METAL COMPLEXES WITH SOME IMIDAZOLE DERIVATIVES

A Thesis submitted

by

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ABSTRACT

Complexes of imidazole, some substituted imidazoles and some substituted benzimidazoles with divalent cobalt, nickel, copper and zinc salts have been prepared in order to investigate the coordination properties of these biologically important ligands.

The stereochemistry of these complexes was studied using the following physical techniques:- electron spin resonance spectroscopy (for the copper complexes), magnetic susceptibility measurements, electronic spectroscopy, and vibrational spectroscopy extending into the low energy region.

The ease of formation of imidazole and substituted imidazole complexes may well be biologically significant, however the substituted benzimidazoles studied here do not readily form metal complexes.

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ABBREVIATIONS

im	imidazole
NMeim	N methyl imidazole
2Meim	2 methyl imidazole
1,2DiMeim	1,2-dimethyl imidazole
beim	benzimidazole
2Mebeim	2-methyl benzimidazole
$2CF_3$ beim	2-trifluoromethyl benzimidazole
2Bubeim	2 tert butyl benzimidazole
$5Cl2CF_3$ beim	5 chloro-2-trifluoromethyl benzimidazole
$5NO_2\ 2CF_3$ beim	5 nitro-2-trifluoromethyl benzimidazole

v	very	s	strong
sh	shoulder	m	medium
br	broad	w	weak

The abbreviations ν_1, ν_2 etc when applied to vibrational spectra refer to the notation of Nakamoto [66], except in the case of the D_{4h} square planar complexes, where the notation of Hendra [217] has been adopted.

The electronic spectral notation is as follows:-

	octahedral Co^{2+},	tetrahedral Ni^{2+}	octanedral Ni^{2+},	tetrahedral Co^{2+}
ν_1	$T_1(F) \rightarrow T_2$		$A_2 \rightarrow T_2$	
ν_2	$T_1(F) \rightarrow A_2$		$A_2 \rightarrow T_1(F)$	
ν_3	$T_1(F) \rightarrow T_1(P)$		$A_2 \rightarrow T_1(P)$	

The subscript g is applied in the case of octahedral (centrosymmetric) complexes.

CHAPTER I

INTRODUCTION

The importance of the imidazole unit in biological processes has been well reviewed[1], as has the usefulness of substituted benzimidazoles as virus, bacteria, fungus and cancer inhibitors and as antihistamines, analgesics, and vasodilatatrics[2]. Recently, investigation of 2-trifluoromethylbenzimidazoles has shown them to have antiviral[3], antibacterial[4], herbicidal[5] and acaricidal[6] properties, and to act as uncouplers of oxidative, and respiratory chain phosphorylation[7,8]. The herbicidal activity of this class of compound aroused the most interest[9-13], however their use as pesticides[14-16], and fungicides[17] was also advocated. It has been suggested that the compounds exhibit herbicidal activity by inhibiting photophosphorylation at low concentrations, and by electron transfer reactions at high concentrations[18].

The complexing of metal ions with imidazole units is extremely common in biological systems[1], although only in vitamin B_{12} has a benzimidazole unit known to be complexed[19]. It has been suggested however, that a series of substituted benzimidazoles which inhibit polio virus multiplication[20], might act by means of chelate complex formation with metal ions[21], and a study of these systems showed that strong metal complexes of the substituted benzimidazoles could be obtained[22]. This study was undertaken to investigate whether the herbicidal properties of the fluorinated benzimidazoles could

be caused by similar means, which seemed possible as "inner" complexes with a variety of metal ions had already been reported[9]. A suitable series of 2-trifluoromethyl benzimidazoles were chosen and studied covering a range of herbicidal activities and of pK_a values, however as herbicidal activity is shown by fluorine free benzimidazoles also[11,12], as well as by substituted imidazoles[23,24], the scope of the study was broadened to include as wide a variety of ligands as possible.

The metal ions chosen were those of divalent zinc, copper, nickel and cobalt. Although nickel is biologically unimportant (except in enzyme activation, e.g.25), the relative ease of determination of structure by spectroscopic means made it a logical choice.

The complexes formed were studied by the following techniques:

Electronic Spectroscopy

General reviews of this subject are plentiful[26-29] and the use of the diffuse reflection technique has also been reviewed[30,31]. In the specific case of copper, the spectra of a range of coordination environments have been published[32-36]. Nickel spectra have been studied in detail in octahedral[37-41], planar[42,43], tetrahedral[37,44-46] and five coordinate[47,48] environments, and similarly, cobalt in octahedral[49,50], tetrahedral[49-52] and five coordinate[53-56] environments.

Magnetic Properties

This subject has been well covered in established texts[26-28,50,57], although only recently has a quantitative approach to low symmetry systems been published[58-61].

Electron Spin Resonance Spectroscopy (of copper ions)

The review by McGarvey[62] covers the field of e.s.r. spectra of metal complexes, more detailed studies of copper systems being given in References 35, 63-65.

Vibrational Spectroscopy

General reviews of both infrared[66] and Raman[67] spectroscopy exist, and the low frequency region has been covered[68,69]. More recent work in the fields of low frequency spectra and of nitrate spectra are given in References 34, 70-72 and References 72-75 respectively.

CHAPTER II

COMPLEXES OF IMIDAZOLE

Introduction

Prior to the commencement of this work, very few coordination complexes of imidazole with zinc, copper, cobalt or nickel ions had been prepared. The complexes $Co(im)_6Cl_2$, $Ni(im)_6Cl_2.2H_2O$ and $Cu(im)_4SO_4\ H_2O$ had been patented[76], and the preparation of the zinc complexes $Zn(im)_6Cl_2.4H_2O$, $Zn(im)_2Cl_2$, $Zn(im)_2(OAc)_2$[77-79] and the copper complexes $Cu(im)_2Cl_2$, $Cu(im)Cl_2$[80] had been published. Subsequent to this work, the following complexes were reported: $Co(im)_6X_2$ (X = Cl, Br, I, NO_3, ClO_4), $Co(im)_4X_2$ (X = ClO_4, NCS, NCSe, NCO), $Co(im)_2X_2$ (X = Cl, Br, I, NO_3, NCS (three forms), NCSe, NCO), $Co(im)X_2$ (X = Cl, Br, I); $Ni(im)_6X_2$ (X = Cl, Br, I, NO_3), $Ni(im)_4X_2$ (X = Cl, Br, I), $Ni(im)_2X_2$ (X = Cl, Br, I), $Ni(im)X_2$ (X = Cl, Br, I) and $Cu(im)_4(NO_3)_2$.[81-83]

The complexes prepared and studied in this work are: $M(im)_6X_2$ (M = Co, Ni, X = Cl, Br, I, NO_3; M = Cu, X = I, NO_3; M = Zn, X = Cl, NO_3), $M(im)_4X_2$ (M = Ni, X = Cl, Br, I; M = Cu, X = Cl, Br, I, NO_3), $Ni(im)_4X_2.2H_2O$ (X = Cl, Br), $M(im)_2X_2$ (M = Co, Zn, X = Cl, Br, I, NO_3; M = Cu, X = NO_3) and $Ni(im)X_2$ (X = Cl, Br). The samples of the complexes $Ni(im)X_2$ (X = Cl, Br) were prepared by Dr M.J. Weeks, and the preparation and electronic spectra of these complexes and of $Ni(im)_4Cl_2.2H_2O$ have been reported[84]. Miss K.A. Price performed the preliminary preparative work on the cobalt halide complexes.

Crystal Structures

$Zn(im)_6Cl_2.4H_2O$[79] This structure contains hexakisimidazole-zinc ions linked together by hydrogen bonds to chloride ions and water molecules, with the zinc-nitrogen bond distances varying from 2.15 to 2.26 Å.

$Cu(im)_4I_2$[85] The cupric tetrakisimidazole iodide complex prepared here seemed sufficiently unusual to make a crystal structure investigation worth while. This was performed by Mrs F. Akhtar and Dr A.C. Skapski of the X-ray Crystallography Department. The coordination about the copper atom is essentially square planar with two distant iodine atoms completing the very distorted octahedron. The copper-nitrogen bond distances vary from 1.98 to 2.04 Å, and the copper-iodine bond distances are 3.42 and 3.87 Å. The latter distances are very long, even for Cu-I bonds (cf. 2.70 Å in iodobis(2,2'-bipyridyl)copperII iodide[86] and 3.17 Å in $Cu(NH_3)_4(CuI_2)_2$[87]). The planes of the imidazole rings lie through the I-Cu-I axis, allowing maximum π-bonding and the least interference between the rings.

$Zn(im)_2Cl_2$[88] This complex has a pseudotetrahedral structure with bond distances of zinc-nitrogen = 2.00 and 2.02 Å and zinc-chlorine = 2.24 and 2.26 Å.

Discussion

Electronic Spectra and Magnetic Properties (Tables 2.1, 2.2 and 2.3)

Both $Co(im)_6(NO_3)_2$ and $Ni(im)_6(NO_3)_2$ have spectra typical of undistorted octahedral complexes. The cobalt complex has a shoulder at 19.1 kK which it is tempting to assign as ν_2, the two electron

transition in the strong field limit[89]; however this would give an unacceptably low value of Δ, and as a sharp band is observed in the low temperature spectrum at this energy also, it is probably the transition to the spin forbidden $^2T_{1g}$ (^2P, ^2H) level[49,90].

The cobalt 2:1 halide complexes give spectra characteristic of C_{2v} pseudotetrahedral complexes, with three components of ν_2[45], which have been assigned, in order of increasing energy, as the $^4A_2 \rightarrow {}^4B_1$, $^4A_2$ and $^4B_2$ transitions[91]. $Co(im)_2(NO_3)_2$ gives a similar spectrum to that of $Co((CH_3)_3PO)_2(NO_3)_2$, a complex which has been shown to have an irregular octahedral structure with chelating nitrate groups[93], and yet whose spectrum resembles more closely those observed for pseudotetrahedral complexes[92].

$Ni(im)_4Cl_2$ is assigned a D_{4h} octahedral structure. The axial distortion must be considerable, as the calculated parameters (Ds = 0.64 kK, Dt = 0.50 kK at room temperature, and Ds = 0.67 kK, Dt = 0.55 kK at 95°K) are large for a NiL_4Cl_2 type complex[39]. The nickel chloride and bromide hydrates, however, have lower, and almost identical splitting parameters (chloride, Ds = 0.53 kK, Dt = 0.22 kK, and bromide, Ds = 0.51 kK, Dt = 0.21 kK), which would appear to indicate that the water molecules rather than the anions are coordinated. It is of interest that for these two complexes, $Ds \approx 2.4\ Dt$, whereas for most D_{4h} nickel octahedral complexes, $Ds \approx 1.3\ Dt$[40].

The complexes $Ni(im)_4Br_2$ and $Ni(im)_4I_2$ are assigned planar structures. The single visible region band is probably the $^1A_{1g} \rightarrow {}^1A_{2g}$ transition[43,94], however the variation in band assignments of square

planar species[29] makes definite assignment impossible. Taylor and Underhill[83] report the 4:1 bromide and iodide complexes prepared by a fusion method as having distorted octahedral structures, thus as has been observed for the benzimidazole system[84,95], the product often depends upon the technique of preparation.

$Ni(im)Cl_2$ and $Ni(im)Br_2$ have very similar spectra to those of the benzimidazole congeners[96], and have been assigned polymeric octahedral structures[84]. $Ni(im)Cl_2$ has the characteristic high magnetic moment of 1:1 nickel chloride complexes[84,96].

The copper complexes all have asymmetric bands in the visible region, as is usually observed for tetragonally distorted octahedral complexes (e.g. 97). The bands are at higher energies than those observed in the benzimidazole complexes[89].

Vibrational Spectra (Table 2.4)

The nitrate bands can be satisfactorily assigned by comparison with the work of Curtis and Curtis[99]. The 6:1 complexes of cobalt, nickel and zinc have ionic nitrate groups, the 4:1 complexes monodentate and the 2:1 complexes bidentate nitrate groups. The nitrate bands of the complexes $Cu(im)_4(NO_3)_2$ and $Cu(im)_6(NO_3)_2$ are almost identical, which would indicate that in the latter case, two imidazole molecules are uncoordinated. This is similar to the copper pyridine system[100], though the splitting of ν_3 in the imidazole complexes is smaller, suggesting a weaker axial coordination. Unsuccessful attempts were made to confirm the presence of uncoordinated imidazole in the 6:1 copper complexes by the study of the ring breathing mode[101].

