

STUDIES OF SOME METAL COMPLEXES WITH SUBSTITUTED BENZIMIDAZOLES

A Thesis submitted

by

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ABSTRACT

The main aim of this study was to investigate the co-ordination chemistry of certain antivirally active derivatives of 2- α -hydroxybenzylbenzimidazole and some inactive 2 substituted benzimidazoles with cobalt(II) and nickel(II) salts, with a view to correlating virus inhibitory activity with chelation properties. In the case of the parent compound, 2- α -hydroxybenzylbenzimidazole, its co-ordination chemistry with some copper(II) salts has been investigated.

A number of complexes have been prepared and attempts made to deduce their structures from their electronic spectral, magnetic and infrared spectral data. All the ligands except 2- α -methoxybenzylbenzimidazole and 2-O-hydroxyphenylbenzimidazole were found to chelate very readily, doing so through their unsaturated nitrogen atom and oxygen atom. 2- α -methoxybenzylbenzimidazole, while not as ready to chelate as the other compounds, is nevertheless capable of doing so, as is evident from its nickel complexes. With 2-O-hydroxyphenylbenzimidazole chelation is uncommon, the ligand either bridging or bonding monodentately. In those complexes in which it is bridging, peculiar magnetic properties are observed. The differences in the co-ordination chemistry of the various ligands have in most cases been explained in terms of steric effects. In the case of 2-O-hydroxyphenylbenzimidazole its difference in co-ordination chemistry to the other compounds is probably due mainly to electronic factors. The behaviour of 2- α -hydroxybenzylbenzimidazole with

copper(II) salts is interesting in that it chelates less readily with these than with cobalt(II) or nickel(II) salts. Several of the copper complexes have very interesting magnetic properties.

Finally, the correlation between antiviral activity and chelation properties is discussed.

ACKNOWLEDGEMENTS

During the course of this study my supervisor, Dr. M. Goodgame, has been a source of constant guidance and encouragement and for this I would like to offer her my many thanks.

I wish to thank the Medical Research Council for their generous support over the past three years.

Finally I would like to express my appreciation to Miss H. Sanger for typing the manuscript.

To my parents.

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ABBREVIATIONS

Ligands

HBB	-	2 α Hydroxybenzylbenzimidazole
nPrHBB	-	1.nPropyl 2 α Hydroxybenzylbenzimidazole
isoPrHBB	-	1.isoPropyl 2 α Hydroxybenzylbenzimidazole
MeOBB	-	2 α Methoxybenzylbenzimidazole
HMeB	-	2 Hydroxymethylbenzimidazole
HPB	-	2.O.Hydroxyphenylbenzimidazole
DMF	-	Dimethylformamide
Ac	-	Acetone
EtOH	-	Ethanol

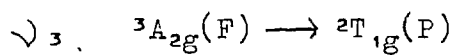
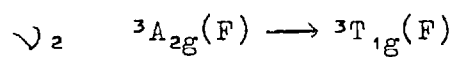
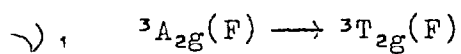
In connection with X-ray powder patterns the symbols d and I are used to represent interplanar spacing (d), and line intensity (I) in arbitrary units.

In describing infrared or electronic spectral bands the following abbreviations are used:

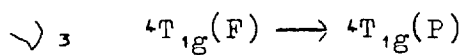
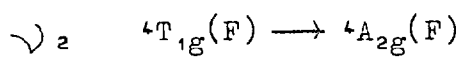
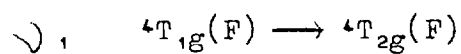
v.s	-	very strong	w	-	weak
s	-	strong	sh	-	shoulder
m	-	medium			

The symbols λ_1 , λ_2 and λ_3 are used to represent the following electronic spectral transitions:

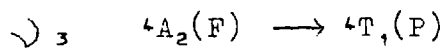
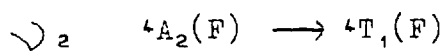
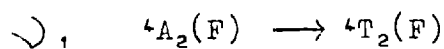
Ni^{II} in an O_h environment



Co^{II} in an O_h environment



Co^{II} in a T_d environment



χ_{M} is the molar susceptibility corrected for the diamagnetism of the ligand. μ_{eff} is the magnetic moment calculated using

χ_{M} .

INTRODUCTION

In 1958 Hollinshead and Smith¹ reported the inhibition of poliovirus multiplication with 2 α -hydroxybenzylbenzimidazole, Fig. 1.

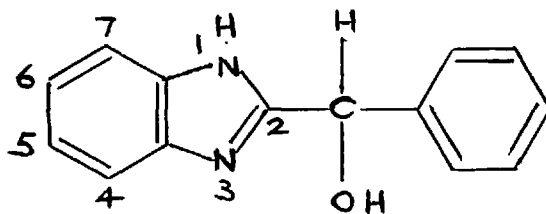


Fig. 1.

Following this Tamm et al² studied the inhibitory activity and selectivity of some twenty-five benzimidazoles and benztriazoles towards poliovirus type 2. From this study it was found that HBB and its 5 chloro derivative are outstanding, showing about 15 times the selectivity ratio [‡] of benzimidazole. Furthermore, these two compounds were the only ones which caused significant inhibition of the cytopathic effects of poliovirus. Cells which have been exposed to non-toxic virus inhibitory concentrations of HBB show no sign of morphological damage when examined microscopically.³ Such concentrations of HBB were also found to have no effect on the oxygen uptake, glucose utilization and lactic acid production of

[‡] This is the lowest toxic concentration divided by the virus inhibitory concentration and is taken as a direct indication of the value of the compound; virus inhibitory concentration is the concentration (μ M) of compound required to produce 75% inhibition of virus multiplication.

cells.⁴ Since other cellular functions were also unaffected⁵ it would appear that HBB does not interfere with the normal working of the cell.⁶ Studies with certain enteroviruses show that HBB specifically inhibits synthesis of viral RNA and suggest that this is responsible for the inhibition of intra cellular replication.⁷

Tamm et al² found that 2 hydroxymethyl benzimidazole, Fig. 2, $R_1 = OH$, $R_2 = H$; 2 hydroxyethyl benzimidazole, Fig. 2, $R_1 = OH$, $R_2 = CH_3$; and 2 benzyl benzimidazole, Fig. 2, $R_1 = H$, $R_2 = C_6H_5$, were inactive, and suggest that the hydroxy benzyl group at position 2 in the benzimidazole ring is of fundamental importance for the selective virus inhibitory action of HBB.

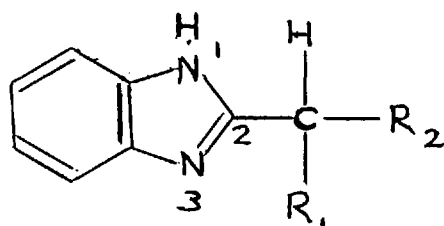


Fig. 2.

O'Sullivan has extended this work⁸ synthesising various derivatives of HBB and testing their antiviral activity, partly with the view of correlating activity with structure and ultimately postulating a mechanism for the inhibitory process. Two properties of HBB and its derivatives which may be involved at some stage in the inhibitory process have been suggested.⁹ These are hydrogen bond formation with for instance some key molecule involved in the

inclusion of nuclear DNA or perinuclear RNA into incomplete virus particles, or chelation with a trace metal in say a protein or enzyme. The hydrogen bonding theory has been investigated by O'Sullivan.¹⁰ It was the purpose of this study to investigate the chelation properties of HBB and some of its derivatives with certain transition metal ions.

The compounds chosen for study were 2- α -hydroxybenzylbenzimidazole, 2-hydroxymethylbenzimidazole, 1-n-propyl-2- α -hydroxybenzylbenzimidazole, Fig. 3, R_1 = n-propyl, R_2 = OH, 1-isopropyl-2- α -hydroxybenzylbenzimidazole, Fig. 3, R_1 = isopropyl, R_2 = OH, 2- α -methoxybenzylbenzimidazole, Fig. 3, R_1 = H, R_2 = OCH₃, and 2-ortho-hydroxyphenylbenzimidazole, Fig. 4.

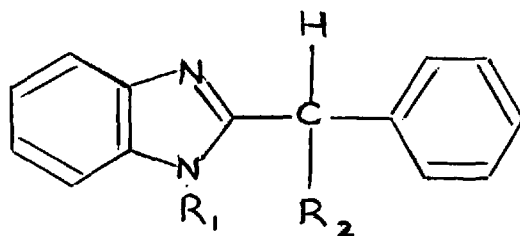


Fig. 3.

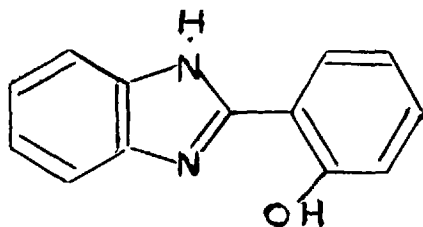


Fig. 4.

The relative activities of these compounds towards poliovirus types 1, 2 and 3¹¹ are listed in Table 1.

TABLE 1.

Polio Virus Type	1	2	3
2 $\propto$ Hydroxybenzylbenzimidazole	$\leq$	δ	$\leq$ [*]
2 Hydroxymethylbenzimidazole	0	0	0
1-n-Propyl 2 $\propto$ Hydroxybenzylbenzimidazole	$\propto$	$\propto$	β
1-iso-Propyl 2 $\propto$ Hydroxybenzylbenzimidazole	$\leq$	δ	$\leq$
2 $\propto$ Methoxybenzylbenzimidazole	$\leq$	δ	$\leq$
2-o-Hydroxyphenylbenzimidazole	-	$< \delta$	-
[*] $\propto$ very high to $\leq$ low, 0 means no activity			

The reasons for studying these particular compounds are given below. Since n Pr HBB is appreciably more active than HBB and iso Pr HBB, it was considered important to study the chelation properties of these particular compounds to see what effect the presence and stereochemistry of a substituent on the 1 N atom would have. Replacement of the phenyl ring in HBB with a proton to give HMeB results in a marked change in activity, whereas replacement of the hydroxyl proton with methyl to give MeOBB produces hardly any change in activity at all. Study of the chelation properties of these two compounds then is important. Finally the chelation properties of the antivirally inactive HPB were studied. In this compound the

hydroxyl group is in a similar position relative to the unsaturated nitrogen atom, as in HBB, but would be expected to have different electronic properties because of its direct substitution into a phenyl ring.

The reason for using salts of the Ni^{II} ion in this study, which after all is not a metal that occurs in biological systems, is because of the ease of interpretation of the electronic spectral and magnetic data of its complexes. Co^{II} salts are an obvious choice because of the importance of this metal in cellular processes and also because like Ni^{II} the electronic spectral and magnetic data of its complexes is extensive and well understood. The Chelates formed by the parent compound, that is HBB, with various Cu^{II} salts were examined since copper is known to occur in some proteins, enzymes, and viruses.

The theoretical principles of the various techniques used in the course of this study which include electronic spectroscopy,¹² magnetochemistry,¹³ infrared spectroscopy¹⁴ and electron spin resonance spectroscopy¹⁵ will not be given here since several excellent texts on these subjects exist.

CHAPTER ONE

Some Cobalt and Nickel Complexes of 2-Hydroxybenzylbenzimidazole.

In order to elucidate the chelation properties of HBB the following compounds were studied, $M(HBB)_3X_2$, $Ni(HBB)_3(ClO_4)_2$, $Co(HBB)_3(ClO_4)_2$, $M(HBB)_2(NO_3)_2$, $M(HBB)_2(SCN)_2$, and $M(HBB)_2(SCN)_2(DMF)_2$, where M is cobalt or nickel, X is chloride, bromide or iodide and DMF is dimethylformamide.

The Nickel Complexes.

The electronic spectra of all the nickel complexes except $Ni(HBB)_2(SCN)_2$ are similar and typical of the type expected for a spin-free Ni^{II} ion in an essentially octahedral environment¹⁶ (Table 1:1). The magnetic data (Table 1:2) are in accord with this observation.¹⁷ Since the Δ values of the complexes $Ni(HBB)_3X_2$, where X is chloride, bromide, iodide, or perchlorate, are similar it may be assumed that the anions are not co-ordinated.

For $Ni(HBB)_3Cl_2$ the energy of the 3P state, P, was calculated from the equation

$$[6DqP - 16(Dq)^2] + [-6Dq - P] E + E^2 = 0$$

where E is the energy of the $^3T_{1g}(F)$ and $^3T_{1g}(P)$ states relative to a spherical field, and Dq has its usual meaning.¹⁸ Taking the value of P' the energy of the 3P state in the free gaseous ion as 15,840,¹⁹ the ratio $P/P' = 0.84$ was calculated. This ratio which gives a measure of the covalence, among other effects,²⁰ is fairly typical for an octahedrally co-ordinated spin-free Ni^{II} ion with nitrogen

TABLE 1: 1

ELECTRONIC SPECTRAL DATA

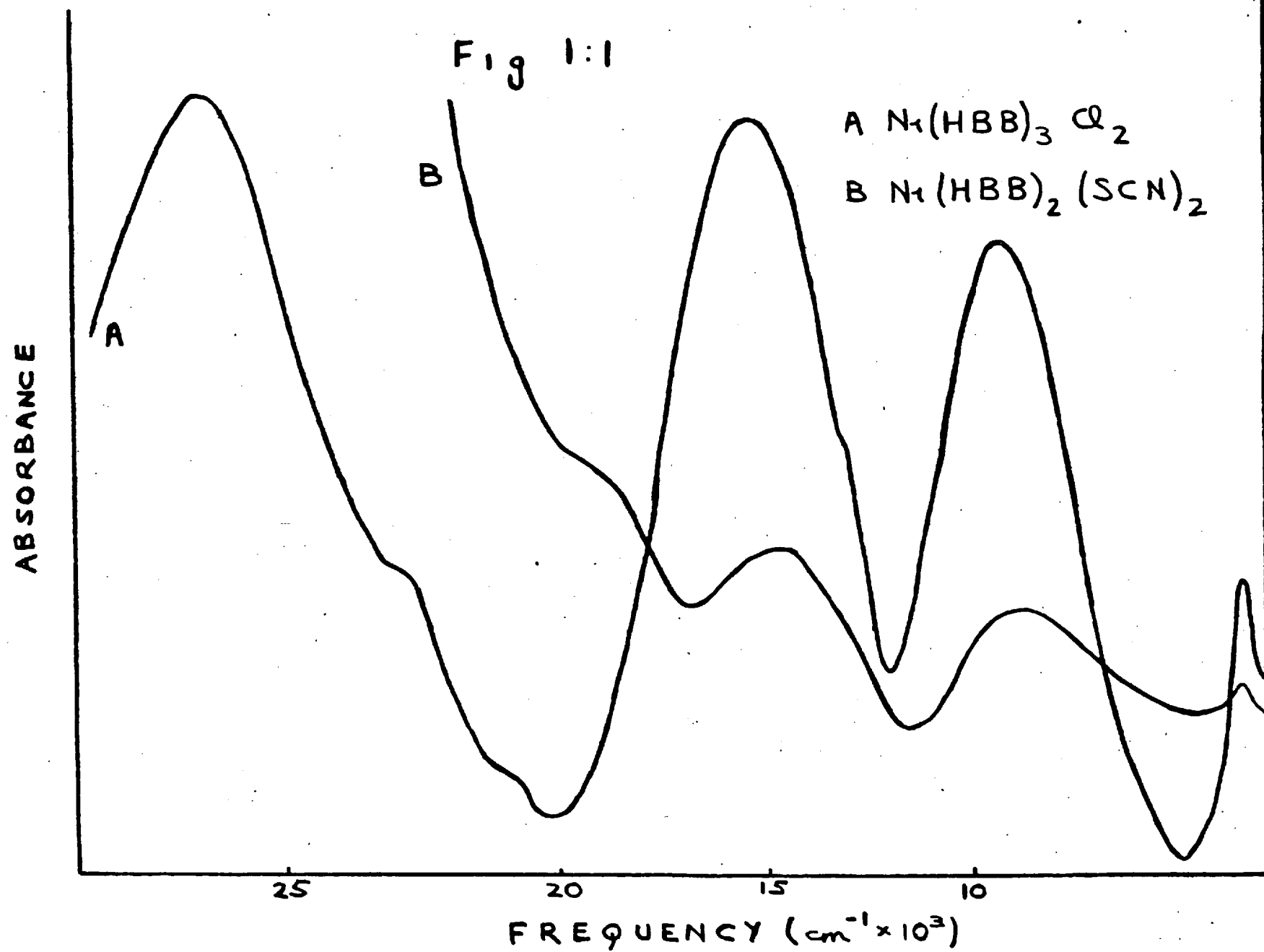
<u>COMPLEX</u>	<u>ABSORPTION MAXIMA cm⁻¹ AND ASSIGNMENT</u>					
	ν_3	ν_2	ν_1 ^f	$^3A_{2g}(F) \rightarrow ^1T_{2g}(D)$	$^3A_{2g}(F) \rightarrow ^1A_{1g}(G)$	$^3A_{2g}(F) \rightarrow ^1E_g(D)$
Ni(HBB) ₃ Cl ₂	26,300	15,850	9,500	≈ 22,700 sh	≈ 21,000 sh	≈ 13,300 sh
Ni(HBB) ₃ Br ₂	28,400	15,850	9,500	≈ 22,700 sh	-	≈ 13,100 sh
Ni(HBB) ₃ I ₂	26,650	15,500	9,350	≈ 23,300 sh	≈ 19,600 sh	≈ 13,200 sh
Ni(HBB) ₂ (NO ₃) ₂	27,000	15,400	9,350	-	-	≈ 13,200 sh
Ni(HBB) ₂ (SCN) ₂	27,000 [⊗] ≈ 18,900sh	15,050	8,850	-	-	-
Ni(HBB) ₂ (SCN) ₂ (DMF) ₂	24,500	15,500	9,500 ≈ 8,700sh	-	≈ 20,800 sh	≈ 13,300 sh
Ni(HBB) ₃ (ClO ₄) ₂	26,300	15,750	9,450 ≈ 9,000sh	≈ 23,300 sh	-	≈ 13,300 sh

^f In all these complexes the position of ν_1 can be taken as ≈ Δ.

[⊗] Not assigned.

TABLE 1:2ROOM TEMPERATURE MAGNETIC DATA

COMPLEX	χ_M' ($\times 10^{-6}$ c.g.s.u.)	μ_{eff} (B.M.)	DIAMAGNETIC CORRECTION ($\times 10^{-6}$ c.g.s.u.)
$\text{Ni}(\text{HBB})_3\text{Cl}_2$	4367	3.21	426
$\text{Ni}(\text{HBB})_3\text{Br}_2$	4253	3.17	448
$\text{Ni}(\text{HBB})_3\text{I}_2$	4130	3.14	480
$\text{Ni}(\text{HBB})_2(\text{NO}_3)_2$	3891	3.07	295
$\text{Ni}(\text{HBB})_2(\text{SCN})_2$	4412	3.27	319
$\text{Ni}(\text{HBB})_2(\text{SCN})_2(\text{DMF})_2$	3546	2.92	407



and oxygen containing ligands.

Fig. (1:1) illustrates the difference in the electronic spectra of $\text{Ni(HBB)}_2(\text{SCN})_2$ and $\text{Ni(HBB)}_3\text{Cl}_2$. It is almost certain that the intense broad band at $27,000 \text{ cm}^{-1}$ in the spectrum of $\text{Ni(HBB)}_2(\text{SCN})_2$ is due to charge transfer but the origin of the shoulder at $18,900 \text{ cm}^{-1}$ is puzzling. It might be thought that this shoulder is due to a partly obscured ν_3 transition (assigned in O_h symmetry), but this is unlikely since this transition would be expected at higher energy, where it would be hidden by the charge transfer band.

The Cobalt Complexes.

The electronic spectra of $\text{Co(HBB)}_3\text{Cl}_2$ and Br_2 (Table 1:3), which are best interpreted in terms of an octahedrally co-ordinated spin-free Co^{II} ion,²¹ indicate that the halide ions are not co-ordinated. The spectra of $\text{Co(HBB)}_3\text{I}_2$, $\text{Co(HBB)}_2(\text{NO}_3)_2$, $\text{Co(HBB)}_2(\text{SCN})_2(\text{DMF})_2$ and $\text{Co(HBB)}_3(\text{ClO}_4)_3$, are similar to that of $\text{Co(HBB)}_3\text{Cl}_2$ in the visible region but differ in the near infrared by the marked asymmetry of the ν_1 band (assigned in O_h symmetry), (Fig. 1:2). Although the bands in these complexes are assigned in O_h symmetry (Table 1:3), the splitting of ν_1 must be taken as an indication of a departure from effective cubic symmetry.²²

The magnetic moments of the above complexes (Table 1:4) are in accord with the electronic spectral data.²³

The electronic spectrum²⁴ and magnetic moment²⁵ of $\text{Co(HBB)}_2(\text{SCN})_2$ indicate that the Co^{II} ions are tetrahedrally

TABLE 1:3
ELECTRONIC SPECTRAL DATA

COMPLEX	ABSORPTION MAXIMA cm.^{-1} AND ASSIGNMENT			
	$\#$	γ_3	γ_1	${}^4T_{1g}(F) \rightarrow {}^2T_{1g}(G)$
$\text{Co(HBB)}_3\text{Cl}_2$	21,300, 20,000, 19,600	18,600	8,450	16,100sh, 13,900
$\text{Co(HBB)}_3\text{Br}_2$	21,050, 20,000sh, 19,400sh	18,500	8,400	15,700, 14,800
$\text{Co(HBB)}_3\text{I}_2$	20,600, 19,600sh	18,200	8,000	13,300sh
$\text{Co(HBB)}_2(\text{NO}_3)_2$	20,800sh, 19,800sh	18,700	8,300	14,700sh
$\text{Co(HBB)}_2(\text{SCN})_2$	20,400sh	18,900	8,200	14,300sh
$(\text{DMF})_2$			7,400sh	
$\text{Co(HBB)}_3(\text{ClO}_4)_1$	21,100sh, 20,000sh	18,200	9,000 6,500	
$\text{Co(HBB)}_2(\text{SCN})_2$	T_d 20,400sh, 17,500sh 16,700, 16,100sh	γ_3	$8,000^\pm \gamma_2$	

$\#$ This fine structure is probably due to spin orbit coupling in the ${}^4T_{1g}(P)$ state

$^\pm$ Δ for this complex is $\approx 4,600 \text{ cm.}^{-1}$.

TABLE 1:4
ROOM TEMPERATURE MAGNETIC DATA

COMPLEX	χ_M' ($\times 10^{-6}$ c.g.s.u.)	μ_{eff} (B.M.)	DIAMAGNETIC CORRECTION ($\times 10^{-6}$ c.g.s.u.)
$\text{Co}(\text{HBB})_3\text{Cl}_2$	9,826	4.86	426
$\text{Co}(\text{HBB})_3\text{Br}_2$	9,964	4.89	448
$\text{Co}(\text{HBB})_3\text{I}_2$	9,363	4.72	480
$\text{Co}(\text{HBB})_2(\text{NO}_3)_2$	9,267	4.71	295
$\text{Co}(\text{HBB})_2(\text{SCN})_2(\text{DMF})_2$	8,560	4.49	407
$\text{Co}(\text{HBB})_3(\text{ClO}_4)_1$	9,259	4.69	411
$\text{Co}(\text{HBB})_2(\text{SCN})_2$	8,628	4.51	319

co-ordinated. The position of the ν_2 band in this complex, which is broad and poorly resolved, is found by taking the centre of gravity of the total intensity.²⁶

Infrared Spectral Studies

Anion Vibrations

The regions of strong broad absorption 1440 to 1360 cm^{-1} and 1360 to 1280 cm^{-1} in the spectra of $\text{Co}(\text{HBB})_2(\text{NO}_3)_2$ and $\text{Ni}(\text{HBB})_2(\text{NO}_3)_2$ can be attributed to vibrations of the nitrate ion.²⁷ The broadness of these bands and absorption by HBB renders their exact location difficult, but they lie at approximately 1430 cm^{-1} and 1300 cm^{-1} , which indicates that the nitrate ions are co-ordinated.²⁷ These bands may be assigned as the asymmetric stretch (ν_4) at 1430 cm^{-1} , and symmetric stretch (ν_1) at 1300 cm^{-1} , of the NO_2 group.²⁷ The position of ν_4 is somewhat lower than that usually found for nitrate complexes while that of ν_1 is fairly typical.²⁷ The NO stretching (ν_2) and non planar rocking (ν_6) modes which would be expected to absorb in the regions 1040 to 970 cm^{-1} and 800 to 780 cm^{-1} respectively²⁷ are almost certainly obscured by HBB absorption.

The very strong band seen at 2079 cm^{-1} in the spectrum of $\text{Co}(\text{HBB})_2(\text{SCN})_2$ and at 2105 cm^{-1} in that of $\text{Ni}(\text{HBB})_2(\text{SCN})_2$ can be assigned as the CN stretch of the thiocyanate ion,²⁸ and indicate that the anions are terminally bonded, probably through their nitrogen atom.²⁸ Examination of the region in which the CS stretch would be

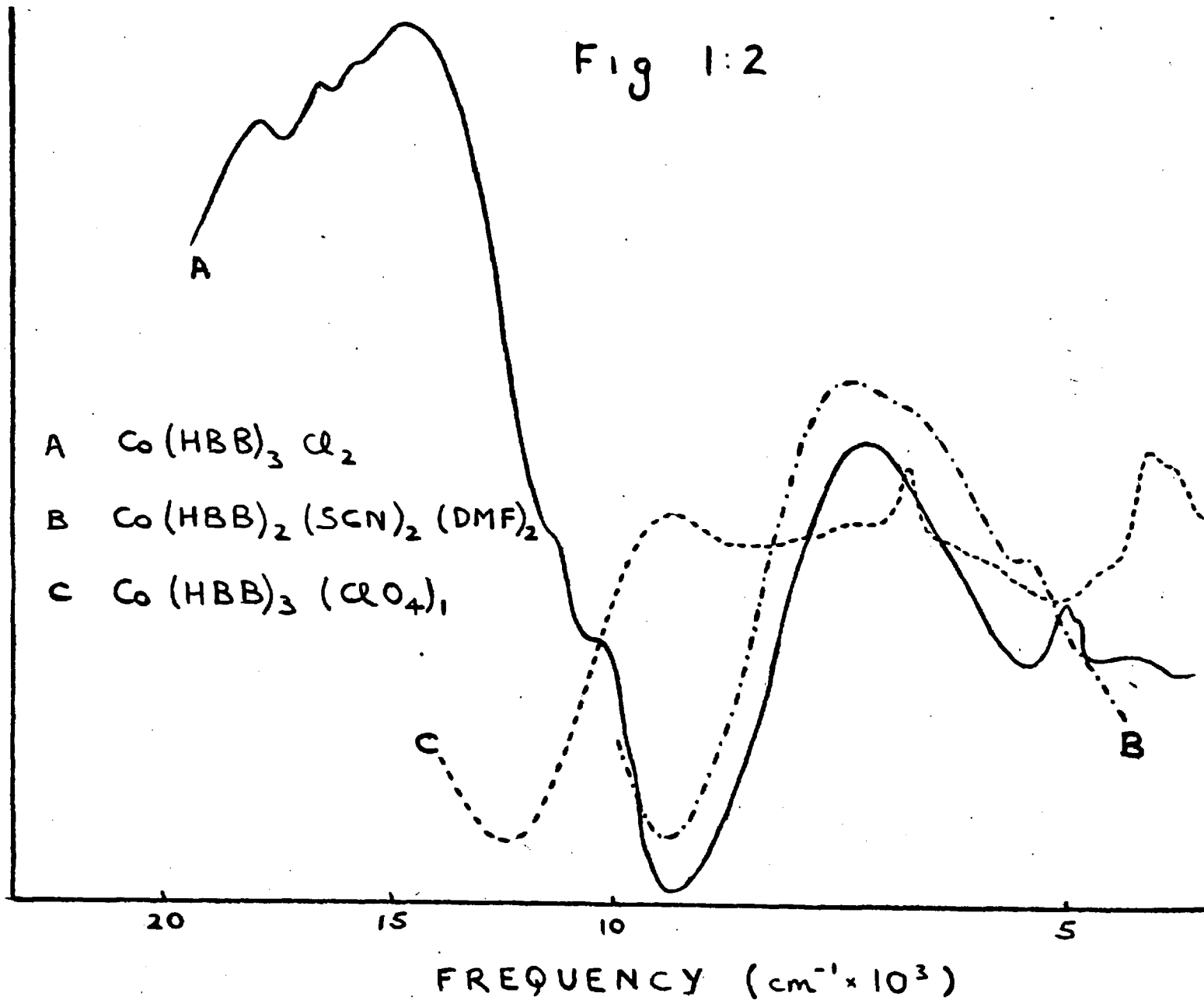
ABSORBANCE

Fig 1:2

A $\text{Co}(\text{HBB})_3 \text{Cl}_2$

B $\text{Co}(\text{HBB})_2 (\text{SCN})_2 (\text{DMF})_2$

C $\text{Co}(\text{HBB})_3 (\text{ClO}_4)_1$



expected²⁸ is rendered difficult due to absorption by HBB.

In $M(HBB)_2(SCN)_2(DMF)_2$ the CN stretch gives rise to two very strong closely spaced bands at 2091 cm^{-1} and 2085 cm^{-1} in the cobalt complex, and 2105 cm^{-1} and 2096 cm^{-1} in the nickel complex, which indicate that the anions are probably terminally nitrogen bonded.²⁸ The strong sharp band at 1656 cm^{-1} in the spectra of both these compounds can be assigned as the CO stretch of dimethylformamide.²⁹ The frequency of this vibration in dimethylformamide vapour is 1716 cm^{-1} ³⁰ and in a non polar solvent such as n hexane, 1696 cm^{-1} .³⁰ The lowering of this frequency upon complex formation is almost certainly due to either co-ordination³¹ or hydrogen bond formation³² but it is not possible to say which. The very strong broad band at 1082 cm^{-1} in the spectrum of $Co(HBB)_3(ClO_4)_1$, can be assigned to vibrations of an ionic perchlorate group.³³ Because of the complexity of the perchlorate ion absorption in $Ni(HBB)_3(ClO_4)_2$ (Table 1:5), it cannot be decided what the role of the anions in this complex is.

Discussion

There is sufficient experimental evidence to indicate that co-ordination of benzimidazoles and substituted benzimidazoles takes place through the unsaturated nitrogen atom.³⁴ This means that in HBB the possible co-ordination sites are the tertiary nitrogen atom and the oxygen atom and it might be anticipated that this molecule will chelate. Indeed most of the electronic spectral and magnetic

TABLE 1:5THE INFRA-RED SPECTRAL DATA OF $\text{Ni}(\text{HBB})_3(\text{ClO}_4)_2$

<u>$\text{Ni}(\text{HBB})_3(\text{ClO}_4)_2$</u>		<u>HBB</u>	
1323	m	1309	m
1311	s	1294	v.s
1280	v.s	1276	v.s
1259	s	1253	m
1232	m	1235	m
1193	s	1220	m
1183	s	1190	s
1152	v.s	1160	m
1138	v.s and broad	1142	w
1094	v.s and broad	1078	m
1060	v.s	1060	sh
1055	v.s	1053	v.s
1044	sh	1024	m
1042	v.s	1001	w.sh
1032	v.s		
1017	v.s and broad		
1014	sh		
1002	v.s		

The bands in the region 1170 to 1050 cm.^{-1} in $\text{Ni}(\text{HBB})_3(\text{ClO}_4)_2$ are not well resolved and form part of a very strong broad absorption trough.

data of the complexes are best rationalised in terms of chelating HBB. For instance, in the isomorphous Co and $\text{Ni}(\text{HBB})_3\text{Cl}_2$ complexes (Table 1:6) the structural data points to there being three chelating ligands in an essentially octahedral array about the metal atom. A similar structure is almost certainly assumed by Co and $\text{Ni}(\text{HBB})_3\text{Br}_2$ and Co and $\text{Ni}(\text{HBB})_3\text{I}_2$.

For Co and $\text{Ni}(\text{HBB})_2(\text{NO}_3)_2$ the infrared spectral data and molar conductance [‡] data (Table 1:7) indicate that the nitrate ions are co-ordinated. Now nitrate ions can co-ordinate either mono- or bidentately, and it is not possible to differentiate between the two forms using infrared spectroscopy.³⁵ However it was decided on the basis of certain features of the electronic spectral and magnetic data that the anions in $\text{Co}(\text{MeOBB})_2(\text{NO}_3)_2$ are chelating (Chapter Five). Since these features are absent from the magnetic and electronic spectral data of $\text{Co}(\text{HBB})_2(\text{NO}_3)_2$ (Fig. 1:3), it can be assumed that the nitrate ions are monodentate in this complex. It is not known whether Co and $\text{Ni}(\text{HBB})_2(\text{NO}_3)_2$ are isomorphous or not because of X-ray fluorescence in the cobalt complex, but it seems reasonable to assume that their structures are similar, that is chelating HBB molecules and monodentate nitrate ions in a distorted cubic array.

The complex $\text{Co}(\text{HBB})_3(\text{ClO}_4)_1$ is an example of a rather interesting aspect of the chelation properties of HBB. Since the infrared spectral data indicates that the perchlorate ion is ionic and the molar conductance is a typical uni-univalent electrolyte value,

[‡] The conductivities of some typical electrolytes in nitrobenzene and nitromethane are given in Chapter Nine.

TABLE 1:6

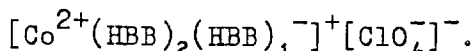
X-RAY POWDER PATTERN DATA

<u>M(HBB)₃Cl₂</u>				<u>M(HBB)₂(SCN)₂(DMF)₂</u>			
Co		Ni		Co		Ni	
d	I	d	I	d	I	d	I
16.66	0.8	16.66	0.9	12.44	0.5	12.44	1.0
10.15	1.4	10.15	2.9	11.04	1.6	11.04	5.3
8.40	2.8	8.42	3.0	10.27	1.6	10.27	5.7
6.70	0.4	6.70	0.4	9.50	1.7	9.40	5.3
5.60	0.3	5.60	0.3			8.93	1.0
5.40	0.2	5.40	0.3			8.42	1.2
5.12	0.3	5.12	0.6	7.62	0.6	7.62	1.9
4.77	0.5	4.79	0.6	6.20	0.5	6.23	1.2
4.60	0.4	4.60	0.4			5.50	1.0
3.90	0.3	3.90	0.4			4.82	0.8
3.40	0.5	3.40	0.7			4.74	1.6

d = Interplanar spacing

I = Line intensity

the following ionic structure is postulated



In this the HBB has gained a negative charge by loss of its hydroxyl proton. The reason for believing that it is this particular proton that is lost stems from studies of the analogous nPrHBB complex, (Chapter Two.)

The loss of a proton by HBB is puzzling since the structure of the complexes discussed above indicates that this hydrogen is not particularly labile. In contrast to the cobalt complex is $\text{Ni}(\text{HBB})_3(\text{ClO}_4)_2$ in which there is no proton loss, and which has a structure similar to that already discussed for $\text{Ni}(\text{HBB})_3\text{Cl}_2$.

With $\text{Co}(\text{HBB})_2(\text{SCN})_2$ the question arises whether the HBB co-ordinates through its unsaturated nitrogen atom or oxygen atom. Since the Δ value of $\text{Co}(\text{MeOBB})_2(\text{SCN})_2$, which is unlikely to contain oxygen bonded MeOBB (Chapter Five), and $\text{Co}(\text{HBB})_2(\text{SCN})_2$ are similar it can be assumed that HBB is nitrogen bonded in this complex. $\text{Co}(\text{HBB})_2(\text{SCN})_2(\text{DMF})_2$ loses two moles of dimethylformamide very quickly to give $\text{Co}(\text{HBB})_2(\text{SCN})_2$, which together with the other structural data indicates that its first co-ordination sphere is that of $\text{Co}(\text{HBB})_2(\text{SCN})_2$ plus two co-ordinated dimethylformamide molecules.

The fact that $\text{Ni}(\text{HBB})_2(\text{SCN})_2(\text{DMF})_2$ loses two moles of dimethylformamide only after prolonged heating at $\approx 140^\circ\text{C}$, and its electronic spectral data etc. are consistent with the observation that it is isomorphous with $\text{Co}(\text{HBB})_2(\text{SCN})_2(\text{DMF})_2$. Since the thiocyanate ions in $\text{Ni}(\text{HBB})_2(\text{SCN})_2$ are probably terminally nitrogen

TABLE 1:7
MOLAR CONDUCTANCE DATA IN NITROBENZENE [/]

COMPLEX	λ_M	COLOUR OF SOLUTION	SOLUBILITY	
			HOT	COLD
$\text{Ni}(\text{HBB})_3\text{Cl}_2$ [⊗]	-	-	Insoluble	Insoluble
$\text{Ni}(\text{HBB})_3\text{Br}_2$ [⊗]	-	-	Insoluble	Insoluble
$\text{Ni}(\text{HBB})_3\text{I}_2$	13.0	No colour change		Soluble
$\text{Ni}(\text{HBB})_2(\text{NO}_3)_2$	3.5	No colour change	Soluble	
$\text{Ni}(\text{HBB})_2(\text{SCN})_2$	0.5	No colour change		Soluble
$\text{Ni}(\text{HBB})_2(\text{SCN})_2(\text{DMF})_2$	0.6	No colour change		Soluble
$\text{Ni}(\text{HBB})_3(\text{ClO}_4)_2$	19.3	Cloudy	Soluble	
$\text{Co}(\text{HBB})_3\text{Cl}_2$	3.7	Blue	Soluble	
$\text{Co}(\text{HBB})_3\text{Br}_2$	5.4	Blue	Soluble	
$\text{Co}(\text{HBB})_3\text{I}_2$	12.2	No colour change		Soluble
$\text{Co}(\text{HBB})_2(\text{NO}_3)_2$	3.3	No colour change	Soluble	
$\text{Co}(\text{HBB})_2(\text{SCN})_2$	5.4	Blue		Soluble
$\text{Co}(\text{HBB})_2(\text{SCN})_2(\text{DMF})_2$	4.9	Blue		Soluble
$\text{Co}(\text{HBB})_3(\text{ClO}_4)_1$	20.0	No colour change		Soluble

[⊗] These are also insoluble in nitromethane.

