (II) complexes) would be square planar, as shown by Figure X. This would be a trans type configuration, although the splitting of the nitrile absorption band in the spectra of the nickel (II) and

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cobalt (II) complexes may be indicative of a cis configuration for these complexes (Figure XI).

ii) Cyanoacetamide Complexes

In addition to the nitrile and carbonyl band frequencies for cyanoacetamide and several of the complexes prepared, the combination N-H and C-N band frequencies and the amide III band frequencies are given in Table X. The carbonyl band frequencies have been observed to decrease slightly upon coordination; a more substantial increase in some of the coordinated-nitrile band frequencies has been observed.

TABLE X

Infrared spectral data for cyanoacetamide complexes.

Compound	Carbonyl band freq.	Shift in carbonyl band freq.	Nitrile band freq.	Shift in nitrile band freq.	N-H & C-N comb. band freq.	Amide III band freq.
cyanoacetamide	1690	--	2260	--	1615	1260
$[\text{Ni}(\text{La})_3](\text{ClO}_4)_2$	1675	15	2300- 2260 (split)	40	1610	1265
$[\text{Co}(\text{La})_2\text{CH}_3\text{OHH}_2\text{O}](\text{ClO}_4)_2$	1675	15	2280	20	1610	1265
$[\text{Zn}(\text{La})_2\text{CH}_3\text{OH}](\text{ClO}_4)_2$	1675	15	2260	0	1605	1265
Mn(II) complex	1675	15	2280	20	1605	1265
Fe(III) complex	1680	10	2270	10	1615	1265

No significant variation in the magnitude of the shift of the carbonyl band frequency was observed for the various complexes. Moreover, the shift is of rather small magnitude. This may be indicative of some steric hinderance by the  $-\text{NH}_2$  group. Although small shifts were observed for the combination N-H and C-N band and amide III band frequencies, coordination through the amide nitrogen is doubtful, both on

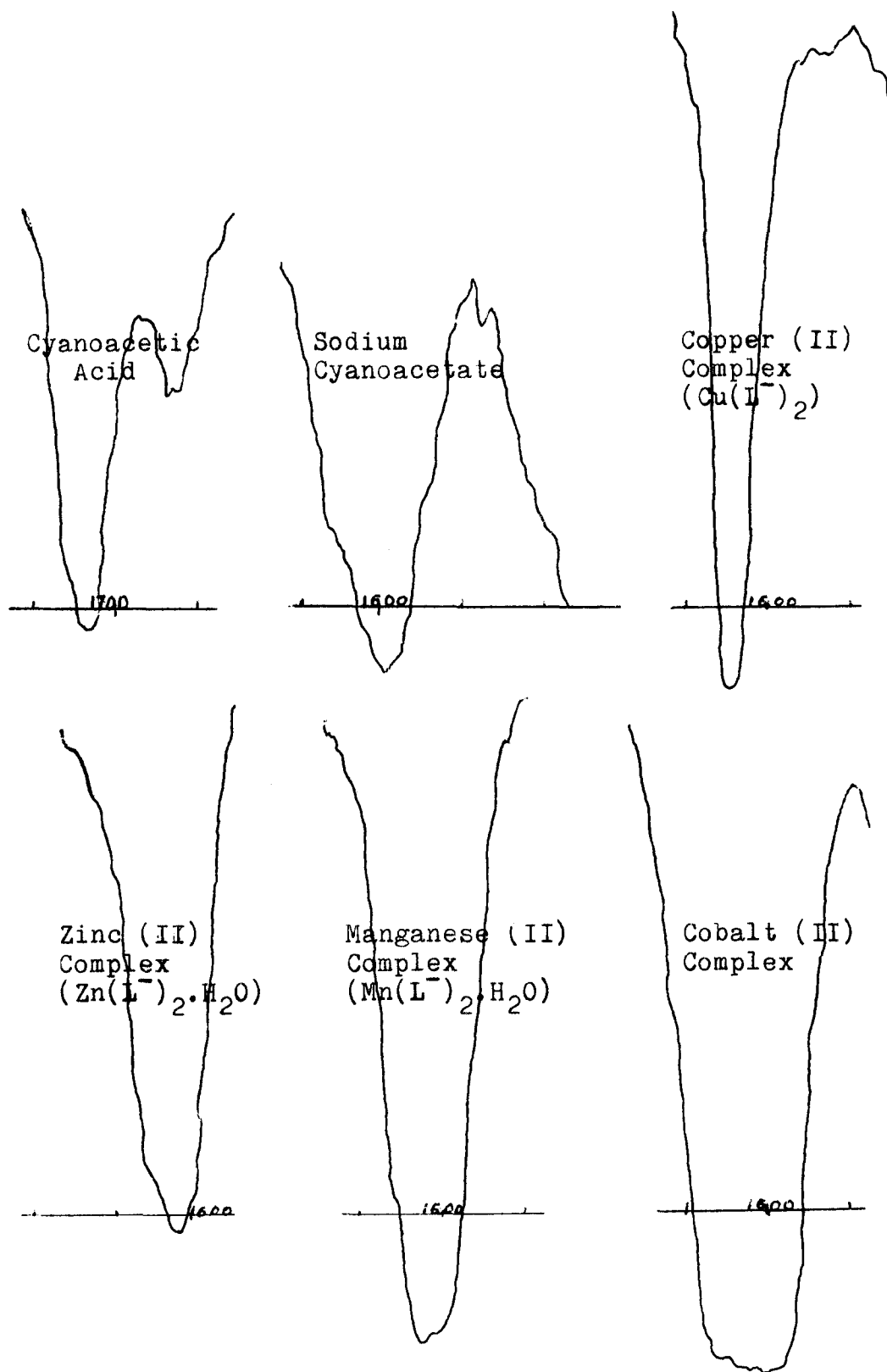


Figure VIII Carbonyl absorption bands for some cyanoacetate anion complexes.