Table 2.1

Diffuse Reflectance Spectra (kK)

$Co(im)_6(NO_3)_2$	[a]	9.66m, 19.1sh, 20.4m
at 95°K		10.15m, 15.9sh, 17.1sh, 18.0w, 19.3m, 20.1sh, 21.3m
$Co(im)_2Cl_2$	[b]	4.85s, 6.38s, 7.50s, 9.15s, 16.1vs, 17.4vs [c]
$Co(im)_2Br_2$	[b]	6.15s, 6.90s, 8.70s, 15.0vs, 16.1vs, 17.2vs [c]
$Co(im)_2I_2$	[b]	6.60s, 8.20s, 14.3vs, 15.6vs, 17.0vs [c], 24.8vs
$Co(im)_2(NO_3)_2$	[b]	6.17s, 7.7s, 9.1s, 11.1sh, 18.4vs
$Ni(im)_6(NO_3)_2$	[a]	10.9m, 13.2sh, 18.1m, 23.8sh, 27.5m
at 95°K		11.4m, 13.3sh, 18.3m, 22.6w, 24.5w, ~ 28.0w
$Ni(im)_4Cl_2$		~6.7m, 11.1m, 14.1m, 17.3m, 21.8sh, 24.5m
at 95°K		7.27m, 11.0sh, 12.1m, 14.7m, 18.0m, 22.7sh, 24.8m
$Ni(im)_4Cl_2.2H_2O$	[e]	9.09m, 11.0m, 13.9m, 16.8m, 27.25m
$Ni(im)_4Br_2$		21.7s
$Ni(im)_4Br_2.2H_2O$	[e]	9.09m, 10.9m, 13.9m, 16.7m, 27.25m
$Ni(im)_4I_2$		21.1s
$Ni(im)Cl_2$	[d]	6.3sh, 7.7, 12.0, 12.95, 18.7sh, 21.1
$Ni(im)Br_2$	[d]	5.9sh, 7.3, 11.3sh, 12.3, 18.0sh, 18.7sh, 21.4
$Cu(im)_4Cl_2$		16.9s
$Cu(im)_4Br_2$		14.8sh, 17.4s
$Cu(im)_4I_2$		14.5sh, 18.2s
$Cu(im)_4I_2.2im$		16.8s, br
$Cu(im)_4(NO_3)_2$		16.7sh, 18.4s
$Cu(im)_4(NO_3)_2.2im$		15.9s
$Cu(im)_2(NO_3)_2$		13.5s, 15.6sh.

[a] The room temperature spectra of the 6:1 chloride, bromide and iodide complexes are identical.

[b] Low energy bands are obscured by ligand modes.

[c] The spin forbidden bands observed above ν_3 have been omitted.

[d] Measured by Dr M.J. Weeks.

[e] The deuterated complexes have identical spectra to the hydrated forms.

Table 2.2

Δ Values (kK)

$Ni(im)_6(NO_3)_2$	10.9	$Ni(im)_4Cl_2$	11.1 (xy)	6.7 (z)
(95°K)	11.4	(95°K)	12.1	7.3
$Co(im)_6(NO_3)_2$	11.0	$Ni(im)_4Cl_2.2H_2O$	11.0	7.2
(95°K)	11.4	$Ni(im)_4Br_2.2H_2O$	10.9	7.3

Table 2.3

Magnetic Moments (B.M.)

$Co(im)_6(NO_3)_2$	5.00	$Ni(im)_4Cl_2.2H_2O$	3.17	$Cu(im)_4Br$	1.84
$Co(im)_2Cl_2$	4.66	$Ni(im)_4Br_2$	diamagnetic	$Cu(im)_4I_2$	1.81
$Co(im)_2Br_2$	4.63	$Ni(im)_4Br_2.2H_2O$	3.18	$Cu(im)_4I_2.2im$	2.19
$Co(im)_2I_2$	4.65	$Ni(im)_4I_2$	diamagnetic	$Cu(im)_4(NO_3)_2$	1.75
$Co(im)_2(NO_3)_2$	4.42	$Ni(im)Cl_2$	3.44	$Cu(im)_4(NO_3)_2.2im$	
$Ni(im)_6(NO_3)_2$	3.07	$Ni(im)Br_2$	3.17		1.84
$Ni(im)_4Cl_2$	3.14 (Θ=-10°)	$Cu(im)_4Cl_2$	1.84	$Cu(im)_2(NO_3)_2$	1.86

Table 2.4

Nitrate Group Frequencies (K)

		ν_3	ν_1	ν_2	ν_3 [a]
$Co(im)_6(NO_3)_2$	ir	1372s	-	824m	710m
	R	-	1045s	-	714m
$Ni(im)_6(NO_3)_2$	ir	1375s	-	823m	710m
	R	-	1045s	-	712m
$Zn(im)_6(NO_3)_2$	ir	1372s	-	824m	711m
	R	-	1043s	-	712m
$Cu(im)_4(NO_3)_2$	ir	1371brs, 1340s	1047m	823m	708m
$Cu(im)_4(NO_3)_2.2im$	ir	1370brs, 1337s	1043m	824m	703w
$Zn(im)_4(NO_3)_2$	ir	1455s, 1400s, 1312s	1033s	811m	717m, 703m
	R	-	1036s	-	720m, 707m
$Co(im)_2(NO_3)_2$	ir	1473s, 1302s, 1273s	1034s, 1005s	806s	703w
$Cu(im)_2(NO_3)_2$	ir	1456brs, 1418brs, 1290brs	1021s	811m, 808m	-
$Zn(im)_2(NO_3)_2$	ir	1473brs, 1332s, 1278s	1037s, 1008s	809s	708w
	R	-	1039s, 1009s	-	723m, 710m

[a] Strong ligand band near 725K

Vibrational Spectra 400 - 90 K

Crystalline imidazole has several active vibrations in the low frequency region (Table 2.5), but these disappear upon complexing. This can be explained from the crystal structure[102] as imidazole is strongly hydrogen bonded, and the intermolecular vibrations would be expected in this region[103].

Table 2.5

Vibrational Spectrum of Imidazole 400 - 70 K

ir	179w, 143s, 115-105w, vbr, 88m	[a]
	179, 142, 114, 103, 89	[103]
R	149s, 89m, 77m	[a]
	149s, 139w, 114w, 106w, 91s, 87s, 78s	[107]

[a] This work

$M(im_6X_2$ Complexes (Table 2.6)

The electronic spectra of the cobalt and nickel complexes show no evidence of distortion, yet assignment of the vibrational bands on the bases of an O_h symmetry unit is difficult. The two Raman active vibrations above 150 K can be assigned as ν_1 (A_{1g}) and ν_2 (E_g), and the highest infrared band as the ν_3 (F_{1u}) vibration. The band at 200 K in the cobalt complexes, which has been assigned as ν_4 (F_{1u}) [104] is more likely to be either ν_1 activated in the infrared or a component

of ν_3. The weak band observed in two of the nickel complexes may be assigned similarly. It is tempting to assign the infrared band found in all the complexes between 160 and 190 K as ν_4, however it has been shown for some ammine complexes that $\nu_3 >> \nu_4$[105,106], thus this assignment would appear unlikely. The alternative is that it is a component of ν_3, split by reduction to S_6 symmetry or lower. The ammine complexes also show ν_1 and ν_2 to be greater than ν_3[105], however no Raman bands were observed at higher energies, though this does not preclude their existence. The weak Raman active band at 203 K in $Zn(im)_6Cl_2$ is probably an overtone (2 x 102). The bands below 150 K are anion dependent, and in fact, appear to be characteristic of the particular anion.

$M(im)_4X_2$ Complexes (Table 2.7)

The two bands above 200 K in $Ni(im)_4Cl_2$ are assigned as the asymmetric nickel-nitrogen (257 K) and nickel-chlorine (232 K) stretches respectively, as a band is observed at 262 K in the octahedral forms of both $Ni(im)_4Br_2$ and $Ni(im)_4I_2$[83]. In the case of $Zn(im)_4(NO_3)_2$, although the infrared band at 271 K can be assigned as the asymmetric zinc-oxygen stretch[108], the Raman band at 268 K could be either the symmetric zinc-oxygen stretch, or the asymmetric stretch activated.

The 270 K band in the hydrated and deuterated nickel halide complexes is probably the nickel-nitrogen stretch, with the lower energy band system being the oxygen-nickel-oxygen bending mode. No band was observed near 400 K where the metal-oxygen stretch is found for $M(OH_2)_6^{2+}$ ions [109] but a band at ~550 K in the region found for

Table 2.6

Vibrational Spectra of $M(im)_6X_2$ Complexes, 400-90 K

		ν_1	ν_2	ν_3	[a]	Other bands
$Co(im)_6Cl_2$	ir			236s, 200m	176ms	145ms, 133m, 114w, 101w
	R	188m	163w			
$Co(im)_6Br_2$	ir			236s,br,197m	174s	110ms
	R	192m	159mw			113m
$Co(im)_6I_2$	ir			238s,br,197m	173m	100mbr
	R	189s	156m			103ms
$Co(im)_6(NO_3)_2$	ir			239s, 199m	175s	127sbr
	R	189ms	162w			140sh, 112sh
$Ni(im)_6Cl_2$	ir			258s, 210vw	189m	148m, 135sh
	R	210m	171w			
$Ni(im)_6Br_2$	ir			259s	186m	111s,br
	R	210s	166wbr			
$Ni(im)_6I_2$	ir			262s	184ms	107mw
	R	207s	164wbr			
$Ni(im)_6(NO_3)_2$				262s, 212vw	188m	130s
	R	208m	175sh			
$Zn(im)_6Cl_2$	ir			199s	171s	154sbr, 133sbr, 110ms
	R	185s	153mbr			203w, 133s, 102m
$Zn(im)_6(NO_3)_2$	ir			201vs	163s	126s
	R	192s	154sh			113s

[a] See text for discussion of this assignment

Table 2.7

Vibrational Spectra of $M(im)_4X_2$ Complexes, 400 - 90 K

Distorted Octahedral		
$Ni(im)_4Cl_2$	ir	257s, 232s, 175-150mbr
$Ni(im)_4(OH_2)_2Cl_2$	ir	270m, 250sh, 241s, 233sh, 205w, 170sh, 147sbr
	R	224w, 178wbr
$Ni(im)_4(OD_2)_2Cl_2$	ir	268m, 245sh, 238s, 226sh, 204w, 169m, 147sbr
	R	223mw, 180mbr
$Ni(im)_4(OH_2)_2Br_2$	ir	263s, 248m, 238s, 227sh, 195m, 169w, 158w, 114ms
	R	221w, 179wbr
$Ni(im)_4(OD_2)_2Br_2$	ir	261m, 243m, 234ms, 220sh, 193ms, 168m, 155w, 113s
	R	220w, 175vwbr
$Cu(im)_4Cl_2$	ir	287ms, 254w, 225m, 176sh, 160s, 126s, 112m
$Cu(im)_4Br_2$	ir	287ms, 254w, 224wbr, 170m, 152w, 125s,br
$Cu(im)_4I_2$	ir	287s, 251ms, 223wbr, 158wbr, 114vs
$Cu(im)_4I_2$ 2im	ir	282s, 255w, 223mw, 176m, 158s, 126ms, 114sh
$Cu(im)_4(NO_3)_2$	ir	290s, 257w, 225w, 168m, 145ms,br, 118s
$Cu(im)_4(NO_3)_2$ 2im	ir	296m, 267ms, 241s, 218s, 155ms,br, 130ms,br
$Zn(im)_4(NO_3)_2$	ir	271ms, 202m, 160vs, 120mw, 105w
	R	268wbr, 219sh, 204mw, 177m, 147s, 90sh
Square Planar		
$Ni(im)_4Br$	ir	393m, 329m, 130s, 98ms
	R	289w, 239mw, 183ms, 113ms
$Ni(im)_4I_2$	ir	389m, 326mw, 124mw, 91mw
	R	288w, 236mw, 179m

the H_2O wagging vibration gives a shift on deuteration (Table 2.8) close to the value found for the nickel oxygen stretch[109].

The copper complexes ($Cu(im)_4X_2$ and $Cu(im_4X_2.2im)$ show no band shifts above 200 K, suggesting that all bands at energies > 200 K are copper-nitrogen vibrations.

The planar nickel complexes are expected to have strong bonding, considering both the change from high spin to low spin, and the change from six to four coordination. One can assign the two infrared bands at ~ 390 K and 330 K as split components of ν_6 (E_u), values slightly lower than those obtained for the planar bisimidazolato nickel inner complex[110]. The two Raman bands at ~ 290 and ~ 240 K are assigned as ν_1 (A_{1g}) and ν_2 (B_{1g}) respectively. For most square planar systems, ν_1, ν_2 and ν_6 lie close together, e.g. $Pt(NH_3)_4Cl_2$[111], $Pt(thiourea)_4Cl_2$[112], thus it may be that the 390 K absorption is caused by activation of a ligand mode (many substituted imidazoles have infrared active bands in that region), and in support of this, the assignments for $Pt(pyridine)_4Cl_2$ are ν_6, ν_1 and ν_2 at 303, 229 and 208 K respectively[113,114].