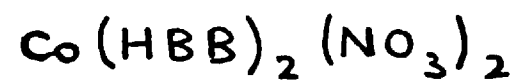
[/] The nitrobenzene itself was pale yellow.

bonded, the structure in which the remaining co-ordination positions are filled by chelating HBB might be suggested. It is however difficult to account for the intense charge transfer band and the shoulder at $18,900\text{ cm}^{-1}$ in the electronic spectrum of this complex (Fig. 1:1) on the basis of this structure. The alternative structure in which the thiocyanate ions are bridging is even more unlikely because of the position of the thiocyanate ion CN stretch and the Δ value, cf $\text{Ni}(\text{HMeB})_2(\text{SCN})_2$.

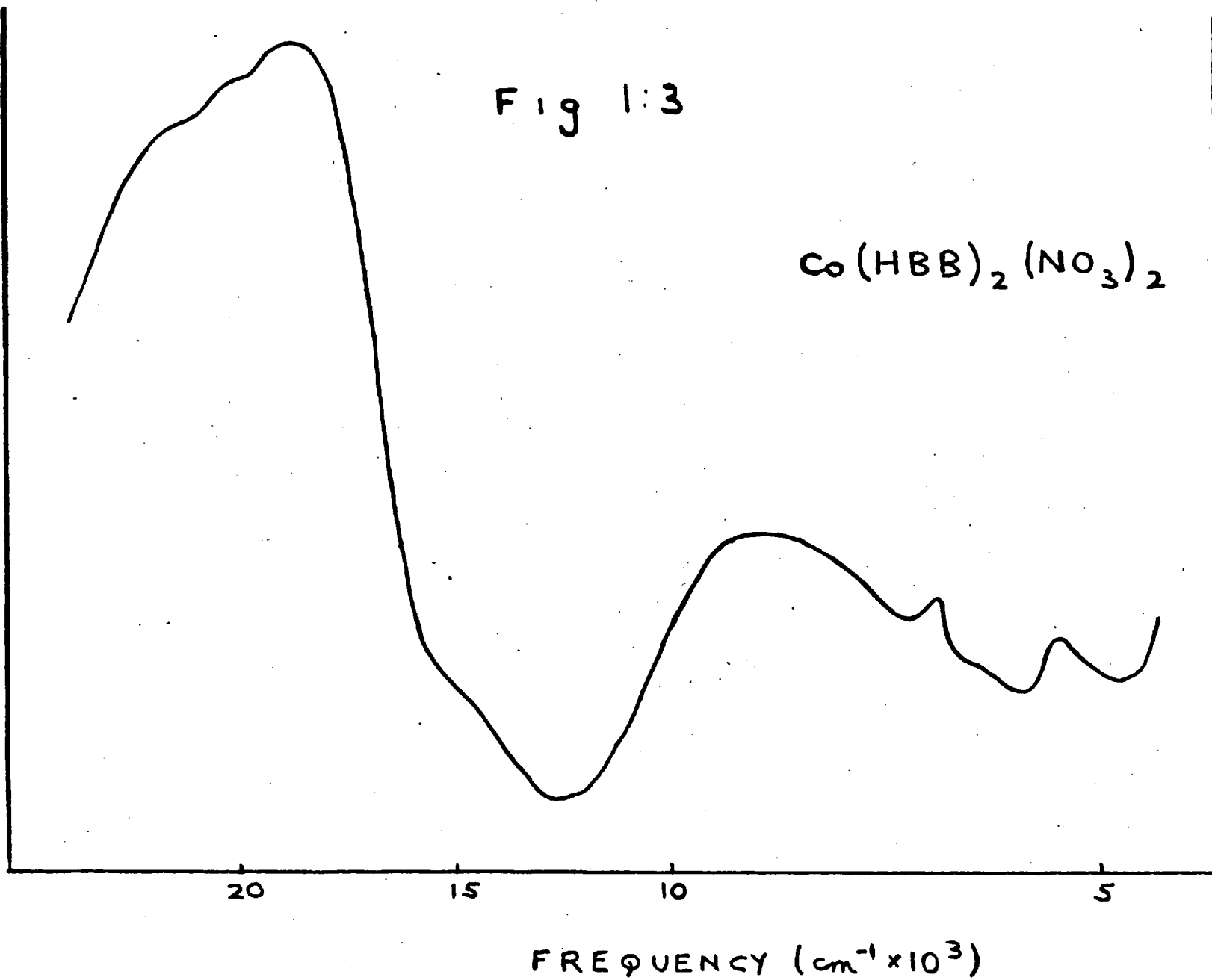
From the preceding discussion it can be seen that HBB is a good chelating agent and co-ordinates with Co^{II} and Ni^{II} ions in a way that in most cases is perhaps predictable. There are however aspects of its co-ordination chemistry that are rather puzzling. For example its behaviour with Co or $\text{Ni}(\text{NO}_3)_2$ is interesting since there seems to be no reason why the 2:1 rather than the 3:1 complex is formed. In Chapter Four an attempt is made to explain this on steric grounds, but it is possible that electronic factors are involved which make the structure in which the axial positions are filled by oxygen bonded ligands highly favourable.

It might be expected that the HBB in $\text{Co}(\text{HBB})_2(\text{SCN})_2$ would chelate since once the unsaturated nitrogen atom co-ordinates the oxygen atom is held in a position highly favourable to co-ordination. However it may be that in this complex the conformation of the HBB is such that the hydroxyl group lies on the same side of the molecule as the imino nitrogen atom, that is trans to the unsaturated nitrogen atom, and consequently is not in a position suitable for co-ordination.

Fig 1:3



ABSORBANCE



This conformation might arise if there is hydrogen bonding between the hydroxyl proton and the thiocyanate ion of an adjacent molecule. If this is also the conformation of HBB in $\text{Ni}(\text{HBB})_2(\text{SCN})_2(\text{DMF})_2$ then its reluctance to lose two moles of dimethylformamide can perhaps be explained. Desolvation of this complex without any solid state rearrangements would very probably lead to the formation of the energetically unfavourable tetrahedral species. However an octahedral stereochemistry could be achieved if the conformation of the HBB molecules altered so that the oxygen atom was cis to the unsaturated nitrogen atom. Such a solid state rearrangement would be expected to be difficult. It is seen from Fig. (1:1) that the electronic spectrum of this complex has an intense charge transfer band at $27,000 \text{ cm}^{-1}$ and a partly obscured band at $18,900 \text{ cm}^{-1}$. Now it would not be expected to find either of these bands in this spectrum, assuming it to have a structure in which the HBB chelates with the anions terminally nitrogen bonded, cf. $\text{Ni}(\text{nPrHBB})_2(\text{SCN})_2$ (Chapter Two), and $\text{Ni}(\text{MeOBB})_2(\text{SCN})_2$ (Chapter Five). The presence of these bands might indicate that electronic effects are operative in this complex which make its structure difficult to attain, this might explain the rate of desolvation of $\text{Ni}(\text{HBB})_2(\text{SCN})_2(\text{DMF})_2$ and also the structure of $\text{Co}(\text{HBB})_2(\text{SCN})_2$.

Finally the formation of $\text{Co}(\text{HBB})_3(\text{ClO}_4)_1$, in which one of the HBB molecules has lost its hydroxyl proton is most interesting since it illustrates the ability of this ligand to undergo structural modification in the presence of a metal ion. This sort

of property could be important biologically. Since $\text{Ni}(\text{ClO}_4)_2$ forms a different complex with this ligand, that is $\text{Ni}(\text{HBB})_3(\text{ClO}_4)_2$, it would seem that any explanation of the behaviour of HBB with $\text{Co}(\text{ClO}_4)_2$ would have to take into account not only the steric and electronic properties of the ligand but also the nature of the metal ion and anion.

CHAPTER TWO

Some Cobalt and Nickel Complexes of 1.nPr.2-Hydroxybenzyl- benzimidazole.

The antiviral activity of HBB is greatly increased by the substitution of a normal propyl group onto the saturated nitrogen atom of the benzimidazole ring. Because of this it was considered of interest to compare the chelation properties of nPrHBB and HBB, and so the following compounds were prepared: $M(nPrHBB)_3(ClO_4)_1$, $M(nPrHBB)_2X_2$, where M is cobalt or nickel and X is nitrate or thiocyanate, $Ni(nPrHBB)_2Cl_2$, $Co(nPrHBB)_2I_2$, $Co(nPrHBB)_{1\frac{1}{2}}Cl_2$ and $Co(nPrHBB)_{1\frac{1}{2}}Br_2$.

Electronic Spectral Studies.

The electronic spectra of $Ni(nPrHBB)_2Cl_2$, $Ni(nPrHBB)_2(SCN)_2$, $Ni(nPrHBB)_3(ClO_4)_1$ (Table 2:1) are all fairly similar and characteristic of the type expected for a Ni^{II} ion in an essentially octahedral ligand field.¹⁶ The spectrum of $Ni(nPrHBB)_2(NO_3)_2$ (Table 2:1 and Fig. 2:1) differs from the others in the splitting of the γ_1 band (assigned in O_h symmetry) which indicates a symmetry lower than effective octahedral.³⁶ For each of the four complexes the magnetic moment (Table 2:2) is in agreement with the interpretation of the electronic spectrum.¹⁷

Of the cobalt complexes the electronic spectra of $Co(nPrHBB)_2I_2$, $Co(nPrHBB)_2(NO_3)_2$, $Co(nPrHBB)_2(SCN)_2$ and $Co(nPrHBB)_3-$

TABLE 2:1
ELECTRONIC SPECTRAL DATA

COMPLEX	ABSORPTION MAXIMA cm.^{-1} AND ASSIGNMENT					
	ν_3	ν_2	ν_1	${}^3A_{2g}(F) \rightarrow {}^1T_{2g}(D)$	${}^3A_{2g}(F) \rightarrow {}^1A_{1g}(G)$	${}^3A_{2g}(F) \rightarrow {}^1E_g(D)$
$\text{Ni}(\text{nPrHBB})_2\text{Cl}_2$	24,100	14,200	8,350 [‡]	$\approx 23,300$ sh.	$\approx 20,000$ sh.	$\approx 12,500$ sh.
$\text{Ni}(\text{nPrHBB})_2(\text{NO}_3)_2$	25,650	15,200	9,250 5,800	$\approx 23,000$ sh.	-	$\approx 12,800$ sh.
$\text{Ni}(\text{nPrHBB})_2(\text{SCN})_2$	25,000	15,400	8,950 [‡]	-	$\approx 21,000$ sh.	$\approx 13,100$ sh.
$\text{Ni}(\text{nPrHBB})_3(\text{ClO}_4)_1$	25,650	15,050	9,100 [‡]	-	-	$\approx 12,900$ sh.

[‡] These energies can be taken as $\approx \Delta$.

TABLE 2:2
ROOM TEMPERATURE MAGNETIC DATA

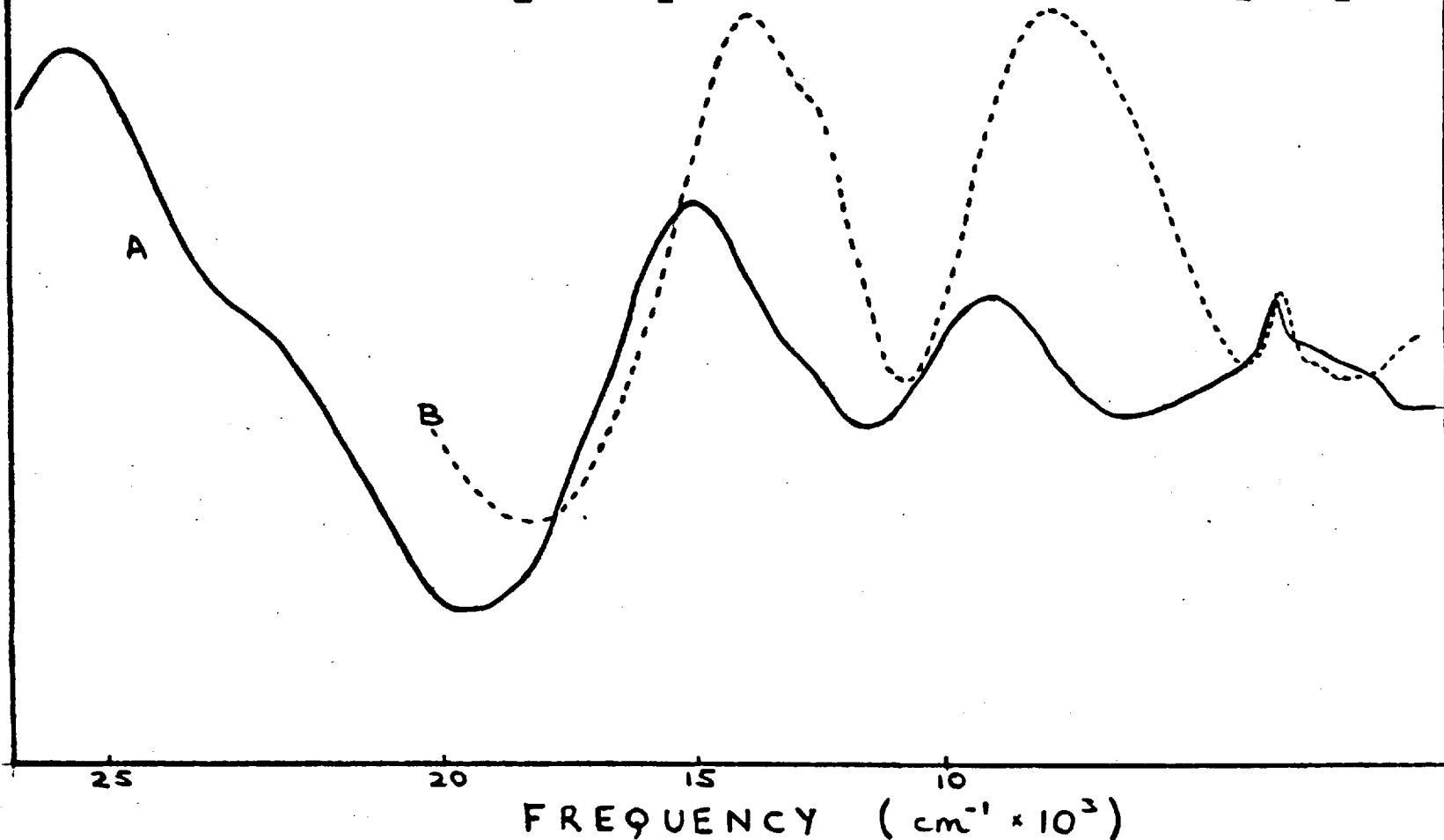
COMPLEX	χ_M ($\times 10^{-6}$ c.g.s.u.)	μ_{eff} (B.M.)	DIAMAGNETIC CORRECTION ($\times 10^{-6}$ c.g.s.u.)
$\text{Ni}(\text{nPrHBB})_2\text{Cl}_2$	4,386	3.24	373
$\text{Ni}(\text{nPrHBB})_2(\text{NO}_3)_2$	4,362	3.23	371
$\text{Ni}(\text{nPrHBB})_2(\text{SCN})_2$	4,013	3.10	395
$\text{Ni}(\text{nPrHBB})_3(\text{ClO}_4)_4$	4,508	3.28	522

Fig 2:1

A $\text{Ni}(\text{nPrHBB})_2(\text{NO}_3)_2$

B $\text{Ni}(\text{nPrHBB})_2\text{Cl}_2$

ABSORBANCE



(ClO_4), are all fairly similar except that the ν_1 band (assigned in O_h symmetry) shows varying degrees of splitting (Table 2:3). Since the spectra of these complexes in the visible region are of the type expected for an octahedrally co-ordinated Co^{II} ion,²¹ the overall spectrum can be interpreted in terms of distorted cubic symmetry.²² The magnetic moments of the complexes (Table 2:4) are somewhat lower than is usually found for spin free octahedrally co-ordinated Co^{II} ions,²³ an observation which may be accounted for in terms of loss of orbital contribution due to the low symmetry ligand field component indicated by the electronic spectra.²³

Discussion

The molar conductance of $\text{Ni}(\text{nPrHBB})_2\text{Cl}_2$ (Table 2:5) indicates that the chloride ions are very probably co-ordinated, and since the Δ value is $\approx 8,300 \text{ cm.}^{-1}$ it is unlikely that they are bridging, cf. $\text{Ni}(\text{MeOBB})_2\text{Cl}_2$ (Chapter Five). On the basis of this evidence and a knowledge of the chelation properties of HBB the most reasonable structure for this complex is one in which the nPrHBB molecules chelate through their unsaturated nitrogen and oxygen atoms, and the chloride ions are bonded monodentately.

The results of the infrared spectral and isomorphism studies are shown in Tables 2:6 and 2:7 respectively.

The position of the anion CN stretch of the isomorphous Co and $\text{Ni}(\text{nPrHBB})_2(\text{SCN})_2$ can be interpreted in terms of either bridging²⁸ or terminally nitrogen bonded thiocyanate ions.²⁸ However the

TABLE 2:3
ELECTRONIC SPECTRAL DATA

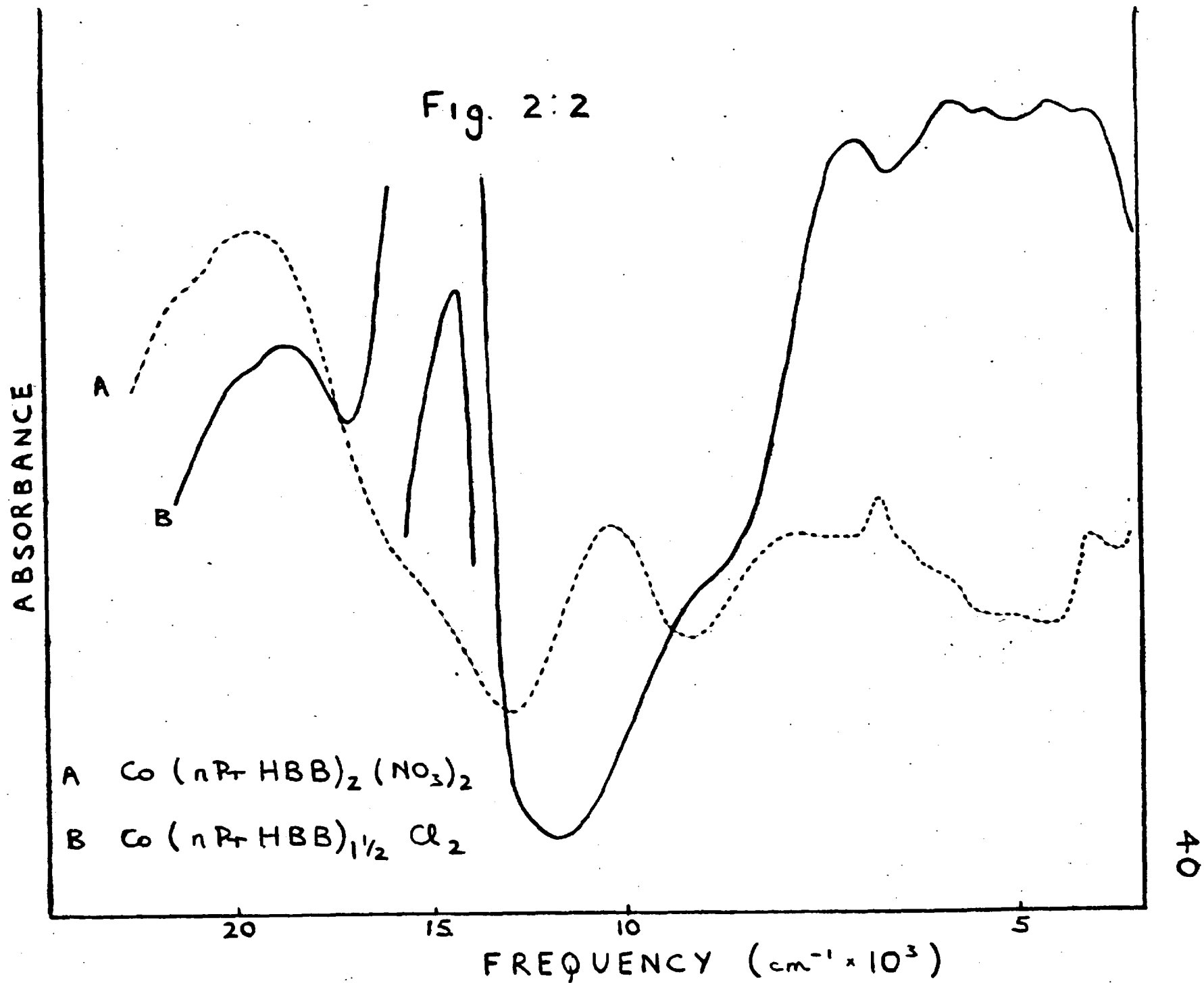
COMPLEX	ABSORPTION MAXIMA cm.^{-1} AND ASSIGNMENT			
	4A_1	$\sqrt{3}$	$\sqrt{1}$	$^4T_{1g}(F) \rightarrow ^2T_{1g}(G)$
$\text{Co}(\text{nPrHBB})\frac{1}{2}\text{Cl}_2$	$C_h \approx 20,200 \text{ sh.}$	18,850	very approx. 7,600 sh.	
	$T_d \approx 15,800 \text{ sh.}$ 14,700 $\sqrt{3}$	6,200; 4,850;	$\approx 5,400$; $\approx 5,200$ $\approx 4,700$ $\sqrt{2}$	
$\text{Co}(\text{nPrHBB})\frac{1}{2}\text{Br}_2$	$O_h \approx 20,000 \text{ sh.}$	17,650	$\approx 7,800 \text{ sh.}$	
	T_d 14,900 $\sqrt{3}$ 13,900	5,700; $\approx 4,500 \text{ sh.}$	5,000; $\approx 4,700$ $\sqrt{2}$	
$\text{Co}(\text{nPrHBB})_2\text{I}_2$	$\approx 18,500 \text{ sh.}$	17,400	9,500 $\approx 6,000$	$\approx 15,900 \text{ sh.}$
$\text{Co}(\text{nPrHBB})_2(\text{NO}_3)_2$	$\approx 21,000 \text{ sh.}$	19,600	10,500 $\approx 6,700$	$\approx 15,400 \text{ sh.}$
$\text{Co}(\text{nPrHBB})_2(\text{SCN})_2$	$\approx 20,500 \text{ sh.}$	18,600	8,700 $\approx 7,700 \text{ sh.}$	$\approx 16,400 \text{ sh.}$
$\text{Co}(\text{nPrHBB})_3(\text{ClO}_4)_1$	$\approx 20,800 \text{ sh.}$	18,450	$\approx 9,100$ $\approx 7,600$	

4A_1 Probably due to spin orbit coupling in the $^4T_{1g}(P)$ state

TABLE 2:4
ROOM TEMPERATURE MAGNETIC DATA

COMPLEX	χ_M' ($\times 10^{-6}$ c.g.s.u.)	μ (B.M.)	DIAMAGNETIC CORRECTION ($\times 10^{-6}$ c.g.s.u.)
$\text{Co}(\text{nPrHBB})\frac{1}{2} \text{Cl}_2$	9,353	4.73	300
$\text{Co}(\text{nPrHBB})\frac{1}{2} \text{Br}_2$	9,459	4.75	322
$\text{Co}(\text{nPrHBB})_2 \text{I}_2$	8,833	4.59	434
$\text{Co}(\text{nPrHBB})_2 (\text{NO}_3)_2$	9,247	4.69	371
$\text{Co}(\text{nPrHBB})_2 (\text{SCN})_2$	8,911	4.60	395
$\text{Co}(\text{nPrHBB})_3 (\text{ClO}_4)_1$	9,385	4.73	522

Fig. 2:2



Δ value of $\text{Ni}(\text{nPrHBB})_2(\text{SCN})_2$, $8,900 \text{ cm.}^{-1}$, is significantly higher than that of $\text{Ni}(\text{HMeB})_2(\text{SCN})_2$, $8,400 \text{ cm.}^{-1}$, in which the thiocyanate ions are thought to be bridging. This evidence is in favour of the interpretation of the infrared spectral data in terms of nitrogen bonded terminal thiocyanate ions. The most likely structure of these two complexes then, is one in which the nPrHBB molecules are chelating and the anions terminally nitrogen bonded, in a distorted cubic array.

The conductivities of the isomorphous Co and $\text{Ni}(\text{nPrHBB})_3-(\text{ClO}_4)$, indicate that they are 1:1 electrolytes and the infrared spectral data is in accord with this suggestion.³³ This evidence together with the electronic spectral and magnetic data suggests that the metal ions in these complexes are in a distorted octahedral ligand field that is produced by one charged and two neutral chelating nPrHBB molecules, cf. $\text{Co}(\text{HBB})_3(\text{ClO}_4)$, (Chapter One).

The complexes Co and $\text{Ni}(\text{HBB})_2(\text{NO}_3)_2$ are isomorphous and their molar conductance data indicate that the anions are co-ordinated; nothing conclusive can be said about this question from the infrared spectral data.²⁷ From a comparison of the magnetic and electronic spectral data of $\text{Co}(\text{nPrHBB})_2(\text{NO}_3)_2$ (Fig. 2:2) and $\text{Co}(\text{MeOBB})_2(\text{NO}_3)_2$ (Chapter Five), it is claimed that the nitrate ions in this complex are not chelating. On the basis of this evidence a structure may be postulated for the complexes similar to that described for Co and $\text{Ni}(\text{nPrHBB})_2\text{SCN}_2$.

The electronic spectra of $\text{Co}(\text{nPrHBB})\frac{1}{2}\text{Cl}_2$ (Fig. 2:2) and $\text{Co}(\text{nPrHBB})\frac{1}{2}\text{Br}_2$ are interesting in that they contain bands which

TABLE 2:5

MOLAR CONDUCTANCE DATA IN NITROBENZENE [‡]

COMPLEX	λ_M	COLOUR OF SOLUTION	SOLUBILITY	
			HOT	COLD
$\text{Ni}(\text{nPrHBB})_2\text{Cl}_2$	1.7	Pale yellow green		Soluble
$\text{Ni}(\text{nPrHBB})_2(\text{NO}_3)_2$	2.2	Pale yellow	Soluble	
$\text{Ni}(\text{nPrHBB})_2(\text{SCN})_2^{\dagger}$	-	-	Insoluble	Insoluble
$\text{Ni}(\text{nPrHBB})_3(\text{ClO}_4)_4$	20.2	Yellow green	Soluble	
$\text{Co}(\text{nPrHBB})_{1\frac{1}{2}}\text{Cl}_2$	2.4	Green	Soluble	
$\text{Co}(\text{nPrHBB})_{1\frac{1}{2}}\text{Br}_2$	5.8	Green	Soluble	
$\text{Co}(\text{nPrHBB})_2\text{I}_2$	8.6	Pale green	Soluble	
$\text{Co}(\text{nPrHBB})_2(\text{NO}_3)_2$	2.6	Straw pink	Soluble	
$\text{Co}(\text{nPrHBB})_2(\text{SCN})_2$	2.7	Straw pink + precipitate		Soluble
$\text{Co}(\text{nPrHBB})_3(\text{ClO}_4)_4$	20.8	Pale yellow	Soluble	

[‡] The nitrobenzene was pale yellow.

[†] This was also insoluble in Nitromethane.

TABLE 2:6

INFRA-RED SPECTRAL DATA

$\text{Co}(\text{nPrHBB})_2(\text{NO}_3)_2$	$\text{Ni}(\text{nPrHBB})_2(\text{NO}_3)_2$	nPrHBB
1484 v.s.	1488 v.s.	1493 sh. 1304 s.
1475 v.s.	1477 v.s.	1486 s. 1287 v.s.
1458 sh.	1462 sh.	1473 v.s. 1266 sh.
1453 v.s. } not well	1456 v.s. } not well	1462 s. 1259 v.s.
1445 v.s. } resolved	1449 v.s. } resolved	1451 v.s. 1250 v.s.
1437 sh.	1439 sh.	1443 v.s.
1401 s. and broad	1395 s. and broad	1412 v.s.
1379 s.	1379 s.	1374 v.s.
1337 sh.	1337 sh.	1359 v.s.
1325 sh.	1326 sh.	1346 s.
1297 v.s. and broad	1300 v.s. and broad	1332 v.s.
1269 v.s. and broad	1266 v.s. and broad	1318 v.s.

Because of the complexity of the spectrum of nPrHBB it is difficult to decide which bands in the spectra of the complexes are due to vibrations of the nitrate ion, and so it cannot be decided from this data whether the anions are co-ordinated or not.

TABLE 2:6 (Contd.)

COMPLEX	BAND POSITION	ASSIGNMENT AND INTERPRETATION
$\text{Co}(\text{HBB})_2\text{SCN}_2$	2079	CN stretch of a terminally nitrogen bonded thiocyanate ion
$\text{Co}(\text{HMeB})_2\text{SCN}_2$	2123	CN stretch of a bridging thiocyanate ion
$\text{Co}(\text{nPrHBB})_2\text{SCN}_2$	2105 v.s. and somewhat broad on low energy side	CN stretch of a terminally nitrogen bonded thiocyanate ion that is either hydrogen bonded or weakly bridging
$\text{Ni}(\text{HBB})_2(\text{SCN})_2(\text{DMF})_2$	2105 2096	CN stretch of a terminally nitrogen bonded thiocyanate ion
$\text{Ni}(\text{HMeB})_2\text{SCN}_2$	2131	CN stretch of a bridging thiocyanate ion
$\text{Ni}(\text{nPrHBB})_2\text{SCN}_2$	2121 v.s. and 2116 sh.	CN stretch of a terminally nitrogen bonded thiocyanate ion that is either hydrogen bonded or weakly bridging
$\text{Co}(\text{nPrHBB})_3(\text{ClO}_4)_4$	1089 v.s. and broad	Vibrations of an ionic perchlorate
$\text{Ni}(\text{nPrHBB})_3(\text{ClO}_4)_4$	1089 v.s. and broad	Vibrations of an ionic perchlorate

can be assigned in octahedral and tetrahedral symmetry. A comparison of the position of the ν_2 and ν_3 transitions observed in the spectra of various salts containing the tetra halo ion $\text{CoCl}_4^{=}$ ³⁷ with those seen in the spectra of $\text{Co}(\text{nPrHBB})_2\text{Cl}_2$, shows them to be very similar. This indicates that the tetrahedral species in this complex is the anion $\text{CoCl}_4^{=}$. An equivalent statement holds for $\text{Co}(\text{nPrHBB})_2\text{Br}_2$ ³⁷. Since the ν_1 band (assigned in O_h symmetry) in $\text{Co}(\text{nPrHBB})_2\text{Cl}_2$ and Br_2 is partly obscured by the ν_2 transition of the tetra halo ion, identification of the octahedral species is difficult. However the ν_1 and ν_3 bands (assigned in O_h symmetry) are in similar positions in both of these complexes which indicates that the octahedral species are almost certainly the same. This observation together with the stoichiometry of the complexes indicates that the octahedral species is very probably $\text{Co}(\text{nPrHBB})_3^{2+}$. The magnetic moment of both these complexes can be explained on the basis of a mixture of octahedrally and tetrahedrally co-ordinated Co^{II} ions.

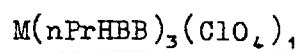
From the electronic spectral and magnetic data of $\text{Co}(\text{nPrHBB})_2\text{I}_2$ and the chelation properties of nPrHBB a structure can be assigned to this complex similar to that already described for the other 2:1 compounds.

Although HBB and nPrHBB form complexes of different stoichiometry with the halides of Co^{II} and Ni^{II} they nevertheless behave similarly in that in each case the ligands chelate. The explanation for the different stoichiometries of these complexes might be that the presence of the normal propyl group in nPrHBB makes

TABLE 2:7

X-RAY POWDER PATTERN DATA

<u>M(nPrHBB)₂(SCN)₂</u>				<u>M(nPrHBB)₂(NO₃)₂</u>			
Co		Ni		Co		Ni	
d	I	d	I	d	I	d	I
11.20	s	11.20	s	12.80	s	12.80	s
8.00	m	8.00	m	9.50	s	11.00	v.w
7.10	m	7.10	m	8.60	s	9.50	s
6.70	m	6.70	m	6.70	s	8.60	s
6.20	v.s	6.20	v.s	6.30	m	6.70	s
5.78	w	5.78	w	5.80	w	6.30	m
5.18	w	5.18	w	5.60	w	5.80	w
4.90	w	4.90	w	5.00	v.w	5.60	w
4.70	w	4.70	w	4.80	v.w	5.00	v.w
4.35	s	4.35	s	4.65	m	4.80	v.w
4.18	s	4.18	s	4.45	m	4.65	m
4.02	s	4.02	s	4.35	w	4.55	w
3.85	w	3.85	w	4.28	m	4.45	m
3.80	m	3.80	m	4.22	w	4.35	w
		3.75	v.w	4.03	m	4.28	m
3.70	w	3.70	w	3.84	w	4.22	w
3.42	m	3.42	m	3.79	w	4.03	w
3.36	w	3.36	w	3.72	v.w	4.01	w
3.29	w	3.29	w	3.65	m	3.84	w
3.22	m	3.22	w	3.50	v.w	3.79	w
3.10	m	3.10	m	3.33	v.w	3.72	v.w
2.93	m	2.93	m	3.30	v.w	3.65	m
						3.50	v.w
						3.33	v.w
						3.30	v.w

TABLE 2:7 (Contd.)

Co		Ni	
d	I	d	I
12.90	s	12.90	s
11.80	s	11.80	s
10.03	w	10.03	w
9.80	s	9.80	s
9.03	v.w	9.03	v.w
8.40	v.w	8.40	v.w
8.30	v.w	8.30	v.w
7.02	v.w	7.02	v.w
6.70	v.w	6.70	v.w
6.50	v.w	6.50	v.w
6.01	v.w	6.01	v.w
5.80	v.w	5.80	v.w
5.59	v.w	5.59	v.w
5.40	v.w	5.40	v.w
5.20	v.w	5.20	v.w
5.00	v.w	5.00	v.w
4.75	s	4.75	s
4.65	v.w	4.65	v.w
4.55	w	4.55	w
4.30	w	4.30	w
4.10	s	4.10	s
4.08	m	4.08	m

formation of complexes of the type Co or $\text{Ni}(\text{nPrHBB})_3\text{X}_2$, where X is an halide ion, sterically unfavourable.

With Co and $\text{Ni}(\text{NO}_3)_2$, HBB and nPrHBB form complexes of similar structure, that is both contain chelating ligand and monodentate nitrate ions. However the difference in the ν_1 band in the electronic spectra of these complexes, that is ν_1 in Ni and $\text{Co}(\text{nPrHBB})_2(\text{NO}_3)_3$ shows quite a large splitting whereas the ν_1 band in Ni and $\text{Co}(\text{HBB})_2(\text{NO}_3)_2$ is virtually unsplit, indicates that the two types of complex are in some way different. Whether this difference is due to steric or electronic factors is not known.

That nPrHBB chelates quite readily with Co and $\text{Ni}(\text{SCN})_2$ whereas HBB is reluctant to do so, is perhaps the most important difference in the co-ordination chemistry of these two ligands. It might be argued that the reason for this difference is that the particular conformation of HBB which gave rise to $\text{Co}(\text{HBB})_2(\text{SCN})_2$ is rendered unfavourable in nPrHBB by the steric hindrance of the normal propyl group on the 1 N atom. The absence from the electronic spectrum of $\text{Ni}(\text{nPrHBB})_2(\text{SCN})_2$ of any of the peculiar features seen in that of $\text{Ni}(\text{HBB})_2(\text{SCN})_2$ might lend support to the suggestion that HBB chelates with $\text{Ni}(\text{SCN})_2$ only with difficulty and not at all with $\text{Co}(\text{SCN})_2$ because of electronic factors which render such structures unfavourable.

With $\text{Co}(\text{ClO}_4)_2$, HBB and nPrHBB form very similar complexes, indeed it is with $\text{Co}(\text{ClO}_4)_2$ that these ligands show most similarity in properties. In contrast to this behaviour is the nature of the complexes formed by HBB and nPrHBB with $\text{Ni}(\text{ClO}_4)_2$, that is

$\text{Ni}(\text{HBB})_3(\text{ClO}_4)_2$ and $\text{Ni}(\text{nPrHBB})_3(\text{ClO}_4)_1$. The reason for the difference in these two complexes is not known but it does perhaps suggest that the hydroxyl proton in nPrHBB is more labile than that in HBB. If formation of this type of complex is due to the lability of the ligand hydroxyl proton, then it is puzzling why only one nPrHBB molecule loses its proton.

CHAPTER THREE

Some Cobalt and Nickel Complexes of 1,isoPropyl,2- α -Hydroxybenzyl-benzimidazole.