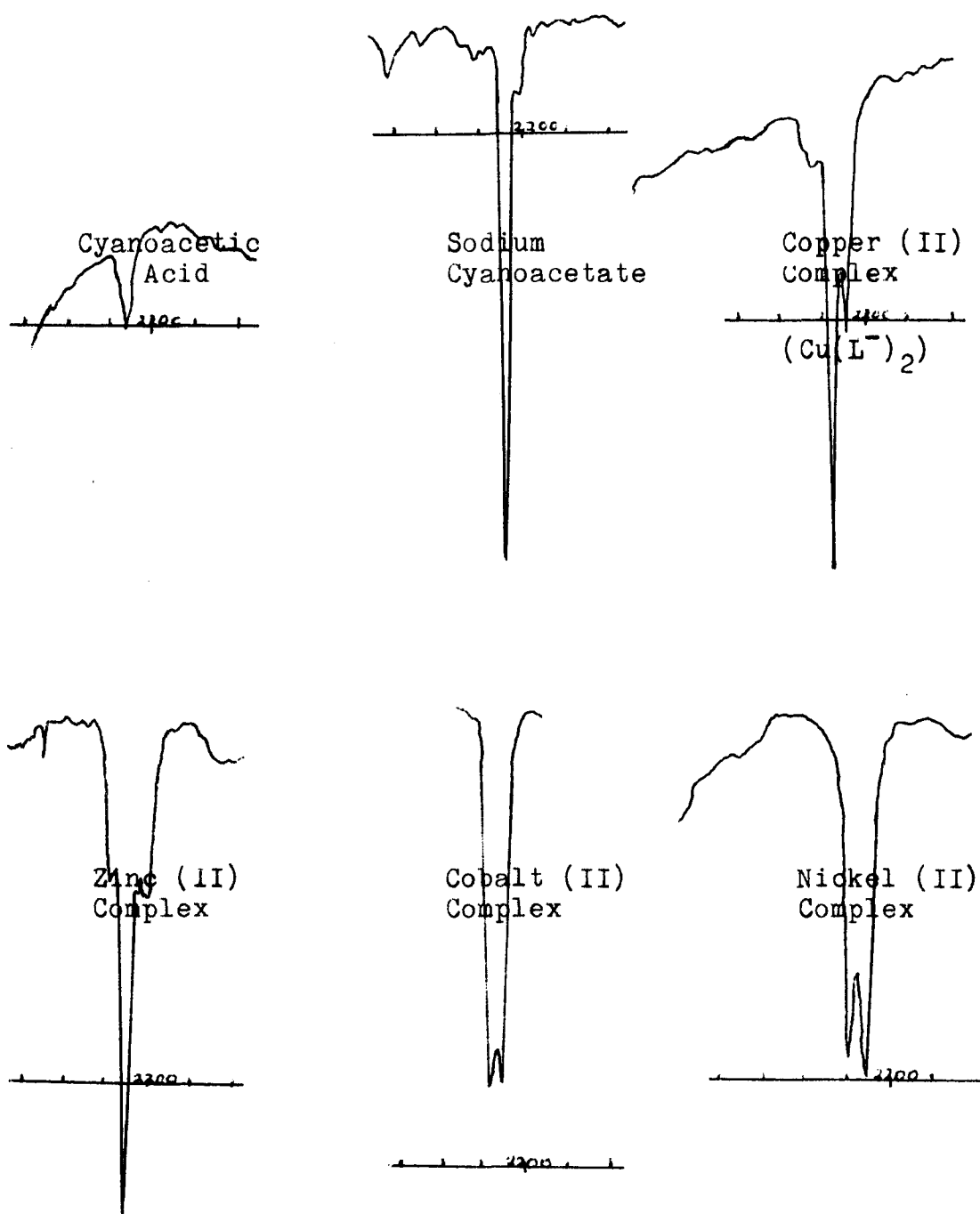


Figure IX Nitrile absorption bands for some cyanoacetate anion complexes.