Bands are reported at ~ 390 and ~ 330 K in the octahedral $Ni(im)_4Br_2$ and $Ni(im)_4I_2$ complexes prepared by Taylor and Underhill, which suggests that their samples contain some of the planar form, especially as they report an abnormally low magnetic moment for the iodide. As they also report bands at these positions in $Ni(im)_2Br_2$ and $Ni(im)_2I_2$, and as they admit that in spite of giving a good analyses, the complex $Co(im)Cl_2$ contains some $Co(im)_2Cl_2$, doubt must be cast as to the worth of their results.

$M(im)_2X_2$ Complexes (Table 2.9)

For the halides of cobalt and zinc, assignment of the metal-nitrogen vibrations is relatively easy, but only for the chlorides are two metal halogen stretching modes readily identified, though assignments can be made for both metal-bromine and the metal-iodine asymmetric stretches, which are compatible with similar systems[71,115]. The band at about 146 K for $Zn(im)_2I_2$ is probably the symmetric zinc-iodine stretching mode, as these are expected to be strongly Raman active[70], however this is at lower energy than has been observed in other ZnL_2I_2 systems[71,116].

For the bidentate nitrate complexes, the metal oxygen stretching vibrations may be tentatively assigned as the bands at 323 and 298 K (cobalt), 330 and 296 K (copper), and 288 and ~ 245 K (zinc)[75,72].

$M(im)X_2$ Complexes (Table 2.10)

As expected for such a low symmetry, most vibrations appear to be Raman and infrared active.

Table 2.8

Shift on deuteration of the 550 K band in $Ni(im)_4(OH_2)_2X_2$

X	H_2O	D_2O	Ratio
Cl	563	532	0.95
Br	540	520	0.96

Table 2.9

Vibrational Spectra 400 - 90 K for $M(im)_2X_2$ Complexes

		$\nu_{(M-N)}$	$\nu_{(M-X)}$	Other bands
Tetrahedral				
$Co(im)_2Cl_2$	ir	274mw, 242w	321s, 308s	196mw, 165s, 153sh, 122m, 105sh
$Co(im)_2Br_2$	ir	284mw, 255sh	260s, 193s	183m, 165w, 155m
$Co(im)_2I_2$	ir	283w, 252m	237ms	182ms, 168mw, 148m
$Zn(im)_2Cl_2$	ir	251mw, 236w	300vs, 288vs	199ms, 160mbr, 124m, 102w
	R	250w, 239m	296vs, 286w	216w, 198m, 177w, 159s, 105s
$Zn(im)_2Br_2$	ir	255sh, 224mw	242vs, 190s	158m, 150m, 111w
	R	-	189s	157w
$Zn(im)_2I_2$	ir	251m, 232m	210s, 148mw	180m, 169m
	R	245m, 190sh,	172s, 145vs	178w, 166m
Nitrates				
$Co(im)_2(NO_3)_2$	ir	323vs, 298m, 278s, 236sh, 188sh, 174s, 145mbr, 98mbr		
$Cu(im)_2(NO_3)_2$	ir	330s, 296s, 246w, 233sh, 222s, 203ms, 146m, 133m, 103m		
$Zn(im)_2(NO_3)_2$	ir	288s, 250mbr, 188w, 169ms, 144m, 131m, 100w		

Table 2.10

Vibrational Spectra 400 - 90 K for $Ni(Im)X_2$ Complexes

$Ni(im)Cl_2$	ir	276m, 255m, 210s, 181s, 150m
	R	278mw, 243w, 210w, 195ms, 182w
$Ni(im)Br_2$	ir	259m, 239s, 220m, 194s, 179s, 155s, 139m
	R	265w, 226w, 198m, 180w, 156m.

CHAPTER III

COMPLEXES OF N-METHYL IMIDAZOLE

Introduction

The substitution of the imino-hydrogen by a methyl group removes the capacity of imidazole to act as an acid, and the importance of N-substituted imidazoles as fungicidal compositions[120,121] made this a ligand of biological interest.

The complexes reported here are: $M(NMeim)_6X_2.2H_2O$ (M = Co, Ni, X = Cl, Br), $M(NMeim)_6X_2$ (M = Co, Ni, X = I, NO_3; M = Zn, X = I), $M(NMeim)_4X_2$ (M = Ni, X = Cl; M = Cu, X = Br, I, NO_3), $Cu(NMeim)_4Cl_2.2H_2O$, $M(NMeim)_2X_2$ (M = Co, Ni, Zn, X = Cl, Br, I; M = Cu, X = Cl, Br, NO_3), $M(NMeim)X_2$ (M = Ni, X = Cl, Br; M = Cu, X = Cl). Dr M.J. Weeks had previously reported the preparation and electronic spectra of $Ni(NMeim)_2Br_2$ and $Co(NMeim)_2X_2$ (X = Cl, Br)[84].

N-methyl substitution of imidazole appears to decrease the stability of the hexakis complexes, with the ease of removal of ligand being in the order Cu > Co > Ni and Cl > Br > I, NO_3. With cobalt, the chloride (and to a lesser extent, the bromide) needed a high ligand to metal ratio in order to obtain a pure compound, and even then the hot solution was blue. The chloride and bromide complexes lost ligand under vacuum, and the finely crushed chloride lost ligand if left in an open container. In the case of copper, addition of free ligand to the tetrakis complexes caused colour changes, but the solids isolated spontaneously lost ligand to revert to the tetrakis species. Only with iodide as the anion could a pure hexakis zinc complex be isolated.

Electronic Spectra and Magnetic Properties (Tables 3.1 and 3.2)

If $Ni(NMeim)_6I_2$ is prepared under strictly anhydrous conditions, a considerable enhancement of the ν_3 band is observed, however this yellow form, and the pale violet form have identical far infrared spectra, magnetic susceptibilities and X-ray powder spectra, and the pale violet form contains no detectable quantities of water. The enhancement is probably caused by the mixing-in of long range charge transfer interactions. (These interactions have been observed for a variety of ML_6I_3 complexes[122]). Presumably the presence of a very few water molecules in the crystal lattice is sufficient to suppress this effect. The anhydrous hexakis cobalt and nickel complexes have a ligand field strength of 10.95 and 10.9 kK respectively, very similar to the values obtained for the equivalent imidazole complexes.

$Ni(NMeim)_4Cl_2$ has a distorted, octahedral structure, giving the parameters Ds = 0.56 kK, Dt = 0.38 kK, Δ_{xy} = 11.2 kK and Δ_z = 4.6 kK. $Ni(pyrazole)_4Cl_2$, whose crystal structure is known[123] (Ni-N = 2.09 and 2.10 Å, Ni-Cl = 2.51 Å), gives a similar spectrum (partially reported in Reference 124, reported in full in Table 3.1) and similar parameters Ds = 0.62 kK, Dt = 0.41 kK, Δ_{xy} = 11.8 kK and Δ_z = 4.5 kK. It would therefore seem safe to assume that the N-methyl imidazole complex has similar values of bond lengths.

The 2:1 nickel complexes have pseudotetrahedral structures. The separation of the observed components of ν_1 is larger than that found for most pseudotetrahedral nickel complexes, and is similar

to the value found for Ni(di-2-pyridylamine)Br_2[125]. The low orbital contributions to the magnetic moment found for these complexes is typical of low symmetry tetrahedral nickel species[126]. Of interest is the iodide complex, where two components appear in the ν_2 region, which are presumably caused by spin orbit coupling with the spin forbidden band arising from the $^1D_2$ free ion state[37].

The complex Cu(NMeim)$_2Br_2$ has a band at the same energy as the complex Cu(pyridine)$_2Br_2$[34], and is therefore assigned a similar polymeric structure[127]. A preliminary crystal structure examination shows that there are repeat units in the crystal lattice of 4 Å length[128], which is characteristic of polymeric halide units. The chloride complex shows an absorption at a considerably lower energy than that of the bromide, this would suggest that the chloride has a markedly different structure to that of the bromide. For comparison, Cu(pyridine)$_2Cl_2$ which has a polymeric octahedral structure[129] shows a maximum at 14.5 kK[34]. A five coordinate dimeric structure is doubtful as Cu(2Me-pyridine)$_2Cl_2$, which has this structure[130], shows a band maximum at 17.1 kK[34]. A pseudotetrahedral structure would account for the band position, however a much more intense, split band is usually observed for such complexes[33] (see also Chapter 4). The spectrum of Cu(NMeim)$_2(NO_3)_2$ closely resembles that of Cu(pyridine)$_2(NO_3)_2$ [100].

Table 3.1

Diffuse Reflectance Spectra (kK)

$Co(NMeim)_6Cl_2.2H_2O$		9.43w, 16.0vw, 19.1sh, 20.4w
$Co(NMeim)_6Br.2H_2O$		9.52w, 15.3sh, 16.1vw, 19.1sh, 20.5m
$Co(NMeim)_6I_2$		9.75w, 14.3vw, 16.4sh, 19.1sh, 20.6w
$Co(NMeim)_6(NO_3)_2$		9.71w, 16.0sh, 19.1sh, 20.5w
$Co(NMeim)_2Cl_2$	[a]	6.40s, 7.05s, 9.09s, 15.9vs, 16.5vs, 17.2sh,s [b]
$Co(NMeim)_2Br_2$	[a]	6.2sh,s, 6.77s, 8.70s, 15.1vs, 16.3vs, 16.9sh,s [b]
$Co(NMeim)_2I_2$	[a]	6.1sh,s, 6.67s, 8.20s, 14.6vs, 15.8vs. 16.6vs [b] 26.5s
$Ni(NMeim)_6Cl_2.2H_2O$		10.6w, 13.5sh, 17.2w, 23.2sh, 26.9w
$Ni(NMeim)_6Br_2.2H_2O$		10.7w, 13.3sh, 17.3w, 23.5sh, 26.9w
$Ni(NMeim)_6I_2$		10.9w, 18.0w, 26.3s
$Ni(NMeim)_6(NO_3)_2$		10.9w, 13.3sh, 17.5w, 23.8vw, 27.2w
$Ni(NMeim)_4Cl_2$		7.87w, 11.2w, 13.2w, 16.1w, 20.5vw, 25.6w
$Ni(pyrazole)_4Cl_2$		8.15w, 11.8w, 13.3w, 16.5w, 21.3vw,sh 26.0w
$Ni(NMeim)_2Cl_2$	[a]	5.7m, 9.0sh, 10.9m, ~12.5sh, 17.4m, 18.5sh,m, 24.4vw
$Ni(NMeim)_2Br_2$	[a]	5.5m, 8.77m, 10.9m, ~12.0sh, 16.5s, 17.4sh,s, 23.9vw
$Ni(NMeim)_2I_2$	[a]	5.7m, 8.15m, 10.2m, 11.0m, 15.2s, ~18.4sh, 24.6vs
$Ni(NMeim)Cl_2$	[c]	~6(sh), 7.6w, 12.1m, 13.1m, 18.5sh, 22.2m
$Ni(NMeim)Br_2$		~6(sh), 7.25w, 11.4sh,m, 12.4m, 18.0sh, 21.4m
$Cu(NMeim)_4Cl_2.2H_2O$		14.3sh, 17.2m
$Cu(NMeim)_4Br_2$		16.7m
$Cu(NMeim)_4I_2$		14.3sh, 16.7m, 25.8m

Table 3.1 (continued)

$Cu(NMeim)_4(NO_3)_2$	17.2m
$Cu(NMeim)_2Cl_2$	12.2s, ~28.7vs
$Cu(NMeim)_2Br_2$	14.6s, 24.4vs
$Cu(NMeim)_2(NO_3)_2$	13.8m, 15.4m
$Cu(NMeim)Cl_2$ [a]	12.5m, ~21.0sh, 28.3s.

[a] Low energy absorptions obscured by vibrational bands

[b] High energy spin forbidden bands omitted

[c] Included for comparison

Table 3.2

Magnetic Moments μ_{eff} (B.M.)