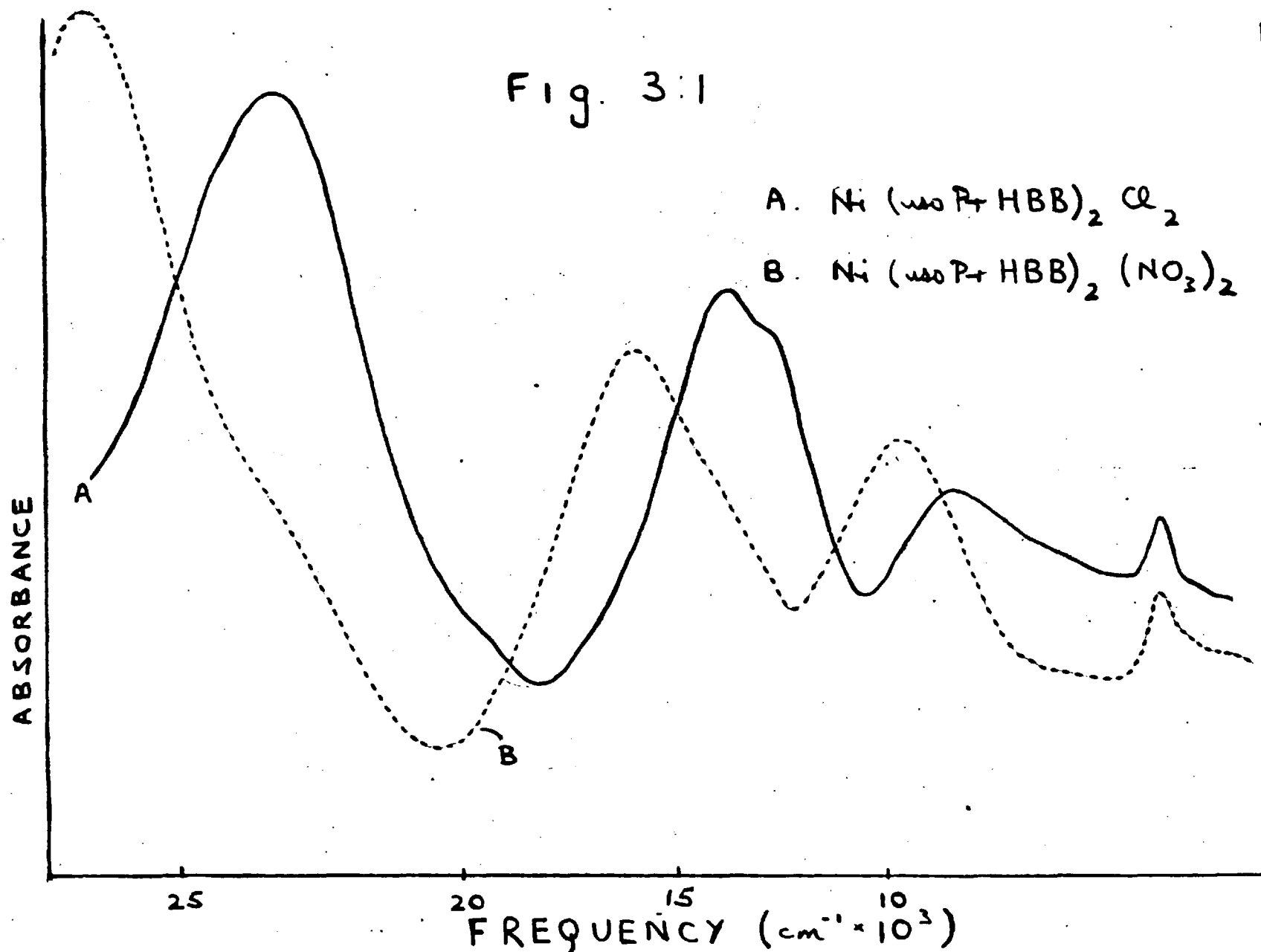
The antiviral activity of nPrHBB and iso nPrHBB are markedly different, and yet structurally they only differ in the stereochemistry of the 1 N substituent. It might be thought that such a difference would be trivial from the point of view of their coordination chemistry. If this proved to be the case it would then be difficult to see how the chelation properties of these molecules could be related to their virus inhibitory activity. Therefore to investigate the chelation properties of isoPrHBB for comparison with nPrHBB the following complexes were prepared: $\text{Co}(\text{isoPrHBB})_x\text{Cl}_2$, $\text{Ni}(\text{isoPrHBB})_2\text{Cl}_2$, $\text{M}(\text{isoPrHBB})_2(\text{NO}_3)_2$, $\text{M}(\text{isoPrHBB})_2(\text{ClO}_4)_2$ and $\text{M}(\text{isoPrHBB})_2(\text{SCN})_2$, where M is cobalt or nickel.

Discussion

From the stoichiometry and similarity in ligands it might be expected that the structures of $\text{Ni}(\text{isoPrHBB})_2\text{Cl}_2$ and $\text{Ni}(\text{nPrHBB})_2\text{Cl}_2$ would be similar. The structural data of $\text{Ni}(\text{isoPrHBB})_2\text{Cl}_2$ indicate that this assumption is essentially correct. However an interesting difference between the two complexes is seen in the position and intensity of their electronic spectral γ_1 transitions, that is γ_1 , in the spectrum of $\text{Ni}(\text{isoPrHBB})_2\text{Cl}_2$ (Table 3:1 and Fig. 3:1) is appreciably less intense and lies at higher energy than the corresponding band in $\text{Ni}(\text{nPrHBB})_2\text{Cl}_2$ (Table 2:1 and Fig. 2:1).

TABLE 3:1
ELECTRONIC SPECTRAL DATA

COMPLEX	ABSORPTION MAXIMA cm^{-1} AND ASSIGNMENT					
	ν_3	ν_2	ν_1	${}^3A_{2g}(F) \rightarrow {}^1T_{2g}(D)$	${}^3A_{2g}(F) \rightarrow {}^1A_{1g}(G)$	${}^3A_{2g}(F) \rightarrow {}^1E_{1g}(D)$
$\text{Ni}(\text{IsoPrHBB})_2\text{Cl}_2$	23,600	13,900	8,550	-	$\approx 19,600$ sh.	$\approx 12,900$ sh.
$\text{Ni}(\text{IsoPrHBB})_2(\text{NO}_3)_2$	26,450	16,150	9,700	$\approx 23,300$ sh	-	$\approx 14,100$
$\text{Ni}(\text{IsoPrHBB})_2(\text{SCN})_2$	25,000	15,250	8,800		$\approx 21,100$ sh.	$\approx 13,500$ sh.
$\text{Ni}(\text{IsoPrHBB})_2(\text{ClO}_4)_2$	25,750	15,050	9,100	$\approx 23,000$ sh.	-	$\approx 13,000$ sh.



The analysis of $\text{Co}(\text{isoPrHBB})_x\text{Cl}_2$ cannot be fitted to any rational stoichiometry and so it is concluded that it is a mixture. A comparison of the electronic spectrum of this complex and $\text{Co}(\text{nPrHBB})_{1/2}\text{Cl}_2$ shows them to be very similar (Tables 3:2 and 2:3 and Figs. 3:2 and 2:2). This may be interpreted as indicating that the predominant component of this mixture is the species $\text{Co}(\text{isoPrHBB})_3^{2+}(\text{CoCl}_4)^{2-}$. Since the analysis indicates that the stoichiometry of $\text{Co}(\text{isoPrHBB})_x\text{Cl}_2$ is less than $1\frac{1}{2}:1$ it would seem reasonable to suppose that the second component is of stoichiometry 1:1, and might be of the form $\text{Co}(\text{isoPrHBB})(\text{Cl})_2$. Such a complex would very probably be tetrahedral and the band at $\approx 16,000 \text{ cm.}^{-1}$ in the electronic spectrum of $\text{Co}(\text{isoPrHBB})_x\text{Cl}_2$ might be due to its partly obscured ν_3 transition, the ν_2 transition being totally obscured by the intense broad ν_2 band of the tetrahalo ion.

The infrared spectral data of Co and $\text{Ni}(\text{isoPrHBB})_2(\text{NO}_3)_2$ (Table 3:3), which are isomorphous (Table 3:4), furnishes no evidence as to the nature of the anions, but the molar conductance data (Table 3:5) indicate that they are probably co-ordinated. That the nitrate ions are monodentate is indicated from a comparison of the electronic spectrum and magnetic datum of $\text{Co}(\text{isoPrHBB})_2(\text{NO}_3)_2$ (Fig. 3:2 and Table 3:6), with that of $\text{Co}(\text{MeOBB})_2(\text{NO}_3)_2$ (Chapter Five). Therefore a structure may be postulated for these complexes similar to that put forward for Co and $\text{Ni}(\text{nPrHBB})_2(\text{NO}_3)_2$.

The electronic spectral data of the isomorphous Co^{22} and $\text{Ni}(\text{isoPrHBB})_2(\text{ClO}_4)_2^{36}$ indicate that the symmetry is distorted

TABLE 3:2
ELECTRONIC SPECTRAL DATA

COMPLEX	ABSORPTION MAXIMA cm.^{-1} AND ASSIGNMENT		
	$\checkmark_3$	$\checkmark_1$	${}^4T_{1g}(F) \rightarrow {}^2T_{1g}(G)$
$\text{Co(isoPrHBB)}_x\text{Cl}_2$	$O_h \quad \approx 20,400 \text{ sh} \quad \approx 18,500 \text{ sh}$	very approx. 8,700 sh	-
	$T_d \quad 16,150 \checkmark_3$ $T_d \quad 14,950 \checkmark_3; 6,175; 5,550; \approx 5,400 \text{ sh} \checkmark_2$ $4,900; 4,650.$		
$\text{Co(isoPrHBB)}_2(\text{NO}_3)_2$	$\approx 21,300 \text{ sh}; 19,900; \approx 19,050 \text{ sh}$	10,300 $\approx 7,100$	
$\text{Co(isoPrHBB)}_2(\text{ClO}_4)_2$	$\approx 20,600 \text{ sh}; \approx 19,800 \text{ sh}; \approx 19,300 \text{ sh}; 18,450$	8,200 $\approx 7,150 \text{ sh}$	$\approx 14,800 \text{ sh}$
$\text{Co(isoPrHBB)}_2(\text{SCN})_2$	$20,500; 18,450; \approx 16,100 \text{ sh}$	8,600 $\approx 7,400$	$\approx 13,300 \text{ sh}$

The fine structure associated with $\checkmark_3$ (assigned in O_h symmetry) probably arises from spin orbit coupling in the ${}^4T_{1g}(P)$ state.

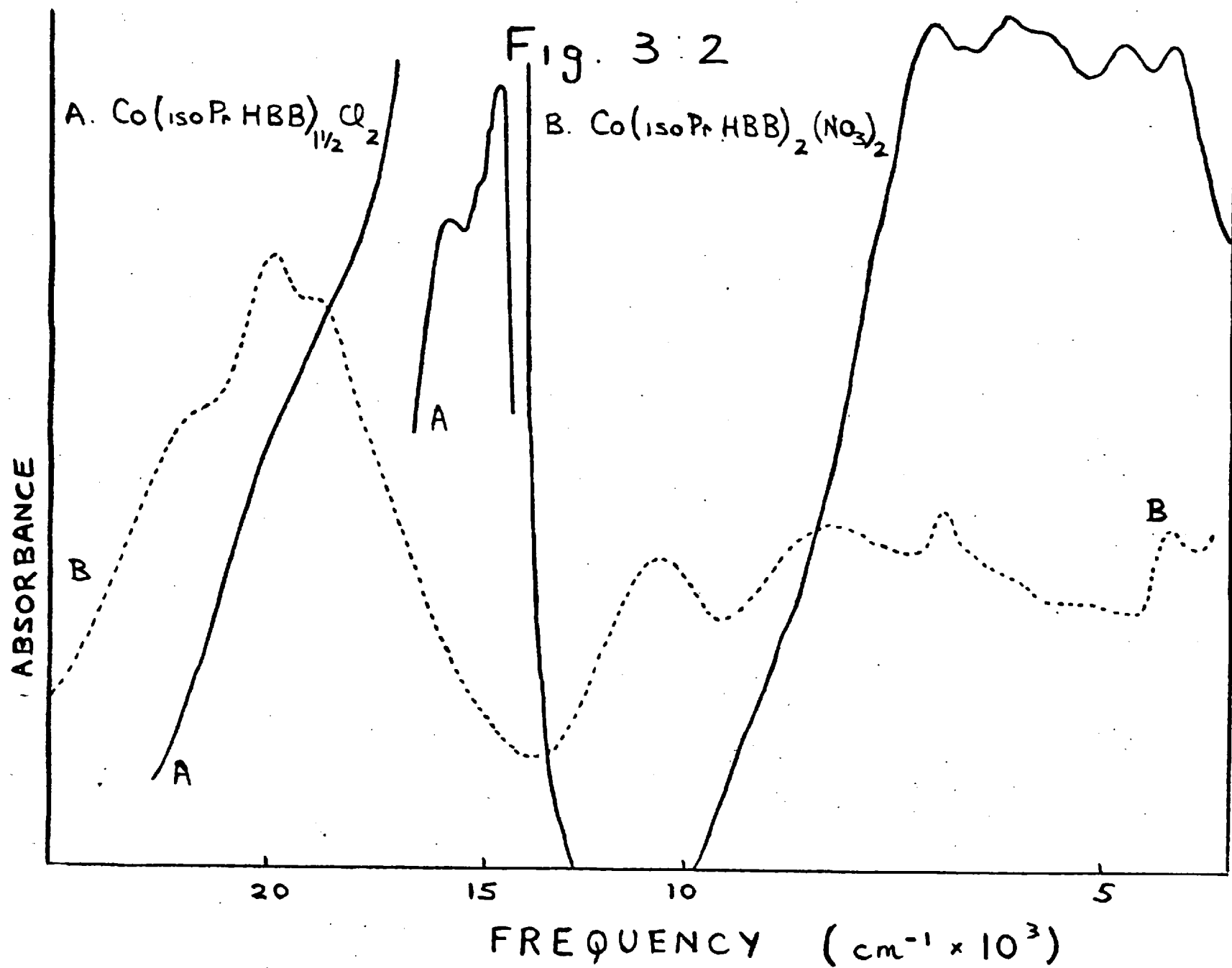


TABLE 3:3
INFRA-RED SPECTRAL DATA

$\text{Co}(\text{isoPrHBB})_2(\text{NO}_3)_2$	$\text{Ni}(\text{isoPrHBB})_2(\text{NO}_3)_2$	isoPrHBB
1488 sh	1490 sh	1493 s 1263 v.s
1471 sh	1475 sh	1458 v.s 1247 v.s
1462 v.s and broad	1464 v.s	1449 v.s
1443 v.s	1447 sh	1412 v.s
1397 sh	1397 sh	1399 v.s
1377 v.s and broad	1359 v.s and broad	1370 s
1337 sh	1340 s and broad	1333 sh
1319 sh	1326 s and broad	1318 s
1299 v.s and broad	1302 v.s	1305 v.s
	1279 s	1287 v.s

It is not possible to decide definitely what bands in the spectra of the complexes are due to vibrations of the nitrate ion and consequently the question as to whether the anions are ionic or co-ordinated cannot be resolved.

TABLE 3:3 (Contd.)

$\text{Co}(\text{isoPrHBB})_2(\text{ClO}_4)_2$	$\text{Ni}(\text{isoPrHBB})_2(\text{ClO}_4)_2$	isoPrHBB
1188 sh	1188 sh	1245 s 1053 v.s
1176 m	1176 m	1192 m 1025 m.s
1159 sh	1157 sh	1170 s 1010 m
1129 sh	1127 s	1161 s
1111 v.s	1111 v.s	1157 s
1094 v.s	1095 v.s	1139 s
1033 s	1087 v.s	1111 s
1017 s	1031 s	1093 s
	1018 s	1078 m.s

The very strong broad absorption band extending from 1205 to 9520 cm^{-1} in the spectra of the complexes is due to vibrations of the perchlorate ion. The poor resolution of this band makes it difficult to decide whether the anions are ionic or co-ordinated.

TABLE 3:3 (Contd. 2)

COMPLEX	BAND POSITION	ASSIGNMENT AND INTERPRETATION
$\text{Co}(\text{HNN})_2\text{SCN}_2$	2079	CN stretch of a terminally nitrogen bonded thiocyanate ion
$\text{Co}(\text{HMeB})_2\text{SCN}_2$	2123	CN stretch of a bridging thiocyanate ion
$\text{Co}(\text{isoPrHBB})_2\text{SCN}_2$	2089 v.s and broad	CN stretch of a terminally nitrogen bonded thiocyanate ion
$\text{Ni}(\text{HBB})_2(\text{SCN})_2(\text{DMF})_2$	2105 2096	CN stretch of a terminally nitrogen bonded thiocyanate ion
$\text{Ni}(\text{HMeB})_2\text{SCN}_2$	2131	CN stretch of a bridging thiocyanate ion
$\text{Ni}(\text{isoPrHBB})_2\text{SCN}_2$	2105 v.s and broad	CN stretch of a terminally nitrogen bonded thiocyanate ion

octahedral, but unfortunately it is not possible to tell from the infrared spectrum whether the perchlorate ions contribute to the ligand field or not. It is to be expected that the anions are not co-ordinated. The magnetic moments of both complexes are somewhat lower than is usually found for six co-ordinate spin free Ni^{II} ¹⁷ and Co^{II} ²³ ions (Tables 3:7 and 3:6), and to try and elucidate the mechanism of this lowering the susceptibilities were measured over the temperature range 300 to 77°A. The experimental results are shown in the form of a plot of T against $1/\chi'$ (Fig. 3:3) from which it can be seen that the complexes follow a Curie Weiss law over the entire temperature range.

Two mechanisms for this sort of magnetic behaviour may be considered, one is spin free - spin paired equilibria³⁸ and the other antiferromagnetism.³⁹ The phenomenon of spin free - spin paired equilibria which is theoretically possible in octahedral complexes of the systems d^4 , d^5 , d^6 , and d^7 arises in octahedral Ni^{II} complexes when the axial ligand field strength is reduced relative to the in-plane field, causing the singlet state to drop in energy.³⁸ This means that at some particular range of values of axial to in-plane ligand field strength, the separation of the singlet and triplet levels should be of the order of kT , that is the upper state should be thermally accessible. If it is assumed that in $\text{Ni}(\text{isoPrHBB})_2(\text{ClO}_4)_2$ the separation of the singlet and triplet states is $\approx kT$ and further that the triplet state lies lowest then the magnetic properties of this complex might be accounted for. A similar argument holds for

Fig 3:3

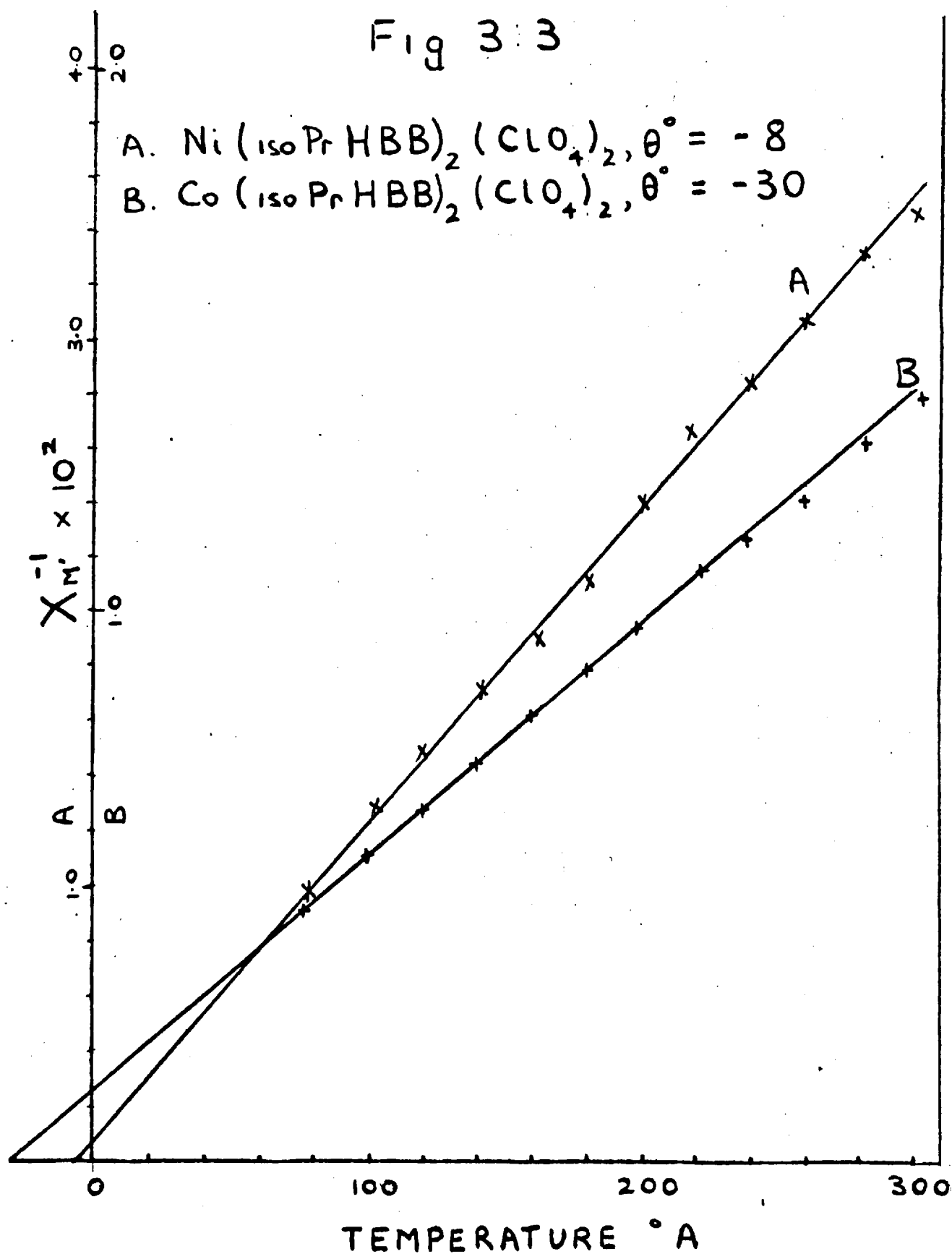


TABLE 3:4

X-RAY POWDER PATTERN DATA

<u>M(isoPrHBB)₂(ClO₄)₂</u>				<u>M(isoPrHBB)₂(NO₃)₂</u>			
Co		Ni		Co		Ni	
d	I	d	I	d	I	d	I
12.8	w	12.8	w	12.3	v.s	12.3	v.s
10.0	s	10.0	s	9.8	w	9.8	w
8.3	m	8.3	m	8.3	w	8.3	w
(unresolved doublet)		(unresolved doublet)		7.2	w	7.2	w
				6.8	s	6.8	s
7.2	v.w	7.3	v.w	6.6	w	6.6	w
(unresolved doublet)		7.1	v.w	6.3	m	6.3	m
6.6	v.w	6.6	v.w	5.8	s	5.8	s
4.32	s	4.32	s	4.82	m	4.82	m
4.20	m	4.20	m	4.63	w	4.63	w
4.00	m	4.00	m	4.46	w	4.46	w
				4.39	m	4.39	m
				4.10	s	4.10	s
				(doublet)		(doublet)	
				3.82	s	3.82	s
				3.70	w	3.70	w
				3.58	m	3.58	m
				3.42	w	3.42	w
				2.69	m	2.69	m

⌘ not resolved.

TABLE 3:5
MOLAR CONDUCTANCE DATA IN NITROBENZENE [‡]

COMPLEX	λ_M	COLOUR OF SOLUTION	SOLUBILITY	
			HOT	COLD
$\text{Co}(\text{isoPrHBB})_x\text{Cl}_2$	-		Insoluble	Insoluble
$\text{Co}(\text{isoPrHBB})_x\text{Cl}_2$ [/]	25.6	Blue	Soluble	
$\text{Co}(\text{isoPrHBB})_2(\text{NO}_3)_2$	2.5	Yellow pink	Soluble	
$\text{Co}(\text{isoPrHBB})_2(\text{SCN})_2$	7.0	Blue green		Soluble
$\text{Co}(\text{isoPrHBB})_2(\text{ClO}_4)_2$	24.3	Pale yellow		Soluble
$\text{Ni}(\text{isoPrHBB})_2\text{Cl}_2$	1.7	Pale green		Soluble
$\text{Ni}(\text{isoPrHBB})_2(\text{NO}_3)_2$	2.4	Yellow green		Soluble
$\text{Ni}(\text{isoPrHBB})_2(\text{SCN})_2$	2.5	Yellow green	Soluble	
$\text{Ni}(\text{isoPrHBB})_2(\text{ClO}_4)_2$	21.4	Yellow green		Soluble

[‡] The nitrobenzene itself was pale yellow.

[/] This was measured in nitromethane.

the cobalt complex.

Antiferromagnetism, which is not uncommon amongst Co^{II} and Ni^{II} , complexes, can arise either by direct metal metal interaction or by "super exchange" through an intervening group.³⁹ If the structure of Co or $\text{Ni}(\text{isoPrHBB})_2(\text{ClO}_4)_2$ is such that the two ligands are chelating and lie in the plane with the axial positions filled by the 1. nitrogen atom of ligand molecules in layers above and below, then it is quite possible that antiferromagnetic coupling might take place through the bridging groups. This sort of mechanism could well lead to the temperature variation of susceptibility shown in Fig. 3:3.

Of the two possible explanations for the magnetic behaviour of these complexes the one involving spin free - spin paired equilibria seems least probable. This is because it is unlikely that the conditions that are necessary to produce partial spin pairing in a d^8 system would also suffice to produce the same phenomenon in a d^7 complex. On the other hand any peculiarities of structure which give rise to antiferromagnetism in the nickel complex are also likely to produce the same effect in the isomorphous $\text{Co}(\text{isoPrHBB})_2(\text{ClO}_4)_2$.

Despite the non-isomorphous nature of Co and $\text{Ni}(\text{isoPrHBB})_2(\text{SCN})_2$ the structural data indicate that their structures are similar, that is, terminally nitrogen bonded thiocyanate ions and chelating ligands in an essentially cubic array.

It can be seen from the preceding discussion that the coordination chemistry of nPrHBB and isoPrHBB with CoCl_2 , NiCl_2 , $\text{Co}(\text{SCN})_2$ and $\text{Ni}(\text{SCN})_2$ is quite similar. These two ligands also form similar

TABLE 3: 6
ROOM TEMPERATURE MAGNETIC DATA

COMPLEX	χ_M' ($\times 10^{-6}$ c.g.s.u.)	μ_{eff} (B.M.)	DIAMAGNETIC CORRECTION ($\times 10^{-6}$ c.g.s.u.)
$\text{Co}(\text{isoPrHBB})_2(\text{NO}_3)_2$	10,175	4.95	371
$\text{Co}(\text{isoPrHBB})_2\text{SCN}_2$	9,479	4.76	395
$\text{Co}(\text{isoPrHBB})_2(\text{ClO}_4)_2$	7,479	4.25	397

TABLE 3:7
ROOM TEMPERATURE MAGNETIC DATA

COMPLEX	χ_M ($\times 10^{-6}$ c.g.s.u.)	μ_{eff} (B.M.)	DIAMAGNETIC CORRECTION ($\times 10^{-6}$ c.g.s.u.)
Ni(isoPrHBB) ₂ Cl ₂	4,473	3.27	380
Ni(isoPrHBB) ₂ (NO ₃) ₂	4,283	3.20	371
Ni(isoPrHBB) ₂ (SCN) ₂	4,425	3.26	395
Ni(isoPrHBB) ₂ (ClO ₄) ₂	2,564	2.67	397

complexes with Co and $\text{Ni}(\text{NO}_3)_2$ but an interesting point of difference is the appearance of the electronic spectral γ_1 band of the nickel complex, that is γ_1 in $\text{Ni}(\text{isoPrHBB})_2(\text{NO}_3)_2$ is unsplit whereas γ_1 in $\text{Ni}(\text{nPrHBB})_2(\text{NO}_3)_2$ shows quite a large splitting, cf. $\text{Ni}(\text{HBB})_2(\text{NO}_3)_2$. In both the cobalt complexes the splitting of γ_1 is fairly similar.

By far the most important difference between the chelation properties of nPrHBB and isoPrHBB is seen in the complexes they form with Co and $\text{Ni}(\text{ClO}_4)_2$, that is Co and $\text{Ni}(\text{nPrHBB})_3(\text{ClO}_4)_1$, and Co and $\text{Ni}(\text{isoPrHBB})_2(\text{ClO}_4)_2$. If it is assumed that the structure of Co and $\text{Ni}(\text{isoPrHBB})_2(\text{ClO}_4)_2$ is that discussed on page 63 then a possible reason for its attainment can be advanced. Since the substituent on the 1.N atom in isoPrHBB is a branched chain alkyl group its inductive effect, that is electron releasing properties might cause a greater build up of electron density on the 1.N atom as compared to the same atom in nPrHBB. The inductive effect of straight chained alkyl groups tends to be less than that of the branched chain isomers⁴⁰. Such an increase in electron density on this nitrogen atom might make it a suitable co-ordination site, particularly if the complex crystallises out with a layer structure in which these atoms are held in a suitable position for co-ordination. This explanation might be acceptable if the only other groups competing for the axial positions are the weak co-ordinators, the perchlorate ions, but there seems to be no reason why the structure found in Co and $\text{Ni}(\text{nPrHBB})_3(\text{ClO}_4)_1$, is not attained.

CHAPTER FOUR

Some Cobalt and Nickel Complexes of 2-Hydroxymethylbenzimidazole.

Since it is thought that the chelation properties of HBB might be related to its antiviral activity, it was considered important to compare its co-ordination chemistry with that of a benzimidazole derivative of similar structure but no virus inhibitory action. For this purpose the compound HMeB was chosen, and the complexes prepared were $M(\text{HMeB})_3\text{X}_2$ and $M(\text{HMeB})_2(\text{SCN})_2$ where M is cobalt or nickel and X is chloride, iodide, nitrate or perchlorate.

Discussion

The electronic spectral¹⁶ and magnetic data¹⁷ of the nickel complexes (Tables 4:1 and 4:2) indicate that the Ni^{II} ions are six co-ordinate. In the case of $\text{Ni}(\text{HMeB})_3\text{Cl}_2$, I_2 , and $(\text{ClO}_4)_2$ it can be further claimed that the metal ions are in an effectively cubic environment.¹⁶ Moreover the position of the γ_1 transition in the electronic spectra of these complexes and $\text{Ni}(\text{HMeB})_3(\text{NO}_3)_2$, although in this spectrum it shows sign of splitting, is similar enough to indicate that the anions are not co-ordinated. For $\text{Ni}(\text{HMeB})_3(\text{NO}_3)_2$ ²⁷ and $(\text{ClO}_4)_2$ ³³ this suggestion is supported by their infrared spectra (Table 4:3).

On the basis of the above data a structure may be postulated for these four complexes in which the Ni^{II} ions are each surrounded by three chelating HMeB molecules. That the chelation of HMeB takes

TABLE 4:1
ELECTRONIC SPECTRAL DATA

COMPLEX	ABSORPTION MAXIMA cm.^{-1} AND ASSIGNMENT				
	ν_3	ν_2	ν_1	${}^3A_{2g}(F) \rightarrow {}^1T_{2g}(D)$	${}^3A_{2g}(F) \rightarrow {}^1E_{1g}(D)$
$\text{Ni(HMeB)}_3\text{Cl}_2$	26,300	$\approx 15,600\text{sh}$ 14,000	9,450 [±]		$\approx 21,000\text{sh}$ $\approx 13,200\text{sh}$
$\text{Ni(HMeB)}_3\text{I}_2$	26,300	$\approx 15,300\text{sh}$ 13,700	9,350 [±]		$\approx 20,600\text{sh}$ $\approx 12,800\text{sh}$
$\text{Ni(HMeB)}_3(\text{NO}_3)_2$	26,200	$\approx 15,600\text{sh}$ 13,900	9,500 [±] $\approx 8,700\text{sh}$		$\approx 21,000\text{sh}$ $\approx 13,200\text{sh}$
$\text{Ni(HMeB)}_3(\text{ClO}_4)_2$	26,000	15,300 $\approx 14,700\text{sh}$	9,500 [±] $\approx 23,000\text{sh}$		$\approx 12,800\text{sh}$
$\text{Ni(HMeB)}_2(\text{SCN})_2$	25,650	16,000	$\approx 9,800\text{sh}$ 8,350		$\approx 20,800\text{sh}$ $\approx 13,500\text{sh}$

[±] These values can be taken as $\approx \Delta$.

TABLE 4:2
ROOM TEMPERATURE MAGNETIC DATA

COMPLEX	χ_M' ($\times 10^{-6}$ c.g.s.u.)	μ_{eff} (B.M.)	DIAMAGNETIC CORRECTION ($\times 10^{-6}$ c g.s.u.)
$\text{Ni}(\text{HMeB})_3\text{Cl}_2$	4,189	3.15	286
$\text{Ni}(\text{HMeB})_3\text{I}_2$	4,523	3.28	341
$\text{Ni}(\text{HMeB})_3(\text{NO}_3)_2$	4,168	3.15	377
$\text{Ni}(\text{HMeB})_3(\text{ClO}_4)_2$	4,328	3.21	304
$\text{Ni}(\text{HMeB})_2(\text{SCN})_2$	4,333	3.21	226

TABLE 4:3
INFRA-RED SPECTRAL DATA

$\text{Ni}(\text{HMeB})_3(\text{NO}_3)_2$	$\text{Co}(\text{HMeB})_3(\text{NO}_3)_2$	HMeB
1481 sh	1481 sh	1481 s
1466 s	1464 s	1449 sh
1449 v.s	1445 v.s	1433 v s
1397 v.s and broad	1429 sh	1393 m
1379 v.s	1418 sh	1376 m
1319 v.s and broad	1374 sh	1353 m
1272 v.s	1362 sh	1340 v.s
	1344 sh } [*]	1309 m
	1326 v.s	1267 v.s
	1311 sh	
	1271 v.s	

^{*} All part of a very strong broad absorption trough.

In the spectrum of the nickel complex are seen two very strong broad bands that probably arise from vibrations of the nitrate ion. The position of the bands indicates that the nitrate ions are probably ionic, but why there should be two is puzzling unless it means that the anions are not equivalent. This might arise through differences in hydrogen bonding between the nitrate ions and HMeB.

The very strong broad absorption region in the cobalt complex almost certainly arises from vibrations of the nitrate ion and this and the absence of absorption at higher energies indicates that the anions are ionic. The width of the absorption band probably means that the

TABLE 4:3 (Contd.)

nitrate ions are absorbing at more than one frequency which suggests that they are non-equivalent cf. the nickel complex.

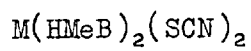
COMPLEX	BAND POSITION	ASSIGNMENT AND INTERPRETATION
$\text{Co}(\text{HBB})_2\text{SCN}_2$	2079	CN stretch of a terminally nitrogen bonded thiocyanate ion
$\text{Co}(\text{nPrHBB})\text{SCN}_2$	2105	CN stretch of a terminally nitrogen bonded thiocyanate ion that is hydrogen bonding or weakly bridging
$\text{Co}(\text{HMeB})_2\text{SCN}_2$	2123 v.s and sharp	CN stretch of a bridging thiocyanate ion
$\text{Ni}(\text{HBB})_2(\text{SCN})_2$ $(\text{DMF})_2$	2105 2096	CN stretch of a terminally nitrogen bonded thiocyanate ion
$\text{Ni}(\text{nPrHBB})_2\text{SCN}_2$	2121 2116	CN stretch of a terminally nitrogen bonded thiocyanate ion that is either hydrogen bonded or weakly bridging.
$\text{Ni}(\text{HMeB})_2\text{SCN}_2$	2131 v.s and sharp	CN stretch of a bridging thiocyanate ion
$\text{Co}(\text{HMeB})_3(\text{ClO}_4)_2$	1082 v.s and broad	Vibration of an ionic perchlorate ion
$\text{Ni}(\text{HMeB})_3(\text{ClO}_4)_2$	1087 v.s and broad	Vibration of an ionic perchlorate ion

place through the unsaturated nitrogen atom and the oxygen atom, that is the same as HBB, is indicated by the similarity in Δ value of $\text{Ni}(\text{HMeB})_3\text{Cl}_2$ and $\text{Ni}(\text{HBB})_3\text{Cl}_2$. From the equations given in Chapter One, the parameter β was calculated for $\text{Ni}(\text{HMeB})_3\text{Cl}_2$ to be 0.85.¹⁸ This is very close to the value found for $\text{Ni}(\text{HBB})_3\text{Cl}_2$ which might be expected since the atoms comprising the first co-ordination sphere are the same in both complexes.

The difference in the position of the γ_1 band in $\text{Ni}(\text{HMeB})_3\text{Cl}_2$ and $\text{Ni}(\text{HMeB})_2(\text{SCN})_2$, and also in $\text{Co}(\text{HMeB})_3\text{Cl}_2$ and $\text{Co}(\text{HMeB})_2(\text{SCN})_2$ is large enough to indicate that the first co-ordination sphere in these two types of complex is widely different. That is the difference is larger than that expected for the structure of Co or $\text{Ni}(\text{HMeB})_2(\text{SCN})_2$ in which the ligand molecules are chelating and the anions terminally nitrogen bonded. From the infrared spectral data it can be seen that the thiocyanate ion CN stretch in Co and $\text{Ni}(\text{HMeB})_2(\text{SCN})_2$ is somewhat higher than that found in Co or $\text{Ni}(\text{HBB})_2(\text{SCN})_2$. Both these observations can best be rationalised in terms of the structure in which the thiocyanate ions are bridging between adjacent metal ions through their nitrogen and sulphur atoms, with the ligand molecules bonded monodentately. Although Co and $\text{Ni}(\text{HMeB})_2(\text{SCN})_2$ are not isomorphous (Table 4:4), their X-ray powder patterns are nevertheless similar enough to indicate that the above deduction that they have similar molecular structures, is essentially correct.