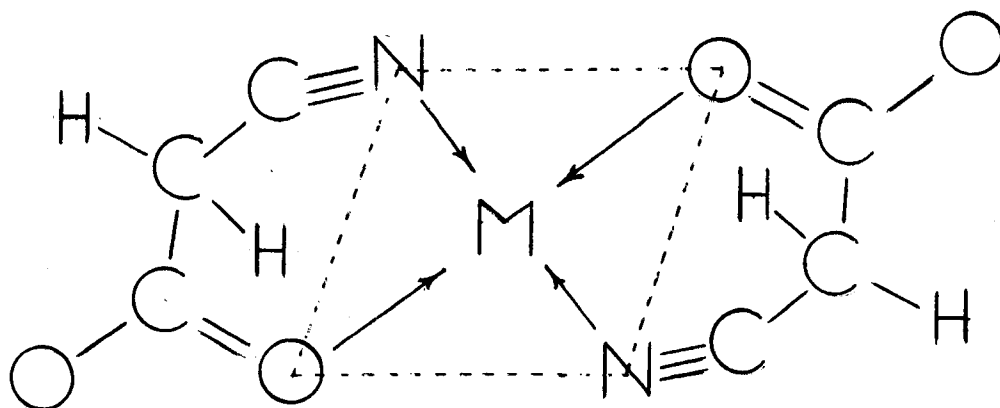


Figure X Trans configuration for cyanoacetate anion chelate.

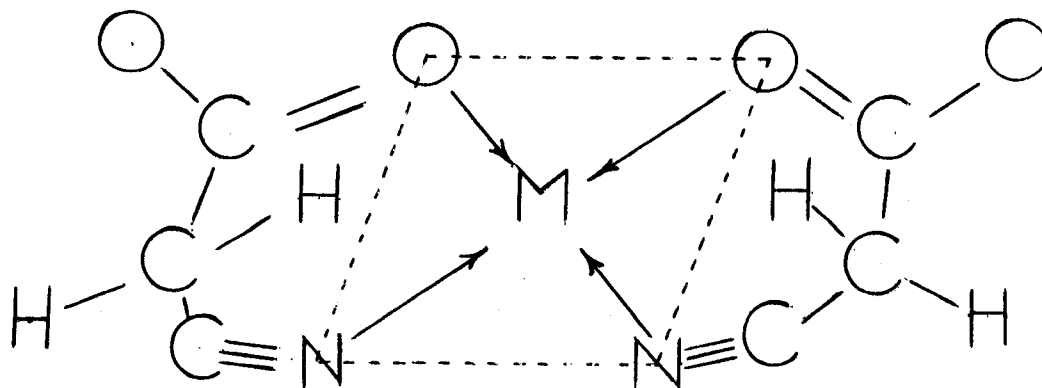


Figure XI Cis configuration for cyanoacetate anion chelate.

the basis of comparison with the work of others with amides as ligands and because of the less stable ring size.

Because of the lack of variation observed for the carbonyl band frequency shifts, nothing can be said about a variation in the coordinating ability of the carbonyl oxygen in cyanoacetamide towards any of the transition metal elements. The variation in the frequency shifts of the nitrile band does permit an ordering of the transition metal elements used in terms of the decreasing ability of the nitrile nitrogen to coordinate. This order is the same, though not so complete, as that observed in the case of the cyanoacetate anion complexes:  $\text{Ni(II)} > \text{Co(II)}$ ,  $\text{Mn(II)} > \text{Fe(III)}$ .

The infrared spectra indicate that two types of complexes have been formed--chelates with nickel (II), cobalt (II), manganese (II), iron (III) and perhaps with copper (II). With zinc (II), however, the ligand cyanoacetamide appears to be monodentate. For this ligand to be bidentate, with no nitrile nitrogen bonding, bonding would have to occur through the amide nitrogen. However, as mentioned previously, such a condition would involve the formation of a four-membered ring. Unless some unusual crystal lattice effects occur with this complex, it is unlikely that a four-membered ring structure (obtained by coordination of the amide nitrogen) would be more stable than the six-membered ring obtainable by coordination of the nitrile nitrogen. The more simple explanation, that the ligand cyanoacetamide is monodentate in this complex, has therefore been put forward.

The nickel (II) complex is probably octahedral and if so, various orientations of the ligand are possible, which may account for the splitting of the nitrile band in the spectrum of this complex. If this complex is octahedral

then the ligand must be able to span adjacent positions in such a configuration. Why the ligand cannot span adjacent positions in a tetrahedral configuration, as the zinc (II) complex would be expected to possess, is not clear.

As in the cyanoacetate anion complexes, the presence of absorption bands in the region of the coordinated water bands prevented any deduction of the mode of incorporation of water molecules in the cyanoacetamide complexes. However, methanol has been included in the coordination sphere of the cobalt (II) complex and the zinc (II) complex, not on the basis of spectral evidence but rather because of the similarity of the preparative method to that used by Drago and Imhof<sup>31</sup> to prepare alcohol complexes of nickel (II).

The perchlorate absorption bands in the spectra of the cyanoacetamide complexes are quite well defined as shown in the comparison of portions of the spectra of the ligand, cyanoacetamide, and the nickel complex in Figure XII.

### iii) Cyanoacetohydrazide Complexes

The absorption band frequencies given in Table XI are those for the carbonyl and nitrile groups of cyanoacetohydrazide and several complexes. In all of the complexes the carbonyl absorption bands have been shifted to lower frequencies, and the nitrile absorption bands have been shifted to higher frequencies.