$Co(NMeim)_6Cl_2.2H_2O$	5.06	$Ni(NMeim)_2Br_2$	3.43
$Co(NMeim)_6Br_2.2H_2O$	5.05	$Ni(NMeim)_2I_2$	3.44
$Co(NMeim)_6I_2$	5.00	$Ni(NMeim)Cl_2$	3.47
$Co(NMeim)_6(NO_3)_2$	5.16	$Ni(NMeim)Br_2$	3.39
$Co(NMeim)_2Cl_2$	4.66	$Cu(NMeim)_4Cl_2.2H_2O$	1.84
$Co(NMeim)_2Br_2$	4.69	$Cu(NMeim)_4Br_2$	1.87
$Co(NMeim)_2I_2$	4.67	$Cu(NMeim)_4I_2$	1.88
$Ni(NMeim)_6Cl_2.2H_2O$	3.16	$Cu(NMeim)_4(NO_3)_2$	1.91
$Ni(NMeim)_6Br_2.2H_2O$	3.11	$Cu(NMeim)_2Cl_2$	1.91
$Ni(NMeim)_6I_2$	3.12	$Cu(NMeim)_2Br_2$	1.88
$Ni(NMeim)_6(NO_3)_2$	3.01	$Cu(NMeim)_2(NO_3)_2$	1.85
$Ni(NMeim)_4Cl_2$	3.18	$Cu(NMeim)Cl_2$	1.84
$Ni(NMeim)_2Cl_2$	3.29		

The complex $Cu(NMeim)Cl_2$ probably has a similar structure to the nickel complex. As has been observed for the substituted pyridine N-oxide complexes, the copper 1:1 halide bridged system exhibits a normal magnetic moment[131].

Vibrational Spectra 400 - 80 K

In the free ligand only two bands are clearly observed, one at about 355 K and the other at 223 K, both being Raman and infrared active. Upon complexing, the higher band moves up to about 370 K, and the lower to about 250 K. Both vibrations could be observed in the Raman, but the infrared showed no absorption which could be consistently assigned as the 250 K band. The far infrared and Raman spectrum of the free ligand has been reported down to 200 K[132], and the bands are assigned as $\delta(CH_3\text{-}N)$ at ~354 K and $\gamma(CH_3\text{-}N)$ at ~222K. An infrared band at 80 K (assigned as a dipole-dipole interaction) has also been reported[103].

$M(NMeim)_6X_2$ Complexes (Table 3.3)

Poor resolution was obtained below 200 K for the hydrated complexes, and these were therefore not listed.

As has been discussed for the imidazole complexes, assignment of the bands is difficult on the basis of O_h symmetry, and the presence of methyl groups would tend to reduce the metal site symmetry still further. For the nickel and cobalt complexes, two bands are observed above 200 K, the higher being in the same position as the highest energy band in the equivalent imidazole complexes, though this could well be fortuitous. The cobalt complexes have a Raman

active band at about the same position as the higher of the two infrared active bands, and as there is little doubt that the Raman band is the ligand vibration (from comparison with the Raman spectra of the zinc complexes), the infrared band might well have the same origin. However in the nickel complexes, both of the infrared active bands are shifted about 10 K to higher energies, suggesting that the two infrared active vibrations in each case are both of a metal-nitrogen stretching nature. The opposite problem arises in the case of the zinc complex, namely the presence of only one infrared active band which can be assigned as a zinc-nitrogen vibration. This presumably is ν_3, but as the cobalt, nickel and zinc iodide complexes are isomorphous, it is difficult to explain the different spectrum observed in the zinc case.

$M(NMeim)_4X_2$ Complexes. (Table 3.4)

From comparison with the equivalent imidazole complex, the two bands above 200 K for $Ni(NMeim)_4Cl_2$ are assigned as the asymmetric nickel-nitrogen stretch at 254 K and the nickel-chlorine stretch at 226 K.

The 4:1 copper complexes have similar spectra to those of the imidazole complexes, except that the unit symmetry would appear to be lower, as the bands observed in the imidazole complexes at about 280 and 220 K are replaced by two pairs of bands centred at about 280 and 200 K respectively. It is possible that the bands at about 200 K are the nitrogen-copper-nitrogen asymmetric bending

modes as has been suggested for the benzimidazole complexes[133]. Unlike the imidazole complexes, no anion dependent bands are observed apart from the 220 K band in $Cu(NMeim)_4(NO_3)_2$, though if this is the copper-oxygen asymmetric stretch, then the axial bonding must be quite strong.

All the anhydrous 4:1 complexes show a significant splitting of the ligand band at ~380 K.

$M(NMeim)_2X_2$ Tetrahedral Complexes (Table 3.5)

The postulated assignments are shown in tabulated form. As has been discussed for the imidazole complexes, the assignment of the symmetric metal-iodine stretch is not certain, however in the zinc case, the Raman spectrum of an acetone solution shows the 142 K band to be intense and strongly polarised. (It has been observed for a variety of systems that metal-iodine symmetric stretches are strongly Raman active in solution[70,134] and of course, being A_1 vibrations, they are expected to be completely polarised).

Surprisingly, the spectrum of $Cu(NMeim)_2Cl_2$ shows an almost identical band system to its nickel and cobalt congeners, and one is therefore tempted to assign its structure, from this evidence, as tetrahedral.

Other Complexes (Table 3.6)

The complexes $Cu(NMeim)_2X_2$, (X = Br, NO_3) presumably have distorted octahedral structures. The band systems of the two complexes are very similar, and although the metal-oxygen stretch in the nitrate

complex may well be superimposed on the metal-nitrogen stretch at 303 K [72,135], it would be unusual if the metal-bromine stretch in the bromide complex is as low as 218 K or as high as 299 K[136].

Table 3.6

Vibrational Spectra 400 - 80 K for Other Complexes

$Cu(NMeim)_2Br_2$	ir	370m, 299s, 218s, 198s, 179s, 127s, 87m
$Cu(NMeim)_2(NO_3)_2$	ir	377w, 303s,br, 222w, 195m, 170w, 137w, 88w
$Ni(NMeim)Cl_2$	ir	372w, 264sh, 247s, 200s, 148m, 83m
$Ni(NMeim)Br_2$	ir	370w, 243m, 216m, 183s, 158s, 146s, 132m
$Cu(NMeim)Cl_2$	ir	380w, 351w, 325m, 284s,vbr, 215w, 187m, 167s 157sh, 142w, 116s, 93s.

Table 3.3

Vibrational Spectra 400 - 80 K for $M(NMeim)_6X_2$ Complexes

$Co(NMeim)_6I_2$	ir	371m, 245m, 220s, 180s, 170m, 150w, 100>
	R	376m, 247m
$Co(NMeim)_6(NO_3)_2$	ir	372m, 242m, 220s, 180s,br, 151w
	R	378m, 246m
$Ni(NMeim)_6I_2$	ir	374w, 259s, 230s, 181s, 161m
$Ni(NMeim)_6(NO_3)_2$	ir	378w, 261s, 231s, 188s, 163w
$Zn(NMeim)_6I_2$	ir	368w, ~239wsh, 188vs
	R	373s, 247s, 190sh, 105sh

Table 3.4

Vibrational Spectra 400 - 80 K for $M(NMeim)_4X_2$ Complexes

$Ni(NMeim)_4Cl_2$	ir	377w, 366w, 254s, 226s, 177s, 150w, 117wbr
$Cu(NMeim)_4Cl_2.2H_2O$	ir	366w, 280s, 271s, 248m, 207m, 191s, 110s,vbr
$Cu(NMeim)_4Br_2$	ir	381w, 374w, 288s, 280s, 256s, 246sh, 213s, 197s, 95s,vbr
$Cu(NMeim)_4I_2$	ir	383w, 372w, 282s, 260m, 204s, 195s, 88s
$Cu(NMeim)_4(NO_3)_2$	ir	384w, 372w, 296s, 282m, 255s, 220s, 206s, 197s, 95s.

Table 3.5

Vibrational Spectra 400 - 80 K for $M(NMeim)_2X_2$ Tetrahedral Complexes

		$\nu_{(M-X)}$	$\nu_{(M-N)}$	Other bands
$Co(NMeim)_2Cl_2$	ir	323s, 296s	267s, 240w	368m, 219w[a] 160w, 142s 105mbr
$Co(NMeim)_2Br_2$	ir	259s, 184s	271w,sh, 248m	367m, 222w,sh[a] 158s, 137s
$Co(NMeim)_2I_2$	ir	219s	270s, 242m	365w, 162s[b], 145s[b]
$Ni(NMeim)_2Cl_2$	ir	323s, 288s	269m, 238w,sh	370w, 227wbr[a], 175mbr, 145s, 114m
$Ni(NMeim)_2Br_2$	ir	259s, 182s	240sh	368m, 161m, 140m, ~90mbr
$Ni(NMeim)_2I_2$	ir	228s	266m, 258s	366m, 175s[b], 154w[b], 137s, 89w
$Cu(NMeim)_2Cl_2$	ir	311s, 279s	262m, 230w	382m, 208m[a], 188s, 167s, 104m
$Zn(NMeim)_2Cl_2$	ir	306s, 285s	235s, 216s	368m, 183w[a], 160s, 144s, 112m
	R	289s	223w	371m, 246w, 189w, 163w, 149w
$Zn(NMeim)_2Br_2$	ir	234s, 187m	223sh	366w, 159m, 137m
	R	190s		371m, 244s, 175w, 157w, 150s
	R[c]	187w		394s
$Zn(NMeim)_2I_2$	ir	206s, 140m	225m	367m, 169s
	R	206w, 142s		371m, 254s, 170m
	R[c]	144vs polarised		395s

[a] Possibly component of $\nu_{(M-N)}$

[b] Possibly other component of $\nu_{(M-X)}$

[c] Solution in acetone

CHAPTER IV

COMPLEXES OF 2-METHYL IMIDAZOLE

Introduction

Substituting a methyl group in the 2 position of the imidazole ring gives a ligand of increased basicity (imidazole pK_a = 6.95, 2-methyl imidazole pK_a = 7.86) and of increased steric hindrance to coordination. No work had been published on the complexing ability of this ligand, and as substituents in the two position occurred in most of the herbicidal compounds, a study of this ligand was undertaken.

During the progress of this work, some complexes were reported[104], these were: $Cu(2Meim)_4Cl_2$, and $M(2Meim)_2X_2$ (M = Co, Ni, X = Cl, Br, I; M = Cu, X = Cl, Br). The complexes prepared here are: $M(2Meim)_4X_2$ (M = Co, X = I, NO_3; M = Ni, X = Cl, Br, I, NO_3; M = Cu, X = Cl, Br; M = Zn, X = NO_3), $Ni(2Meim)_{3.5}I_2$, $M(2Meim)_2X_2$ (M = Co, Ni, Zn, X = Cl, Br, I, NO_3; M = Cu, X = Cl, Br) and $Ni(2Meim)Cl_2$. As would be expected, no 6:1 complexes could be prepared, and small quantities of the "inner" complexes were often formed upon mixing the ligand and the metal salt solution.

Electronic Spectra and Magnetic Properties (Tables 4.1 and 4.2)

$Co(2Meim)_4I_2$ has a spectrum suggesting a tetrahedral structure. From comparison with $Co(im)_4(ClO_4)_2$ [82] and $Co(beim)_4(ClO_4)_2$ [137], the ligand field strength in a tetrahedral environment of 2-methyl imidazole (Δ = 5.25 kK) is greater than that of benzimidazole (Δ = 5.10 kK) but less than that of imidazole.

Two forms of the complex $Co(2Meim)_4(NO_3)_2$ were obtained. Form A was obtained by crystallisation of the complex from acetone solution whereas form B could be prepared only by rapid precipitation as an oil (Chapter 9). Form A is assigned as a tetragonally distorted octahedral structure. Assignment of the band at 6.8 kK as the E_g component of ν_1, and the band at 10.0 kK as the B_{2g} component gives a value of 0.37 kK for Dt. Form B has an electronic spectrum very similar to that of $Co(2Meim)_4I_2$, but the magnetic moment is too high for a tetrahedral environment. It could be that form B has both tetrahedral and octahedral sites in the lattice, or alternatively, the complex could be five coordinate square pyramidal, as a number of complexes of that coordination are known[56] which fit exactly a tetrahedral ligand field model, but which have high magnetic moments.

The complexes $Co(2Meim)_2X_2$ (X = Cl, Br, I) are assigned pseudo-tetrahedral structures, and the complex $Co(2Meim)_2(NO_3)_2$ has a similar spectrum to that of $Co(im)_2(NO_3)_2$, and presumably has a similar structure.

$Ni(2Meim)_4(NO_3)_2$ has an octahedral structure. It is interesting to note that for this complex, no band splitting is observed, whereas the equivalent cobalt complex shows a splitting of ν_1 of over 3kK as mentioned previously.