Although the lowest energy transitions in the electronic spectra of $\text{Co}(\text{HMeB})_3\text{Cl}_2$, I_2 , $(\text{NO}_3)_2$ and $(\text{ClO}_4)_2$ show varying degrees

TABLE 4:4
X-RAY POWDER PATTERN DATA



Co		Ni	
d	I	d	I
7.50	w	7.50	w
7.10	s	7.20	w
7.00	s	6.90	v.s
6.10	s	6.10	s
5.75	v.w	4.43	s
4.43	s	4.26	s
4.35	s	4.15	s
4.19	s	4.07	s
4.03	s	3.93	m
3.93	m	3.85	s
3.82	m	3.80	w
3.80	m	3.77	s
3.67	w	3.61	s
3.61	s	3.39	s
3.39	s	3.31	w
3.31	w	3.22	v.w
3.22	v.w	3.16	w
3.07	v.w	3.07	v.w
2.97	v.w	3.00	v.w
2.88	m	2.88	m
2.81	s	2.84	v.w
2.73	s	2.78	s
2.67	m	2.69	s
2.63	m	2.64	m

of broadening (Table 4:5), the spectra are still best interpreted in terms of effective cubic symmetry.²¹ The magnetic data,²³ (Table 4:6) is in accord with this interpretation. Furthermore the positions of ν_1 in the spectra of $\text{Co}(\text{HMeB})_3\text{Cl}_2$, I_2 and $(\text{NO}_3)_2$, although not identical, are similar enough to indicate that the anions are not co-ordinated. The infrared spectral data of $\text{Co}(\text{HMeB})_3(\text{NO}_3)_2$ ²⁷ and $(\text{ClO}_4)_2$ ³³ (Table 4:3) point to the anions being ionic. This implies that the first co-ordination sphere of $\text{Co}(\text{HMeB})_3\text{Cl}_2$ and $\text{Co}(\text{HMeB})_3-(\text{ClO}_4)_2$ are the same, which makes it difficult to explain the difference in their Δ value. In view of this data it can be assumed that the structure of these four complexes is essentially that already discussed for the nickel compounds.

From the preceding discussion it can be seen that with NiCl_2 , CoCl_2 , NiI_2 , CoI_2 and $\text{Ni}(\text{ClO}_4)_2$ the chelation properties of HMeB and HBB are virtually identical. Further, since the parameters Δ and β of $\text{Ni}(\text{HMeB})_3\text{Cl}_2$ and $\text{Ni}(\text{HBB})_3\text{Cl}_2$ are very similar, it would seem that the absence of the phenyl ring from HMeB has little or no effect on the electronic factors which determine their magnitude.

However the complexes formed by these ligands with $\text{Co}(\text{ClO}_4)_2$ are different. This suggests that the hydroxyl proton in HBB is more labile than that in HMeB, which might be related to the electron attracting properties of the phenyl ring in HBB.

It may be that the different stoichiometries achieved by HBB and HMeB with Co and $\text{Ni}(\text{NO}_3)_2$ are due to steric factors. For instance Co and $\text{Ni}(\text{HBB})_3(\text{NO}_3)_2$ are probably less favourable sterically

TABLE 4:5
ELECTRONIC SPECTRAL DATA

COMPLEX	ABSORPTION MAXIMA cm.^{-1} AND ASSIGNMENT				
	$\#$	ν_3	ν_1	$\approx \Delta$	${}^4T_{1g}(F) \rightarrow {}^2T_{2g}(G)$
$\text{Co(HMeB)}_3\text{Cl}_2$	21,500	18,450	8,600	9,200	$\approx 15,000\text{sh}$
	20,000				
$\text{Co(HMeB)}_3\text{I}_2$	21,750	18,600	8,550	9,100	$\begin{matrix} \times \\ \{ 14,500 \\ 13,000 \end{matrix}$
	20,000				
$\text{Co(HMeB)}_3(\text{NO}_3)_2$	21,000	18,200	8,550	9,100	$\approx 15,400\text{sh}$
	$\approx 19,600\text{sh}$				
$\text{Co(HMeB)}_3(\text{Cl}_4)_2$	$\approx 21,000\text{sh}$	18,000	8,200	8,900	$\approx 15,200\text{sh}$
	$\approx 19,700\text{sh}$		$\approx 6,700\text{sh}$		
$\text{Co(HMeB)}_2\text{SCN}_2$	$\approx 20,800\text{sh}$	19,200	7,600	8,300	$\approx 15,400\text{sh}$

$\times$ Not assigned.

$\#$ This absorption is probably a consequence of spin orbit coupling in the ${}^4T_{1g}(P)$ state.

TABLE 4:6
ROOM TEMPERATURE MAGNETIC DATA

COMPLEX	χ_M ($\times 10^{-6}$ c.g.s.u.)	μ_{eff} (B.M.)	DIAMAGNETIC CORRECTION ($\times 10^{-6}$ c.g.s.u.)
$\text{Co}(\text{HMeB})_3\text{Cl}_2$	9,889	4.83	286
$\text{Co}(\text{HMeB})_3\text{I}_2$	10,288	4.93	341
$\text{Co}(\text{HMeB})_3(\text{NO}_3)_2$	9,775	4.81	377
$\text{Co}(\text{HMeB})_3(\text{ClO}_4)_2$	9,512	4.74	304
$\text{Co}(\text{HMeB})_2(\text{SCN})_2$	9,559	4.75	226

than Co and $\text{Ni}(\text{HBB})_2(\text{NO}_3)_2$, and since nitrate ions are fairly strong ligands the 2:1 complex is formed. In Co and $\text{Ni}(\text{HMeB})_3(\text{NO}_3)_2$ the steric hindrance due to the three phenyl rings, which would be expected in the 3:1 HBB complexes, is absent, and since HMeB is probably a better co-ordinating agent than the nitrate ion this complex is formed rather than the 2:1 form.

It is interesting that like HBB, HMeB seems reluctant to chelate with cobalt in the presence of thiocyanate ions. The reason why the thiocyanate ions bridge in $\text{Co}(\text{HMeB})_2(\text{SCN})_2$ and not in $\text{Co}(\text{HBB})_2(\text{SCN})_2$ might be explainable on steric grounds. With $\text{Co}(\text{HBB})_2(\text{SCN})_2$ the phenyl rings might prevent close enough approach by a neighbouring metal ion to enable the thiocyanate groups to bridge. In $\text{Co}(\text{HMeB})_2(\text{SCN})_2$ there would be less restriction on the approach of an adjacent Co^{II} ion so that bridge formation could be achieved. If it is assumed that in $\text{Ni}(\text{HBB})_2(\text{SCN})_2$ the HBB is chelating, then the above argument can still be applied to explain the differences in structure of this and $\text{Ni}(\text{HMeB})_2(\text{SCN})_2$.

TABLE 4:7
MOLAR CONDUCTANCE DATA IN NITROBENZENE [/]

COMPLEX	λ_M	COLOUR OF SOLUTION	SOLUBILITY	
			HOT	COLD
$\text{Co}(\text{HMeB})_3\text{Cl}_2$	1.1	Green blue	Soluble	
$\text{Co}(\text{HMeB})_3\text{I}_2$	9.0	Pale green	Soluble	
$\text{Co}(\text{HMeB})_3(\text{NO}_3)_2$	0.7	Solution cloudy	Soluble	
$\text{Co}(\text{HMeB})_3(\text{ClO}_4)_2$	25.7	Pink	Soluble	
$\text{Co}(\text{HMeB})_2(\text{SCN})_2$	1.0	Deep blue	Soluble	
$\text{Ni}(\text{HMeB})_3\text{Cl}_2$ [≡]	-		Insoluble	Insoluble
$\text{Ni}(\text{HMeB})_3\text{I}_2$ [≡]	-		Insoluble	Insoluble
$\text{Ni}(\text{HMeB})_3(\text{NO}_3)_2$	0.8	Solution cloudy	Soluble	
$\text{Ni}(\text{HMeB})_3(\text{ClO}_4)_2$	-		Insoluble	Insoluble
$\text{Ni}(\text{HMeB})_2(\text{SCN})_2$ [≡]	-		Insoluble	Insoluble
$\text{Ni}(\text{HMeB})_3(\text{ClO}_4)_2$	137.0	Pale green	MEASURED IN COLD NITRO-METHANE	

[/] The nitrobenzene was pale yellow.

[≡] Also insoluble in nitromethane.

CHAPTER FIVE

Some Cobalt and Nickel Complexes of 2-Methoxybenzylbenzimidazole

Since HBB and MeOBB have similar antiviral properties and yet differ structurally in a way that would be expected to have a marked effect on their chelation properties it was considered important to investigate the co-ordination chemistry of MeOBB for comparison with HBB. The complexes prepared were $M(\text{MeOBB})_2\text{Cl}_2$, $\text{Ni}(\text{MeOBB})_2\text{I}_2$, $M(\text{MeOBB})_2(\text{NO}_3)_2$, $M(\text{MeOBB})_2(\text{SCN})_2$, $\text{Co}(\text{MeOBB})_2(\text{SCN})_2(\text{Acetone})_2$, $\text{Ni}(\text{MeOBB})_2(\text{SCN})_2(\text{Dimethylformamide})_2$ and $M(\text{MeOBB})_3(\text{ClO}_4)_2$, where M is cobalt or nickel. It might be anticipated that the effect of replacing the hydroxyl proton of HBB with a methyl group to give MeOBB would be to sterically hinder the approach of a metal ion to this atom so making it a poorer co-ordinator. Indeed most of the structural data of these complexes is best rationalised on this assumption.

The Nickel Complexes.

The electronic spectral^{16, 36} and magnetic data¹⁷ of these complexes (Tables 5:1 and 5:2) indicate that in each of them the Ni^{II} ions are spin free and six co-ordinate.

The electronic spectral data of $\text{Ni}(\text{MeOBB})_2\text{Cl}_2$ is open to two interpretations. From Fig. 5:1 it can be seen that the band at $5,970 \text{ cm}^{-1}$ which is assigned as a vibrational overtone shows considerable broadening on the low energy side. The same band in $\text{Ni}(\text{MeOBB})_3(\text{ClO}_4)_2$ (Fig. 5:1) is seen to be quite symmetrical.

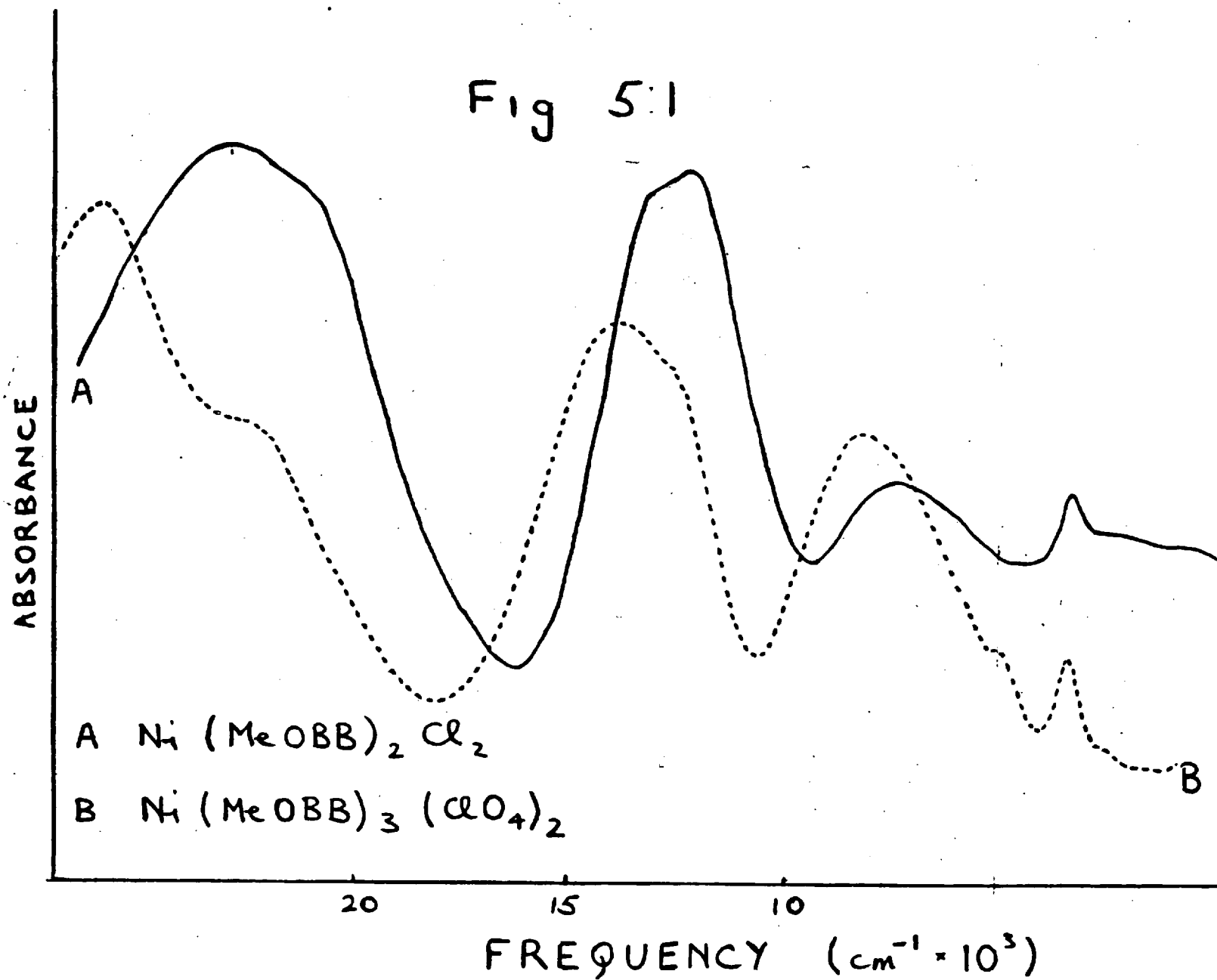
TABLE 5:1
ELECTRONIC SPECTRAL DATA

COMPLEX	ABSORPTION MAXIMA cm.^{-1} AND ASSIGNMENT			
	$\checkmark_3$	$\checkmark_2$	$\checkmark_1$	
$\text{Ni}(\text{MeOBB})_2\text{Cl}_2$	22,450	$\approx 13,300\text{sh}$ $\approx 12,500$	7,950 $\approx 5,600 ?$	${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^1\text{T}_{2g}(\text{G}) \approx 27,600\text{sh}$ ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^1\text{T}_{2g}(\text{D}) \approx 17,900\text{sh}$
$\text{Ni}(\text{MeOBB})_2\text{I}_2$	$\approx 23,800\text{sh}$	12,900	7,700	Charge transfer - 27,000 ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^1\text{T}_{2g}(\text{D}) \approx 20,400\text{sh}$
$\text{Ni}(\text{MeOBB})_2(\text{NO}_3)_2$	24,100	$\approx 14,500$ $\approx 13,300\text{sh}$	9,500 $\approx 9,000\text{sh}$ 6,800	
$\text{Ni}(\text{MeONN})_2(\text{SCN})_2$	24,700	14,900	$\approx 8,700\text{sh}$ 7,300	${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^1\text{E}_g(\text{D}) \approx 13,300\text{sh}$
$\text{Ni}(\text{MeOBB})_2(\text{SCN})_2$ (LiF) ₂	24,400	15,000	$\approx 9,300\text{sh}$ 7,400	${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^1\text{E}_g(\text{D}) \approx 13,300\text{sh}$
$\text{Ni}(\text{MeOBB})_3(\text{ClO}_4)_2$	24,700	14,000	8,600	${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^1\text{A}_g(\text{G}) \approx 22,000\text{sh}$ ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^1\text{E}_g(\text{D}) \approx 12,700\text{sh}$

TABLE 5:2
ROOM TEMPERATURE MAGNETIC DATA

COMPLEX	χ_M' ($\times 10^{-6}$ c.g.s.u.)	μ_{eff} (B.M.)	DIAMAGNETIC CORRECTION ($\times 10^{-6}$ c.g.s.u.)
$Ni(MeOBB)_2Cl_2$	4,620	3.30	328
$Ni(MeOBB)_2I_2$	4,813	3.37	369
$Ni(MeOBB)_2(NO_3)_2$	3,931	3.04	319
$Ni(MeOBB)_2(SCN)_2$	4,387	3.23	345
$Ni(MeOBB)_2(SCN)_2$ (DMF) ₂	4,100	3.08	433
$Ni(MeOBB)_3(ClO_4)_2$	3,954	3.06	478

Fig 5:1



Assuming that this broadening is due to an electronic transition or component thereof its position is very approximately $5,600 \text{ cm.}^{-1}$ and the entire spectrum may be interpreted as follows. The bands at $7,900 \text{ cm.}^{-1}$ and $\approx 5,600 \text{ cm.}^{-1}$ may be taken as the components of a split ν_1 band (assigned in O_h symmetry), the remaining transitions being assigned as in Table 5:1. This spectrum is very similar to that of $\text{Ni(Pyridine)}_2\text{Cl}_2$ and $\text{Ni(Quinoline)}_2\text{Cl}_2$, the structures of which are known to consist of planar bridging chloride ions with the heterocyclic rings bonded axially.⁴¹ Moreover the value of Δ calculated for $\text{Ni(MeOBB)}_2\text{Cl}_2$ from the positions of the ν_1 components is $7,300 \text{ cm.}^{-1}$ ⁴² which lies between those found for $\text{Ni(Pyridine)}_2\text{Cl}_2$, $7,600 \text{ cm.}^{-1}$ and $\text{Ni(Quinoline)}_2\text{Cl}_2$, $7,100 \text{ cm.}^{-1}$.⁴¹ On the basis of this data, assignment to $\text{Ni(MeOBB)}_2\text{Cl}_2$ of a structure similar to that of $\text{Ni(Pyridine)}_2\text{Cl}_2$ seems reasonable.

This structure can also account for the rather high magnetic moment of this complex. The Ni^{II} ion in an octahedral environment has a $^3A_{2g}$ ground state¹⁶ for which no orbital contribution to the magnetic moment is expected and leads to a spin only value of 2.83 B.M.¹⁷ It is possible however particularly in complexes in which the ligand field is rather weak to get mixing in of the $^3T_{2g}$ state, for which orbital contribution to the magnetic moment is expected, by spin orbit coupling.⁴³ Now in this complex the ligand field is rather weak and higher state mixing in may occur leading to an observed moment of 3.3 B.M.

Alternatively, if it is assumed that the broadening of the

5,970 cm^{-1} band is not due to an electronic transition then the spectrum can be rationalised on the basis of the following structure. Since the ν_1 transition in this spectrum is the band at 7,950 cm^{-1} a Δ value of about the same magnitude may be assumed. Now the Δ value of $\text{Ni}(\text{nPrHBB})_2\text{Cl}_2$, in which it is thought that the nPrHBB is chelating and the chloride ions are monodentate, is $\approx 8,300 \text{ cm}^{-1}$. Although this is some 400 cm^{-1} larger than the Δ value of $\text{Ni}(\text{MeOBB})_2\text{Cl}_2$ the possibility that the MeOBB is chelating is not ruled out. The metal oxygen bond in this complex would probably be longer than the corresponding bond in $\text{Ni}(\text{nPrHBB})_2\text{Cl}_2$ because of steric hindrance by the methyl group, so leading to a reduction in Δ , see page 93. The conductivity of $\text{Ni}(\text{MeOBB})_2\text{Cl}_2$ (Table 5:3) which indicates that the chloride ions are co-ordinated is in accord with both these structures.

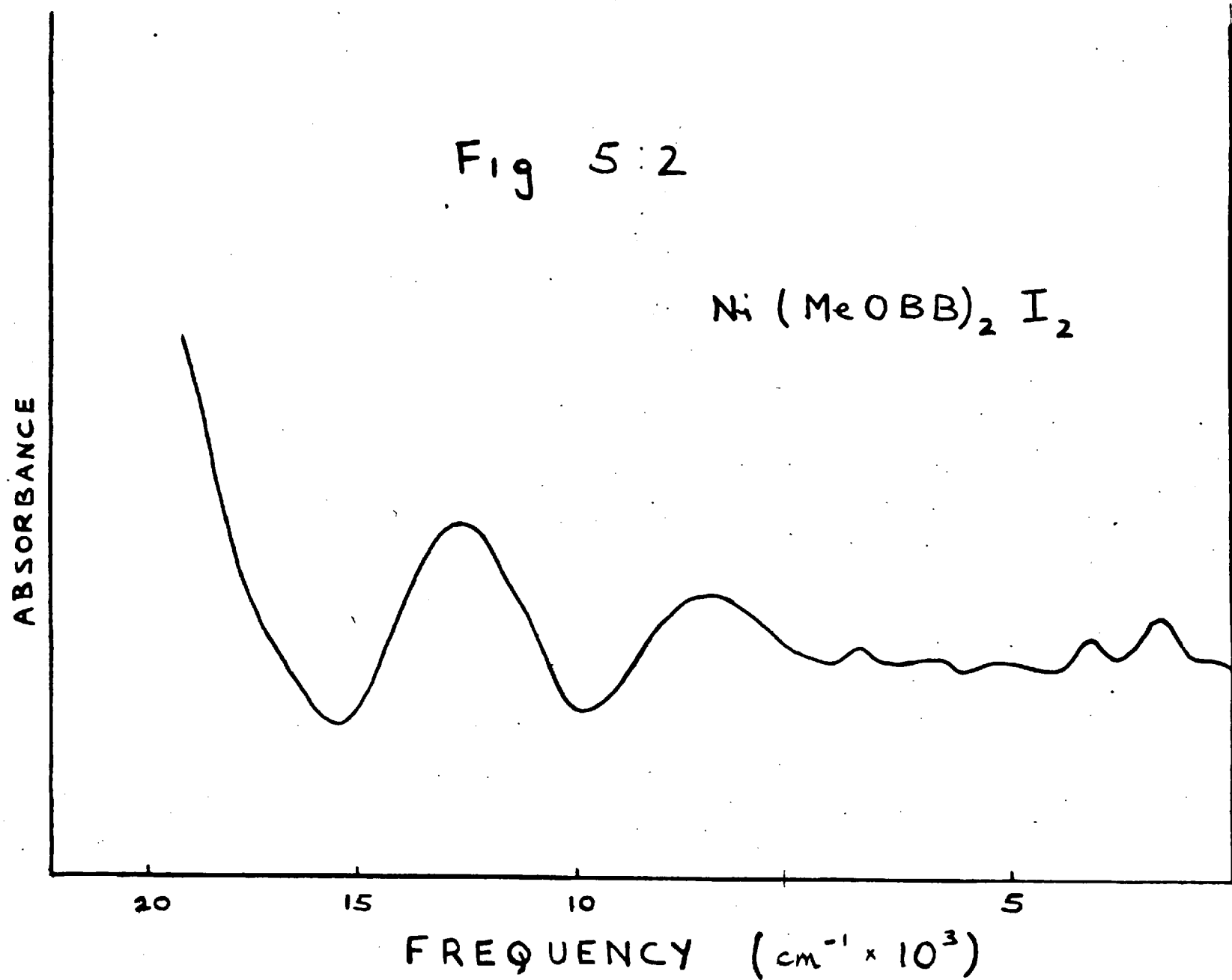
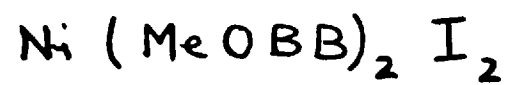
In the electronic spectrum of $\text{Ni}(\text{MeOBB})_2\text{I}_2$ the base line is very high and almost obscures the vibrational overtones (Fig. 5:2). Consequently, if the band at 7,650 cm^{-1} is the higher energy component of a split ν_1 band (assigned in O_h symmetry), the lower lying component would very probably be obscured. However interpreting the spectrum on the basis of those bands that can be seen, the 7,650 cm^{-1} band may be assigned as the ν_1 transition in O_h symmetry and the others as in Table 5:1. A Δ value of $\approx 7,700 \text{ cm}^{-1}$ is likely to be consistent with the structure in which the MeOBB is chelating through its tertiary nitrogen atom and oxygen atom with the iodide ions monodentate. The magnetic moment of this

TABLE 5:3

MOLAR CONDUCTANCE DATA IN NITROBENZENE

COMPLEX	λ_M	COLOUR OF SOLUTION	SOLUBILITY	
			HOT	COLD
$\text{Co}(\text{MeOBB})_2\text{Cl}_2$	2.0	Deep green		Soluble
$\text{Co}(\text{MeOBB})_2(\text{NO}_3)_2$	4.0	Deep pink		Soluble
$\text{Co}(\text{MeOBB})_2(\text{SCN})_2$	2.5	Deep blue		Soluble
$\text{Co}(\text{MeOBB})_2(\text{SCN})_2$ (acetone) ₂	2.6	Deep blue		Soluble
$\text{Co}(\text{MeOBB})_3(\text{ClO}_4)_2$	39.1	No colour change		Soluble
$\text{Ni}(\text{MeOBB})_2\text{Cl}_2$	1.2	Yellowish green	Soluble	
$\text{Ni}(\text{MeOBB})_2\text{I}_2$	12.8	Deep yellow brown	Soluble	
$\text{Ni}(\text{MeOBB})_2(\text{NO}_3)_2$	5.0	Green yellow	Soluble	
$\text{Ni}(\text{MeOBB})_2(\text{SCN})_2$	-	-	Insoluble	Insoluble
$\text{Ni}(\text{MeOBB})_2(\text{SCN})_2$	29.1	Very pale green	SOLUBLE IN METHANE	HOT NITRO-
$\text{Ni}(\text{MeOBB})_2(\text{SCN})_2$ (dimethylformamide) ₂	3.4	Green		Soluble
$\text{Ni}(\text{MeOBB})_3(\text{ClO}_4)_2$	46.3	Green yellow	Soluble	

Fig 5:2



complex can be explained in terms of upper state mixing in,⁴³ cf. $\text{Ni}(\text{MeOBB})_2\text{Cl}_2$. The molar conductance of $\text{Ni}(\text{MeOBB})_2\text{I}_2$ which is rather high for a non electrolyte may be indicative of some degree of dissociation in solution.

That the symmetry of $\text{Ni}(\text{MeOBB})_2(\text{NO}_3)_2$ is lower than cubic is indicated by the splitting of the γ_1 band (assigned in O_h symmetry).³⁶ Because of the complexity of the infrared spectrum of this complex (Table 5:4), it is not possible to decide whether the nitrate ions are co-ordinated or not. However the conductance datum shows that the anions are very likely co-ordinated. The structure of the complex then is probably similar to that proposed for $\text{Ni}(\text{MeOBB})_2\text{I}_2$. On page 97 it is argued that a chelating nitrate ion can be treated as a large diffuse group which renders the symmetry of the complex quasi tetrahedral.⁴⁴ Now a Ni^{II} ion in such an environment would probably have an electronic spectrum different from that produced by a distorted cubic field. For example it might be expected that the spectral bands would be more intense, amongst other things. Since the spectrum of $\text{Ni}(\text{MeOBB})_2(\text{NO}_3)_2$ is fairly typical of the type expected for a Ni^{II} ion in a distorted octahedral environment³⁶ it is assumed that the nitrate ions are not chelating in this complex. This is also, to some extent, suggested by the non isomorphous nature of this complex and $\text{Co}(\text{MeOBB})_2(\text{NO}_3)_2$ (Table 5:5).

The infrared spectral data of $\text{Ni}(\text{MeOBB})_2(\text{SCN})_2$ (Table 5:4) indicates that the thiocyanate group is terminally nitrogen bonded.²⁸ Because of the splitting of the γ_1 transition (assigned in O_h

TABLE 5:4
INFRA-RED SPECTRAL DATA

$\text{Co}(\text{MeOBB})_2(\text{NO}_3)_2$	$\text{Ni}(\text{MeOBB})_2(\text{NO}_3)_2$	MeOBB
1506 sh	1486 m	1488 m 1267 v.s
1479 s	1464 sh	1484 m
1460 s	1462 sh	1462 sh
1445 v.s	1449 v.s	1458 sh
1431 sh	1420 v.s	1445 v.s
1379 m	1385 sh	1439 v.s
1305 sh	1381 v.s	1422 v.s
1294 v.s and broad	1342 sh	1381 m
1277 sh	1326 v.s	1337 m
	1312 v.s	1323 m
	1300 sh	1312 s

The marked increase in intensity of the bands at 1312 and 1381 cm^{-1} in going from MeOBB to $\text{Ni}(\text{MeOBB})_2(\text{NO}_3)_2$ is probably due to absorption by the nitrate ion. However it is not possible to say definitely whether the anions are co-ordinated or not.

In the cobalt complex the two bands at 1290 and 1460 cm^{-1} probably arise from vibrations of the nitrate ion. The position of these bands can be interpreted as indicating that the anions are co-ordinated.

TABLE 5:4 (Contd.)

COMPLEX	BAND POSITION	ASSIGNMENT AND INTERPRETATION
$\text{Co(HBB)}_2\text{SCN}_2$	2079 cm.^{-1}	CN stretch of a terminally nitrogen bonded thiocyanate ion
$\text{Co(HMeB)}_2\text{SCN}_2$	2123	CN stretch of a bridging thiocyanate ion
$\text{Co(MeOBB)}_2\text{SCN}_2$	2066 v.s and 2075 broad	CN stretch of a terminally nitrogen bonded thiocyanate ion. The reason for the splitting of this band is not known.
$\text{Co(MeOBB)}_2\text{SCN}_2$ (acetone) ₂	2083	CN stretch of a terminally nitrogen bonded thiocyanate ion
Acetone vapour	1740	CO stretching frequency
Acetone in aniline	1703	CO stretching frequency of hydrogen bonded acetone
Acetone + InCl_2	1670	CO stretching frequency of co-ordinated acetone
$\text{Co(MeOBB)}_2(\text{SCN})_2$ (acetone) ₂	1695 v.s	CO stretching frequency of either co-ordinated or hydrogen bonded acetone
$\text{Ni(HBB)}_2(\text{SCN})_2$ (DMF) ₂	2105 2096	CN stretch of a terminally nitrogen bonded thiocyanate
$\text{Ni(HMeB)}_2\text{SCN}_2$	2131	CN stretch of a bridging thiocyanate ion
$\text{Ni(MeOBB)}_2\text{SCN}_2$	2100 v.s and broad on low energy side	CN stretch of a terminally nitrogen ion
$\text{Ni(MeOBB)}_2(\text{SCN})_2$ (DMF) ₂	2105 sh 2098 v.s 2079 sh	CN stretch of a terminally nitrogen bonded thiocyanate ion
$\text{Ni(MeOBB)}_2(\text{SCN})_2$ (DMF) ₂	1653 v.s	CO stretch of either co-ordinated or hydrogen bonded dimethylformamide cf. $\text{Ni(HBB)}_2(\text{SCN})_2(\text{DMF})_2$

TABLE 5:4 (Contd. 2)

$\text{Co}(\text{MeOBB})_3(\text{ClO}_4)_2$	$\text{Ni}(\text{MeOBB})_3(\text{ClO}_4)_2$	MeOBB
1193 m	1227 sh	1193 m
1178 w	1211 sh	1114 v.s
1149 s	1199 sh	1089 v.s and broad
1136 sh	1193 s and broad	1067 v.s
1119 v.s and broad	1186 sh	1036 v.s
1114 sh	1148 m	1022 sh
1067 v.s and broad	1096 v.s and broad	1006 m
1064	1087 sh	
1027 v.s and broad	1074 sh	
1024	1026	
1010 s	1012 sh	
	[‡] These shoulders are part of the very strong broad band centred at 1193 cm^{-1}	

The increased absorption in the 1100 cm^{-1} region in the nickel complex is due to vibrations of the perchlorate ion. If this is assumed to be the only absorption due to the anions then it can be interpreted as indicating that they are ionic.

Unequivocal assignment of any of the bands in $\text{Co}(\text{MeOBB})_3(\text{ClO}_4)_2$ to vibrations of the perchlorate ion is difficult, but it does seem that the anions are absorbing at two different energies. If this is the case then it suggests that the perchlorate ions are not equivalent in this complex and whether this indicates that the anions are ionic or co-ordinated is not known.

symmetry) it can be claimed that the symmetry is lower than effective octahedral,³⁶ but nothing can be said about the magnitude of Δ . This makes it difficult to decide what the first co-ordination sphere of the complex is. However on the basis of the infrared spectral data and of course the fact that the complex is six co-ordinate, a structure is proposed in which the MeOBB is chelating.

The electronic spectra of $\text{Ni}(\text{MeOBB})_2(\text{SCN})_2$ and $\text{Ni}(\text{MeOBB})_2-(\text{SCN})_2(\text{DMF})_2$ are very similar except for the splitting of the γ , band, which is less pronounced in the dimethylformamide adduct. Another difference is the charge transfer tail seen in $\text{Ni}(\text{MeOBB})_2-(\text{SCN})_2$, cf. $\text{Ni}(\text{HBB})_2(\text{SCN})_2$, but not in the solvate. The position of the CN stretching frequency of the thiocyanate ion in $\text{Ni}(\text{MeOBB})_2-(\text{SCN})_2(\text{DMF})_2$ (Table 5:4) is similar to that found in $\text{Ni}(\text{MeOBB})_2(\text{SCN})_2$ and is interpreted in the same way. The CO stretching frequency of the dimethylformamide in this complex is almost identical to that found in $\text{Ni}(\text{HBB})_2(\text{SCN})_2(\text{DMF})_2$ for which it was indicative that the dimethylformamide was either co-ordinated³¹ or hydrogen bonded.³² Another point of structural interest is the rate of loss of the dimethylformamide from this complex, which is fairly rapid, cf. $\text{Ni}(\text{HBB})_2(\text{SCN})_2(\text{DMF})_2$. On the basis of the above evidence two structures may be proposed, one involving co-ordinated solvent, terminally nitrogen bonded thiocyanate and monodentate MeOBB, the other being similar to that suggested for $\text{Ni}(\text{MeOBB})_2(\text{SCN})_2$ but with hydrogen bonded dimethylformamide. The main objection to the structure in which the solvent is co-ordinated is its ease of removal.

TABLE 5:5

X-RAY POWDER PATTERN DATA

<u>M(MeOBB)₂(NO₃)₂</u>				<u>M(MeOBB)₃(ClO₄)₂</u>			
Co		Ni		Co		Ni	
d	I	d	I	d	I	d	I
8.90	s	9.00	v.s	10.00	m	12.90	s
7.40	w	7.40	v.w	7.70	v.w	11.80	s
5.58	v.w	7.20	w	6.82	v.w	10.25	s
4.50	m	6.60	w	4.80	v.w	7.55	m
4.41	v.w	6.30	s			7.02	v.w
4.22	v.w	5.02	w			6.40	v.w
		4.98	s			5.02	v.w
		3.84	v.w			4.80	w
		3.75	v.w			4.62	w
		3.68	v.w			4.43	v.s
		3.57	v.w			4.19	s
		3.42	s			4.17	w
		3.39	s			4.00	s
						3.57	s
						3.22	s
						2.97	m

This would involve the solid state rearrangement, monodentate MeOBB to chelating MeOBB which might be expected to be difficult. However if the metal oxygen bond in $\text{Ni}(\text{MeOBB})_2(\text{SCN})_2$ is considered to be rather long, due to steric hindrance by the methyl group, then the above change might not be so difficult. Evidence in favour of this structure is the similarity in position of the CO stretch in $\text{Ni}(\text{HBB})_2(\text{SCN})_2(\text{DMF})_2$ and this complex, and the differences in electronic spectra of $\text{Ni}(\text{MeOBB})_2(\text{SCN})_2$ and the solvate. The latter difference would be difficult to account for if the dimethylformamide was merely hydrogen bonded.

The molar conductance of $\text{Ni}(\text{MeOBB})_3(\text{ClO}_4)_2$ is a typical 2:1 electrolyte value and as such shows that the perchlorate ions are unlikely to be co-ordinated. This claim can also be made on the basis of the infrared spectral data³³ (Table 5:4). This evidence together with the electronic spectral and magnetic data suggests that the Ni^{II} ions are in an effectively cubic environment created by three chelating MeOBB molecules. This is interesting since it is the only complex so far discussed in which there are three chelating MeOBB groups, a feature which is very common with HBB. Also since this complex and $\text{Ni}(\text{HBB})_3(\text{ClO}_4)_2$ have similar structures then a reasonably valid comparison of the Δ value of HBB and MeOBB may be made. For example, Δ for $\text{Ni}(\text{HBB})_3(\text{ClO}_4)_2$ is $\approx 9,400 \text{ cm.}^{-1}$ and for $\text{Ni}(\text{MeOBB})_3(\text{ClO}_4)_2$ $\approx 8,500 \text{ cm.}^{-1}$. This difference is quite large and might be explained in terms of the steric hindrance created by the methyl group in MeOBB preventing close approach of the oxygen atom to the metal ion.

The Cobalt Complexes

The electronic spectral²⁴ and magnetic data²⁵ of $\text{Co}(\text{MeOBB})_2\text{-Cl}_2$ and SCN_2 (Tables 5:6 and 5:7) is consistent with the view that the arrangement of ligands about the metal ion is essentially tetrahedral. The conductivities indicate that the anions in both are co-ordinated. In the case of $\text{Co}(\text{MeOBB})_2(\text{SCN})_2$ the infrared spectral data (Table 5:4) is in agreement with this observation and further indicates that the thiocyanate ions are very probably nitrogen bonded and terminal.²⁸ These observations together with a knowledge of the co-ordination properties of MeOBB suggest that the structure of these two complexes is one in which the co-ordination sphere is comprised of two MeOBB nitrogen atoms and two anions.