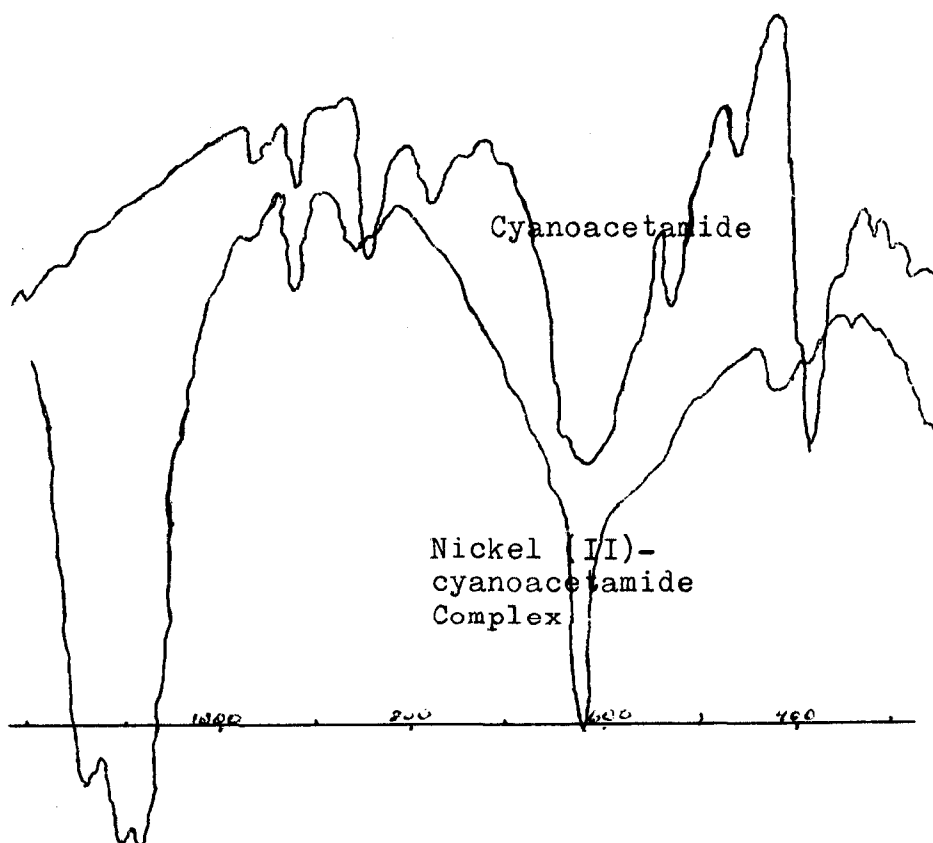
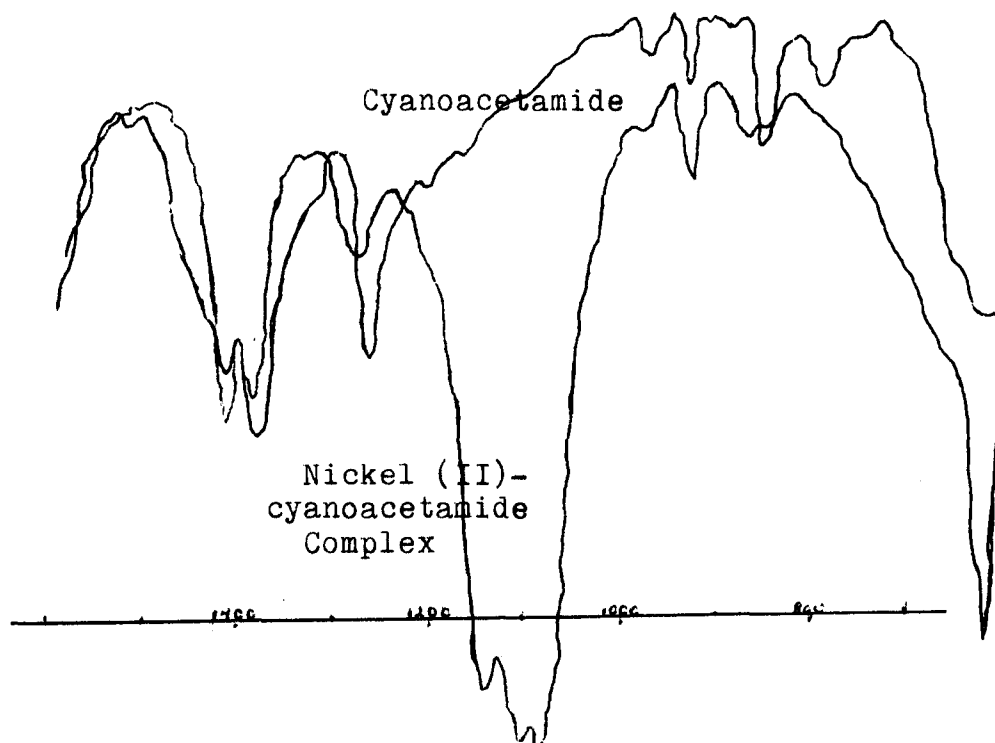


Figure XII Perchlorate absorption bands for nickel (II)-  
cyanoacetamide complex.