As is shown by the X-ray crystal structure, $Ni(2Meim)_4Br_2$, and the isomorphous $Ni(2Meim)_4Cl_2$, have a C_{4v} symmetry. Almost identical strong band systems are observed for the two complexes and these closely resemble the spectrum observed for $Ni(benzimidazole)_4Cl_2$,

Table 4.1

Electronic Spectra

$Co(2Meim)_4I_2$	~5.0vbr, 8.93s, 17.6vs, 18.6sh [a]
$Co(2Meim)_4(NO_3)_2$ [A]	6.80m, 10.0m, 18.9s, 19.9s, 21.2sh
$Co(2Meim)_4(NO_3)_2$ [B]	6.35br,sh, 8.90m, 17.1s, 18.5sh, [a]
$Co(2Meim)_2Cl_2$	4.65m, 6.20s, 7.45s, 8.90s, 16.0v s, 16.5vs, 17.3vs [a]
$Co(2Meim)_2Br_2$	~4.5m, 5.90sh,s, 6.85s, 8.50s, 15.1vs, 15.9vs, 17.3vs [a]
$Co(2Meim)_2I_2$	4.30s, 5.75s, 6.90s, 8.33s, 14.6vs, 15.4vs, 16.7vs [a] 27.0vs
$Co(2Meim)_2(NO_3)_2$	[b] 7.87m, 9.50m, 14.5m, 18.6s
$Ni(2Meim)_4Cl_2$	4.7m,br, 10.0w, 14.5m, ~17.4sh, 20.2sh, 24.4m
$Ni(2Meim)_4Br_2$	4.7m,br, 9.7w, 14.5m, ~17.1sh, ~20.0sh, 24.4s
(at 95°K)	5.0m,br, 10.3w, ~12.1sh, 15.0m, 17.3w, 21.5sh, 24.6s
$Ni(2Meim)_4I_2$	14.9vw, 22.0m
$Ni(2Meim)_4(NO_3)_2$	9.43w, 16.1w, 25.9w
$Ni(2Meim)_{3.5}I_2$	4.7br,w, 8.77w, 11.4m, 12.3m, 18.9s, 26.9vs
(at 95°K)	4.5br,w, 8.85w, 11.4m, 12.3w, 18.9s, 22.4sh, 25.9s
Ni(benzimidazole)$_2$ inner complex	5.4m, 8.9w, 12.1sh,w, 13.0w, ~16.3sh, 17.3m, 22.0m, 27.9s
$Ni(2Meim)_2Cl_2$	6.95m, 12.7m, 18.9sh, 22.6s
(at 95°K)	6.90m, ~8.2sh, 9.5sh, ~10.9sh, 13.1m, 18.6sh, 20.0sh, 22.8m
5% in $Zn(2Meim)_2Cl_2$	[b] 10.3, 12.2sh, 16.8sh, 18.3
$2x10^{-3}$ molar soln in acetone	-, 10.3 (ϵ = 46), 12.1sh, 17.8 (ϵ = 128)

Table 4.1 (continued)

$Ni(2Meim)_2Br_2$	5.8br,s, 6.7sh, 10.1s, 16.1s, 17.7s		
$Ni(2Meim)_2I_2$	[b] 6.9s, 10.0s, 15.4vs, 22.0vs, 23.8sh,vs, 27.6vs		
$Ni(2Meim)_2(NO_3)_2$	8.65w, ~13.3sh, 15.1m, 24.8m		
$Ni(2Meim)Cl_2$	~6.0sh, 7.30w, 11.8w, 12.8w, ~18.5sh, 20.6w		
$Cu(2Meim)_4Cl_2$	15.0vs	$Cu(2Meim)_2Cl_2$	9.5vs, 12.0vs, ~21.0sh, 26.8vs
$Cu(2Meim)_4Br_2$	15.9vs	$Cu(2Meim)_2Br_2$	8.77vs, 11.4vs, 20.6sh 25.0vs

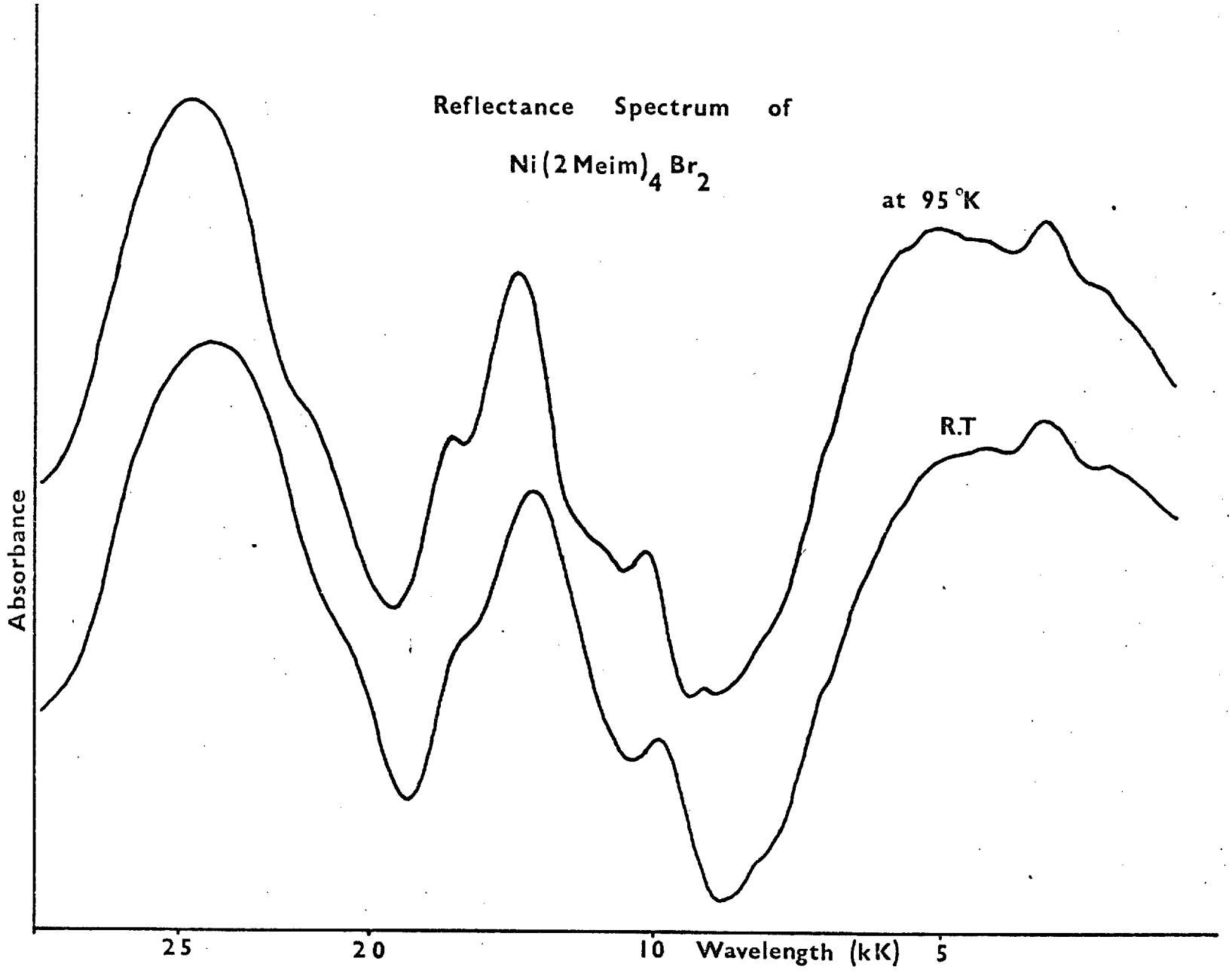
[a] Spin forbidden bands above 17 kK omitted

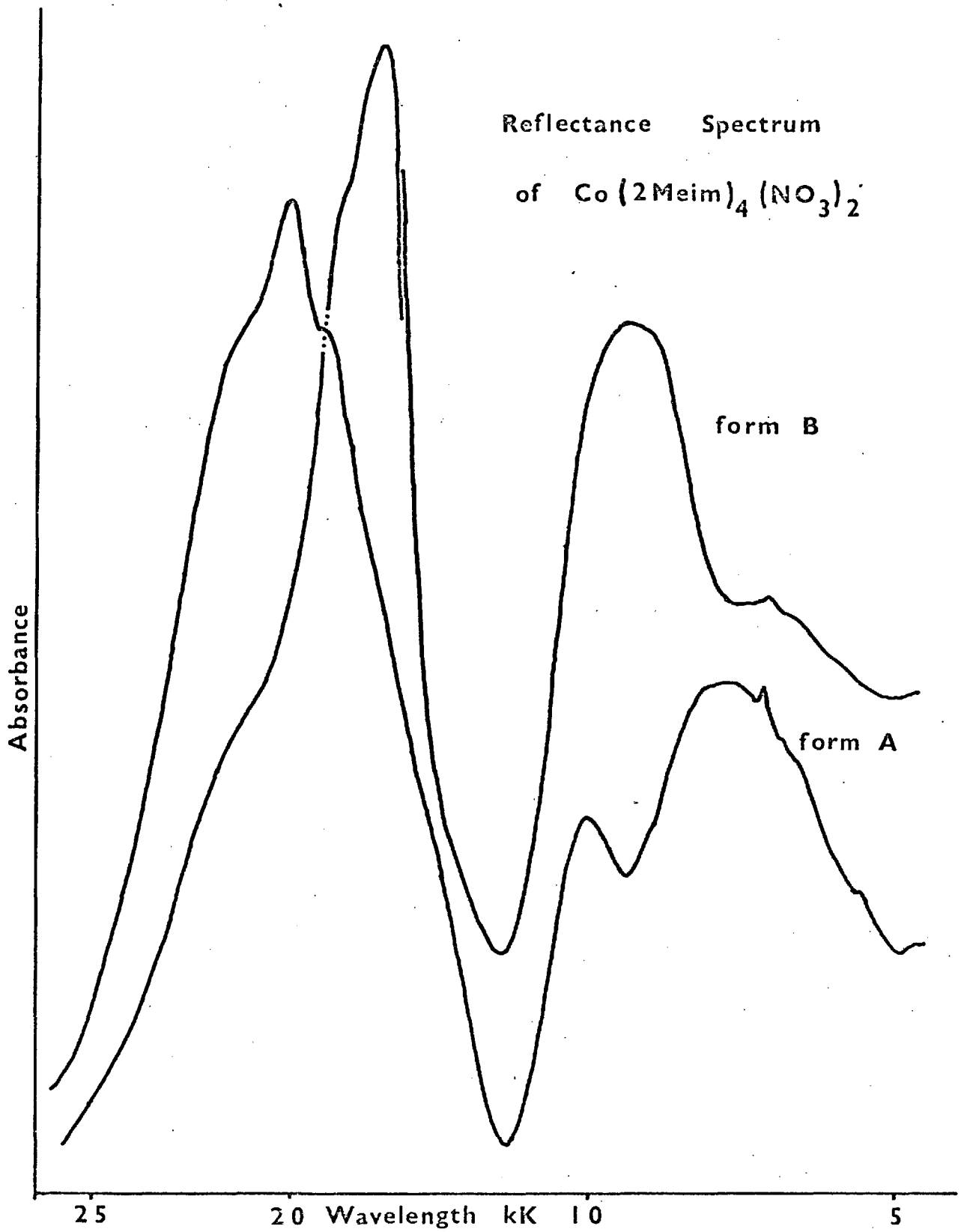
[b] Low energy bands obscured by ligand vibrations

Table 4.2

Magnetic Moments μ (B.M.)