Apart from the rather high intensity of the bands, the electronic spectrum of $\text{Co}(\text{MeOBB})_2(\text{SCN})_2(\text{Acetone})_2$ can be interpreted in terms of distorted cubic symmetry.²³ The structural data, that is infrared and molar conductance, indicate that the thiocyanate ions are terminally nitrogen bonded.²⁸ Since this complex loses two moles of acetone fairly readily to give $\text{Co}(\text{MeOBB})_2(\text{SCN})_2$, the structure in which the co-ordination sphere is that of $\text{Co}(\text{MeOBB})_2(\text{SCN})_2$ plus two co-ordinated acetone molecules is suggested, cf. $\text{Co}(\text{HBB})_2(\text{SCN})_2\text{-(DMF)}_2$. The structure in which the MeOBB is chelating with the acetone hydrogen bonded is another possibility. Unfortunately it cannot be decided from the position of the CO stretch whether the acetone in this complex is co-ordinated or hydrogen bonded⁴⁵ (Table 5:4).⁴⁶

TABLE 5:6

ELECTRONIC SPECTRAL DATA

COMPLEX	ABSORPTION MAXIMA cm.^{-1} AND ASSIGNMENT
$\text{Co}(\text{MeOBB})_2\text{Cl}_2$	$T_d \approx 23,000\text{sh}, \approx 19,600\text{sh}, \approx 17,000\text{sh}, 15,700 \checkmark_3$ Centre of Gravity $\approx 16,100$ $\approx 8,600\text{sh}, 7,150, \approx 6,200\text{sh}$ $\checkmark_2$ Centre of Gravity $\approx 7,000$
$\text{Co}(\text{MeOBB})_2(\text{SCN})_2$	$T_d \approx 20,200\text{sh}, \approx 17,400\text{sh}, 16,700 \checkmark_3$ Centre of Gravity $\approx 17,400$ $\approx 8,100, \approx 7,200$ $\checkmark_2$ Centre of Gravity $\approx 7,700$ [‡]
$\text{Co}(\text{MeOBB})_2(\text{NO}_3)_2$	$O_h ? 19,200\text{sh}, 18,000 \checkmark_3$ 12,800 ? $8,600, \approx 7,700\text{sh} \checkmark_1$
$\text{Co}(\text{MeOBB})_2(\text{SCN})_2$ (acetone) ₂	$O_h 20,500, 18,600 \checkmark_3$ ${}^4T_{1g}(\text{F}) \rightarrow {}^2T_{2g}(\text{P}) \approx 23,300\text{sh}$ $\approx 7,900\text{sh}, 6,850 \checkmark_1$ ${}^4T_{1g}(\text{F}) \rightarrow {}^2T_{1g}(\text{G}) \approx 14,300\text{sh}$
$\text{Co}(\text{MeOBB})_3(\text{ClO}_4)_2$	$O_h 21,500, \approx 19,500 \checkmark_3$ $\approx 17,500\text{sh}, 16,700$ ${}^4T_{1g}(\text{F}) \rightarrow {}^2T_{1g}(\text{G}) \approx 14,300\text{sh}$ $7,400, \approx 6,400\text{sh} \checkmark_1$

[‡] The Δ value of this complex is $\approx 4,400 \text{ cm.}^{-1}$

The fine structure associated with $\checkmark_3$ (assigned in O_h symmetry) is probably due to spin orbit coupling in the ${}^4T_{1g}(\text{P})$ state.

TABLE 5:7
ROOM TEMPERATURE MAGNETIC DATA

COMPLEX	χ_M' ($\times 10^{-6}$ c.g.s.u.)	μ_{eff} (B.M.)	DIAMAGNETIC CORRECTION ($\times 10^{-6}$ c.g.s.u.)
$\text{Co}(\text{MeOBB})_2\text{Cl}_2$	9,086	4.57	328
$\text{Co}(\text{MeOBB})_2(\text{NO}_3)_2$	8,487	4.52	319
$\text{Co}(\text{MeOBB})_2(\text{SCN})_2$	9,137	4.60	345
$\text{Co}(\text{MeOBB})_2(\text{SCN})_2$ (acetone) ₂	9,273	4.70	412
$\text{Co}(\text{MeOBB})_3(\text{ClO}_4)_2$	9,245	4.70	479

The electronic spectrum of $\text{Co}(\text{MeOBB})_2(\text{NO}_3)_2$ (Fig. 5:3) may be interpreted as indicating a co-ordination sphere of six atoms about Co^{II} ions and most of the bands can be assigned as in Table 5:6. The infrared spectral²⁷ and molar conductance data both point to the nitrate ions being co-ordinated. It would seem reasonable to postulate a structure for this complex in which the MeOBB is chelating with the nitrate ions monodentate. However there are three features of the electronic spectrum, namely the high intensity of the bands, the very pronounced shoulder at $\sim 12,800 \text{ cm.}^{-1}$, and the magnetic moment, that are inexplicable on the basis of this structure. But if the structure is considered in which both the nitrate ions are regarded as chelating, these spectral and magnetic peculiarities can be explained. Now the oxygen atoms through which the nitrate ion chelates are relatively close together and instead of regarding them as discrete entities the entire ion may be considered as a rather large diffuse group.⁴⁴ This means that in $\text{Co}(\text{MeOBB})_2(\text{NO}_3)_2$ the Co^{II} ion can be thought to be in a quasi tetrahedral environment,⁴⁴ which would explain the high intensity of the electronic spectral bands and the low magnetic moment.⁴⁴ Moreover the lack of structure on the band at $18,000 \text{ cm.}^{-1}$ can also be explained using the above argument. This band very probably represents a transition to a state that arises out of the ^4P state of the free ion and it appears that its threefold orbital degeneracy is not appreciably lifted, which would not be expected in a quasi tetrahedral environment.⁴⁴

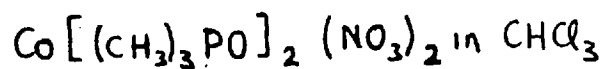
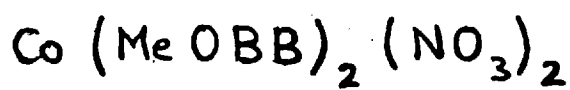
The features of the electronic spectrum and magnetic moment

of $\text{Co}(\text{MeOBB})_2(\text{NO}_3)_2$ discussed above are also encountered with $\text{Co}[(\text{CH}_3)_3\text{PO}]_2(\text{NO}_3)_2$.⁴⁴ Indeed the spectra of these two complexes are very similar (Fig. 5:3) and it is known from single crystal X-ray studies that the nitrate ions in the phosphine oxide complex are chelating.⁴⁴ The magnetic moment of $\text{Co}[(\text{CH}_3)_3\text{PO}]_2(\text{NO}_3)_2$ is 4.65 B.M.⁴⁴ Throughout this thesis then, the criteria applied to decide whether nitrate ions are chelating or not is the similarity of the electronic spectral and magnetic data of the complex in question to that of $\text{Co}(\text{MeOBB})_2(\text{NO}_3)_2$.

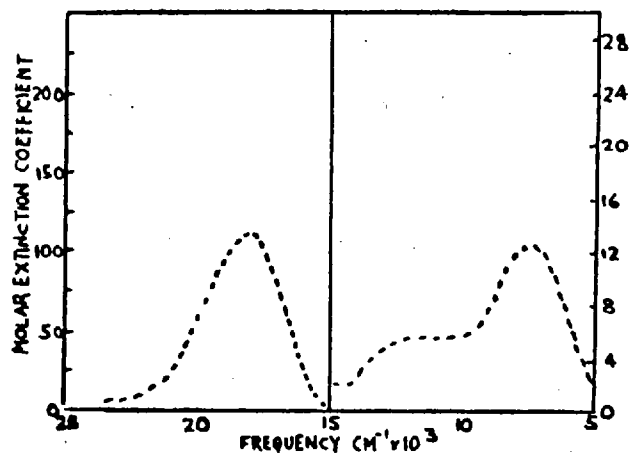
The magnetic, electronic spectral, and molar conductance data of $\text{Co}(\text{HBB})_3(\text{ClO}_4)_2$ indicate that its structure is similar to that of $\text{Ni}(\text{MeOBB})_3(\text{ClO}_4)_2$. The infrared spectrum is complicated and interpretation of it is difficult. Although the structures of Co and $\text{Ni}(\text{MeOBB})_3(\text{ClO}_4)_2$ are similar the X-ray powder pattern data shows that they are not isomorphous (Table 5:5). This observation is in accord with the difference in the infrared spectral data of the two complexes. The way in which the structures differ is not known. It is interesting that $\text{Co}(\text{MeOBB})_3(\text{ClO}_4)_2$ is the only cobalt complex studied in which the MeOBB chelates.

From the preceding discussion it can be seen that the suggestion that the presence of the methyl group on the oxygen atom of MeOBB makes it a poorer co-ordinator, relative to the oxygen in HBB, is fairly valid. For example, it is probably for this reason that with CoCl_2 , NiCl_2 and $\text{Co}(\text{NO}_3)_2$, MeOBB forms complexes in which it is monodentate, and why with NiI_2 it forms $\text{Ni}(\text{MeOBB})_2\text{I}_2$, in which it

Fig 5:3



ABSORBANCE



20

15

10

FREQUENCY ($\text{cm}^{-1} \times 10^3$)

is chelating, rather than $\text{Ni}(\text{MeOBB})_3\text{I}_2$, cf. HBB. Whether this is why it is also monodentate in $\text{Co}(\text{MeOBB})_2(\text{SCN})_2$ will be discussed later on.

However this behaviour is by no means general and with $\text{Ni}(\text{NO}_3)_2$, $\text{Ni}(\text{SCN})_2$, NiI_2 , and Co and $\text{Ni}(\text{ClO}_4)_2$ the ligand chelates quite readily.

An interesting similarity between $\text{Ni}(\text{MeOBB})_2(\text{SCN})_2$ and $\text{Ni}(\text{HBB})_2(\text{SCN})_2$ is the charge transfer band seen towards the u.v. end of their electronic spectra. The reason why this band lies further into the visible region in $\text{Ni}(\text{HBB})_2(\text{SCN})_2$ might be connected with the length of the nickel oxygen band, this band presumably being longer in the MeOBB complex. If the suggestion made in Chapter One that HBB is reluctant to chelate with Co and $\text{Ni}(\text{SCN})_2$ because of electronic effects associated with the type of structure that would be produced, is applied to this ligand it might, in part, explain why MeOBB is monodentate in $\text{Co}(\text{MeOBB})_2(\text{SCN})_2$.

It is interesting that like HBB, MeOBB forms solvates of the type $\text{M}(\text{MeOBB})_2(\text{SCN})_2(\text{Solvent})_2$, for example $\text{Ni}(\text{MeOBB})_2(\text{SCN})_2$ -(dimethylformamide)₂. This together with the similarity in complexes formed with $\text{Co}(\text{SCN})_2$, $\text{Ni}(\text{SCN})_2$, $\text{Ni}(\text{NO}_3)_2$ and $\text{Ni}(\text{ClO}_4)_2$ indicates that of ligands investigated in this study the one most similar to HBB is MeOBB. This is despite the fact that of the modifications carried out on HBB, substitution of the hydroxyl proton by a methyl group is the one which might have been expected to bring about the largest change in chelation properties.

The difference in the type of complex formed by HBB and MeOBB with $\text{Co}(\text{ClO}_4)_2$ can be explained in terms of the relative strengths of the O - C bond in MeOBB and the O - H bond in HBB. The hydroxyl bond should be much more easily broken than the O - C bond, so that formation of a complex of the type $\text{Co}^{2+}(\text{HBB})_2(\text{HBB}),^-(\text{ClO}_4),^-$ is feasible whereas formation of the corresponding MeOBB complex in which a methyl group is lost is not expected.

CHAPTER SIX

Some Cobalt and Nickel Complexes of 2.0.hydroxyphenylbenzimidazole

In HBB and the antivirally inactive HPB the hydroxyl group is in a similar position relative to the unsaturated nitrogen atom, and it might be expected that the chelation properties of the two ligands would be similar. However since the hydroxyl group in HPB is substituted directly into the phenyl ring its electronic properties should be different from those of the corresponding group in HBB. This could have the effect of making the HPB hydroxyl proton relatively more labile, which in turn would almost certainly influence the type of complexes formed. For example inner complex formation should occur more readily with HPB than HBB. Another difference between these two ligands which would probably cause differences in their co-ordination chemistry is the conjugation of the double bonds in HPB, HBB is not a conjugated system.

The Nickel Complexes

The nickel complexes studied in this chapter are Ni(HPB)_2 , $\text{Ni(HPB)}_3\text{Cl}_2$, $\text{Ni(HPB)}_3\text{Br}_2$, $\text{Ni(HPB)}_3(\text{NO}_3)_2$, $\text{Ni(HPB)}_2(\text{SCN})_2$ and $\text{Ni(HPB)}_2(\text{SCN})_2(\text{EtOH})_2$ and their electronic spectral, magnetic and infrared spectral data are given in Tables 6:1, 6:2 and 6:3 respectively. From Table 6:1 it can be seen that the Ni^{II} ions in all these complexes except Ni(HPB)_2 are six co-ordinate. The magnetic susceptibilities of $\text{Ni(HPB)}_3(\text{NO}_3)_2$, $\text{Ni(HPB)}_3\text{Br}_2$ and $\text{Ni(HPB)}_2(\text{SCN})_2$ and its ethanolate are interesting in that they are

TABLE 6:1
ELECTRONIC SPECTRAL DATA

COMPLEX	ABSORPTION MAXIMA cm.^{-1} AND ASSIGNMENT				
	ν_3	ν_2	ν_1	${}^3A_{2g}(F) \rightarrow {}^1T_{2g}(D)$	${}^3A_{2g}(F) \rightarrow {}^1A_{1g}(G)$
$\text{Ni(HPB)}_3\text{Cl}_2$	$\approx 24,400^\ddagger$	15,300	$\approx 9,300^\dagger$ $\approx 8,900\text{sh}$	$\approx 22,500\text{sh}$	$\approx 20,800\text{sh}$
$\text{Ni(HPB)}_3\text{Br}_2$	$\approx 24,400^\ddagger$	15,600	$9,550^\dagger$ $\approx 8,900\text{sh}$		$\approx 20,800\text{sh}$
$\text{Ni(HPB)}_3(\text{NO}_3)_2$	$\approx 23,800^\ddagger$	16,500	$9,500^\dagger$ $\approx 8,900\text{sh}$		
$\text{Ni(HPB)}_2(\text{SCN})_2$		14,700	$\approx 9,100\text{sh}$ 7,350		
$\text{Ni(HPB)}_2(\text{SCN})_2(\text{EtOH})_2$	$\approx 25,000^\ddagger$	15,500	9,800 $\approx 8,300\text{sh}$		

‡ Partly obscured by charge transfer band.

† This splitting is very slight.

TABLE 6:2
ROOM TEMPERATURE MAGNETIC DATA

COMPLEX	χ_M' ($\times 10^{-6}$ c.g.s.u.)	μ_{eff} (B.M.)	DIAMAGNETIC CORRECTION ($\times 10^{-6}$ c.g.s.u.)
Ni(HPB)_2	486	1.1	233
$\text{Ni(HPB)}_3\text{Cl}_2$	3,702	2.98	390
$\text{Ni(HPB)}_3\text{Br}_2$	5,603	3.66	403
$\text{Ni(HPB)}_3(\text{NO}_3)_2$	6,646	3.98	381
$\text{Ni(HPB)}_2(\text{SCN})_2$	6,325	3.89	295
$\text{Ni(HPB)}_2(\text{SCN})_2$ (EtOH) ₂	5,139	3.51	405

appreciably higher than the values usually found for six co-ordinate spin free Ni^{II} complexes.¹⁷ In view of this the susceptibilities of $\text{Ni}(\text{HPB})_3(\text{NO}_3)_2$ and Br_2 were measured over the temperature range 300 to 77°A , and the results are shown in Fig. 6:1, from which it can be seen that a Curie Weiss law is followed from 300 to $\approx 120^\circ\text{A}$ by $\text{Ni}(\text{HPB})_3(\text{NO}_3)_2$ and 300 to $\approx 90^\circ\text{A}$ by $\text{Ni}(\text{HPB})_3\text{Br}_2$. A detailed interpretation of these results will not be attempted.

On the basis of the differences in magnetic properties alone it would seem reasonable to assume that the structures of $\text{Ni}(\text{HPB})_3(\text{NO}_3)_2$ and Br_2 are different from that of $\text{Ni}(\text{HPB})_3\text{Cl}_2$. This assumption is supported by the electronic spectra which shows the position of the γ_1 band (assigned in O_h symmetry) of $\text{Ni}(\text{HPB})_3\text{Cl}_2$ to be different from that of $\text{Ni}(\text{HPB})_3(\text{NO}_3)_2$ and Br_2 . The similarity in electronic spectral and magnetic properties of the latter two complexes suggests that their structures are similar. Since the splitting of the γ_1 band in $\text{Ni}(\text{HPB})_3\text{Cl}_2$ is very small its position can be taken as an approximate measure of the value of Δ , that is $\approx 9,300 \text{ cm}^{-1}$. This value is higher than that expected for a structure in which the chloride ions are co-ordinated, and the first co-ordination sphere of this complex probably consists of three chelating HPB molecules. The reason for rejecting structures in which the HPB is bridging will become apparent when $\text{Ni}(\text{HPB})_3\text{Br}_2$, etc., are discussed. Since the Δ value of $\text{Ni}(\text{HPB})_3\text{Cl}_2$ is $\approx 9,300 \text{ cm}^{-1}$ and that of $\text{Ni}(\text{HBB})_3\text{Cl}_2$ is $\approx 9,400 \text{ cm}^{-1}$ it can be claimed that HPB produces a slightly weaker ligand field than HBB.

Fig 6:1

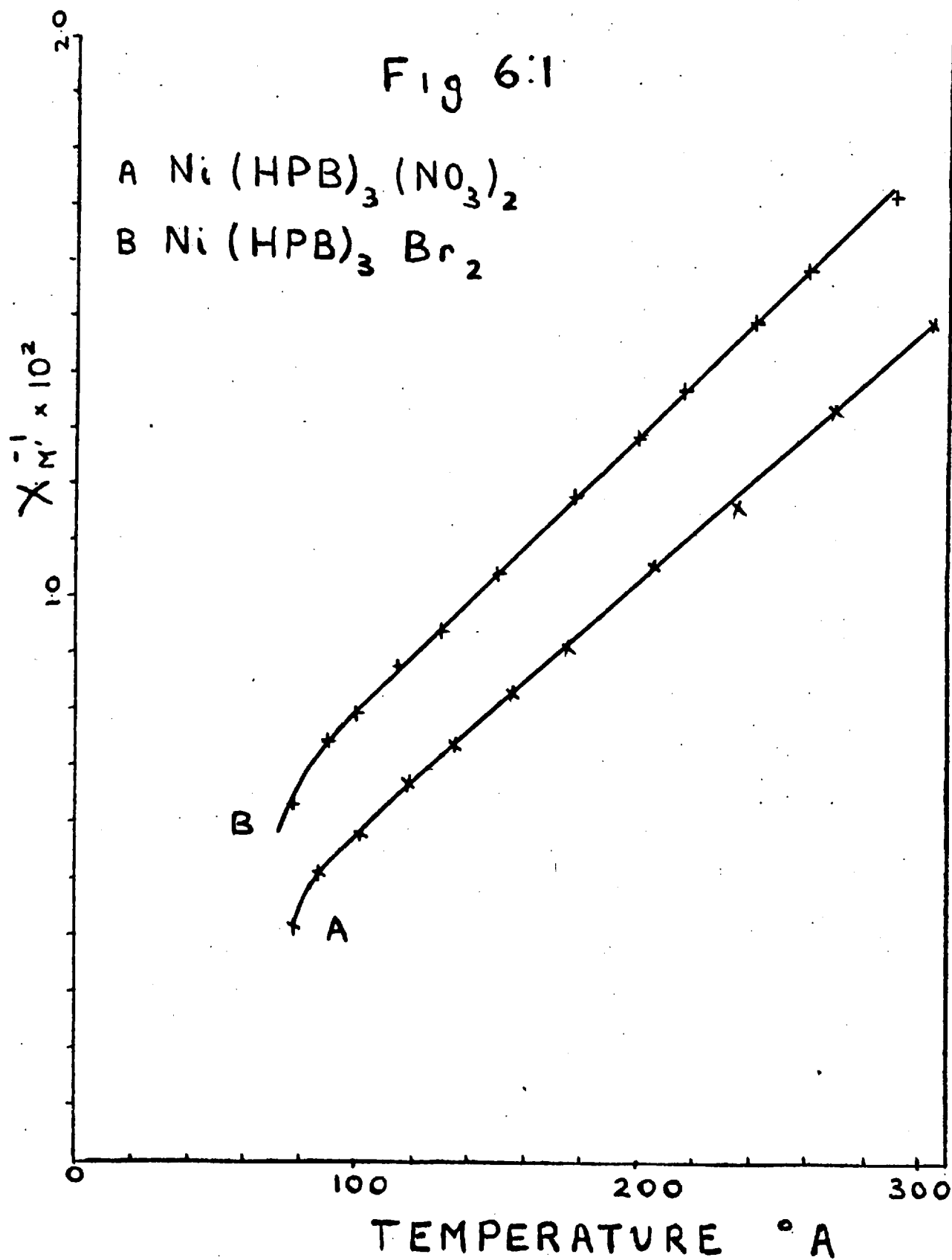


TABLE FOR FIG. 6:1The Temperature Variation in the Magnetic Susceptibility ofNi(HPB)₃Br₂ and Ni(HPB)₃(NO₃)₂

<u>Ni(HPB)₃Br₂</u>		<u>Ni(HPB)₃(NO₃)₂</u>	
T°A	$\chi_M' (x 10^{-3} \text{ c.g.s.u.})$	T°A	$\chi_M' (x 10^{-3} \text{ c.g.s.u.})$
291	5.80	305	6.68
260	6.29	269	7.62
241	6.69	234	8.60
216	6.87	205	9.42
200	7.74	175	10.96
177	8.42	155	12.03
150	9.58	135	13.52
130	10.58	120	15.15
100	12.58	110	16.31
77	15.86	100	17.58
		77	23.80

TABLE 6:3
INFRARED SPECTRAL DATA

$\text{Co(HPB)}_3(\text{NO}_3)_2$	$\text{Ni(HPB)}_2(\text{NO}_3)_2$	HPB
1527 sh	1531 s	1529 s and sharp
1477 v.s and sharp	1479 v.s	1484 v.s and sharp
[⌘] 1456 v.s and sharp	1453 v.s	1449 s and sharp
1441 sh	[⌘] 1429 v.s and broad	1412 v.s and sharp
1389 sh	1377 s	1389 v.s
1381 s	1323 v.s and broad	1318 v.s and sharp
1351 s	[⌘] 1302 sh	1271 v.s and sharp
1312 sh	1285 s	1253 v.s and sharp
[⌘] 1290 v.s and broad		
1266 sh		

[⌘] Some of the absorption in these regions might be due to vibrations of the nitrate ion but it is difficult to be certain, and consequently no definite conclusions about the nature of the nitrate ion can be drawn from this data.

TABLE 6:3 (Contd.)

COMPLEX	BAND POSITION	ASSIGNMENT AND INTERPRETATION
$\text{Co}(\text{HMeB})_2(\text{SCN})_2$	2123	CN stretch of a bridging thiocyanate ion
$\text{Co}(\text{HBB})_2(\text{SCN})_2$	2079	CN stretch of a terminally nitrogen bonded thiocyanate ion
$\text{Co}(\text{HPB})_{\frac{1}{2}}(\text{SCN})_2$	2123	CN stretch of a bridging thiocyanate ion
$\text{Co}(\text{HPB})_{\frac{1}{2}}(\text{SCN})_2$ (Acetone),	2121	CN stretch of a bridging thiocyanate ion
Acetone vapour	1740	CO stretching frequency
Acetone in aniline	1703	CO stretching frequency of hydrogen bonded acetone
Acetone + InCl_2	1670	CO stretching frequency of co-ordinated acetone
$\text{Co}(\text{HPB})_{\frac{1}{2}}(\text{SCN})_2$ (Acetone),	1692	CO stretching frequency of either co-ordinated or hydrogen bonded acetone
$\text{Ni}(\text{HMeB})_2(\text{SCN})_2$	2131	CN stretch of a bridging thiocyanate ion
$\text{Ni}(\text{nPrHBB})_2(\text{SCN})_2$	2121 2116 sh	CN stretch of a terminally nitrogen bonded thiocyanate ion that is either hydrogen bonded or weakly bridging
$\text{Ni}(\text{HPB})_2(\text{SCN})_2$	2126 2117 sh 2051 sh	CN stretch of a terminally nitrogen bonded thiocyanate ion that is either hydrogen bonded or weakly bridging

TABLE 6:3 (Contd. 2)

$\text{Ni}(\text{isoPrHBB})_2(\text{SNC})_2$	2105	CN stretch of a terminally nitrogen bonded thiocyanate ion
$\text{Ni}(\text{HPB})_2(\text{SCN})_2(\text{EtOH})_2$	2110	CN stretch of a terminally nitrogen bonded thiocyanate ion

$\text{Ni}(\text{HPB})_2(\text{SCN})_2$	$\text{Ni}(\text{HPB})_2(\text{SCN})_2(\text{EtOH})_2$
3226 v.s	3319 sh
3058 v.s	3244 } v.s unresolved
2985 sh	3231 } doublet
2961 sh	3165 sh
	3049 s

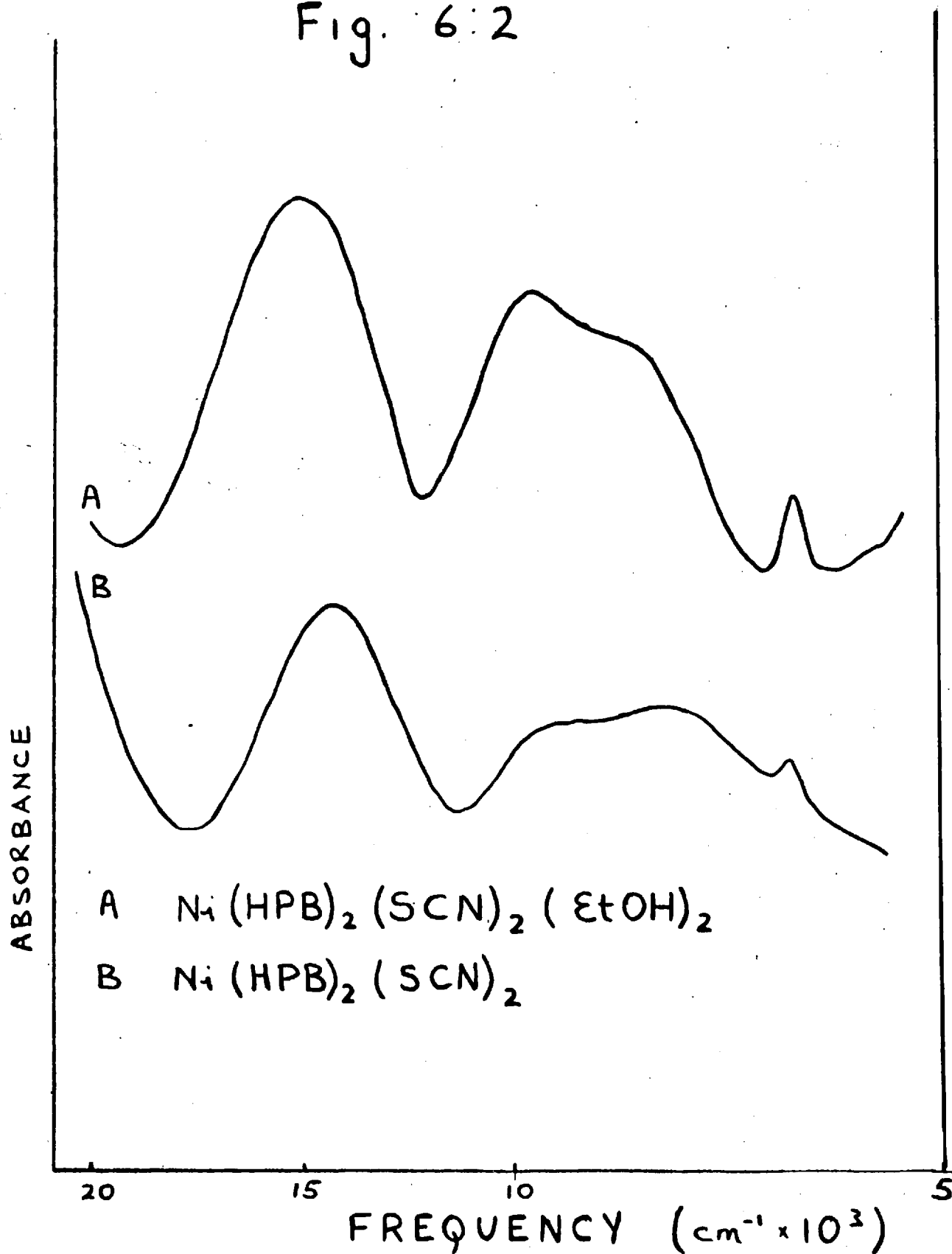
The differences between the spectrum of $\text{Ni}(\text{HPB})_2(\text{SCN})_2$ and $\text{Ni}(\text{HPB})_2(\text{SCN})_2(\text{EtOH})_2$ are undoubtedly due in part to the ethanol but whether this is co-ordinated or hydrogen bonded it is not possible to decide on the basis of this data.

The similarity in the position of the ν_1 band (assigned in O_h symmetry) in $Ni(HPB)_3(NO_3)_2$ and $Ni(HPB)_3Br_2$ indicates that the anions are not co-ordinated. It is not possible to tell anything about the role of the nitrate ion in $Ni(HPB)_3(NO_3)_2$ from its infrared spectrum. Two structures may be considered for these complexes, both of which might rationalise the electronic spectral and magnetic data. These are, one in which two of the HPB molecules are chelating and two are bridging, and the other in which there are six bridging ligands in an essentially cubic array. The magnetic properties of these complexes might be explained on the basis of either structure if it is assumed that ferromagnetic coupling⁴⁷ takes place between adjacent Ni^{II} ions through an intervening HPB molecule.

Since the room temperature susceptibilities of $Ni(HPB)_2(SCN)_2$ and its solvate are similar to that of $Ni(HPB)_3(NO_3)_2$ and Br_2 (Table 6:2), it would seem reasonable to suppose that they have structural features in common, that is bridging HPB molecules.

It is not possible to decide from the infrared spectrum of $Ni(HPB)_2(SCN)_2(EtOH)_2$ whether the ethanol is co-ordinated or not. However since the ν_1 bands in the electronic spectra of this complex and $Ni(HPB)_2(SCN)_2$ are quite different (Fig. 6:2), it would seem reasonable to suppose that the first co-ordination sphere of the two complexes is different. This difference might arise, in part, from co-ordination of the ethanol. The difference in position of the thiocyanate ion CN stretch in $Ni(HPB)_2(SCN)_2$ and its ethanolate (Table 6:3) indicates that the anions in these two complexes are either

Fig. 6:2



co-ordinated terminally²⁸ and subject to varying degrees of hydrogen bonding or co-ordinated differently. For example the anion in $\text{Ni(HPB)}_2(\text{SCN})_2$ might be bridging²⁸ and in the ethanolate it might be terminally nitrogen bonded.²⁸

The electronic spectrum of Ni(HPB)_2 is shown in Fig. 6:3 but no attempt will be made to interpret it or the magnetic moment, beyond saying that it might indicate that the complex is square planar.⁴⁸

The Cobalt Complexes

The electronic spectra of Co(HPB)_2 and $\text{Co(HPB)}_2\text{X}_2$, where X is chloride, bromide or iodide (Table 6:4), are typical of the type expected for a Co^{II} ion in an essentially tetrahedral environment.²⁴ Moreover the spectra of $\text{Co(HPB)}_2\text{X}_2$ indicate that the halide ions are co-ordinated. The magnetic data of the four complexes is in accord with these observations, that is the values fall within the range expected for tetrahedrally co-ordinated Co^{II} ions²⁵ and increase in the order $\text{Co(HPB)}_2 \lesssim \text{Co(HPB)}_2\text{Cl}_2 \lesssim \dots \text{Co(HPB)}_2\text{I}_2$ (Table 6:5), as is expected from the suggestion that the orbital contribution is an inverse function of Δ .⁴⁹

The electronic spectrum of $\text{Co(HPB)}_3(\text{NO}_3)_2$ (Table 6:4 and Fig. 6:4) may be interpreted in terms of distorted cubic symmetry.²² The magnetic moment is in accord with this.²³ However a puzzling feature of the spectrum is the lack of structure on what is probably the ν_3 transition. No information can be obtained from the infrared

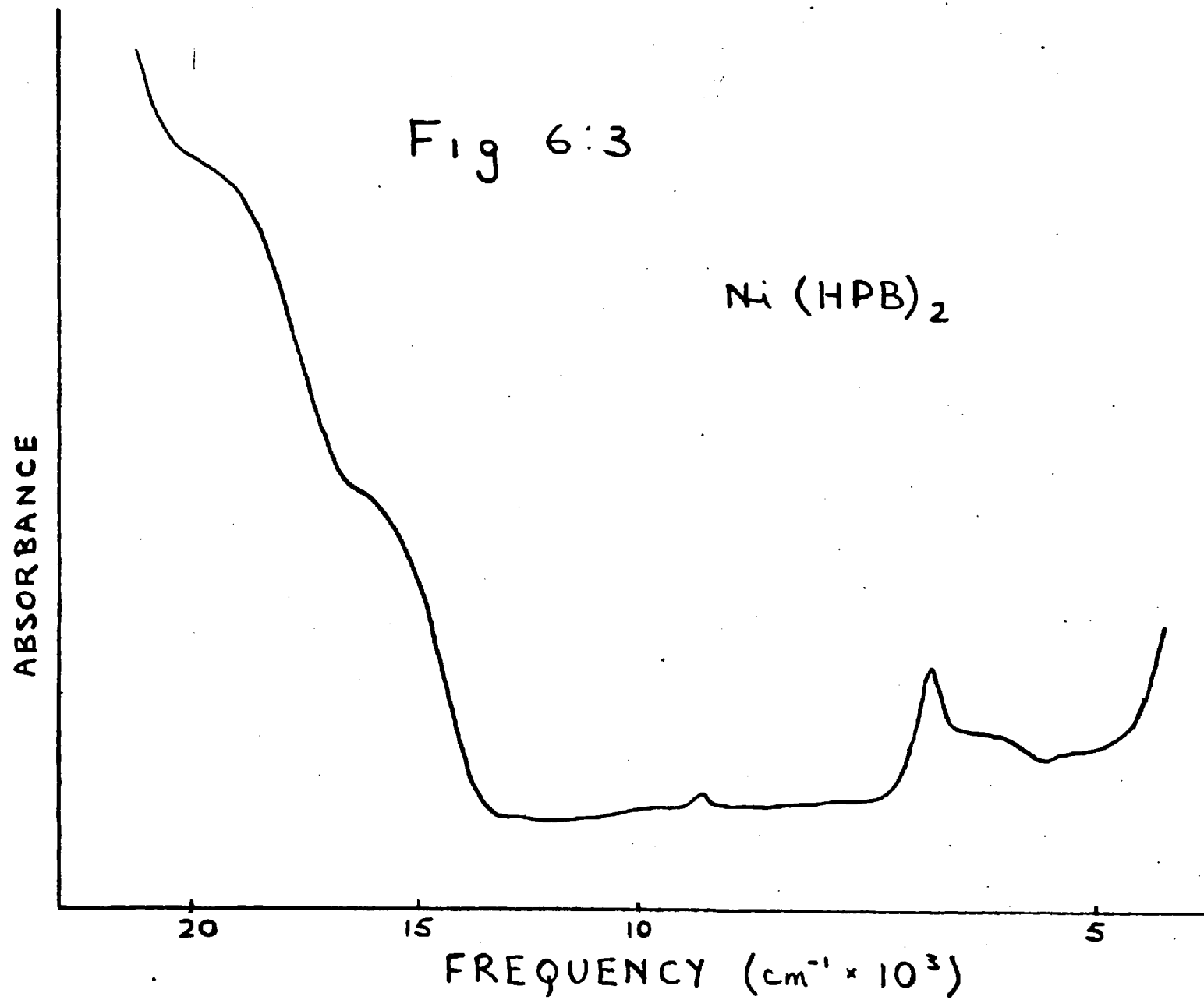
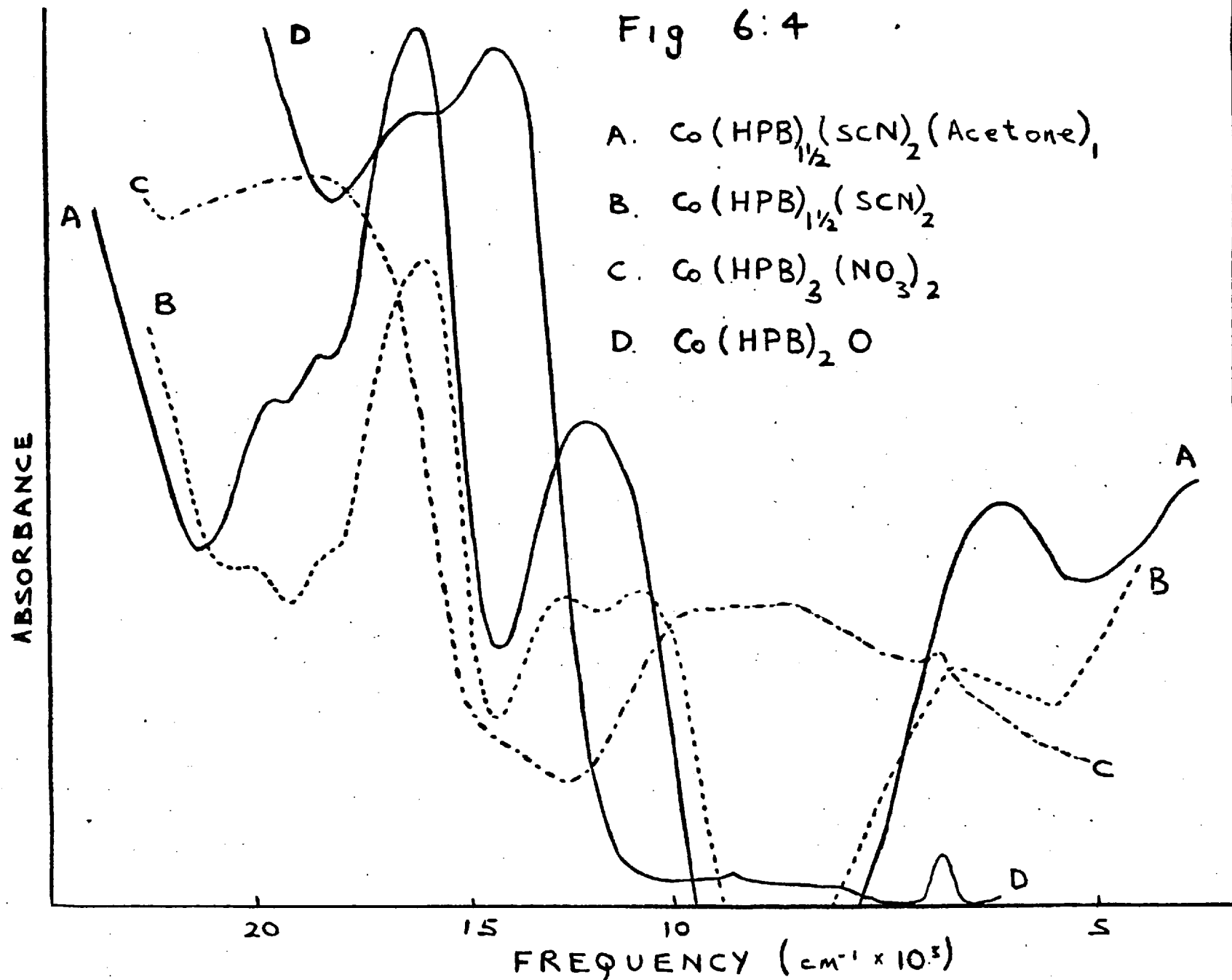


TABLE 6:4
ELECTRONIC SPECTRAL DATA

COMPLEX	ABSORPTION MAXIMA cm.^{-1} AND ASSIGNMENT		
	T_d	ν_3	ν_2
Co(HPB)_2		$\approx 20,400\text{sh}, 18,900, \approx 17,200\text{sh}$	$\approx 8,500\text{sh}, 7,650$
$\text{Co(HPB)}_2\text{Cl}_2$		$\approx 18,200\text{sh}, \approx 17,900\text{sh}, 16,700$ $15,900$	$9,550, 7,700, 6,450$
$\text{Co(HPB)}_2\text{Br}_2$		$\approx 17,900\text{sh}, 16,700, 15,500$	$9,250, 7,500, \approx 6,400$
$\text{Co(HPB)}_2\text{I}_2$		$\approx 17,000, 16,400, 14,800$	$9,100, 7,350, \approx 6,100$
$\text{Co(HPB)}_3(\text{NO}_3)_2$	O_h	$18,500 (\nu_3 - \nu_2)$	$\approx 9,400, \approx 7,800 (\nu_1)$
$\text{Co(HPB)}\frac{1}{2}(\text{SCN})_2$		Not assigned: $20,400, \approx 18,900\text{sh}, 16,650, 13,000, 11,000$ $\approx 5,700$	
$\text{Co(HPB)}\frac{1}{2}(\text{SCN})_2$ (acetone),		Not assigned: $\approx 19,800, \approx 18,900, 16,750, 12,500, 5,650$	
$\text{Co(HPB)}_2\text{O}$		Not assigned: $\approx 16,700, 14,700$	

Fig 6:4



spectrum (Table 6:3) as to the nature of the anions in this complex. Although the lines in the X-ray powder photograph of this complex are extremely indistinct it is just possible to distinguish a few, and a comparison of this photograph with that of $\text{Ni(HPB)}_3(\text{NO}_3)_2$, which shows many distinct lines, indicates that the two complexes are not isomorphous. A probable structure is one in which the three HPB molecules are chelating with the nitrate groups ionic.