TABLE XI

Infrared spectral data for cyanoacetohydrazide complexes.

Compound	Carbonyl band freq.	Shift in carbonyl band freq.	Nitrile band freq.	Shift in nitrile band freq.
cyanoacetohydrazide	1690	-	2245	-
$[\text{Co}(\text{L}_h)_2 2(\text{CH}_3)_2\text{CO}](\text{ClO}_4)_2$	1655	35	2260	15
$[\text{Ni}(\text{L}_h)_2 2(\text{CH}_3)_2\text{CO}](\text{ClO}_4)_2$	1660	30	2265	20
Mn(II) complex	1640	50	2255	10
Zn(II) complex	1660	30	2260	15
Cu(II) complex	1675	15	2250- 2210 (split)	-

These frequency shifts have been considered to be sufficient evidence that cyanoacetohydrazide forms chelates with the various transition metal elements used. In addition, the bonding in these chelate compounds occurs through the carbonyl oxygen and the nitrile nitrogen. It is interesting to note in this latter connection that a substantial shift in the nitrile frequency of the zinc (II) complex has been observed, whereas none was observed in the cyanoacetamide-zinc (II) complex. For this latter complex it was suggested that the ligand, cyanoacetamide, was monodentate. Cyanoacetohydrazide, on the other hand, seems to function as a bidentate ligand in the zinc (II) complex. However, a satisfactory stoichiometry for the cyanoacetohydrazide complex with zinc (II) could not be found. Therefore, no attempt has been made to reconcile the above observations.

A portion of the spectra of cyanoacetamide, cyanoacetohydrazide and the nickel (II) complex of the latter has been reproduced in Figure XIII. The absorption bands shown for cyanoacetohydrazide are the only ones that did

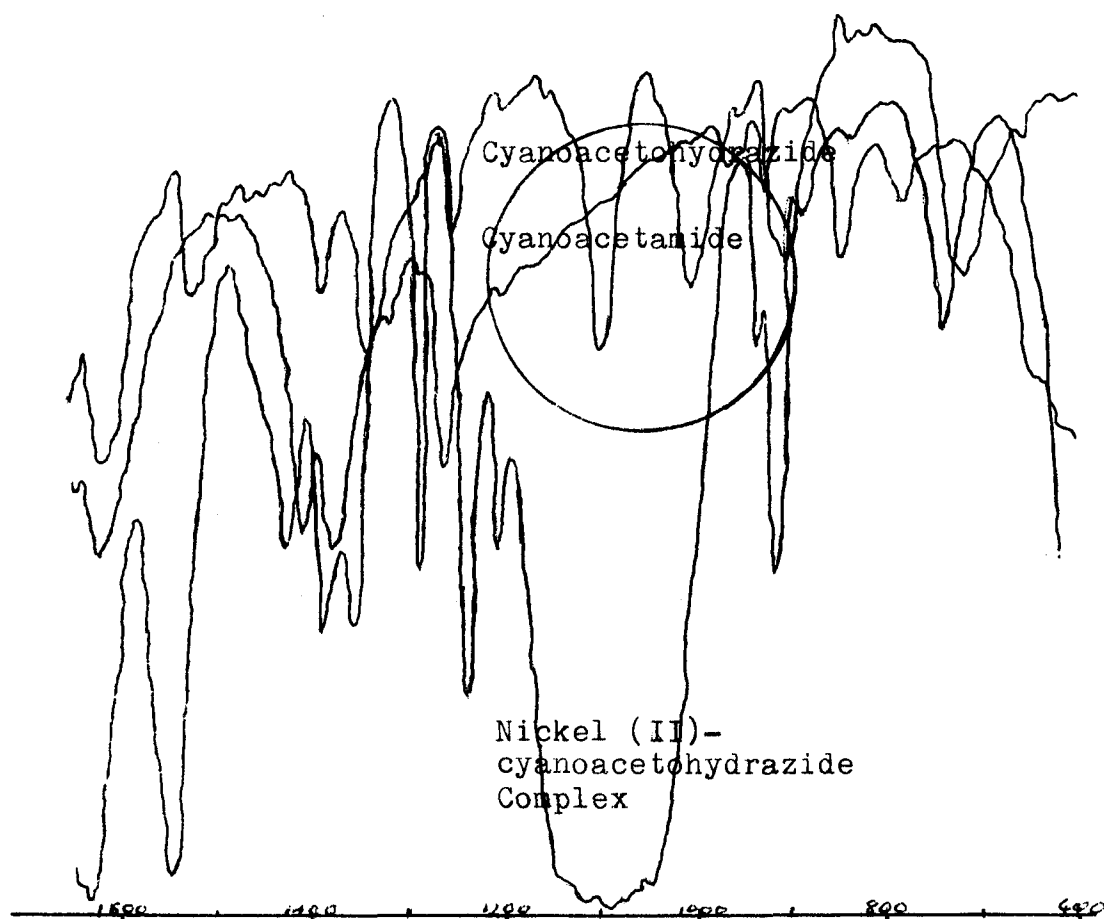


Figure XIII A portion of the spectra of cyanoacetamide, cyanoacetylhydrazide, and nickel (II)-cyanoacetylhydrazide complex.

not appear in the spectrum of cyanoacetamide. It was hoped that these bands were characteristic of the second nitrogen in the hydrazide group; no corroboration of this could be found in the literature. Furthermore, it was anticipated that, if these bands were in fact due to the hydrazide group, any shift in their frequencies would be indicative of bonding through the hydrazide nitrogen. However, as is shown in Figure XIII, the strong perchlorate anion absorption in this region marked these bands and therefore no evidence could be obtained to prove or disprove the postulate that bonding could occur through the hydrazide nitrogen, giving a five-membered ring chelate.