$Co(2Meim)_4I_2$	4.28	$Ni(2Meim)_4(NO_3)_2$	3.19
$Co(2Meim)_4(NO_3)_2$ [A]	4.96	$Ni(2Meim)_2Cl_2$	3.20
$Co(2Meim)_4(NO_3)_2$ [B]	4.99	$Ni(2Meim)_2Br_2$	3.53
$Co(2Meim)_2Cl_2$	4.49	$Ni(2Meim)_2I_2$	3.41
$Co(2Meim)_2Br_2$	4.56	$Ni(2Meim)_2(NO_3)_2$	3.24
$Co(2Meim)_2I_2$	4.58	$Ni(2Meim)Cl_2$	3.48
$Co(2Meim)_2(NO_3)_2$	4.51	$Cu(2Meim)_4Cl_2$	1.79
$Ni(2Meim)_4Cl_2$	3.28	$Cu(2Meim)_4Br_2$	1.78
$Ni(2Meim)_4Br_2$	3.19	$Cu(2Meim)_2Cl_2$	1.88
$Ni(2Meim)_4I_2$	Diamagnetic	$Cu(2Meim)_2Br_2$	1.85
$Ni(2Meim)_{3.5}I_2$	2.61		


Reflectance Spectrum of
Ni(2Meim)4 Br2
at 95°K
R.T
Absorbance
25
20
10
Wavelength (kK)
5

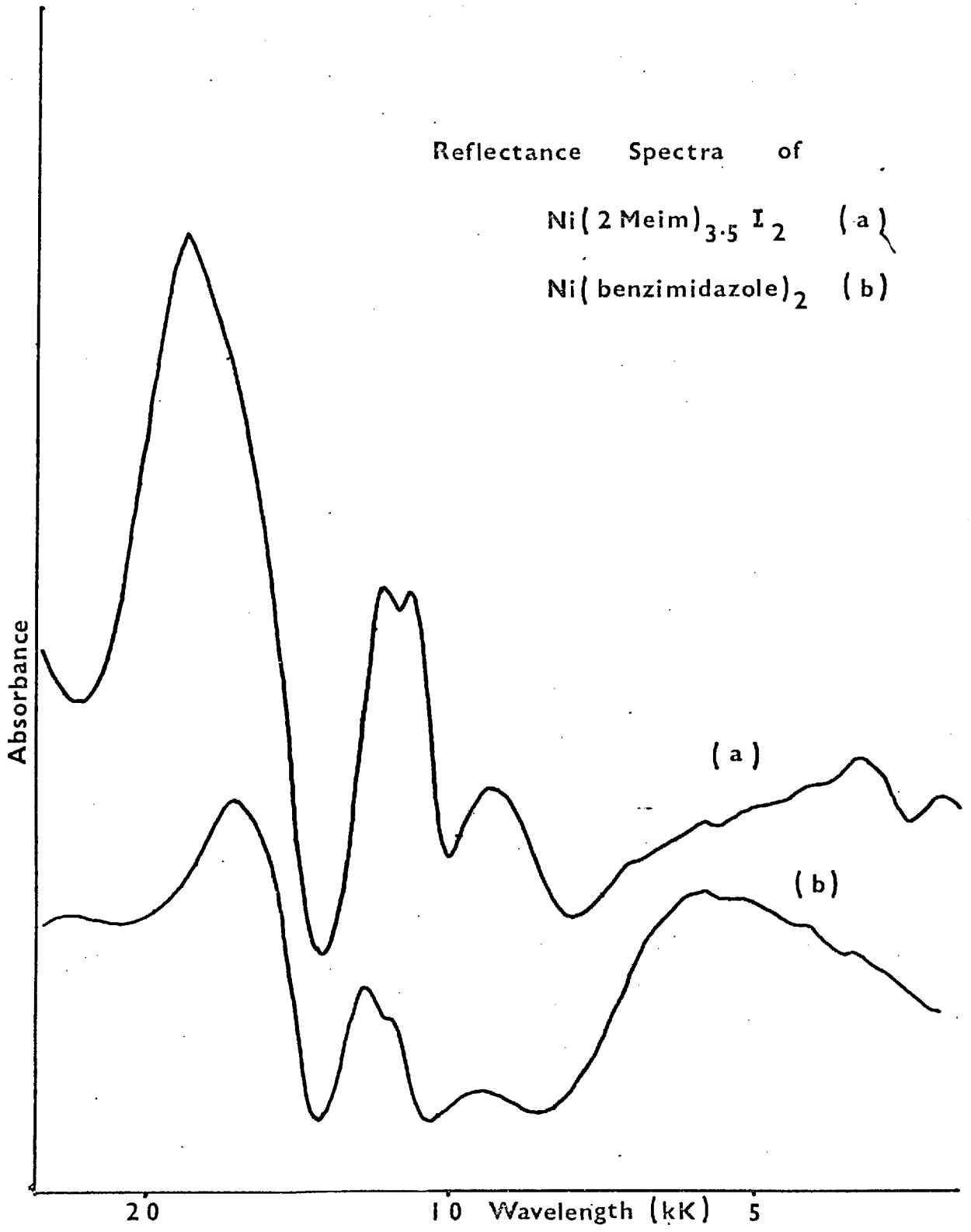

Reflectance Spectrum
of Co(2Meim)4(NO3)2
form B
form A
Absorbance
25
20
Wavelength kK
10
5

form V[95] (N.B., Ni(benzimidazole)$_4$Cl$_2$.2acetone (green form) has a dimeric structure[138], again with each nickel environment having C_{4v} symmetry). If the molecules are considered to have an essentially five coordinate, square pyramidal environment of the nickel atom, then Crampolini's model[47] may be used to assign the spectrum. Taking the ligands as five equivalent dipoles of strength 3.8D, with an angle of 100° between the vertical and the basal plane gives assignments of $^3B_1 \rightarrow {}^3E$ at 4.7 kK, $^3B_1 \rightarrow {}^3A_2$ and $^3B_1 \rightarrow {}^3B_2$ at ~ 10.0 kK, $^3B_1 \rightarrow {}^3E$ at 14.5 kK and $^3B_1 \rightarrow {}^3E(P)$ at 24.4 kK. It is doubtful if the $^3B_1 \rightarrow {}^3A_2(P)$ transition could be observed as it is a two electron transition in the strong field limit. Considering that the dipole strength increases with decrease in temperature, fitting these assignments to the spectrum of Ni(2Meim)$_4$Br$_2$ at 95°K gives the same band assignments except that the band at ~ 10.0 kK is split into two components, the lower component being $^3B_1 \rightarrow {}^3A_2$ and the higher being $^3B_1 \rightarrow {}^3B_2$ according to the model. A reversed assignment would seem more reasonable considering that the $^3B_1 \rightarrow {}^3B_2$ transition is a measure of the in plane ligand field, which is very unlikely to increase by as much as 2.4 kK on cooling. The band at 17.3 kK is difficult to explain. It could be the spin forbidden transitions to the coincident $^1B_1$ or ^1E levels, or alternatively, it could be that this is the $^3B_1 \rightarrow {}^3A_2(P)$ transition. The assignments suggested above are somewhat speculative, as in the case of these complexes there must be some interaction with the weakly bonded halide atom filling the sixth coordination position. To illustrate the difficulties of identifying

types of five coordination, one may consider the complex Ni(N-β-Diethylamine ethyl-5-chlorosalicylaldimine)$_2$, which has been shown to have a square pyramidal structure[139], and yet has a spectrum[140] which bears little resemblance to that observed here, whilst Ni(bis(2-methylaminoethyl)methyamine)Cl_2, a complex which is believed to have a very different structure[142] from that reported here, nevertheless has a remarkably similar spectrum.[141]

$Ni(2Meim)_4I_2$ has a planar structure. As has been mentioned for the planar imidazole complexes, the strong band observed in the visible spectrum is possibly the $^1A_{1g} \rightarrow {}^1A_{2g}$ transition. This assignment has been confirmed in the case of Ni(ethylenebisbiguanide)$_2$[143] though single crystal studies and a molecular orbital treatment on Ni(dipivaloylmethane)$_2$ indicate that all four spin allowed transitions occur under the single band envelope[144] for that complex. A weak band is observed here at 14.9 kK, (this has also been seen for some planar nickel benzimidazole complexes[95]) and may be assigned as one of the spin forbidden transitions.[94,145]

If this complex is heated at 80°K under vacuum, a complex is sometimes obtained of formula $Ni(2Meim)_{3.5}I_2$ (Chapter 9) which has an unusual electronic spectrum, unlike that of either the 4:1 or the 2:1 complex. It resembles that of very distorted pseudotetrahedral complexes, with the two components of ν_1 at 4.7 and 8.8 kK, ν_2 and the spin forbidden band arising from the $^1D_2$ free ion state (interacting by spin orbit coupling) at 11.4 and 12.3 kK, and the band at 18.9 kK being a component of ν_3. Nevertheless this does not explain


Reflectance Spectra of
Ni(2Meim)3·5 I2 (a)
Ni(benzimidazole)2 (b)
Absorbance
(a)
(b)
20
10
Wavelength (kK)
5

the low magnetic moment of 2.61 BM, combined with Curie Weiss law behaviour down to 80°K ($\theta = -48^{\circ}$). Postulation of an interallogon complex, namely equal numbers of planar $(NiN_4)^{2+}$ and pseudotetrahedral $(NiN_3I)^{+}$ chromophores in the lattice, would explain this, as the magnetic moment is the mean value of a low spin and a high spin nickel complex. A similar band system is observed in $Ni(NMeim)_2I_2$ (Chapter 3), though in that case there is no absorption in the 20 kK region. A more comparable system is the nickel "inner" benzimidazole complex. This complex was originally prepared by Ghosh[147], who reported it to have a magnetic moment of 3.09 BM, though as has been pointed out[137], his work appears to be far from reliable.

Dr M. Goodgame has made repeated attempts, using various preparative techniques, to obtain acceptable analysis results for samples of this compound but without success (of interest is that some samples give an inexplicable band in the electronic spectrum at 9.3 kK). Cordes and Walter[110] prepared the compound using the procedure reported for the cobalt inner complex[148], and made no mention of any difficulties in obtaining good analysis results. They report the infrared spectrum of the complex down to 33 K and assign the bands on the basis of a tetrahedral nickel environment, using the paramagnetism reported by Ghosh as the only evidence for this structure. Samples of this compound were prepared here using the technique of Brown and Aftergut[149], which also gave unacceptable analysis results, but which did appear to have reproducible electronic spectra. The spectrum of this compound, and the magnetic moment (~ 2.4 BM) suggests

the presence of both tetrahedral and planar (NiN_4) chromophores in the lattice. (One of the forms of the cupric inner imidazole complex[150] has alternate planar and flattened tetrahedral copper environments[151]). Thus as both (NiN_4) and (NiN_2I_2) units have been suggested as having very distorted pseudotetrahedral structures it seems not unreasonable to postulate the existence of (NiN_3I) pseudo-tetrahedral units in the complex $Ni(2Meim)_{3.5}I_2$ on the basis of a similar spectrum. Attempts to isolate the $[Ni(2Meim)_3I]^+$ species were unsuccessful, however ethanol solutions of $Ni(2Meim)_4I_2$ gave spectra similar to that of solid $Ni(2Meim)_{3.5}I_2$ suggesting that the $[Ni(2Meim)_3L]^{n+}$ (L = solvent or I) species exists in solution.