The magnetic data (Table 6:5) and electronic spectral data (Table 6:4 and Fig. 6:4) of $\text{Co(HPB)}\frac{1}{2}(\text{SCN})_2$ and $\text{Co(HPB)}\frac{1}{2}(\text{SCN})_2(\text{Acetone})$, cannot be rationalised in terms of either octahedral,^{21,23} tetrahedral^{24,25} or square planar⁵⁰ stereochemistry. The infrared spectral data (Table 6:3) can be interpreted in terms of bridging thiocyanate ions but beyond this nothing approaching even a tentative structure can be put forward for these complexes.

The complex that analyses for $\text{Co(HPB)}_2\text{O}$ gives an electronic spectrum (Fig. 6:4), and effective magnetic moment that are completely different from those expected for either an octahedrally^{21,23} or tetrahedrally^{24,25} co-ordinated Co^{II} ion. It may well be that some of the cobalt ions are in a higher oxidation state, that is Co^{III} , which might account for the magnetic moment. The difficulty in assigning a structure to this complex arises from the uncertainty as to the exact empirical formula, for example the formulae $\text{Co}^{2+}(\text{HPB})_2^{2-}\text{O}$, $\text{Co}^{2+}(\text{HPB})_2^-(\text{OH})^-$, $\text{Co}^{3+}(\text{HPB})_2^{2-}(\text{OH})^-$ etc., would all give very similar analyses. Consequently further discussion of the structure of this complex is not justified.

TABLE 6:5
ROOM TEMPERATURE MAGNETIC DATA

COMPLEX	χ_M' ($\times 10^{-6}$ c.g.s.u.)	μ_{eff} (B.M.)	DIAMAGNETIC CORRECTION ($\times 10^{-6}$ c.g.s.u.)
Co(HPB)_2	8,085	4.39	174
$\text{Co(HPB)}_2\text{Cl}_2$	8,857	4.59	273
$\text{Co(HPB)}_2\text{Br}_2$	9,064	4.65	302
$\text{Co(HPB)}_2\text{I}_2$	9,929	4.87	322
$\text{Co(HPB)}_3(\text{NO}_3)_2$	9,514	4.69	381
$\text{Co(HPB)}_1\frac{1}{2}(\text{SCN})_2$	15,260	6.03	240
$\text{Co(HPB)}_1\frac{1}{2}(\text{SCN})_2$ (acetone) ₁	13,480	5.66	274
$\text{Co(HPB)}_2\text{O}$	365	0.92	237

It can be seen by comparing the complexes formed by HPB and HBB that apart from $\text{Ni}(\text{HBB})_3\text{Cl}_2$ and $\text{Ni}(\text{HPB})_3\text{Cl}_2$ the co-ordination chemistry of these two ligands is completely different.

Since HPB is a conjugated system it might be expected that it would be more easily polarised by a metal ion than HBB, in which the double bonds are not conjugated. If this assumption is valid it is probably the reason why with the cobalt halides HPB forms tetrahedral complexes⁵¹, in which it is monodentate, rather than complexes of the type formed by HBB, that is $\text{Co}(\text{HBB})_3\text{Cl}_2$ etc.

This property of HPB to co-ordinate monodentately is just one of the differences between HPB and HBB, the tendency for HPB to bridge in the complexes $\text{Ni}(\text{HPB})_3(\text{NO}_3)_2$, $\text{Ni}(\text{HPB})_3\text{Br}_2$, $\text{Ni}(\text{HPB})_2(\text{SCN})_2$, $\text{Ni}(\text{HPB})_2(\text{SCN})_2(\text{EtOH})_2$ and probably $\text{Co}(\text{HPB})_{\frac{1}{2}}(\text{SCN})_2$ and its solvate, is another important difference between the co-ordination chemistry of these two ligands.

It is interesting that with $\text{Co}(\text{ClO}_4)_2$, HBB undergoes complex formation with the loss of one proton whereas with HPB proton loss is more pronounced, the inner complex, amongst other things, being formed quite readily. Indeed it is probably true to say that hydroxyl proton loss is a dominant feature of the co-ordination chemistry of HPB.

The complex $\text{Co}(\text{HPB})_3(\text{NO}_3)_2$ is interesting since it is the only example known for this ligand in which a Co^{II} ion is in a ligand field produced by three chelating HPB molecules, a feature which is quite common with HBB. The reason why a complex of this

nature is formed is not known, but it illustrates yet another difference between HPB and HBB, that is HBB forms a 2:1 complex with $\text{Co}(\text{NO}_3)_2$.

In conclusion then of the ligands studied in this survey HPB is the one least similar in co-ordination chemistry to HBB, an observation which is probably related more to differences in electronic rather than stereochemical properties.

CHAPTER SEVEN

Some Copper Complexes of 2-Hydroxybenzylbenzimidazole

So far this study has been concerned solely with the chelation properties of HBB and its derivatives with divalent cobalt and nickel salts. Now copper is a metal of considerable biological importance and so an investigation of the co-ordination chemistry of the parent compound, that is HBB, with this metal was carried out. The complexes prepared were $\text{Cu}(\text{HBB})_2\text{X}_2$, where X is Cl^- , Br^- , NO_3^- and SCN^- , $\text{Cu}(\text{HBB})_2\text{Cl}_2(\text{Ethanol})_2$, $\text{Cu}(\text{HBB})_2\text{Br}_2(\text{Ethanol})_2$, $\text{Cu}(\text{HBB})_2(\text{SCN})_2(\text{Acetone})_2$, $\text{Cu}(\text{HBB})_3(\text{NO}_3)_2$, $\text{Cu}(\text{HBB})_3(\text{ClO}_4)_2$ and $\text{Cu}(\text{HBB})_2\text{I}_2$.

Discussion

The electronic spectra of all these complexes except $\text{Cu}(\text{HBB})_2\text{I}_2$, which very probably contains Cu^{I} , indicate that the Cu^{II} ions are six co-ordinate⁵² (Table 7:1). With the exception of $\text{Cu}(\text{HBB})_3(\text{NO}_3)_2$, $\text{Cu}(\text{HBB})_3(\text{ClO}_4)_2$ and $\text{Cu}(\text{HBB})_2(\text{SCN})_2$ which are probably not magnetically dilute, the magnetic moments of the Cu^{II} complexes are fairly normal⁵³ and in agreement with the electronic spectral data (Table 7:2).

On the basis of the structural data of $\text{Cu}(\text{HBB})_2\text{Cl}_2$ and the chelation properties of HBB two structures may be proposed for this complex. The structure in which the chloride ions lie in the plane and bridge, with the HBB bonded axially might be considered in view of the structure of $\text{Cu}(\text{Pyridine})_2\text{Cl}_2$ ⁵⁴ and $\text{Cu}(2 \text{ methylquinoxaline})_2\text{Cl}_2$.⁵⁵ Now the electronic spectral band of $\text{Cu}(\text{Pyridine})_2\text{Cl}_2$,

TABLE 7:1
ELECTRONIC SPECTRAL DATA

COMPLEX	ABSORPTION MAXIMA cm.^{-1}
$\text{Cu(HBB)}_2\text{Cl}_2$	12,100
$\text{Cu(HBB)}_2\text{Cl}_2(\text{EtOH})_2$	11,800
$\text{Cu(HBB)}_2\text{Br}_2$	12,400
$\text{Cu(HBB)}_2\text{Br}_2(\text{EtOH})_2$	12,300
$\text{Cu(HBB)}_2(\text{NO}_3)_2$	10,400, $\approx 12,500$ sh
$\text{Cu(HBB)}_2(\text{SCN})_2$	$\approx 19,000$ sh, 17,300, $\approx 14,300$ sh
$\text{Cu(HBB)}_2(\text{SCN})_2(\text{Acetone})_2$	16,700 - broad on low energy side
$\text{Cu(HBB)}_3(\text{NO}_3)_2$	15,400
$\text{Cu(HBB)}_3(\text{ClO}_4)_2$	14,800
$\text{Cu(MeOBB)}_2\text{Cl}_2$	12,400, $\approx 10,500$ sh.

TABLE 7:2
ROOM TEMPERATURE MAGNETIC DATA

COMPLEX	$\chi M'$ ($\times 10^{-6}$ c.g.s.u.)	μ_{eff} (B.M.)	DIAMAGNETIC CORRECTION ($\times 10^{-6}$ c.g.s.u.)
$\text{Cu}(\text{HBB})_2\text{Cl}_2$	1,287	1.75	304
$\text{Cu}(\text{HBB})_2\text{Cl}_2(\text{EtOH})_2$	1,587	1.94	372
$\text{Cu}(\text{HBB})_2\text{Br}_2$	1,245	1.72	326
$\text{Cu}(\text{HBB})_2\text{Br}_2(\text{EtOH})_2$	1,606	1.96	394
$\text{Cu}(\text{HBB})_2(\text{NO}_3)_2$	1,641	1.97	295
$\text{Cu}(\text{HBB})_2(\text{SCN})_2$	925	1.43	319
$\text{Cu}(\text{HBB})_2(\text{SCN})_2$ (acetone) ₂	1,491	1.88	387
$\text{Cu}(\text{HBB})_3(\text{NO}_3)_2$	92	0.47	417
$\text{Cu}(\text{HBB})_3(\text{ClO}_4)_2$	485	1.07	443
$\text{Cu}(\text{HBB})_2\text{I}_2$	DIAMAGNETIC		
$\text{Cu}(\text{MeOBB})_2\text{Cl}_2$	1,446	1.86	327

$\sim 14,100 \text{ cm.}^{-1}$ lies at appreciably higher energy than that of $\text{Cu(HBB)}_2\text{Cl}_2$, $12,100 \text{ cm.}^{-1}$. This is a rather large difference for two complexes which are supposed to have similar first co-ordination spheres. However this difference might partly be explained if it is assumed that for steric reasons the HBB molecule is unable to approach as close to the Cu atom as pyridine.⁵⁴ Another factor that might account for the above difference in spectra is that pyridine is almost certainly a stronger ligand than nitrogen bonded HBB. From Chapter One it will be seen that HBB chelates readily with Co^{II} and Ni^{II} salts and the same behaviour might be expected with CuCl_2 . However a structure in which the Cu^{II} ion is surrounded by two essentially planar chelating HBB molecules with axially bonded chloride ions is difficult to reconcile with the position of the electronic spectral band of $\text{Cu(HBB)}_2\text{Cl}_2$ (Fig. 7:1).

To try and elucidate the structure of $\text{Cu(HBB)}_2\text{Cl}_2$, the complex $\text{Cu(MeOBB)}_2\text{Cl}_2$ was prepared. Now it will be seen from Chapter Five that MeOBB is a weaker chelating agent than HBB and it might be argued that with CuCl_2 it would form a complex of similar structure to that of $\text{Cu(Pyridine)}_2\text{Cl}_2$.⁵⁴ The electronic spectral band of $\text{Cu(MeOBB)}_2\text{Cl}_2$ (Fig. 7:1) lies at similar energy to that of $\text{Cu(HBB)}_2\text{Cl}_2$, which might indicate that the two complexes have a similar structure. It would be difficult to account for the similarity of electronic spectral band positions if the ligands in these two complexes were chelating.

The molar conductance of $\text{Cu(HBB)}_2\text{Cl}_2(\text{EtOH})_2$ (Table 7:3)

Fig. 7:1.

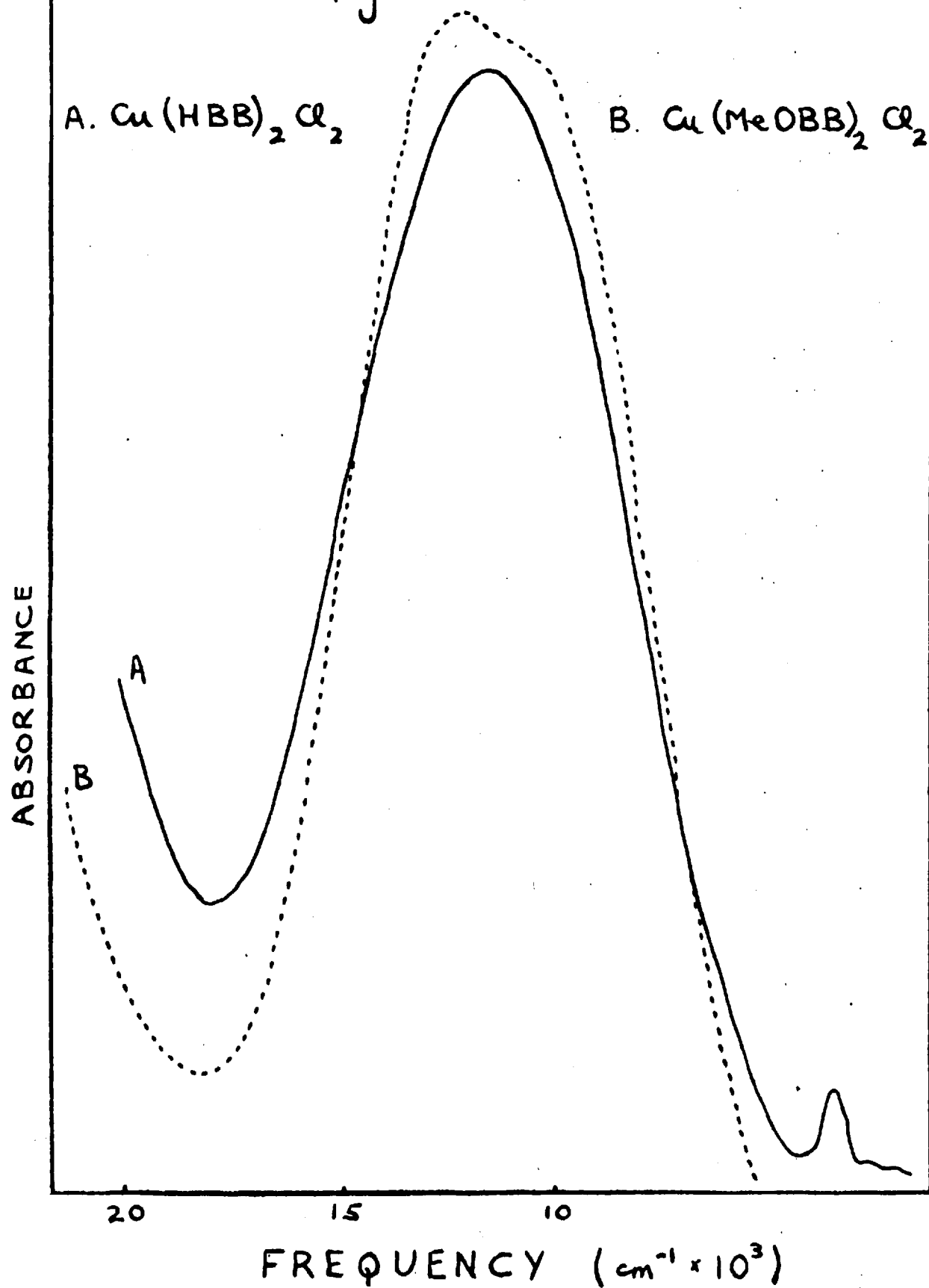


TABLE 7:3
MOLAR CONDUCTANCE DATA IN NITROBENZENE [/]

COMPLEX	λ_M	COLOUR OF SOLUTION	SOLUBILITY	
			HOT	COLD
$\text{Cu}(\text{HBB})_2\text{Cl}_2$	4.3	Green yellow		Soluble
$\text{Cu}(\text{HBB})_2\text{Cl}_2(\text{EtOH})_2$	2.4	Green yellow		Soluble
$\text{Cu}(\text{HBB})_2\text{Br}_2$	5.3	Dark greenish yellow		Soluble
$\text{Cu}(\text{HBB})_2\text{Br}_2(\text{EtOH})_2$	4.4	Dark greenish yellow		Soluble
$\text{Cu}(\text{HBB})_2(\text{NO}_3)_2$	-	-	Insoluble	
[⌘] $\text{Cu}(\text{HBB})_2(\text{SCN})_2$	-	-	Insoluble	
[⌘] $\text{Cu}(\text{HBB})_2(\text{SCN})_2$ (acetone) ₂	-	-	Insoluble	
[⌘] $\text{Cu}(\text{HBB})_3(\text{NO}_3)_2$	-	-	Insoluble	
$\text{Cu}(\text{HBB})_3(\text{ClO}_4)_2$	23.2	Greenish blue		Soluble
$\text{Cu}(\text{HBB})_2\text{I}_2$	18.0	Golden yellow		Soluble
[⌘] $\text{Cu}(\text{MeOBB})_2\text{Cl}_2$	-	-	Insoluble	
$\text{Cu}(\text{HBB})_2(\text{NO}_3)_2$	39.1	Greenish blue	SOLUBLE IN WARM NITROMETHANE	

[/] The nitrobenzene was pale yellow.

[⌘] Also insoluble in nitromethane.

like that of $\text{Cu}(\text{HBB})_2\text{Cl}_2$ indicates that the chloride ions are co-ordinated. It cannot be decided from the infrared spectrum (Table 7:4) whether the ethanol in the solvate is co-ordinated or hydrogen bonded. Since the electronic spectra and magnetic moments of the two complexes are different it might indicate that the first co-ordination spheres are different, that is the ethanol in $\text{Cu}(\text{HBB})_2\text{Cl}_2 \cdot (\text{EtOH})_2$ is co-ordinated.

It might be thought that the structures of $\text{Cu}(\text{HBB})_2\text{Cl}_2$ and $\text{Cu}(\text{HBB})_2\text{Br}_2$ would be rather similar, that is either a structure based on chelating HBB or on bridging halide ions. The appearance of the d-d band of $\text{Cu}(\text{HBB})_2\text{Br}_2$ at slightly higher energy than that of $\text{Cu}(\text{HBB})_2\text{Cl}_2$ might be explained on the basis of the structure in which the HBB is chelating, in terms of the greater tetragonal distortion to be expected from an axially bonded bromide ion than a chloride ion. However the structure in which the bromide ions are bridging need not be ruled out because of this difference in spectra since similar behaviour is shown by $\text{Cu}(\text{2 methylquinoxaline})_2\text{Cl}_2$ and Br_2 .⁵⁵

The molar conductances of $\text{Cu}(\text{HBB})_2\text{Br}_2 \cdot (\text{EtOH})_2$ and $\text{Cu}(\text{HBB})_2\text{Br}_2$ indicate that the bromide ions are co-ordinated, but nothing as definite can be said about the nature of the ethanol in the ethanolate from its infrared spectrum. However the electronic spectra of these two complexes are very similar which might indicate that their structures are similar, that is that the ethanol is hydrogen bonded, though this is not certain.

The infrared spectrum of $\text{Cu}(\text{HBB})_2(\text{NO}_3)_2$ indicates that the

TABLE 7:4

INFRARED SPECTRAL DATA

$\text{Cu(HBB)}_2(\text{NO}_3)_2$	$\text{Cu(HBB)}_3(\text{NO}_3)_2$	HBB
1449 v.s	1453 v.s	1451 v.s
$\#$ 1408 v.s	1439 sh	1433 v.s
1337 sh	$\#$ 1412 v.s	1383 m
$\#$ 1326 v.s and broad	1385 sh	1374 sh
1314 sh	1364 sh	1337 w
1287 s	1323 v.s	1309 s
	$\#$ 1304 v.s	1289 v.s
	1289 sh	1272 v.s

$\#$ Some of the absorption in these regions is probably due to the nitrate ions, which indicates that they are very likely co-ordinated.

$\text{Cu(HBB)}_3(\text{ClO}_4)_2$	HBB
1372 s	1377 v.s (Nujol)
1339 sh	1309 m
1309 w	1294 v.s
1285 s	1276 v.s
1256 sh	1253 m
1242 m	1235 m
1190 m	1220 m
1149 sh	1190 s
1117 sh	1160 m

TABLE 7:4 (Contd.)

$\text{Cu}(\text{HBB})_3(\text{ClO}_4)_2$	HBB
1095 v.s and broad	1142 w
1086 sh	1078 m
1064 v.s	1060 sh
1039 v.s	1053 v.s
1024 s	1024 m
1004 m	1001 sh

It is not possible to decide on the basis of this evidence whether the perchlorate ions are co-ordinated or not.

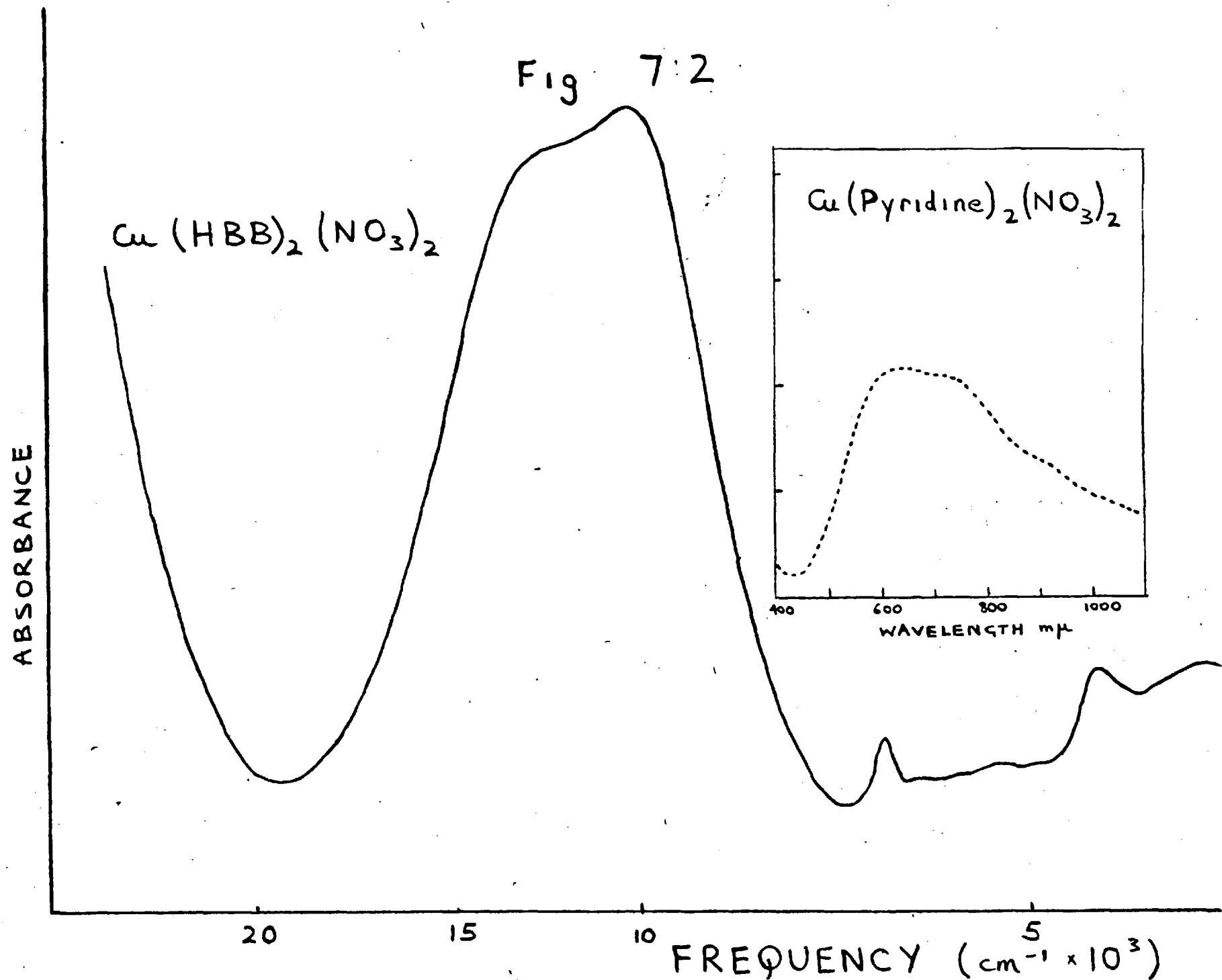
COMPLEX	BAND POSITION	ASSIGNMENT AND INTERPRETATION
$\text{Cu}(\text{HBB})_2(\text{SCN})_2$ (Acetone) ₂	2084	CN stretch of a terminally bonded thiocyanate ion
$\text{Cu}(\text{HBB})_2(\text{SCN})_2$ (Acetone) ₂	1684	CO stretch of acetone that is either hydrogen bonded or co-ordinated
$\text{Cu}(\text{HBB})_2(\text{SCN})_2$	2111	CN stretch of a thiocyanate ion that is either bridging or strongly hydrogen bonded

TABLE 7:4 (Contd. 2)

The spectra of $\text{Cu(HBB)}_2\text{Cl}_2$, $\text{Cu(HBB)}_2\text{Cl}_2(\text{EtOH})_2$, $\text{Cu(HBB)}_2\text{Br}_2$ and $\text{Cu(HBB)}_2\text{Br}_2(\text{EtOH})_2$ are similar in that they contain a very strong broad region of absorption that extends from $3,600 \text{ cm.}^{-1}$ to $2,500 \text{ cm.}^{-1}$ and it is not possible to decide whether the ethanol in the ethanولات is co-ordinated or hydrogen bonded.

nitrate ions are probably co-ordinated²⁷ and it might be assumed that this complex would have a structure similar to that of Co and $\text{Ni}(\text{HBB})_2(\text{NO}_3)_2$. However a comparison of the X-ray powder photographs of $\text{Cu}(\text{HBB})_2(\text{NO}_3)_2$ and $\text{Ni}(\text{HBB})_2(\text{NO}_3)_2$ (Table 7:5) shows that they are not isomorphous. This difference might arise from the Jahn Teller distortion in the copper complex. However if the structure of $\text{Cu}(\text{HBB})_2(\text{NO}_3)_2$ was essentially the same as that of $\text{Ni}(\text{HBB})_2(\text{NO}_3)_2$, it would be difficult to account for the position of the d-d band in the spectrum of the copper complex. In $\text{Cu}(\text{Pyridine})_2(\text{NO}_3)_2$ the nitrate ions are thought to be either bridging or chelating⁵⁶ and similar modes of bonding of the anions might be proposed for $\text{Cu}(\text{HBB})_2(\text{NO}_3)_2$. The difference in the electronic spectra of these two complexes (Fig. 7:2) might be explained in terms of the arguments put forward in the discussion of $\text{Cu}(\text{HBB})_2\text{Cl}_2$.

The complex $\text{Cu}(\text{HBB})_2(\text{NO}_3)_2$ is converted quite rapidly in solution to the blue insoluble $\text{Cu}(\text{HBB})_3(\text{NO}_3)_2$, the infrared spectrum of which indicates that the nitrate ions are co-ordinated.²⁷ The d-d band in the spectrum of $\text{Cu}(\text{HBB})_3(\text{NO}_3)_2$ occurs at much higher energy than that in the spectrum of $\text{Cu}(\text{HBB})_2(\text{NO}_3)_2$, but its magnetic moment is considerably lower, which almost certainly indicates the presence of copper to copper magnetic interactions. This can occur either by direct interaction, that is by the formation of a bond between the Cu^{II} ions as in copper(II) acetate monohydrate,⁵⁷ or by 'super exchange' in which a π pathway is established between the Cu^{II} ions using an intervening bridging ligand.⁵⁷ It is also possible



for both mechanisms to operate in a complex.⁵⁸ Which of these mechanisms is responsible for the anomalous magnetism of this complex it is not possible to say. On the basis of the stoichiometry of $\text{Cu}(\text{HBB})_3(\text{NO}_3)_2$ and the fact that the nitrate ions are probably co-ordinated it is possible to suggest a structure in which the nitrate ions and two of the HBB molecules are monodentately co-ordinated with two HBB molecules bridging between adjacent Cu^{II} ions. This type of structure would account for the electronic spectrum (~~Fig.~~ 7:1), and it might also account for the anomalous magnetic moment.

It cannot be decided from the infrared spectrum whether the perchlorate ions in $\text{Cu}(\text{HBB})_3(\text{ClO}_4)_2$ are co-ordinated or not,³³ but the molar conductance value which is typical for a 1:1 electrolyte might be interpreted in terms of ionic perchlorate groups which undergo association in solution. Now the magnetic moment of this complex is also anomalous and because of this and the fact that the position of its electronic spectral band is not too different from that of $\text{Cu}(\text{HBB})_3(\text{NO}_3)_2$ it might be thought that the two complexes have structural features in common, for example bridging HBB molecules. However an interesting difference between these two complexes for which no attempt at an explanation will be made is seen in their electron spin resonance spectra, that is $\text{Cu}(\text{HBB})_3(\text{NO}_3)_2$ shows a signal at $g_{\perp} = 1.894$ but no signal is observed for $\text{Cu}(\text{HBB})_3(\text{ClO}_4)_2$ even on sweeping through to 10,000 gauss.

The position of the thiocyanate ion CN stretch in the

TABLE 7:5X-RAY POWDER PATTERN DATA

$\text{Ni(HBB)}_2(\text{NO}_3)_2$		$\text{Cu(HBB)}_2(\text{NO}_3)_2$	
d	I	d	I
13.0	v.w	12.2	v.w
11.0	w doublet	10.9	w
10.1	w	9.3	m
8.5	v.w	7.1	v.w
8.3	v.w	6.6	v.w
		5.9	v.w

infrared spectrum of $\text{Cu}(\text{HBB})_2(\text{SCN})_2(\text{Acetone})_2$ may be interpreted as indicating that the anions are terminally bonded.²⁸ Now this complex loses two molecules of acetone on desolvation to give $\text{Cu}(\text{HBB})_2(\text{SCN})_2$ and two very interesting changes are seen. The first of these is that the anion CN stretch in $\text{Cu}(\text{HBB})_2(\text{SCN})_2$ absorbs at some 26 cm.^{-1} higher than this mode in the acetate, and secondly is the decrease in the room temperature magnetic moment in going from $\text{Cu}(\text{HBB})_2(\text{SCN})_2 \cdot (\text{Acetone})_2$ to $\text{Cu}(\text{HBB})_2(\text{SCN})_2$. The latter change indicates that an alteration in first co-ordination sphere takes place during the desolvation process, which might imply that the acetone in the solvate is co-ordinated. This is also partly suggested by the frequency of the acetone CO stretch in the infrared spectrum of $\text{Cu}(\text{HBB})_2(\text{SCN})_2 \cdot (\text{Acetone})_2$, that is 1684 cm.^{-1} . On the basis of this information a structure may be proposed for the acetate in which the thiocyanate ions are terminally nitrogen bonded with monodentate HBB and co-ordinated acetone, in a distorted cubic array. This sort of structure might also account for the electronic spectrum. The change in the position of the anion CN stretch on desolvation of the acetate might indicate that the thiocyanate ions in $\text{Cu}(\text{HBB})_2(\text{SCN})_2$ are bridging, a possible structure being one in which the anions form planar bridges with the HBB bonded axially. It might be possible to account for the difference in the electronic spectra of $\text{Cu}(\text{HBB})_2(\text{SCN})_2$ and its acetate if it is assumed that the in-plane field in $\text{Cu}(\text{HBB})_2(\text{SCN})_2$ is produced by four nitrogen atoms and the axial field by two relatively distant sulphur atoms. The large tetragonal

distortion in this complex may well produce a splitting of the Cu^{II} ion d electron energy levels such that the electronic spectral band occurs at higher energy than that of the acetate.

Whether the above structure would account for the magnetic behaviour of this complex it is not possible to say. Fig. 7:3 shows a plot of $1/\chi'$ against T for $\text{Cu}(\text{HBB})_2(\text{SCN})_2$ in the region 200 to 77 Å. Since the susceptibility is seen to increase with decreasing temperature it is highly unlikely that the order of the energy levels and their separation is that found in a dimeric species such as copper(II) acetate monohydrate in which there is magnetic interaction between adjacent Cu^{II} ions.⁵⁷ In this complex there is a lower lying singlet level separated by $\approx kT$ from an upper triplet level.⁵⁷

The electronic spectrum, magnetic moment and electron spin resonance spectrum all indicate that the copper in $\text{Cu}(\text{HBB})_2\text{I}_2$ is present as Cu^{I} . Now it is known that the imino hydrogen of imidazole is capable of undergoing substitution by iodine.⁵⁸ For example iodination of 2,4,5 trimethylimidazole leads to the formation of 1-iodo-2,4,5 trimethylimidazole.⁵⁹ If it is assumed that the imino hydrogen of HBB undergoes substitution by iodine then the peculiar stoichiometry of $\text{Cu}(\text{HBB})_2\text{I}_2$ can be rationalised, that is the complex might be of the form $\text{Cu}^+[(\text{C}_4\text{H}_4\text{N}_2\text{OI})(\text{C}_4\text{H}_4\text{N}_2\text{O})]\text{I}^-$. The molar conductance value of this complex which is a typical uni-univalent electrolyte value is in accord with this ionic formulation.