The order of the transition metal elements to which the carbonyl oxygen of cyanoacetohydrazide has a decreasing tendency to coordinate is  $Mn(II) > Co(II) > Ni(II)$ ,  $Zn(II) > Cu(II)$ . This order is based on the magnitude of the carbonyl band frequency shifts in the spectra of the various complexes. This order is significantly different from that for the same characteristic of the ligand cyanoacetate anion; copper (II) has completely reversed its position, and the positions of cobalt (II) and nickel (II) now show an increased tendency for carbonyl oxygen to coordinate. The sequence, indicative of the decreasing ability of the nitrile nitrogen of cyanoacetohydrazide to coordinate to the various transition metal elements-- $Ni(II) > Co(II)$ ,  $Zn(II) > Mn(II)$ --is similar to those for cyanoacetate anion and cyanoacetamide.

The splitting of the nitrile absorption band in the spectrum of the copper (II) complex was not of so great a magnitude as that observed in the spectra of the nickel (II) complex with cyanoacetamide. That a satisfactory stoichiometry for the copper (II) complex was not found, has precluded any discussion of the significance of this

band splitting and the small carbonyl band frequency shift in the spectrum of this complex.

iv) N-methyl-2-pyrrolidinone Complexes

The ligand N-methyl-2-pyrrolidinone was known from previous work in this laboratory<sup>9</sup> to coordinate through its carbonyl group oxygen. In Table XII the frequencies for the carbonyl band are given for N-methyl-2-pyrrolidinone and several complexes. In addition the shifts in the frequency of this band in the various complexes are listed in this table.

TABLE XII

Infrared spectral data for N-methyl-2-pyrrolidinone complexes

Compound	Carbonyl band frequency	Shift in carbonyl band frequency
N-methyl-2-pyrrolidinone	1675	--
$[\text{Cr}(\text{L}_p)_6](\text{ClO}_4)_3$	1625	50
$[\text{Fe}(\text{L}_p)_6](\text{ClO}_4)_3$	1625	50
$\text{MnL}_p\text{Cl}_2$ ( $\text{MnL}_p\text{H}_2\text{OCl}_2$ )?	1625	50
$\text{Zn}(\text{L}_p)_2\text{Cl}_2$	1620	55
$\text{Ni}(\text{L}_p)_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ ( $\text{Ni}(\text{L}_p)_2\text{H}_2\text{OCl}_2$ )?	1620	55

In keeping with observations made for the complexes with the other ligands, cyanoacetamide and cyanoaceto-hydrazide, the carbonyl band frequency is decreased by coordination. This band showed a slight shoulder in the spectrum of N-methyl-2-pyrrolidinone but this shoulder is not discernible in the spectra of the complexes. Moreover the spectra of the complexes are more diffuse than that of the ligand. This latter spectrum was obtained by placing a smear of the liquid N-methyl-2-pyrrolidinone

between two potassium bromide disks.

Both the nickel (II) and manganese (II) complexes were extremely hygroscopic. Their spectra, however, included a broad absorption band in the region  $800-650\text{ cm}^{-1}$ . Such a band frequency has been assigned to the rocking or wagging mode of coordinated water.<sup>32</sup> It is therefore possible that the manganese (II) complex includes a molecule of water, which would bring the coordination number to the expected four. The nickel (II) complex may be a six coordinate octahedral diaquo complex, on this same basis, instead of a four coordinate dihydrate.

#### B Ultraviolet and Visible Spectra

The spectrum of the nickel (II) cyanoacetamide complex in the region  $305-800\text{ m}\mu$  is reproduced in Figure XIV. Except for those absorption bands around  $310\text{ m}\mu$ , the bands shown for this complex are typical in shape of those bands observed in the other spectra. Some of the other complexes, however, exhibited a more intense and more sharply defined band around  $310\text{ m}\mu$ .

The frequencies of the band maxima, extinction coefficients and descriptions of some of the electronic transitions involved are given in Table XIII. Assignments of electronic transitions to their corresponding absorption bands were made by comparison with data recorded in the article by Dunn,<sup>27</sup> cited earlier, and with data obtained by Drago and co-workers.<sup>6</sup>

The maximum value observed for the extinction coefficient of any of the bands was less than 100. It is therefore concluded that none of the bands observed were charge transfer bands.