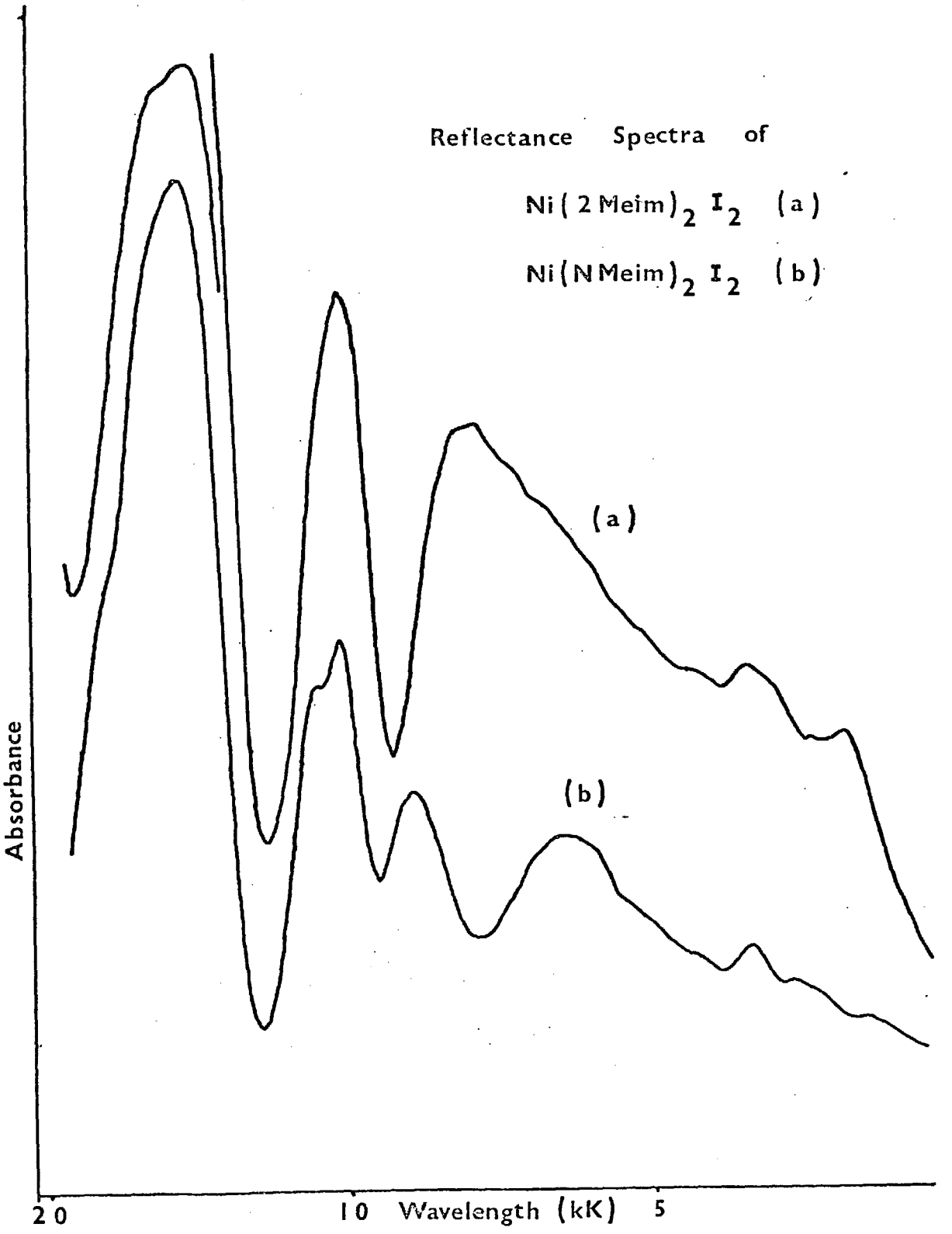
The spectrum of $Ni(2Meim)_2Cl_2$ indicates an octahedral structure for the complex. Although the spectrum has been dismissed as being typical of a polymeric octahedral complex[104], a three band system of medium intensity is extremely unusual for complexes of this type, and even at 95°K, no detectable band splitting is observed, indicating there is little departure from O_h symmetry. This is surprising, considering that the ligand field strengths of 2-methylimidazole and chloride ions are 9-10 kK and 6.6 kK[96] respectively, but it can be explained by considering that the steric hindrance of the 2-methyl group prevents a close approach of the ligand to the nickel-chlorine polymeric chain, thus weakening the axial ligand field to a similar value to that of the in-plane field. The steric effects may also cause loss of the centre of symmetry, which would account for the enhanced intensity of the bands. As $Ni(NMeim)_2Cl_2$ is pseudotetrahedral,

it seems surprising that with the much more sterically hindered $Ni(2Meim)_2Cl_2$, a polymeric octahedral structure is preferred. This structure can be only marginally favoured as the complex exists in a pseudotetrahedral environment in acetone solution and diluted in the tetrahedral $Zn(2Meim)_2Cl_2$ complex. The magnetic moment of the complex measured here is lower than that reported previously[104], and is lower than the values usually observed for complexes of this class[153].

The complexes $Ni(2Meim)_2Br_2$ and I_2 have spectra characteristic of pseudotetrahedral structures. The bands are less split than in the N-methyl imidazole complexes, which would indicate an electronic symmetry closer to that of T_d. The lower intensity ratio of ν_2/ν_1 in the 2-methyl imidazole complexes also suggests this, as although the two electron transition in the strong field limit is ν_2 in T_d symmetry, in C_{2v} symmetry it is a component of ν_3[45], thus qualitatively the ratio would be expected to increase upon increasing the distortion of the ligand field.

The spectrum of $Ni(2Meim)_2(NO_3)_2$ more closely resembles that of an octahedral complex than does that of the cobalt analogue, in spite of the fact that the X-ray spectra are very similar. This has been observed previously for other bidentate nitrato complexes[154].

The complexes $Cu(2Meim)_2Cl_2$ and Br_2 have a very intense pair of absorption bands, in the near infrared, as is observed for pseudotetrahedral complexes[33]. The magnetic moment of these two


Reflectance Spectra of
Ni(2Meim)2 I2 (a)
Ni(NMeim)2 I2 (b)
(a)
(b)
Absorbance
20
10
Wavelength (kK)
5

pseudotetrahedral complexes is not much higher than the values for the 4:1 complexes, which would confirm that electronic symmetry is less than T_d [155].

Vibrational Spectra 2000 - 400 K

Studies were made of the infrared (and Raman for zinc) spectra in order to determine the position of the nitrate vibrations. Unfortunately, 2-methyl imidazole vibrations were found to make unambiguous assignment of the nitrate vibrations impossible. The spectra of both forms of $Co(2Meim)_4(NO_3)_2$ were very similar.

Vibrational Spectra 400 - 80 K

2-methyl imidazole has the following active bands in this region:

I.R. 374m, 353s, 265s, 163m, 149s, 128w, 114m, 96s

R 268m, 168w, 148vs

Upon complexing, the infrared active bands at 374 and 353 K are replaced by a single band in the 380 - 390 K region, which is also observed in the Raman spectrum. The band at 265 K moves to about 280 K and can be identified in all of the complexes. This band probably obscures metal-ligand stretching vibrations in many of the complexes.

$M(2Meim)_4X_2$ Complexes (Table 4.4)

The spectra of $Co(2Meim)_4I_2$ and $Zn(2Meim)_4(NO_3)_2$ show considerable resemblance. From the electronic spectrum and magnetic moment of the former and the infrared and Raman nitrate band positions of the latter, they are both considered to have tetrahedral structures, with assignments of the antisymmetric M-N stretch at ~ [illegible] K (Zn, Co)

Table 4.4

Vibrational Spectra 400 - 90 K for $M(2Meim)_4X_2$ Complexes

$Co(2Meim)_4I_2$		Ir	388s, 286s, 277sh, 163s
$Co(2Meim)_4(NO_3)_2$	[A]	Ir	384s,br, 280s, 230s,vbr, 110s,br
$Co(2Meim)_4(NO_3)_2$	[B]	Ir	423s, 383s, 312m, 278s, ~180 vbr, 110s,br
$Ni(2Meim)_4Cl_2$		Ir	385s, 277s, 243s, 135s,br
$Ni(2Meim)_4Br_2$		Ir	386s, 281s, 243m, 218m, 133w, 111m, 92s
$Ni(2Meim)_4I_2$		Ir	424s, 400w, 365w, 292w, 280w, 95w
		R	406w, 373w, 309w, 228m, 214s, 196w
$Ni(2Meim)_{3.5}I_2$	[a]	Ir	414s, 384s, 357m, 283s,br, 259m, 191s, 175s, 164s, 152s, 92s,vbr
$Ni(2Meim)_4(NO_3)_2$		Ir	391s,br, 286s, 257m, 213w, ~195m,vbr, 110mbr
$Cu(2Meim)_4Cl_2$		Ir	389s, 283s, 256w, 215m, 125s,br
$Cu(2Meim)_4Br_2$		Ir	388s, 284s, 260w, 214s, 160s, 93s
$Zn(2Meim)_4(NO_3)_2$		Ir	388mbr, 275s, 174s
		R	382s, 280s, 213w

[a] Included here for comparison with $Ni(2Meim)_4I_2$

(coincident with the ligand mode), the symmetric M-N stretch at 213 K (Zn), and possibly the F_1 bending mode at ~ 170 K (Zn, Co), though it seems surprising that the zinc complex vibrations should be at similar energies to those of the cobalt complex.

One would expect the metal-oxygen asymmetric stretch in the other nitrate complexes to appear at about 280 K[108], however it may be that steric interaction reduces this to 257 K (Ni) and 230 (Co, form B). The presence of the bands at 423 and 312 K in $Co(2Meim)_4(NO_3)_2$ form A is confirmatory evidence that this is not a tetrahedral species, and surprisingly the band system resembles that of $Ni(2Meim)_4I_2$.

If the 4:1 nickel chloride and bromide complexes are assumed to have the structure $[Ni(2Meim)_4X]X$, then two nickel-nitrogen and one nickel-halogen vibrations should be infrared active. One of the nickel-nitrogen bands is at 243 K and the other may be obscured by the ligand band at 280 K. The nickel-bromine stretch is at 218 K, and taking the relationship $\nu(M-Br)/\nu(M-Cl) = 0.74$[168], the nickel-chlorine stretch would be expected to occur in the region of the 280 K ligand vibration.

Assignment of bands for the planar $Ni(2Meim)_4I_2$ complex is discussed in Chapter 5.

<u>$M(2Meim)_2X_2$ and $M(2Meim)X_2$ Complexes</u> (Tables 4.5 and 4.6)

Assignments of these complexes are given in Table 4.5. As in the case of $Zn(NMeim)_2I_2$, the solution Raman spectrum of $Zn(2Meim)_2I_2$ would suggest the zinc-iodine stretch to be at about 145 K.

Table 4.6

Vibrational Spectra 400 - 90 K for $M(2Meim)_2X_2$ Tetrahedral Complexes

		ν(M-X)	ν(M-N)	Other Bands
$Co(2Meim)_2Cl_2$	Ir	316s, 305s	233w	384s, 272m[a], 163s,br, 114m
$Co(2Meim)_2Br_2$	Ir	241m[a], 189s	-	382s, 269s,br[a], 178m, 145s, 94m
$Co(2Meim)_2I_2$	Ir	212s	260m	382s, 272s[a], 167s[b], 140m
$Ni(2Meim)_2Br_2$	Ir	233s[a], 189s	-	382s, 268s[a], 150sh, 137s, 92w
$Ni(2Meim)_2I_2$	Ir	208s	~250sh	382s, 267s[a], 180s[b] 137s
$Cu(2Meim)_2Cl_2$	Ir	294s,br	237w	385s, 266m[a], 217m, 173s, 151s, 130w,br, 110m
$Cu(2Meim)_2Br_2$	Ir	251m[a], 199m	-	383s, 271s[a], 180s, 158s, ~100m,br
$Zn(2Meim)_2Cl_2$	Ir	302sh, 287s	240m	382s, 257s, 162s,br, 125s
	R	295m	237m	388w, 280s, 151w
$Zn(2Meim)_2Br_2$	Ir	216s[a], 192s	246s,br	381s, 268s, 161s, 147m, 92s
	R	195s	246w	367w, 288m, 276s, 195s, 179m, 145w
	R[c]	191s,polarised	-	392m, 278m, 174w
$Zn(2Meim)_2I_2$	Ir	195s, 140m	242s, 226m	380s, 265s, 175s
	R	148s	-	385w, 277m, 180m
	R[c]	145s,polarised	-	392m, 275m, ~180sh

[a] Possibly also contains ν(M-N) band
[b] Possibly component of ν(M-I)
[c] Acetone solution

Table 4.5

Vibrational Spectra 400 - 90 K for Other Complexes

$Co(2Meim)_2(NO_3)_2$	Ir 382m, 286s, br, 270sh, 185s, 140m, vbr, 96m
$Ni(2Meim)_2(NO_3)_2$	Ir 384m, 306s, 287s, 194m, 177m, 100w
$Zn(2Meim)_2(NO_3)_2$	Ir 386s, 294sh, 277s, br, 254sh, 170m, ~125vbr
	R 394w, 277m, 237m, 169m
$Ni(2Meim)_2Cl_2$	Ir 388m, br, 267m, br, ~225s, vbr, ~180s, vbr
$Ni(2Meim)Cl_2$	Ir 387w, br, 267m, ~200s, vbr

In contrast to the spectra obtained for $Ni(im)X_2$ and $Ni(NMeim)X_2$ (X = Cl, Br), the band systems observed for both the 2:1 and 1:1 nickel chloride complexes are very broad. Similar broad absorption has been observed in the case of $Ni(di\text{-}2\text{-}pyridylamine)Cl_2$ [125].

CHAPTER V

COMPLEXES OF 1,2-DIMETHYL IMIDAZOLE

Introduction

1,2-Dimethyl imidazole has been patented as a herbicidal compound,[216] and, as a preliminary investigation of its reactions with metal salts showed a quite different coordination behaviour from 2-methyl imidazole, a detailed study was undertaken.

The complexes prepared were:- $Co(1,2\ DiMeim)_4X_2$ (X = I, NO_3), $Co(1,2\ DiMeim)_2X_2$ (X = Cl, Br, I, NO_3), $Ni(1,2\ DiMeim)_4X_2$ (X = Cl, Br, I, NO_3), $Cu(1,2\ DiMeim)_4X_2$ (X = Br, NO_3), $Cu(1,2\ DiMeim)_3Cl_2$, $Cu(1,2\ DiMeim)_2X_2$ (X = Cl, NO_3), $Zn(1,2\ DiMeim)_4(NO_3)_2.H_2O$, $Zn(1,2\ DiMeim)_2X_2$ (X = Cl, Br, I, NO_3).