Since it is not known exactly what the mode of co-ordination of HBB is in most of the above complexes a valid discussion of its

Fig. 7:3

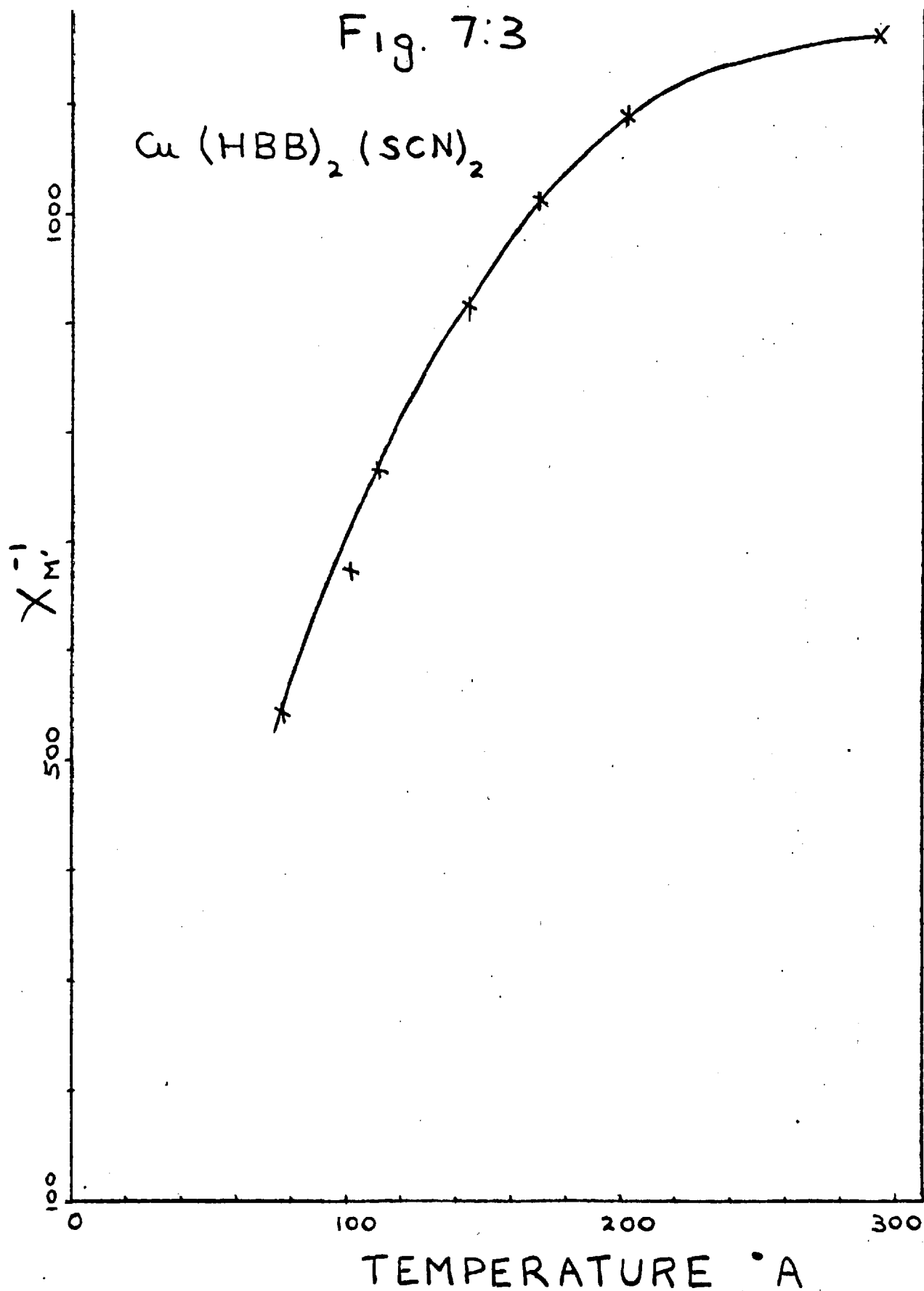
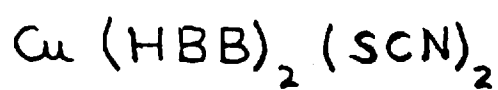


TABLE FOR FIG. 7:3

The Temperature Variation in the Magnetic Susceptibility
of $\text{Cu}(\text{HBB})_2(\text{SCN})_2$

$T^{\circ}\text{A}$	$M' (\times 10^{-6} \text{ c.g.s.u.})$
294	858
202	915
170	987
145	1087
112	1309
101	1482
77	1831

co-ordination chemistry with copper(II) salts is difficult. It does seem however that HBB is more inclined to co-ordinate monodentately with Cu^{II} ions than it is with Co^{II} and Ni^{II} ions. An interesting similarity is shown by Cu, Co and $\text{Ni}(\text{SCN})_2$ in the type of complex they form with HBB, that is $\text{M}(\text{HBB})_2(\text{SCN})_2(\text{Solvent})_2$. When $\text{Cu}(\text{HBB})_2(\text{SCN})_2(\text{Acetone})_2$ is desolvated it is thought that it goes to a form in which the HBB molecules are still monodentate. Whether this reluctance of HBB to chelate in $\text{Cu}(\text{HBB})_2(\text{SCN})_2$ is related to the electronic factors mentioned for Co and $\text{Ni}(\text{HBB})_2(\text{SCN})_2$, is an interesting point for conjecture.

Another feature of the co-ordination chemistry of HBB with Cu^{II} ions that is not shown with Co^{II} or Ni^{II} salts is its ability to bridge between adjacent copper atoms and perhaps act as an effective π pathway for electron delocalisation.

Although the solid state form of $\text{Cu}(\text{HBB})_2(\text{SCN})_2$ is stable, in solution it slowly decomposes. During this decomposition which probably involves Cu^{II} going to Cu^{I} the HBB undergoes modification to a compound that has quite a strong mercaptan like smell. Attempts to identify this compound were not successful because during its isolation it seemed to be oxidising. The mass spectrum of this unknown compound was compared with that of HBB but none of the fragments could be identified. A suggestion as to the way in which HBB is modified is that during the reduction $\text{Cu}^{\text{II}} \longrightarrow \text{Cu}^{\text{I}}$ a thiocyanate ion or radical is generated which attacks the HBB molecule probably bringing about incorporation of a sulphur atom. Despite

the conjectural nature of this proposal it is obvious that HBB is capable of undergoing quite drastic change in the presence of certain metal salts, an observation that could be highly significant biologically.

CHAPTER EIGHT

Conclusion

The main aim of this study was to investigate the co-ordination chemistry of HBB and some related compounds with a view to correlating antiviral activity with chelation properties. However, it would be necessary to investigate the co-ordination chemistry of many more derivatives of HBB than have been studied in this thesis, with a greater variety of metal ions, before a meaningful relationship between antiviral activity and chelation properties would emerge. Now it was mentioned in the introduction that the presence of the hydroxybenzyl group, or more precisely, in view of the

antiviral activity of MeOBB, the group $\begin{array}{c} \text{H} \\ | \\ \text{C} \text{---} \text{C}_6\text{H}_5 \\ | \\ \text{OR} \end{array}$, at position 2

in the benzimidazole ring is of fundamental importance for the virus inhibitory action of HBB. Therefore it might be more rewarding to try to correlate the co-ordination chemistry of the various ligands

studied in this thesis with the presence of the group $\begin{array}{c} \text{H} \\ | \\ \text{C} \text{---} \text{C}_6\text{H}_5 \\ | \\ \text{O} \end{array}$, rather than directly with antiviral activity.

It can be seen from the discussion of the co-ordination chemistry of the various ligands that on the basis of their behaviour with cobalt and nickel halides they can be divided into three groups. For example HBB and HMeB both form complexes of the type $\text{M}(\text{L})_3\text{X}_2$ where M is cobalt or nickel, L is HBB or HMeB and X is Cl or I,

and because of this it might be argued that HBB and HMeB have very similar chelation properties. This may or may not be true, but it is worth noting that since HBB forms tris chelates with cobalt and nickel halides it is difficult to see how HMeB could act differently, since it represents a steric change in HBB which favours formation of this type of complex. It is to be expected that there would be no significant change in polarizability in going from HBB to HMeB.

nPrHBB and isoPrHBB behave similarly with CoCl_2 and NiCl_2 , that is they form complexes of the type $\text{Co}(\text{L})_3^{2+}\text{CoCl}_4^{2-}$ and $\text{Ni}(\text{L})_2\text{Cl}_2$ where L is nPrHBB or isoPrHBB. nPrHBB also forms $\text{Co}(\text{nPrHBB})_3^{2+}\text{CoBr}_4^{2-}$ and $\text{Co}(\text{nPrHBB})_2\text{I}_2$, and it is very probable that isoPrHBB would form similar complexes. The reason why these two ligands behave differently from HBB can probably be explained in terms of the increased steric effect of the propyl group.

With CoX_2 , where X is Cl, Br or I, HPB forms the tetrahedral complexes $\text{Co}(\text{L})_2\text{X}_2$ in which the anions are co-ordinated. MeOBB forms a similar type of complex with CoCl_2 and would presumably behave similarly with CoBr_2 and CoI_2 . The reason for the differences in chelation properties of HPB and HBB might be explained in terms of the relative polarizability of these ligands. The steric effect of the methyl group on the oxygen atom in MeOBB is probably the cause of the difference in behaviour of this ligand and HBB with CoCl_2 . In their co-ordination chemistry with the nickel halides HPB and MeOBB are completely different from one another and from the other ligands.

On the basis of the above classification it seems that except for nPrHBB and isoPrHBB there is no tendency for ligands

containing the group $\begin{array}{c} \text{H} \\ | \\ \text{C} \text{---} \text{C}_6\text{H}_5 \\ | \\ \text{OR} \end{array}$ to behave similarly with cobalt and nickel halides, apart of course from the fact that in most cases they chelate.

An alternative classification of these ligands is that based on their chelation properties with Co and $\text{Ni}(\text{NO}_3)_2$, Co and $\text{Ni}(\text{SCN})_2$, and Co and $\text{Ni}(\text{ClO}_4)_2$.

With $\text{Ni}(\text{NO}_3)_2$, Co and $\text{Ni}(\text{SCN})_2$ and $\text{Ni}(\text{ClO}_4)_2$, the chelation properties of HBB and MeOBB are very similar, see Chapter Five. The reason for the difference in behaviour with $\text{Co}(\text{ClO}_4)_2$ can perhaps be attributed to the greater ease with which the O - H bond in HBB can be broken as compared to the O - C bond in MeOBB. The steric effect of the methoxy methyl group in MeOBB is probably the cause of the difference in behaviour of this ligand and HBB with $\text{Co}(\text{NO}_3)_2$. It would seem then that the modification of HBB necessary to give MeOBB does not have the drastic effect on the chelation properties of the former that might have been expected.

In their co-ordination chemistry with Co and $\text{Ni}(\text{NO}_3)_2$, Co and $\text{Ni}(\text{SCN})_2$ and $\text{Co}(\text{ClO}_4)_2$, HMeB and HPB behave completely differently from each other, and, what is perhaps more important, from HBB also.

The ligands HBB and nPrHBB form very similar complexes with Co and $\text{Ni}(\text{NO}_3)_2$ and $\text{Co}(\text{ClO}_4)_2$. However two interesting differences between these ligands are seen in their behaviour with Co and $\text{Ni}(\text{SCN})_2$.

and $\text{Ni}(\text{ClO}_4)_2$. With $\text{Co}(\text{SCN})_2$, HBB forms the complex $\text{Co}(\text{HBB})_2(\text{SCN})_2$ in which it is monodentate, whereas $n\text{PrHBB}$ forms a complex of the same stoichiometry but in which it is chelating. It is only possible to prepare $\text{Ni}(\text{HBB})_2(\text{SCN})_2$, in which the HBB is chelating, indirectly by desolvation of the dimethylformamide adduct, $n\text{PrHBB}$ chelates directly with $\text{Ni}(\text{SCN})_2$. HBB undergoes proton loss only with $\text{Co}(\text{ClO}_4)_2$, that is to give $\text{Co}^{2+}(\text{HBB})_2(\text{HBB}),^-(\text{ClO}_4),^-$, $n\text{PrHBB}$ forms this type of complex with $\text{Ni}(\text{ClO}_4)_2$ also. In view of the above observations it is perhaps best to treat these differences not as radical changes in chelation properties, but rather as a smooth transition to structures that HBB is not quite capable of forming, probably because of electronic factors.

The only obvious difference in the chelation properties of $n\text{PrHBB}$ and isoPrHBB is seen in the complexes they form with Co and $\text{Ni}(\text{ClO}_4)_2$, that is Co and $\text{Ni}(\text{isoPrHBB})_2(\text{ClO}_4)_2$ and Co and $\text{Ni}(n\text{PrHBB})_2(n\text{PrHBB}),^-(\text{ClO}_4),^-$. Therefore it would seem that isoPrHBB is also similar in chelation properties to HBB.

On the basis of this classification then it can be seen

that ligands containing the group $\begin{array}{c} \text{H} \\ | \\ \text{C} \text{ --- } \text{C}_6\text{H}_5 \\ | \\ \text{OR} \end{array}$ are quite similar

in their chelation properties. HMeB and HPB which do not contain this group are very different in their co-ordination chemistry from each other and more significantly from HBB etc.

The question now arises as to which of the above classifications is more significant, that is which one best illustrates

trends in co-ordination chemistry. It is claimed that for the purpose of this discussion the classification based upon chelation properties with Co and $\text{Ni}(\text{NO}_3)_2$ etc. is more significant than that based upon co-ordination chemistry with cobalt and nickel halides. The reason for this is that with Co and $\text{Ni}(\text{NO}_3)_2$, Co and $\text{Ni}(\text{SCN})_2$ and Co and $\text{Ni}(\text{ClO}_4)_2$ one is dealing with much more drastic changes in anion than with Co and NiCl_2 , Br_2 and I_2 . This is important since it is with very different anions that one would expect to see better the effects of changes in steric and electronic properties of the various ligands.

CHAPTER NINEExperimentalAnalyses

The determination of carbon, hydrogen, nitrogen and halogen were carried out by members of the Microanalytical Department, Imperial College.

Preparation of the CompoundsCHAPTER ONE2-O-Hydroxyphenylbenzimidazole⁶⁰

One mole of mandelic acid (142 gms.) and one mole of O. phenylene diamine (108 gms.) were refluxed in 200 mls. of distilled water and 200 mls. of concentrated hydrochloric acid, that is approximately 6 M, for about one hour. On cooling, the resulting dark blue oily liquid was neutralised with .880 ammonium hydroxide, when the crude product precipitated as an off-white solid. The crude product was filtered, washed with distilled water and recrystallised from 95% ethanol using activated charcoal for decolourising. The final product was in the form of white crystalline plates.

Melting point = 207°C (literature melting point 207-208°C).

Yield = 120 gms. (56%).

Co(HBB)₃Cl₂

A solution of 1.2 gms. of CoCl₂.6H₂O in 25 mls. of acetone was added to 3.4 gms. of HBB in 200 mls. of acetone. The resulting

deep blue solution was then left to evaporate in an open dish at room temperature. After a few days dark pink crystals formed. These were filtered off, washed with acetone, gently crushed and refluxed for about an hour in nitromethane. The now light pink solid was filtered off and dried in vacuo.

(Found: C, 62.73; H, 4.47; Cl, 8.85; N, 10.41.

Calculated for $\text{Co}(\text{C}_{14}\text{H}_{12}\text{N}_2\text{O})_3\text{Cl}_2$

C, 62.84; H, 4.52; Cl, 8.84; N, 10.47%).

$\text{Co}(\text{HBB})_3\text{Br}_2$

A solution of 1.6 gms. of $\text{CoBr}_2 \cdot 6\text{H}_2\text{O}$ in 25 mls. of acetone was added to 3.4 gms. of HBB in 200 mls. of acetone. The rest of this preparation is identical to that given above.

(Found: C, 56.41; H, 4.11; Br, 17.85; N, 9.64.

Calculated for $\text{Co}(\text{C}_{14}\text{H}_{12}\text{N}_2\text{O})_3\text{Br}_2$

C, 56.56; H, 4.07; Br, 17.93; N, 9.43%).

$\text{Co}(\text{HBB})_3\text{I}_2$

2.9 gms. of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 3.4 gms. KI were refluxed in about 50 mls. of acetone for about two hours. The resulting solution was filtered, evaporated to about 20 mls. and left standing in the fridge overnight. The solution was filtered again and to the filtrate was added 6.7 gms. of HBB which dissolved readily on shaking. After filtering, the solution was evaporated to dryness and the solid remaining was dissolved in 100 mls. of nitromethane. This solution was filtered, heated to boiling and

allowed to cool very slowly to room temperature. The dark pink crystals that formed were filtered off, washed with a small amount of nitromethane and dried in vacuo.

(Found: C, 51.77; H, 4.03; I, 25.42.

Calculated for $\text{Co}(\text{C}_{14}\text{H}_{12}\text{N}_2\text{O})_3\text{I}_2$ C, 51.18; H, 3.67; I, 25.75%).

$\text{Co}(\text{HBB})_2(\text{NO}_3)_2$

To a solution of 4.5 gms. of HBB in about 200 mls. of acetone was added one of 2.9 gms. of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 25 mls. of acetone. The resulting deep pink solution was filtered, evaporated to about 50 mls. and left standing. After several weeks dark pink feathery crystals formed, which were filtered off and dried in vacuo at about 100°C until the last traces of acetone were removed.

(Found: C, 53.11; H, 4.20; N, 13.18; O, 20.27.

Calculated for $\text{Co}(\text{C}_{14}\text{H}_{12}\text{N}_2\text{O})_2(\text{NO}_3)_2$

C, 53.26; H, 3.83; N, 13.31; O, 20.27%).

$\text{Co}(\text{HBB})_2(\text{SCN})_2(\text{DMF})_2$

4.5 gms. of HBB and 1.7 gms. of $\text{Co}(\text{SCN})_2$ were dissolved in 20 mls. of dimethylformamide with vigorous shaking and warming to give a deep blue solution. This solution was filtered and the filtrate on standing overnight produced tiny purple crystals, which were filtered off, washed quickly with a small amount of diethyl ether and dried in vacuo.

(Found: C, 55.43; H, 6.07.

Calculated for $\text{Co}(\text{C}_{14}\text{H}_{12}\text{N}_2\text{O})_2(\text{SCN})_2(\text{H} \cdot \text{CON}(\text{CH}_3)_2)_2$ C, 56.16; H, 4.91%).

Weight loss study

Found: = 20%

Calculated for $\text{Co}(\text{C}_{14}\text{H}_{12}\text{N}_2\text{O})_2(\text{SCN})_2(\text{H}.\text{CON}(\text{CH}_3)_2)_2$

————→ $\text{Co}(\text{C}_{14}\text{H}_{12}\text{N}_2\text{O})_2(\text{SCN})_2$ = 19.0%.

The poor analysis of this compound is very probably due to hydrogen bonded dimethylformamide.

$\text{Co}(\text{HBB})_2(\text{SCN})_2$

A sample of $\text{Co}(\text{HBB})_2(\text{SCN})_2(\text{DMF})_2$ was heated in vacuo at about 100°C until all the dimethyl formamide had been removed. The resulting compound was deep blue.

(Found: C, 57.22; H, 4.36.

Calculated for $\text{Co}(\text{C}_{14}\text{H}_{12}\text{N}_2\text{O})_2(\text{SCN})_2$ C, 57.77; H, 3.85%).

$\text{Co}(\text{HBB})_3(\text{ClO}_4)_1$

6.7 gms. of HBB and 3.6 gms. of $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ were covered with 20 mls. of nitromethane and shaken vigorously. The resulting dark pink solution was filtered and the filtrate left standing in the fridge for some weeks, after which time a dark pink solid separated out. This was filtered off, dissolved in about 20 mls. of aceto-nitrile and the solution evaporated to about half volume. On standing overnight a pink solid crystallised out which was filtered off and dried in vacuo.

(Found: C, 60.59; H, 4.35; Cl, 3.86; N, 10.28; O, 14.13.

Calculated for $\text{Co}(\text{C}_{14}\text{H}_{12}\text{N}_2\text{O})_2(\text{C}_{14}\text{H}_{11}\text{N}_2\text{O})_1(\text{ClO}_4)_1$,

C, 60.10; H, 4.33; Cl, 4.23; N, 10.16; O, 13.35%).

Ni(HBB)₃Cl₂

To a hot solution of 3.4 gms. of HBB in about 150 mls. of acetone was added a solution of 1.2 gms. of NiCl₂.6H₂O in 25 mls. of absolute alcohol. The resulting light green solution was vigorously shaken and on standing for a few minutes a bluish green solid crystallised out. This product was filtered off and dried in vacuo.

(Found: C, 62.62; H, 4.54; Cl, 8.60; N, 10.23.

Calculated for Ni(C₁₄H₁₂N₂O)₃Cl₂

C, 62.87; H, 4.52; Cl, 8.84; N, 10.47%).

Ni(HBB)₃Br₂

6.7 gms. of HBB and 3.3 gms. of NiBr₂.6H₂O were dissolved in 50 mls. of absolute alcohol to give a green solution. After filtering this solution was evaporated to about 20 mls. and left standing for about six weeks. The large bluish green crystals that formed were filtered off, washed with a small amount of absolute alcohol, crushed and dried in vacuo.

(Found: C, 56.26; H, 4.27; Br, 18.09.

Calculated for Ni(C₁₄H₁₂N₂O)₃Br₂

C, 56.59; H, 4.07; Br, 17.93%).

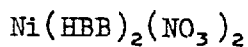
Ni(HBB)₃I₂

The large green crystals produced by a solution of 3.4 gms. of HBB and 2.1 gms. of NiI₂.6H₂O in 25 mls. of nitromethane on standing overnight, were filtered off, gently crushed and dried in

vacuo.

(Found: C, 51.24; H, 3.55; I, 25.74.

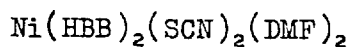
Calculated for $\text{Ni}(\text{C}_{14}\text{H}_{12}\text{N}_2\text{O})_3\text{I}_2$ C, 51.21; H, 3.68; I, 25.76%).



See $\text{Co}(\text{HBB})_2(\text{NO}_3)_2$.

(Found: C, 53.33; H, 4.27.

Calculated for $\text{Ni}(\text{C}_{14}\text{H}_{12}\text{N}_2\text{O})_2(\text{NO}_3)_2$ c, 53.30; H, 3.83%).



A solution of $\text{Ni}(\text{SCN})_2$ was prepared by dissolving 4.4 gms. of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 2.91 gms. of KSCN in 50 mls. of acetone, filtering off the precipitated KNO_3 , evaporating the solution to about 20 mls. and standing in the fridge overnight. To this solution was added 4.5 gms. of HBB, which dissolved readily on shaking, and then the dark green solution was evaporated to dryness. The residue was dissolved in 25 mls. of dimethylformamide and this solution on standing for a short time produced green crystals. The product was filtered off, gently crushed, washed with diethyl ether and dried in vacuo.

(Found: C, 55.47; H, 4.85.

Calculated for $\text{Ni}(\text{C}_{14}\text{H}_{12}\text{N}_2\text{O})_2(\text{SCN})_2(\text{H} \cdot \text{CON}(\text{CH}_3)_2)_2$ C, 56.22; H, 4.98%).

Weight loss study

Found: = 20.5%

Calculated for $\text{Ni}(\text{C}_{14}\text{H}_{12}\text{N}_2\text{O})_2(\text{SCN})_2(\text{H} \cdot \text{CON}(\text{CH}_3)_2)_2$

————→ $\text{Ni}(\text{C}_{14}\text{H}_{12}\text{N}_2\text{O})_2(\text{SCN})_2$ = 19.0%.

$\text{Ni}(\text{HBB})_2(\text{SCN})_2$

A sample of $\text{Ni}(\text{HBB})_2(\text{SCN})_2(\text{DMF})_2$ was vacuum dried at about 140°C until all the dimethylformamide had been removed; this took about two weeks to achieve. The resulting compound was dark fawn in colour.

(Found: C, 57.54; H, 4.27.

Calculated for $\text{Ni}(\text{C}_{14}\text{H}_{12}\text{N}_2\text{O})_2(\text{SCN})_2$ C, 57.80; H, 3.88%).

$\text{Ni}(\text{HBB})_3(\text{ClO}_4)_2$

6.7 gms. of HBB and 3.6 gms. of $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 25 mls. of acetone and the solution filtered. The filtrate was then evaporated to dryness and the residue dissolved in 10 mls. of acetonitrile. On standing for about 5 weeks the small amount of blue green crystals that had formed was filtered off. These crystals were crushed and dried in vacuo.

(Found: C, 54.11; H, 3.85; N, 8.77; O, 17.56.

Calculated for $\text{Ni}(\text{C}_{14}\text{H}_{12}\text{N}_2\text{O})_3(\text{ClO}_4)_2$

C, 54.21; H, 3.90; N, 9.04; O, 18.91%).

CHAPTER TWO

1. nPr 2 $\propto$ Hydroxybenzylbenzimidazole⁶¹

One mole of o chloro nitrobenzene (158 gms.) and two moles of n propylamine (118 gms.) were heated in sealed Carius tubes at 150°C for about five hours. On cooling the dark red oily product was extracted with ether, thoroughly washed with

distilled water and then dried over CaCl_2 . After drying the ether was removed and the dark red oil, that is the N substituted nitro-aniline was weighed, dissolved in about 200 mls. of methanol and then hydrogenated at atmospheric pressure using about 1 gm. of Adams platinum oxide catalyst. When hydrogen uptake was complete, the solution now being a pale straw colour, the methanol was removed under vacuum, since the N substituted diamine oxidises very rapidly, and the resulting oily liquid condensed with mandelic acid. This was achieved by refluxing 1 mole of diamine and 1 mole of mandelic acid in 6 M hydrochloric acid for about five hours under nitrogen. On cooling the very dark blue solution was neutralised with .880 ammonium hydroxide when the product separated as a viscous sticky mass which solidified when left standing in the fridge. The crude product was purified by recrystallisation from 95% ethanol and washing with acetone.

Melting point = 141°C (literature melting point $141-142^\circ\text{C}$)

The yield of N substituted nitroaniline is very high being about 100%.

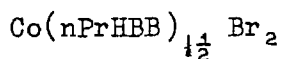
Yield of nPrHBB = 89 gms. (55%)

$\text{Co}(\text{nPrHBB})_2 \cdot \frac{1}{2} \text{Cl}_2$

5.4 gms. of nPrHBB and 2.4 gms. of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 50 mls. of acetone with vigorous shaking and the resulting deep blue solution was filtered. On standing for a short time a blue solid crystallised out which was filtered off and dried in vacuo at about 90°C . This product was then recrystallised from nitromethane and the small feathery crystals dried in vacuo.

(Found: C, 57.38; H, 5.00; N, 7.97.

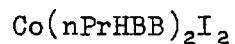
Calculated for $\text{Co}(\text{C}_{17}\text{H}_{18}\text{N}_2\text{O})\frac{1}{2}\text{Cl}_2$ C, 57.84; H, 5.14; N, 7.98%).



4.0 gms. of nPrHBB and 2.4 gms. $\text{CoBr}_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 20 mls. of acetone and the resulting deep blue solution was filtered. The filtrate was evaporated to dryness and the residue dissolved in 10 mls. of nitromethane. The nitromethane solution on standing for about a week produced purple crystals which were filtered off, crushed and dried in vacuo.

(Found: C, 49.39; H, 4.31; N, 7.01.

Calculated for $\text{Co}(\text{C}_{17}\text{H}_{18}\text{N}_2\text{O})\frac{1}{2}\text{Br}$ C, 49.53; H, 4.40; N, 6.80%).



1.5 gms. of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 1.5 gms. of NaI were dissolved in 25 mls. of acetone and the precipitated NaNO_3 filtered off. The filtrate was evaporated to about 10 mls. and left standing in the fridge overnight. After filtering the CoI_2 solution 2.7 gms. of nPrHBB were dissolved in it and the deep purple solution was filtered. The filtrate was evaporated to dryness, the residue dissolved in 20 mls. of nitromethane and the very dark brown solution filtered. On standing overnight a mass of blue crystals formed which were filtered off, crushed and dried in vacuo.

(Found: C, 48.65; H, 4.40; N, 6.78.

Calculated for $\text{Co}(\text{C}_{17}\text{H}_{18}\text{N}_2\text{O})_2\text{I}_2$ C, 48.31; H, 4.49; N, 6.64%).

$\text{Co}(\text{nPrHBB})_2(\text{NO}_3)_2$

5.4 gms. of nPrHBB and 2.9 gms. of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 50 mls. of acetone with shaking and warming and after filtration the solution was evaporated to about 10 mls. On standing overnight in the fridge copious dark red crystals formed which were filtered off and dried in vacuo. This compound was recrystallised from acetone.

(Found: C, 57.59; H, 4.85.

Calculated for $\text{Co}(\text{C}_{17}\text{H}_{18}\text{N}_2\text{O})_2(\text{NO}_3)_2$ C, 57.07; H, 5.07%).

 $\text{Co}(\text{nPrHBB})_2(\text{SCN})_2$

The deep blue solution prepared by shaking together 4.0 gms. of nPrHBB and 1.3 gms. of $\text{Co}(\text{SCN})_2$ in 50 mls. of acetone, filtering and evaporating the filtrate to about 20 mls., on standing produced a pink crystalline solid. This compound was filtered off, very gently crushed and dried in vacuo.

(Found: C, 60.77; H, 5.20; N, 11.92.

Calculated for $\text{Co}(\text{C}_{17}\text{H}_{18}\text{N}_2\text{O})_2(\text{SCN})_2$ C, 61.09; H, 5.13; N, 11.88%).

 $\text{Co}(\text{nPrHBB})_3(\text{ClO}_4)_1$

4.0 gms. of nPrHBB and 1.9 gms. of $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 25 mls. of acetone with shaking to give a dark pink solution which was filtered and evaporated to about half volume. On standing for about two weeks this solution produced pink crystals. The crystals were filtered off, gently crushed and dried in vacuo.

(Found: C, 63.06; H, 5.66; O, 12.30.

Calculated for $\text{Co}(\text{C}_{17}\text{H}_{18}\text{N}_2\text{O})_2(\text{C}_{17}\text{H}_{17}\text{N}_2\text{O})_1(\text{ClO}_4)_1$,
C, 63.98; H, 5.68; O, 11.69%.

$\text{Ni}(\text{nPrHBB})_2\text{Cl}_2$

5.4 gms. of nPrHBB and 2.4 gms. of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 25 mls. of nitromethane with vigorous shaking and warming. After filtering this solution the filtrate was evaporated to about 10 mls. and left standing. On standing for some days pale green crystals formed which were filtered off, crushed and dried in vacuo at about 100°C .

(Found: C, 60.39; H, 5.37; N, 8.27.

Calculated for $\text{Ni}(\text{C}_{17}\text{H}_{18}\text{N}_2\text{O})_2\text{Cl}_2$ C, 61.60; H, 5.48; N, 8.46%.

$\text{Ni}(\text{nPrHBB})_2(\text{NO}_3)_2$

5.4 gms. of nPrHBB and 2.9 gms. of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 50 mls. of acetone with warming and shaking to give a green solution which after filtration was evaporated to about 10 mls. Since no crystals formed on standing in the fridge overnight the solution was evaporated to dryness and the residue dissolved in 20 mls. of nitromethane. The nitromethane solution on standing for a few days produced green crystals which were filtered off, crushed and dried in vacuo. This compound was recrystallised by dissolving in absolute alcohol, evaporating to dryness and dissolving the residue in nitromethane.

(Found: C, 57.28; H, 5.19.

Calculated for $\text{Ni}(\text{C}_{17}\text{H}_{18}\text{N}_2\text{O})_2(\text{NO}_3)_2$ C, 57.07; H, 5.07%.

$\text{Ni}(\text{nPrHBB})_2(\text{SCN})_2$

2.7 gms. of nPrHBB were dissolved in 25 mls. of hot absolute alcohol and to this was added 17 mls. of a solution prepared by dissolving 1.94 gms. of KSCN and 2.91 gms. of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 35 mls. of absolute alcohol. The resulting green solution was filtered and left standing. The green solid which crystallised out was filtered off and dried in vacuo.

(Found: C, 60.84; H, 5.16; N, 11.69
Calculated for $\text{Ni}(\text{C}_{17}\text{H}_{18}\text{N}_2\text{O})_2(\text{SCN})_2$ C, 60.10; H, 5.13; N, 11.88%).

 $\text{Ni}(\text{nPrHBB})_3(\text{ClO}_4)_4$

4.0 gms. of nPrHBB and 1.9 gms. of $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 25 mls. of hot acetone, the solution filtered and the filtrate evaporated to about 15 mls. After standing for about 10 days this solution produced a small amount of a green crystalline solid which was filtered off, crushed and dried in vacuo.

(Found: C, 62.63; H, 5.79; O, 12.20.
Calculated for $\text{Ni}(\text{C}_{17}\text{H}_{18}\text{N}_2\text{O})_3(\text{ClO}_4)_4$ C, 63.98; H, 5.68; O, 11.70%).

CHAPTER THREE1.isoPr.2-Hydroxybenzylbenzimidazole⁶¹

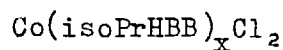
One mole of o chloro nitrobenzene (158 gms.) and two moles of isopropylamine (118 gms.) were heated in sealed Carius tubes at about 140°C for twelve hours. On cooling, the substituted nitro-aniline, which was in the form of a dark brown oil was extracted

with ether, washed with distilled water and dried over CaCl_2 . The ether was removed from the product, which was weighed, dissolved in ether and hydrogenated at atmospheric pressure using about 1 gm. of Adams platinum oxide catalyst. When the calculated volume of hydrogen had been consumed the N substituted diamine, which oxidises very rapidly, was isolated and refluxed with the appropriate amount of mandelic acid in 6 M hydrochloric acid for about four hours under nitrogen. The crude isoPrHBB was isolated from this reaction mixture by neutralisation with .880 ammonium hydroxide and purified by recrystallisation from aqueous ethanol and decolourisation with activated charcoal.

Melting point = 176°C (literature melting point 176°C).

The yield of N substituted nitroaniline is very high, being about 100%.

Yield of isoPrHBB = 80 gms. (36%).



2.7 gms. of isoPrHBB and 1.2 gms. of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, that is a 2:1 ratio, were dissolved in 20 mls. of acetone to give a blue solution which was filtered and evaporated to dryness. The residue was dissolved in 10 mls. of nitromethane and the solution left standing overnight. The blue crystals that formed were filtered off and dried in vacuo.

(Found: C, 55.95; H, 4.41; N, 6.78.

Calculated for $\text{Co}(\text{C}_{17}\text{H}_{18}\text{N}_2\text{O})_{1\frac{1}{2}}\text{Cl}_2$ C, 57.84; H, 5.14; N, 7.98%).

The above compound was recrystallised from nitromethane.

(Found: C, 55.80; H, 4.83; N, 7.52.

Calculated for $\text{Co}(\text{C}_{17}\text{H}_{18}\text{N}_2\text{O})_4\text{Cl}_2$ C, 51.53; H, 4.58; N, 7.07%).

2.7 gms. of isoPrHBB and 2.4 gms. of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, that is a 1:1 ratio, were dissolved in 30 mls. of acetone to give a deep blue solution which was filtered and then evaporated to about half volume. On standing for about four days the copious yield of blue crystals that had formed was filtered off, crushed and dried in vacuo.

(Found: C, 56.22; H, 4.92; N, 7.90%).

It is evident from the above that the composition of this mixture is independent of the solvent used and the ratio of ligand to metal salt.

$\text{Co}(\text{isoPrHBB})_2(\text{NO}_3)_2$

5.4 gms. of isoPrHBB and 2.9 gms. of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in about 50 mls. of acetone and to the deep pink solution were added a few grams of molecular sieves. The mixture was shaken for about ten minutes after which time the solution was filtered and evaporated to dryness under vacuum. N.B. if this solution is heated it very quickly turns brown; this may be due to oxidation of the Co^{2+} to Co^{3+} . The residue was dissolved in 10 mls. of nitromethane and the deep pink solution was left standing for a few days after which time the pink crystals that had formed were filtered off, crushed and dried in vacuo.

(Found: C, 56.31; H, 4.82; N, 11.55.

Calculated for $\text{Co}(\text{C}_{17}\text{H}_{18}\text{N}_2\text{O})_2(\text{NO}_3)_2$ C, 57.07; H, 5.07; N, 11.74%).

Co(isoPrHBB)₂(SCN)₂

2.7 gms. of isoPrHBB and 0.9 gms. of Co(SCN)₂ were dissolved in 50 mls. of acetone and the resulting deep blue solution was filtered and evaporated to about half volume. After standing for several days no crystals formed and so the solution was evaporated to dryness and the residue dissolved in 5 mls. of nitromethane. This solution on standing overnight produced tiny pink crystals which were filtered off and dried in vacuo

(Found: C, 60.57; H, 5.11; N, 11.91.

Calculated for Co(C₇H₁₃N₂O)₂(SCN)₂ C, 61.09; H, 5.13; N, 11.88%).

Co(isoPrHBB)₂(ClO₄)₂

5.4 gms. of isoPrHBB and 3.6 gms. of Co(ClO₄)₂·6H₂O were dissolved in 25 mls. of acetone and the deep pink solution was filtered and evaporated to dryness. The residue was then dissolved in about 20 mls. of nitromethane and the solution was evaporated under vacuum to remove the last traces of acetone. Equal volumes of carbon tetrachloride and dichloromethane were added until the solution became very faintly turbid, then it was left standing overnight. The copious yield of pink crystals that formed was filtered off and dried in vacuo.