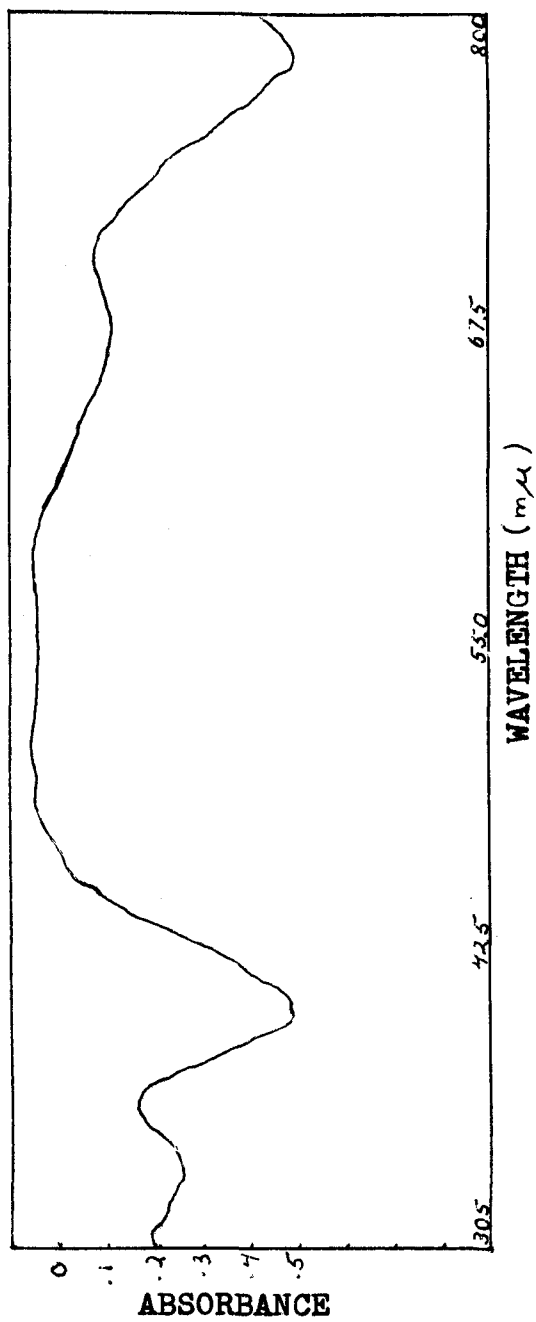


Figure XIV Ultraviolet and visible spectrum of nickel (II)-cyanoacetamide complex.

TABLE XIII

## Ultraviolet and visible spectral data

Complex	Frequency of band maximum	$\epsilon_{\max}$ (maximum extinction coefficient)	Electronic transition
$[\text{Cu}(\text{La})_2](\text{ClO}_4)_2$	30,581	64.57	$2T_{2g} \rightarrow 2E_g$
	13,298	26.82	
$[\text{Co}(\text{La})_2\text{CH}_3\text{OHH}_2\text{O}](\text{ClO}_4)_2$	32,468	27.08	$4T_{1g} \rightarrow 4T_{1g}(\text{P})$
	20,833	6.00	
	19,417	6.88	$4T_{1g} \rightarrow 4A_{2g}(\text{F})$
	13,369	12.75	
$[\text{Co}(\text{L}_h)_2^2(\text{CH}_3)_2\text{CO}](\text{ClO}_4)_2$	31,447	46.00	$4T_{1g} \rightarrow 4T_{1g}(\text{P})$
	20,833	8.63	
	19,493	9.45	$4T_{1g} \rightarrow 4A_{2g}(\text{F})$
	13,605	6.63	
$[\text{Ni}(\text{La})_3](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$	30,120	4.30	$3A_{2g} \rightarrow 3T_{1g}(\text{P})$
	25,000	7.45	
	14,493	2.75)	$3A_{2g} \rightarrow 3T_{1g}(\text{F})$
	12,658	7.38)	
$[\text{Ni}(\text{L}_h)_2^2(\text{CH}_3)_2\text{CO}](\text{ClO}_4)_2$	32,573	26.63	$3A_{2g} \rightarrow 3T_{1g}(\text{P})$
	26,316	7.13	
	14,749	3.63)	$3A_{2g} \rightarrow 3T_{1g}(\text{F})$
	12,853	6.88)	

Moreover, assignments of the electronic transitions to various bands have been made by assuming square planar geometry for the copper (II) complex and octahedral geometry for the cobalt (II) and nickel (II) complexes. This latter assumption is justified by the similarity of the spectra for these complexes to each other and to the spectra of known octahedral complexes.<sup>26</sup>

Since no spectra were recorded in the near infrared region, no values of  $\log \epsilon$  could be obtained for the complexes. Therefore, no attempt has been made to position the ligands in the spectrochemical series.



### C Conductivity Measurements

Molar conductances have been obtained for some of the complexes for which stoichiometries have been assigned. Where possible, the complexes were dissolved in nitromethane; the complex ions are believed to retain their identity in this solvent because in general the complexes were found to be more soluble in nitromethane than the corresponding metal salts. It is thought, however, that extensive dissociation occurs in the solvent water and that the complexes are destroyed. These latter measurements are useful only in that similarities and differences between the various complexes involved may be implied by a qualitative more than quantitative interpretation of the value obtained. The molar conductances of both types of solutions are given in Table XIV along with a description of the type of electrolyte formed upon dissolution of the complex in the solvent.