(Found: C, 52.13; H, 4.40; N, 6.93; O, 20.49.

Calculated for Co(C₇H₁₃N₂O)₂(ClO₄)₂

C, 51.66; H, 4.59; N, 7.08; O, 20.24%).

Ni(isoPrHBB)₂Cl₂

3 gms. of isoPrHBB were dissolved in 25 mls. of acetone and

1.2 gms. of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in 10 mls. of absolute alcohol. The nickel chloride and ligand solutions were mixed and after filtration the light green solution was evaporated to dryness. The residue was dissolved in 10 mls. of nitromethane and on standing for a few days the green-yellow crystals that formed were filtered off, crushed and dried in vacuo at about 80°C .

(Found: C, 60.03; H, 5.64;

Calculated for $\text{Ni}(\text{isoPrHBB})_2\text{Cl}_2$ C, 61.60; H, 5.48%).

$\text{Ni}(\text{isoPrHBB})_2(\text{NO}_3)_2$

2.7 gms. of isoPrHBB and 1.4 gms. of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 50 mls. of acetone with shaking and the resulting green solution was filtered. On standing for a short time a greenish blue solid crystallised out which was filtered off, washed with acetone and dried in vacuo.

(Found: C, 57.45; H, 5.00; N, 11.39;

Calculated for $\text{Ni}(\text{C}_{17}\text{H}_{10}\text{N}_2\text{O})_2(\text{NO}_3)_2$ C, 57.07; H, 5.07; N, 11.74%).

$\text{Ni}(\text{isoPrHBB})_2(\text{SCN})_2$

A solution of $\text{Ni}(\text{SCN})_2$ was prepared by dissolving 1.45 gms. of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.95 gms. of KSCN in 25 mls. of absolute alcohol, filtering, evaporating to about 10 mls. and leaving to stand in the fridge overnight. After filtering this solution 2.7 gms. of iso-PrHBB were added to it and the resulting green solution was evaporated to dryness. The residue was dissolved in 30 mls. of nitromethane and on standing for a short time the green solid that crystallised

out was filtered off and dried in vacuo.

(Found: C, 60.75; H, 5.05; N, 11.98;

Calculated for $\text{Ni}(\text{C}_{17}\text{H}_{18}\text{N}_2\text{O})_2(\text{SCN})_2$ C, 61.10; H, 5.13; N, 11.88%).

$\text{Ni}(\text{isoPrHBB})_2(\text{ClO}_4)_2$

5.4 gms. of isoPrHBB and 3.6 gms. of $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 10 mls. of acetone and the solution filtered and evaporated to dryness. The residue was dissolved in 10 mls. of nitromethane and this was evaporated to about 5 mls. Carbon tetrachloride was added to the dark green nitromethane solution until it became faintly turbid, and on standing overnight the green crystals that formed were filtered off, crushed and dried in vacuo.

(Found: C, 51.89; H, 4.41; N, 6.95; O, 20.32;

Calculated for $\text{Ni}(\text{isoPrHBB})_2(\text{ClO}_4)_2$

C, 51.68; H, 4.59; N, 7.09; O, 20.24%).

CHAPTER FOUR

2. Hydroxymethylbenzimidazole⁶²

One mole of glycollic acid (76 gms.) and one mole of o.phenylene diamine (108 gms.) were refluxed for six hours in 200 mls. of 6 M hydrochloric acid. On cooling the solution was neutralised with .880 ammonium hydroxide and the precipitated solid filtered off, washed with water and recrystallised from 95% ethanol.

Melting point = 171°C (literature melting point 171°C).

Yield = 95 gms. (64%).

Co(HMeB)₃Cl₂

5 gms. of HMeB and 2.4 gms. of CoCl₂.6H₂O were heated in 25 mls. of absolute alcohol with frequent shaking until a clear deep blue solution was obtained. This solution was then filtered and evaporated to about 15 mls. On cooling the solution became deep pink and after standing for a couple of days produced dark pink crystals, which were filtered off, very gently crushed and vacuum dried at about 50°C.

(Found: C, 49.75; H, 4.05; N, 14.54;

Calculated for Co(C₈H₈N₂O)₃Cl₂ C, 50.20; H, 4.21; N, 14.63%).

Co(HMeB)₃I₂

2.3 gms. of HMeB and 1.7 gms. of CoI₂.2H₂O were dissolved in 40 mls. of acetone to give a deep blue solution which on standing overnight produced a pink crystalline solid. This was filtered off and dried in vacuo.

(Found: C, 37.80; H, 3.13; N, 11.04;

Calculated for Co(C₈H₈N₂O)₃I₂ C, 38.07; H, 3.19; N, 11.10%).

Co(HMeB)₃(NO₃)₂

To a rapidly stirred, warm solution of 4.5 gms. of HMeB in 200 mls. of acetone was added dropwise a solution of 2.9 gms. of Co(NO₃)₂.6H₂O in 15 mls. of absolute alcohol. A pink solid soon began to form, which was filtered off and vacuum dried at about 50°C.

(Found: C, 46.16; H, 3.79; N, 17.73;

Calculated for Co(HMeB)₃(NO₃)₂ C, 45.99; H, 3.86; N, 17.86%).

$\text{Co}(\text{HMeB})_2(\text{SCN})_2$

A solution prepared by shaking 1.7 gms. of $\text{Co}(\text{SCN})_2$ and 3 gms. of HMeB in 50 mls. of acetone was filtered and evaporated to about 30 mls. On standing overnight this deep blue solution produced dark pink crystals which were filtered off and dried in vacuo.

(Found: C, 45.98; H, 3.60; N, 18.06;

Calculated for $\text{Co}(\text{C}_8\text{H}_8\text{N}_2\text{O})_2(\text{SCN})_2$ C, 45.88; H, 3.42; N, 17.84%).

 $\text{Co}(\text{HMeB})_3(\text{ClO}_4)_2$

4.5 gms. of HMeB and 3.6 gms. of $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 10 mls. of acetonitrile and the resulting deep pink solution was filtered. To this filtrate was added about 50 mls. of dichloromethane with vigorous shaking. On standing for a few minutes pink crystals started to form and after a couple of hours they were filtered off, washed with a little dichloromethane, crushed and dried in vacuo.

(Found: C, 41.90; H, 3.74; Cl, 10.52; N, 12.25; O, 25.00;

Calculated for $\text{Co}(\text{C}_8\text{H}_8\text{N}_2\text{O})_3(\text{ClO}_4)_2$

C, 41.06; H, 3.44; Cl, 10.09; N, 11.97; O, 25.06%).

 $\text{Ni}(\text{HMeB})_3\text{Cl}_2$

5 gms. of HMeB and 2.4 gms. of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 15 mls. of cold absolute alcohol to give a bluish green solution which was filtered and left standing for a couple of days. The bluish green crystals that formed were filtered off, crushed and vacuum dried at about 50°C .

(Found: C, 50.18; H, 4.18; N, 14.27;
 Calculated for $\text{Ni}(\text{C}_8\text{H}_8\text{N}_2\text{O})_3\text{Cl}_2$ C, 50.23; H, 4.21; N, 14.64%).

$\text{Ni}(\text{HMeB})_3\text{I}_2$

2.3 gms. of HMeB and 2.1 gms. of $\text{NiI}_2 \cdot 6\text{H}_2\text{O}$ were dissolved in about 40 mls. of acetone to give a deep green solution. This solution was filtered and the filtrate warmed slightly, when a green solid began to crystallise out. After standing overnight the product was filtered off, washed with acetone and dried in vacuo.

(Found: C, 38.14; H, 3.18; N, 10.94;
 Calculated for $\text{Ni}(\text{HMeB})_3\text{I}_2$ C, 38.09; H, 3.20; N, 11.10%).

$\text{Ni}(\text{HMeB})_3(\text{NO}_3)_2$

See $\text{Co}(\text{HMeB})_3(\text{NO}_3)_2$. The product was in the form of bluish green crystals.

(Found: C, 45.05; H, 3.65; N, 17.45;
 Calculated for $\text{Ni}(\text{HMeB})_3(\text{NO}_3)_2$ C, 45.97; H, 3.86; N, 17.87%).

$\text{Ni}(\text{HMeB})_2(\text{SCN})_2$

1.9 gms. of KSCN and 3.6 gms. of $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 40 mls. of absolute alcohol and the solution left standing in the fridge overnight. The $\text{Ni}(\text{SCN})_2$ solution was filtered into 3 gms. of HMeB in 100 mls. of ethanol and the resulting green solution filtered and evaporated to about half volume. On standing this solution produced a bluish green micro crystalline solid which was filtered off and dried in vacuo.

(Found: C, 45.96; H, 3.27; N, 17.98;
 Calculated for $\text{Ni}(\text{C}_8\text{H}_8\text{N}_2\text{O})_2(\text{SCN})_2$ C, 45.88; H, 3.42; N, 17.84%).

$\text{Ni}(\text{HMeB})_3(\text{ClO}_4)_2$

4.5 gms. of HMeB and 3.6 gms. of $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 15 mls. of acetonitrile and the resulting deep green solution was filtered. To the filtrate was added dichloromethane until it became very faintly turbid and on standing large green crystals formed which were filtered off, crushed and dried in vacuo.

(Found: C, 41.18; H, 3.35; Cl, 10.30; N, 11.91; O, 24.44;

Calculated for $\text{Ni}(\text{C}_8\text{H}_8\text{N}_2\text{O})_3(\text{ClO}_4)_2$

C, 41.07; H, 3.45; Cl, 10.10; N, 11.98; O, 25.07%).

CHAPTER FIVE

2. α Methoxybenzylbenzimidazole ⁶³

26 gms. of α methoxyphenylacetic acid and 17 gms. of o.phenylene diamine, that is a 1:1 mole ratio, were refluxed in 200 mls. of distilled water and 100 mls. of concentrated hydrochloric acid for about four hours. On cooling the solution was neutralised with .880 ammonium hydroxide and the crude product purified by recrystallisation from 95% ethanol and decolourisation with activated charcoal.

Melting point = 160°C (literature melting point 160°C).

Yield = 18 gms. (48%).

Co(MeOBB)₂Cl₂

2.4 gms. of MeOBB and 1.2 gms. of CoCl₂.6H₂O were dissolved in about 20 mls. of absolute alcohol and the resulting deep blue solution was filtered. On standing overnight blue crystals formed which were filtered off and vacuum dried at 95°C. The resulting light blue solid was recrystallised from absolute alcohol.

(Found: C, 59.69; H, 4.95; Cl, 11.73;

Calculated for Co(C₁₅H₁₄N₂O)₂Cl₂ C, 59.41; H, 4.65; Cl, 11.69%).

Co(MeOBB)₂(SCN)₂(Acetone)₂

Upon dissolving 2.4 gms. of MeOBB and 0.9 gms. of Co(SCN)₂ in about 30 mls. of acetone, to give a deep blue solution, a pink solid crystallised out almost immediately. After standing overnight these crystals were filtered off and refluxed for a short time in analar carbon tetrachloride, when they became blue. This blue solid was dissolved in acetone and the solution left standing for a couple of days, then the pink crystals that had formed were filtered off and air dried.

(Found: C, 58.34; H, 4.93; N, 11.02;

Calculated for Co(C₁₅H₁₄N₂O)₂(SCN)₂((CH₃)₂CO)₂

C, 59.41; H, 5.25; N, 10.94%).

Weight loss study

Found = 14%

Calculated for Co(C₁₅H₁₄N₂O)₂(SCN)₂((CH₃)₂CO)₂

————→ Co(C₁₅H₁₄N₂O)₂(SCN)₂ = 15.1%.

$\text{Co}(\text{MeOBB})_2(\text{SCN})_2$

A sample of the above pink crystalline solid was desolvated at about 100°C in vacuo. The product was deep blue.

(Found: C, 58.27; H, 4.13; N, 12.89;

Calculated for $\text{Co}(\text{C}_{15}\text{H}_{14}\text{N}_2\text{O})_2(\text{SCN})_2$ C, 58.95; H, 4.33; N, 12.89%).

 $\text{Co}(\text{MeOBB})_2(\text{NO}_3)_2$

2.4 gms. of MeOBB and 1.5 gms. of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 20 mls. of acetone, and the solution filtered and evaporated to about 10 mls. On standing for about a week a mass of deep purple crystals formed, these were filtered off and crushed to give a dark pink solid which was dried in vacuo at about 50°C .

(Found: C, 54.55; H, 4.32; N, 12.84;

Calculated for $\text{Co}(\text{C}_{15}\text{H}_{14}\text{N}_2\text{O})_2(\text{NO}_3)_2$ C, 54.64; H, 4.28; N, 12.75%).

 $\text{Co}(\text{MeOBB})_3(\text{ClO}_4)_2$

4.0 gms. of MeOBB and 1.8 gms. of $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 25 mls. of acetone and the solution was evaporated to dryness. The residue was dissolved in 10 mls. of nitromethane and after standing for a few days the pink crystalline solid that had formed was filtered off, crushed and dried in vacuo. When the compound is dry it is a pinkish blue colour.

(Found: C, 54.94; H, 4.29; N, 8.24; O, 18.55;

Calculated for $\text{Co}(\text{C}_{15}\text{H}_{14}\text{N}_2\text{O})_3(\text{ClO}_4)_2$

C, 55.56; H, 4.35; N, 8.64; O, 18.09%).

$\text{Ni}(\text{MeOBB})_2\text{Cl}_2$

1.2 gms. of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 10 mls. of absolute alcohol and 2.4 gms. of MeOBB in 40 mls. of acetone. The two solutions were mixed and left standing. After a short time golden yellow crystals formed which were filtered off and dried in vacuo at about 50°C .

(Found: C, 58.91; H, 4.98; Cl, 11.32;
Calculated for $\text{Ni}(\text{C}_{15}\text{H}_{14}\text{N}_2\text{O})_2\text{Cl}_2$ C, 59.44; H, 4.66; Cl, 11.69%).

 $\text{Ni}(\text{MeOBB})_2\text{I}_2$

1.66 gms. of KI and 1.45 gms. of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 20 mls. of acetone and the solution left standing in the fridge overnight. The NiI_2 solution was filtered and 2.4 gms. of MeOBB were added to the filtrate and the resulting solution evaporated to about half volume. On standing for about two weeks the crystals that had formed were filtered off, crushed, and vacuum dried at about 80°C . The final product was a yellowish colour.

(Found: C, 46.34; H, 3.54; N, 6.89;
Calculated for $\text{Ni}(\text{C}_{15}\text{H}_{14}\text{N}_2\text{O})_2\text{I}_2$ C, 45.65; H, 3.58; N, 7.09%).

 $\text{Ni}(\text{MeOBB})_2(\text{NO}_3)_2$

2.4 gms. of MeOBB and 1.5 gms. of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 20 mls. of acetone, the solution was filtered and evaporated to about 10 mls. On standing for a few weeks green crystals formed which were filtered off, crushed and dried in vacuo.

(Found: C, 54.12; H, 4.10; N, 12.20;
Calculated for $\text{Ni}(\text{C}_{15}\text{H}_{14}\text{N}_2\text{O})_2(\text{NO}_3)_2$ C, 54.66; H, 4.28; N, 12.75%).

Ni(MeOBB)₂(SCN)₂(DMF)₂

1.45 gms. of Ni(NO₃)₂·6H₂O and 0.98 gms. of KSCN were dissolved in 30 mls. of acetone and the solution after standing overnight in the fridge was filtered into a solution of 2.4 gms. of MeOBB in 25 mls. of acetone. This solution on standing soon produced a green crystalline solid which was filtered off and recrystallised from dimethylformamide. The green crystalline product was dried in vacuo.

(Found: C, 56.26; H, 5.23; N, 14.00;

Calculated for Ni(C₁₅H₁₄N₂O)₂(SCN)₂(H.CO.N(CH₃)₂)₂

C, 57.22; H, 5.31; N, 14.05%).

Weight loss study

Found: = 23%

Calculated for Ni(C₁₅H₁₄N₂O)₂(SCN)₂(H.CO.N(CH₃)₂)₂

————→ Ni(C₁₅H₁₄N₂O)₂(SCN)₂ = 22.4%

Ni(MeOBB)₂(SCN)₂

A sample of the above compound was dried in vacuo at about 100°C. The resulting product was green.

(Found: C, 58.28; H, 4.42; N, 13.08;

Calculated for Ni(C₁₅H₁₄N₂O)₂(SCN)₂ C, 59.00; H, 4.33; N, 12.90%).

Ni(MeOBB)₃(ClO₄)₂

1.8 gms. of Ni(ClO₄)₂·6H₂O were dissolved in 20 mls. of acetone and the solution partially dried by standing over 3 gms. of anhydrous Na₂SO₄. This solution was then filtered onto 2.4 gms. of

MeOBB and the resulting dark green solution evaporated to about 5 mls. On standing for a couple of weeks the green crystals that formed were filtered off and dried in vacuo at about 80°C.

(Found: C, 55.68; H, 4.56; O, 18.62;
Calculated for $\text{Ni}(\text{C}_{15}\text{H}_{14}\text{N}_2\text{O})_3(\text{ClO}_4)_2$ C, 55.58; H, 4.35; O, 18.09%).

CHAPTER SIX

2.o.Hydroxyphenylbenzimidazole ⁶⁴

One mole of o phenylenediamine (108 gms.) and one mole of salicylamide (137 gms.) were mixed in a mortar until finely powdered and then heated in a flask immersed in an oil bath. The mixture melted at about 160°C and evolved NH_3 and H_2O . After the melting was complete the temperature was raised to 200°C and maintained there until the evolution of NH_3 had ceased. The molten mixture was transferred to a distillation flask and distilled under atmospheric pressure. The yellow coloured distillate was recrystallised from 95% ethanol.

Melting point = 242°C (literature melting point 242°C).

Yield = 70 gms. (33%).

$\text{Co}(\text{HPB})_2$

1.8 gms. of HPB were dissolved in about 30 mls. of hot absolute alcohol and to it was added a solution of 1.4 gms. of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 3 mls. of water, which had been made neutral with very dilute ammonium hydroxide. A red crystalline solid formed

immediately. This product was filtered off, the filtrate being kept⁺⁺, washed with acetone and dried in vacuo. Because of the very low solubility of this complex in the common organic solvents it was not possible to recrystallise it.

(Found: C, 64.62; H, 4.07; N, 11.49; O, 6.73;

Calculated for $\text{Co}(\text{C}_{13}\text{H}_9\text{N}_2\text{O})_2$

C, 65.42; H, 3.80; N, 11.80; O, 6.70%).

⁺⁺ This filtrate on standing for about six weeks produced shiny black crystals, which were filtered off and dried in vacuo. When dry these crystals powder very easily to give a green solid.

(Found: C, 63.46; H, 4.22; O, 8.24;

Calculated for $\text{Co}(\text{C}_{13}\text{H}_{10}\text{N}_2\text{O})(\text{C}_{13}\text{H}_9\text{N}_2\text{O})(\text{OH})$

C, 63.02; H, 4.04; O, 9.69%).

$\text{Co}(\text{HPB})_2\text{Cl}_2$

2.1 gms. of HPB were dissolved in about 50 mls. of acetone and to this was added a solution of 1.2 gms. of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in 10 mls. of acetone. The resulting deep blue solution was filtered and left standing in an open flask. After a few days the blue crystals that had formed were filtered off and dried in vacuo.

(Found: C, 56.96; H, 3.94; Cl, 12.88; N, 9.95;

Calculated for $\text{Co}(\text{C}_{13}\text{H}_{10}\text{N}_2\text{O})_2\text{Cl}_2$

C, 56.74; H, 3.66; Cl, 12.88; N, 10.18%).

$\text{Co}(\text{HPB})_2\text{Br}_2$

The preparation of this complex was identical to that of

$\text{Co(HPB)}_2\text{Cl}_2$ except that 1.7 gms. of $\text{CoBr}_2 \cdot 6\text{H}_2\text{O}$ were used. This complex was turquoise in colour.

(Found: C, 48.94; H, 3.24; Br, 24.84; N, 8.24;

Calculated for $\text{Co}(\text{C}_{13}\text{H}_{10}\text{N}_2\text{O})_2\text{Br}_2$

C, 48.85; H, 3.24; Br, 25.00; N, 8.76%).

$\text{Co(HPB)}_2\text{I}_2$

3.0 gms. of NaI and 2.9 gms. of $\text{Co(NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in about 25 mls. of acetone and the solution left standing in the fridge overnight. The NaNO_3 was filtered off and the filtrate added to a hot solution of 4.2 gms. of HPB in about 100 mls. of acetone. On standing in an open flask for some days the green crystals that formed were filtered off and dried in vacuo.

(Found: C, 42.49; H, 3.36; N, 7.34; I, 34.89;

Calculated for $\text{Co}(\text{C}_{13}\text{H}_{10}\text{N}_2\text{O})_2\text{I}_2$

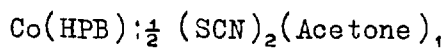
C, 42.58; H, 2.75; N, 7.64; I, 34.61%).

$\text{Co(HPB)}_3(\text{NO}_3)_2$

3.2 gms. of HPB were dissolved in about 100 mls. of hot acetone and to this was added a solution of 1.5 gms. of $\text{Co(NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 20 mls. of acetone. The resulting solution was then left standing when a redish brown solid crystallised out which was filtered off and dried in vacuo.

(Found: C, 57.72; H, 4.18;

Calculated for $\text{Co}(\text{C}_{13}\text{H}_{10}\text{N}_2\text{O})_3(\text{NO}_3)_2$ C, 57.54; H, 3.74%).



4.2 gms. of HPB and 1.7 gms. of Co(SCN)_2 were dissolved in about 200 mls. of acetone and the resulting deep blue solution was filtered. The filtrate was evaporated to about 100 mls. and then the solution was left standing in an open flask. On standing for a few days the blue crystalline solid that formed was filtered off and dried in vacuo.

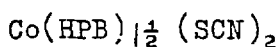
(Found: C, 53.31; H, 3.76;
Calculated for $\text{Co(C}_{13}\text{H}_{10}\text{N}_2\text{O}) \cdot \frac{1}{2} (\text{SCN})_2 ((\text{CH}_3)_2\text{CO})_1$ C, 53.62; H, 3.86%).

Weight loss study

Found: = 10.4%

Calculated for $\text{Co(C}_{13}\text{H}_{10}\text{N}_2\text{O}) \cdot \frac{1}{2} (\text{SCN})_2 ((\text{CH}_3)_2\text{CO})_1$

————→ $\text{Co(C}_{13}\text{H}_{10}\text{N}_2\text{O}) \cdot \frac{1}{2} (\text{SCN})_2$ = 10.6%.



A sample of the above complex was taken and heated at about 100°C in vacuo to give a grey green solid.

(Found: C, 52.93; H, 3.27;

Calculated for $\text{Co(C}_{13}\text{H}_{10}\text{N}_2\text{O}) \cdot \frac{1}{2} (\text{SCN})_2$ C, 52.64; H, 3.08%).

To a solution of 3.2 gms. of HPB in about 100 mls. of acetone was added a solution of 1.8 gms. of $\text{Co(ClO}_4)_2$ in 10 mls. of acetone. The resulting solution was dark pink and on standing for a short time it became much darker in colour and produced a red crystalline solid. These crystals were filtered off, the filtrate being retained, and identified as the inner complex Co(HPB)_2 . The filtrate on repeated evaporation became intensely black and on standing

produced a dark green crystalline solid. This product was recrystallised from aqueous acetone until complete removal of the perchlorate ion was achieved, the final green solid being dried in vacuo. The analysis of this compound indicates that it is probably the same as $\text{Co(HPB)}_2\text{O}$.

(Found: C, 63.85; H, 4.10;
Calculated for $\text{Co(C}_{13}\text{H}_{10}\text{N}_2\text{O})(C}_{13}\text{H}_9\text{N}_2\text{O})(\text{OH})$ C, 63.02; H, 4.04%).

Ni(HPB)_2

4.2 gms. of HPB was titrated with a solution of NaOH in absolute alcohol, using phenol phthalein indicator. The sodium salt solution was decolourised with activated charcoal and to it was added a solution of 3.7 gms. of $\text{Ni(ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in about 25 mls. of absolute ethanol. On standing for a few minutes a yellowish brown solid precipitated out which was filtered off and dried in vacuo.

(Found: C, 64.69; H, 4.05;
Calculated for Ni(HPB)_2 C, 65.19; H, 3.79%).

$\text{Ni(HPB)}_3\text{Cl}_2$

A solution of 1.2 gms. of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in about 20 mls. of absolute alcohol was added to 3.2 gms. of HPB dissolved in 50 mls. of acetone. The dark green solution was then evaporated to about 30 mls. After standing overnight the green crystals that had formed were filtered off and dried in vacuo.

(Found: C, 61.08; H, 4.73;
Calculated for $\text{Ni(C}_{13}\text{H}_{10}\text{N}_2\text{O})_3\text{Cl}_2$ C, 61.57; H, 3.98%).

$\text{Ni(HPB)}_3\text{Br}_2$

A solution of 6.3 gms. of HPB in 70 mls. of acetone and 3.3 gms. of $\text{NiBr}_2 \cdot 6\text{H}_2\text{O}$ in 30 mls. of acetone were mixed and left standing overnight. The green crystals that formed were filtered off and dissolved in absolute alcohol. The ethanol solution was evaporated to a small volume and acetone was added causing the complex to crystallise out. The product was filtered off and dried in vacuo.

(Found: C, 54.53; H, 4.37;

Calculated for $\text{Ni(C}_{13}\text{H}_{10}\text{N}_2\text{O)}_3\text{Br}_2$ C, 55.13; H, 3.56%).

 $\text{Ni(HPB)}_3(\text{NO}_3)_2$

3.2 gms. of HPB were dissolved in about 75 mls. of acetone and to the solution was added a solution of 1.5 gms. of $\text{Ni(NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 10 mls. of acetone. The resulting green solution on standing produced a green crystalline product, which was recrystallised from absolute ethanol.

(Found: C, 57.72; H, 3.48; O, 18.41;

Calculated for $\text{Ni(C}_{13}\text{H}_{10}\text{N}_2\text{O)}_3(\text{NO}_3)_2$ C, 57.57; H, 3.72; O, 17.70%).

 $\text{Ni(HPB)}_2(\text{SCN})_2(\text{C}_2\text{H}_5\text{OH})_2$

1.5 gms. of $\text{Ni(NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.95 gms. of KSCN were dissolved in 25 mls. of acetone and the solution left standing in the fridge overnight. The Ni(SCN)_2 solution was then filtered into 2.1 gms. of HPB dissolved in about 100 mls. of absolute ethanol and the resulting green solution evaporated to about 50 mls. On standing overnight a green crystalline solid formed which was filtered off

and dried in vacuo.

(Found: C, 52.71; H, 4.44; N, 11.59;

Calculated for $\text{Ni}(\text{C}_{13}\text{H}_{10}\text{N}_2\text{O})_2(\text{SCN})_2(\text{C}_2\text{H}_5\text{OH})_2$

C, 52.38; H, 4.65; N, 12.22%).

Weight loss study

Found: = 14%

Calculated for $\text{Ni}(\text{C}_{13}\text{H}_{10}\text{N}_2\text{O})_2(\text{SCN})_2(\text{C}_2\text{H}_5\text{OH})_2$

————→ $\text{Ni}(\text{C}_{13}\text{H}_{10}\text{N}_2\text{O})$ = 13.4%.

$\text{Ni}(\text{HPB})_2(\text{SCN})_2$

A sample of the above ethanolate was taken and vacuum dried at 110°C. The desolvated complex is dark green.

(Found: C, 57.16; H, 3.45; N, 14.03;

Calculated for $\text{Ni}(\text{C}_{13}\text{H}_{10}\text{N}_2\text{O})_2(\text{SCN})_2$ C, 56.46; H, 3.39; N, 14.12%).

CHAPTER SEVEN

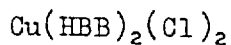
$\text{Cu}(\text{HBB})_2(\text{Cl})_2(\text{C}_2\text{H}_5\text{OH})_2$

4.5 gms. of HBB were dissolved in about 50 mls. of absolute alcohol and to this solution was added 1.7 gms. of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ dissolved in 10 mls. of ethanol. The resulting green solution was then left standing in an open flask and after a few days the bright green crystals that had formed were filtered off and gently crushed.

(Found: C, 57.06; H, 5.42; Cl, 10.86; N, 8.32; O, 9.75;

Calculated for $\text{Cu}(\text{C}_{14}\text{H}_{12}\text{N}_2\text{O})_2(\text{Cl})_2(\text{C}_2\text{H}_5\text{OH})_2$

C, 56.89; H, 5.33; Cl, 10.51; N, 8.30; O, 9.48%).



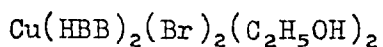
A sample of the above complex was vacuum dried at about 80°C to give a dark green solid.

Weight loss study

Found: = 12.4%

Calculated for $\text{Cu}(\text{C}_{14}\text{H}_{12}\text{N}_2\text{O})_2(\text{Cl})_2(\text{C}_2\text{H}_5\text{OH})_2$

————→ $\text{Cu}(\text{C}_{14}\text{H}_{12}\text{N}_2\text{O})_2(\text{Cl})_2$ = 13.6%.

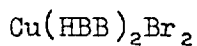


2.2 gms. of CuBr_2 were dissolved in 10 mls. of absolute alcohol and added to 4.5 gms. of HBB dissolved in about 50 mls. of absolute alcohol. The resulting deep green solution was left standing when green crystals very quickly formed. These crystals were filtered off and gently crushed.

(Found: C, 50.37; H, 4.98; Br, 20.97; N, 7.62; O, 8.75;

Calculated for $\text{Cu}(\text{C}_{14}\text{H}_{12}\text{N}_2\text{O})_2(\text{Br})_2(\text{C}_2\text{H}_5\text{OH})_2$

C, 50.30; H, 4.75; Br, 20.92; N, 7.34; O, 8.38%).



A sample of the above complex was desolvated by heating at about 80°C in vacuo. The product was a very dark green colour.

Weight loss study

Found: = 11.5%

Calculated for $\text{Cu}(\text{C}_{14}\text{H}_{12}\text{N}_2\text{O})_2(\text{Br})_2(\text{C}_2\text{H}_5\text{OH})_2$

————→ $\text{Cu}(\text{C}_{14}\text{H}_{12}\text{N}_2\text{O})_2(\text{Br})_2$ = 12.1%.

$\text{Cu}(\text{HBB})_3(\text{NO}_3)_2$

1.2 gms. of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ were dissolved in about 25 mls. of acetone and shaken vigorously with about 5 gms. of anhydrous Na_2SO_4 . This solution was then filtered into 3.4 gms. of HBB dissolved in about 150 mls. of acetone and the resulting blue solution evaporated down to about half volume. On standing for a few days the blue solid which crystallised out was filtered off and dried in vacuo.

(Found: C, 58.25; H, 4.16; N, 12.79; O, 14.83;

Calculated for $\text{Cu}(\text{C}_{14}\text{H}_{12}\text{N}_2\text{O})_3(\text{NO}_3)_2$

C, 58.62; H, 4.22; N, 13.02; O, 14.88%).

 $\text{Cu}(\text{HBB})_2(\text{NO}_3)_2$

2.4 gms. of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ were dissolved in 20 mls. of acetone and shaken with 5 gms. of anhydrous Na_2SO_4 . After standing for about one hour this solution was filtered onto 3 gms. of HBB. The resulting clear green solution was then left standing for a few days after which time the mass of needle-like green crystals that had formed was filtered off and dried in vacuo at about 100°C .

(Found: C, 52.85; H, 3.86;

Calculated for $\text{Cu}(\text{C}_{14}\text{H}_{12}\text{N}_2\text{O})_2(\text{NO}_3)_2$ C, 52.85; H, 3.77%).

N.B. any attempt to recrystallise this compound results in the formation of the blue 3:1 form, that is $\text{Cu}(\text{HBB})_3(\text{NO}_3)_2$.

 $\text{Cu}(\text{HBB})_3(\text{ClO}_4)_2$

3.7 gms. of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and 4.5 gms. of HBB were dissolved in 10 mls. of absolute alcohol and the resulting blue

solution was filtered using a further 5 mls. of absolute alcohol. On standing for about two weeks the large blue crystals that formed were filtered off, gently crushed and dried in vacuo.

(Found: C, 53.92; H, 4.44; O, 18.72; N, 8.42;

Calculated for $\text{Cu}(\text{C}_{14}\text{H}_{12}\text{N}_2\text{O})_3(\text{ClO}_4)_2$

C, 53.93; H, 3.88; O, 18.82; N, 8.99%).

$\text{Cu}(\text{HBB})_2(\text{SCN})_2(\text{Acetone})_2$

4.5 gms. of HBB and 3.6 gms. of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 10 mls. of acetone and to the clear blue solution was added a solution of 2 gms. of KSCN in 25 mls. of acetone. After standing in the fridge overnight the precipitated KClO_4 was filtered off and the filtrate allowed to evaporate at room temperature in an open petri dish. The green crystals that formed were filtered off and recrystallised from acetone. N.B. care was taken to ensure that the system $\text{CuHBBSCN}/\text{acetone}$ was never left standing for longer than one day. This is because after standing for a few days the solution smells quite strongly of what is probably an organic sulphur compound. Attempts to isolate and identify this compound were not successful.

(Found: C, 57.52; H, 4.87; N, 11.33;

Calculated for $\text{Cu}(\text{C}_{14}\text{H}_{12}\text{N}_2\text{O})_2(\text{SCN})_2((\text{CH}_3)_2\text{CO})_2$

C, 58.09; H, 4.87; N, 11.29%).

Weight loss study

Found: = 15.2%

Calculated for $\text{Cu}(\text{C}_{14}\text{H}_{12}\text{N}_2\text{O})_2(\text{SCN})_2((\text{CH}_3)_2\text{CO})_2$

————→ $\text{Cu}(\text{C}_{14}\text{H}_{12}\text{N}_2\text{O})_2(\text{SCN})_2$ = 15.7%.

$\text{Cu}(\text{HBB})_2(\text{SCN})_2$

A sample of the above complex was vacuum dried at about 100°C to give a greenish brown solid.

(Found: C, 57.54; H, 4.06; N, 13.72;
Calculated for $\text{Cu}(\text{C}_{14}\text{H}_{12}\text{N}_2\text{O})_2(\text{SCN})_2$ C, 57.36; H, 3.85; N, 13.39%).

 $\text{Cu}(\text{HBB})_2(\text{I})_2$

4.5 gms. of HBB and 3.7 gms. of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in about 50 mls. of absolute alcohol, the resulting solution being green. To this solution was added 3.2 gms. of KI to give a deep yellow green solution which also became quite warm. This solution was filtered using 25 mls. of absolute alcohol and the filtrate left to cool in the fridge, after which it was evaporated to about 30 mls. The now very dark golden brown solution on standing overnight produced dark greenish crystals which were filtered off and crushed to give a dark red brown powder.

(Found: C, 44.70; H, 3.54; N, 6.91;
Calculated for $\text{Cu}(\text{C}_{14}\text{H}_{12}\text{N}_2\text{O})_2\text{I}$ C, 52.62; H, 3.79; N, 8.77%).

The above product was recrystallised from absolute alcohol, in which it is not very soluble, and the dark brown crystals crushed and dried in vacuo at about 50°C .

(Found: C, 43.39; H, 3.83; I, 32.07;
Calculated for $\text{Cu}(\text{C}_{14}\text{H}_{12}\text{N}_2\text{O})_2\text{I}_2$ C, 43.90; H, 3.16; I, 33.13%).

 $\text{Cu}(\text{MeOBB})_2\text{Cl}_2$

0.7 gms. of CuCl_2 were dissolved in 25 mls. of acetone and

added to a solution of 2.4 gms. of MeOHBB in 40 mls. of acetone. The resulting deep green solution was evaporated to about 50 mls. and left standing overnight. The green crystals that formed were filtered off, and dried in vacuo.

(Found: C, 59.23; H, 4.91;

Calculated for $\text{Cu}(\text{C}_{15}\text{H}_{15}\text{N}_2\text{O})_2\text{Cl}_2$ C, 58.98; H, 4.62%).

Physical Measurements

The electrolytic conductances were measured with a Philips PR 9,500 Bridge and a standard cell. The values obtained were reckoned as being significant if the complex dissolved in the cold solvent, or on gentle warming with no obvious colour change. Some typical values of κ for various electrolyte types are given below.

Solvent	Non electrolyte	1:1 electrolyte	2:1 electrolyte
Nitrobenzene	0	20	40 - 50
Nitromethane	0	80	180

X-ray powder photographs were taken with an Enraf Nonius Guimer-De Wolff camera using monochromatised copper K_α radiation. The intensities were estimated visually.

The solid state diffuse reflectance spectra were obtained with a Beckmann D.K.2 recording spectrophotometer or with a Unicam S.P. 500 spectrophotometer.

Infra-red spectra in the range 0.6 to 25 μ were recorded with a Grubb Parsons Spectromaster Mark I grating spectrometer using KBr discs and Nujol or hexachlorobutadiene as mulling agent.

Electron spin resonance spectra were obtained with a Varian V 4502 - 15 spectrometer operating at about 9,300 Mc/s using a field modulation of 100 Kc/s.

Room temperature magnetic susceptibilities were measured using a standard Gouy balance with a permanent magnet, the samples being packed in standard glass tubes. For magnetic susceptibility measurements in the temperature range 77 - 300°A a balance of essentially the same design as that described by Figgis and Nyholm⁶⁵ was used, the samples being packed in perspex tubes of standard length.

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