Since most of the perchlorate containing complexes, except those with iron (III) and chromium (III), form 2:1 electrolytes in nitromethane, it may be said that no coordination of the perchlorate anion is involved. The molar conductance value for the aqueous solution of the nickel (II) complex with N-methyl-2-pyrrolidinone is rather high for a 2:1 electrolyte, which should be formed in water if the assigned stoichiometry is correct. This stoichiometry was assigned on the basis of a carbon and hydrogen analysis only, and may be incorrect.

The zinc (II) complex with N-methyl-2-pyrrolidinone formed a non-electrolyte in nitromethane. Because of the similarity in the molar conductance values for this complex and that for the manganese (II) complex with N-methyl-2-pyrrolidinone, it may be valid to assume that this latter would also form a non-electrolyte in nitro-

methane. On this basis, it is therefore doubtful that the manganese (II) complex is a dimer, but it is possible that it is a monaquo complex.

TABLE XIV

Conductance measurements.  $K = .203448 \text{ cm}^{-1}$ 

Compound	Conc.	Solvent	$\Lambda$	Nature of electrolyte formed
$[\text{Ni}(\text{La})_3](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$	.001	$\text{CH}_3\text{NO}_3$	169.54	2:1
$[\text{Co}(\text{La})_2 \text{CH}_3\text{OH} \cdot \text{H}_2\text{O}](\text{ClO}_4)_2$	.001	$\text{CH}_3\text{NO}_3$	161.47	2:1
$[\text{Cu}(\text{La})_2](\text{ClO}_4)_2$	.001	$\text{CH}_3\text{NO}_3$	173.15	2:1
$[\text{Co}(\text{L}_h)_2 \cdot 2(\text{CH}_3)_2\text{CO}](\text{ClO}_4)_2$	.001	$\text{CH}_3\text{NO}_3$	121.10	2:1
$[\text{Ni}(\text{L}_h)_2 \cdot 2(\text{CH}_3)_2\text{CO}](\text{ClO}_4)_2$	.001	$\text{CH}_3\text{NO}_3$	145.32	2:1
$[\text{Zn}(\text{La})_2 \cdot 2\text{CH}_3\text{OH}](\text{ClO}_4)_2$	.001	$\text{CH}_3\text{NO}_3$	178.46	2:1
$[\text{Cr}(\text{L}_p)_6](\text{ClO}_4)_3$	.001	$\text{CH}_3\text{NO}_3$	243.65	3:1
$[\text{Fe}(\text{L}_p)_6](\text{ClO}_4)_3$	.001	$\text{CH}_3\text{NO}_3$	236.57	3:1
$\text{Zn}(\text{L}_p)_2 \text{Cl}_2$	.001	$\text{CH}_3\text{NO}_3$	6.26	non elect.
$\text{Mn}(\text{L}_p) \text{Cl}_2$	.001	$\text{H}_2\text{O}$	250.55	2:1
$\text{Zn}(\text{L}_p)_2 \text{Cl}_2$	.001	$\text{H}_2\text{O}$	286.55	2:1
$\text{Ni}(\text{L}_p)_2 \text{Cl}_2 \cdot \text{H}_2\text{O}$	.001	$\text{H}_2\text{O}$	336.28	2:1
$\text{Cu}(\text{L}^-)_2$	.001	$\text{H}_2\text{O}$	191.03	2:1
$[\text{Cu}(\text{L}^-)_2 \text{Cl}_2] \text{Na}_2$	.001	$\text{H}_2\text{O}$	444.13	-

## CHAPTER IV

### SUMMARY

A partial series of coordination compounds of chromium (III), manganese (II), iron (III), cobalt (II), nickel (II), copper (II) and zinc (II) with the related ligands cyanoacetate anion, cyanoacetamide and cyanoacetohydrazide have been prepared. In most instances, chelates were formed in which the ligand-metal ion bonding occurred through the carbonyl oxygen and the nitrile nitrogen. Characterization of these complexes has been made primarily by interpretation of their infrared spectra. The spectra in the ultraviolet and visible region, as well as the conductivity measurements have been used to corroborate the evidence from the infrared spectra.

The relative ease with which the complexes could be prepared would suggest a sequence of cyanoacetate anion, cyanoacetamide and then cyanoacetohydrazide within the spectrochemical series. No values for  $\log K$  were obtained that would enable the sequence to be positioned in this series; nor is there any other evidence that the sequence given is correct.

The use of N-methyl-2-pyrrolidinone as ligand has been extended from species with perchlorate as the anion to satisfy the primary valence of the metal to species involving chloride ion which partially satisfies the secondary valence as well as the primary valence. Again characterization has been based on infrared spectral data with corroboration from conductivity measurements.

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The author was born in York Township, Ontario, on the thirteenth day of November 1941, the first son of Vaughn and Eleanor Courrier. He completed his public school education in St. Thomas, Ontario, at Homedale Public School. In 1959 he graduated from Woodstock Collegiate Institute, having completed his secondary school education. In 1960 he enrolled at Assumption University of Windsor, and was granted an honours Bachelor of Science degree in 1964.

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