A ligand to metal ratio of 4:1 was far more difficult to obtain with this ligand. Whereas with 2 methyl imidazole 4:1 nickel halide complexes were all readily obtainable, with 1,2 dimethyl imidazole the chloride and bromide complexes were only obtainable with difficulty.

Most pseudotetrahedral nickel halide complexes are hygroscopic, but the complexes of this type reported here are quite stable.

Electronic Spectra and Magnetic Properties (Tables 5.1 and 5.2)

$Co(1,2\ DiMeim)_4I_2$ and $Co(1,2\ DiMeim)_4(NO_3)_2$ have spectra suggesting a tetrahedral structure, with a ligand field strength (Δ = 5.2 kK) slightly less than that of $Co(2\ Meim)_4I_2$.

The 2:1 cobalt and nickel halide complexes have spectra characteristic of pseudotetrahedral species. The highest energy compound of ν_2 in the spectrum of $Co(1,2\ DiMeim)_2Cl_2$ at 8.58 kK is at noticeably lower energy than the same band in the equivalent N methyl imidazole (9.09 kK) and 2 methyl imidazole (8.90 kK) complexes, whereas the other two components are only shifted by much smaller amounts. This would support the theory that the highest energy component is more sensitive to steric effects of the ligands[91], though the band shifts in the spectra of the bromide and iodide complexes do not show this effect so clearly.

The planar complexes $Ni(1,2DiMeim)_4Cl_2$ and $Ni(1,2DiMeim)_4Br_2$ are yellow, but the microcrystalline iodide complex is red. This colouration is observed in the electronic spectrum as strong absorption on the high energy side of the single band at 22.0 kK, which would indicate an interaction with the iodide ions.

The complex $Ni(1,2DiMeim)_4(NO_3)_2.CCl_4$ has an octahedral structure, and the spectra of $Co(1,2DiMeim)_2(NO_3)_2$ and $Ni(1,2DiMeim)_2(NO_3)_2$ closely resemble those of the equivalent 2 methyl imidazole complexes.

Various structures can be postulated for the complex $Cu(1,2DiMeim)_3Cl_2$, the most likely being that of a monomeric trigonal bipyramid. The spectrum resembles that of $dienH_3CuCl_5$[218], and reasonable values of the parameters of Allen and Hush [218] of $\Delta_1^* = 1.2$ and $\Delta_2^* = 1.1$ kK may be obtained if the assignments $^2A_1' \rightarrow {}^2E'$ at 10.5 kK and $^2A_1' \rightarrow {}^2E''$ at 13.2 kK are adopted. Though the $^2A_1' \rightarrow {}^2E''$ transition is symmetry forbideen, it has become generally accepted that it appears

Table 5.1

Diffuse Reflectance Spectra (kK)

$Co(1,2DiMeim)_4I_2$		~ 4.7m,br, 8.80s, 14.7sh, 17.4vs, 18.4s,sh [a]
$Co(1,2DiMeim)_4(NO_3)_2$		~ 4.7m,br, 8.77s, 17.4vs, 18.4s,sh [a]
$Co(1,2DiMeim)_2Cl_2$		~ 5m,br, 6.25s, 6.99s, 8.58s, 15.7vs, 16.2vs, 17.0vs [a]
$Co(1,2DiMeim)_2Br_2$		~ 4.5m,br, 6.25s, 6.78s, 8.54s, 15.1vs, 15.9vs, 16.8vs [a]
$Co(1,2DiMeim)_2I_2$		~ 4.3m,br, 5.7s,sh, 6.62s, 8.30s, 14.5vs,sh, 15.3vs, 16.5vs [a], 26.8vs
$Co(1,2DiMeim)_2(NO_3)_2$	[d] [c]	7.9m, 8.8m, 13.4m, 18.5s
$Ni(1,2DiMeim)_4Cl_2$	[d]	23.2m
$Ni(1,2DiMeim)_4Br_2$		13.3w, 22.8s
$Ni(1,2DiMeim)_4I_2$		22.2vs [b]
$Ni(1,2DiMeim)_4(NO_3)_2.CCl_4$		9.52m, 15.8m, 25.8m
$Ni(1,2DiMeim)_2Cl_2$	[c]	5.83s, 8.47m, 10.65s, 12.1sh, 17.5vs
$Ni(1,2DiMeim)_2Br_2$	[c]	5.92s, 7.81m, 10.3s, 11.8sh, 17.2vs.
$Ni(1,2DiMeim)_2I_2$	[c]	6.41s, 7.7s, 9.95s, 15.4sh, 16.3vs, 22.7vs, 24.4vs
$Ni(1,2DiMeim)_2(NO_3)_2$	[d]	8.86m, 15.6s, 24.7s
$Cu(1,2DiMeim)_4Br_2$	[d]	16.4m
$Cu(1,2DiMeim)_4(NO_3)_2$	[d]	18.2m
$Cu(1,2DiMeim)_3Cl_2$	[d]	10.5s,sh, 13.2s
$Cu(1,2DiMeim)_2Cl_2$	[d]	8.7s, 11.1s, 28.6vs
$Cu(1,2DiMeim)_2(NO_3)_2$	[d]	15.4vs.

[a] The spin forbidden bands observed above ν_3 have been omitted.

[b] Shoulder on high energy side of band.

[c] Absorption below 5 kK.

[d] These spectra were obtained using a linear wavelength model, Beckman DK2-A.

Table 5.2

Magnetic Moments (B.M.)

$Co(1,2DiMeim)_4I_2$	4.46	$Ni(1,2DiMeim)_2Cl_2$	3.51
$Co(1,2DiMeim)_4(NO_3)_2$	4.45	$Ni(1,2DiMeim)_2Br_2$	3.49
$Co(1,2DiMeim)_2Cl_2$	4.69	$Ni(1,2DiMeim)_2I_2$	3.42
$Co(1,2DiMeim)_2Br_2$	4.57	$Ni(1,2DiMeim)_2(NO_3)_2$	3.14
$Co(1,2DiMeim)_2I_2$	4.70	$Cu(1,2DiMeim)_4Br_2$	1.79
$Co(1,2DiMeim)_2(NO_3)_2$	4.45	$Cu(1,2DiMeim)_4(NO_3)_2$	1.79
$Ni(1,2DiMeim)_4Cl_2$	diamagnetic	$Cu(1,2DiMeim)_3Cl_2$	1.76
$Ni(1,2DiMeim)_4Br_2$	diamagnetic	$Cu(1,2DiMeim)_2Cl_2$	1.84
$Ni(1,2DiMeim)_4I_2$	diamagnetic	$Cu(1,2DiMeim)_2(NO_3)_2$	1.87
$Ni(1,2DiMeim)_4(NO_3)_2.CCl_4$	3.21		

as a strong absorption[53,193,218,219]. It has been suggested that the two bands which are often observed in the 10 kK region are in fact components of the $^2A_1' \rightarrow {}^2E''$ transition split by the Jahn Teller effect[53].

The strong pair of bands observed in the spectrum of $Ci(1,2DiMeim)_2Cl_2$ centred about 10 kK would suggest a pseudotetrahedral structure.

Vibrational Spectra

The complex $Ni(1,2DiMeim)_4(NO_3)_2$ could only be obtained with solvent molecules in the lattice, any attempt at removal of the solvent causing simultaneous loss of ligand. Acetone, 2,2dimethoxypropane, or carbon tetrachloride can be occluded in the lattice, but only with carbon tetrachloride could an acceptable analysis be obtained. A band is observed at 1738 K in the acetone containing complex, indicating that the solvent is not bonded[157]. The complex containing carbon tetrachloride shows bands at 787 K and 452 K which may be assigned as a component of ν_3 and ν_1 respectively, of the CCl_4 molecule[214,215]. The other component of ν_3 at about 760 K and ν_2 and ν_4 are obscured by vibrations of the complex.

The free ligand has the following active bands in the low energy region(-

I.r.	~ 295 w,sh, 264 m, 93w,
R	295 w,sh, 273s, 210s.

From comparison with the spectra of N methyl imidazole and 2 methyl imidazole, the Raman band at 273 K would appear to be

$\gamma(CH_3\text{-}C)$ and that at 210 K to be $\gamma(CH_3\text{-}N)$, but it is surprising that bands are not present in the infra red spectrum at these values. Bands are observed at about 310 and 270 K in the infra red spectra and at about 310, 280 and 250 K in the Raman spectra of most of the complexes, thus identification of ν(M-N) and ν(M-X) vibrations is difficult.

M(1,2DiMeim)$_4X_2$ complexes (Table 5.3)

The similarity of the spectra of Co(1,2DiMeim)$_4(NO_3)_2$ and Zn(1,2DiMeim)$_4(NO_3)_2.H_2O$, both in the infrared and far infrared regions, would suggest that both complexes have tetrahedral metal environments. Between 400 and 90K, these two complexes and Co(1,2DiMeim)$_4I_2$ show infrared active bands at 282K (Co) and 257K (Zn) which may be assigned as the antisymmetric M-N stretch, and the band at about 230K in the cobalt complexes may well be the symmetric M-N stretch.

The bands of the planar nickel complexes are very difficult to assign. Using similar assignments to those in Chapter 2, the components of ν_6 (E_u) would either be the two bands at ~ 380 K (424 K in Ni(2Meim)$_4I_2$) or else part of the band system at ~ 260K. The bands in the Raman spectra of the bromide and chloride at ~ 330K and ~ 280 K are most probably ligand vibrations (though no banfs are observed in these positions in the iodide complex), in which case the bands below 240 K must be ν_1 (A_{1g}) and ν_2 (B_{1g}). The iodide shows considerable band splitting, which would suggest

Table 5.3

Vibrational Spectra 400-90 K of $M(1,2Dimeim)_4X_2$ Complexes

$Ni(1,2DiMeim)_4Cl_2$	i.r.	387s, 378s, 310w,sh, 272s, 262sh, 184w, 125s, 100sh
	R	328m, 278m, 208sh, 194m
$Ni(1,2DiMeim)_4Br_2$	i.r.	386s, 377s, 310w, 278sh, 263s, 248sh, 183m, 100s,br
	R	327s, 275s, 237w, 207s, 192m
$Ni(1,2DiMeim)_4I_2$	i.r.	392s, 360m, 302m, 265m, 249s, 230m, 92s.
	R	218w, 143vs
$Ni(1,2DiMeim)_4(NO_3)_2.CCl_4$	i.r.	330w,sh, 285s, 261s, 232s, 200-80w,vbr
$Co(1,2DiMeim)_4I_2$	i.r.	305m, 282s, 267sh, 232w, 135w, 98w
$Co(1,2DiMeim)_4(NO_3)_2$	i.r.	305m, 283s, 234w, 132s,br, 95s
$Cu(1,2DiMeim)_4Br_2$	i.r.	290s,br, 237m, 200m, 100s,br
$Cu(1,2DiMeim)_4(NO_3)_2$	i.r.	290s,br, 243m, 204w, 125w,vbr, 98m
$Zn(1,2DiMeim)_4(NO_3)_2.H_2O$	i.r.	305w,sh, 272s, 256s, 230sh,br, 125m,vbr.
	R	308m, 278s, 244m, 186w.

that the iodide ions are close enough to cause steric hindrance.

M(1,2DiMeim)$_2$X$_2$ pseudotetrahedral complexes (Table 5.4)

Assignments of the metal halogen stretching modes are given in Table 5.4. The shifts in position of the ligand vibrations in this series of complexes would indicate that coupling is occurring between these vibrations and the skeletal vibrations of the complexes, thus making definitive assignment of the ν(M-N) modes difficult.

Table 5.4

Vibrational Spectra 400 - 90 K of Pseudotetrahedral $M(1,2DiMeim)_2X_2$ complexes

	ν(M-X)	Other bands
$Co(1,2DiMeim)_2Cl_2$	i.r. 319s, 300s	271sh, 264s, 232m, 127s, vbr, 107sh
$Co(1,2DiMeim)_2Br_2$	i.r. 249s[a] 181s	302w, sh, 270s, 230sh, 131s, br
$Co(1,2DiMeim)_2I_2$	i.r. 213s, 165s	304w, sh, 270s, 249m, 237m, 223sh, 130s
$Ni(1,2DiMeim)_2Cl_2$	i.r. 321s, 290s	265m, 251w, 233w, 129s, 105sh
$Ni(1,2DiMeim)_2Br_2$	i.r. 248s[a] 179s	310w, sh, 272s, 232s, 141m, br
$Ni(1,2DiMeim)_2I_2$	i.r. 210s, 168m	274s, 262m, 254m, 238m, 136m
$Cu(1,2DiMeim)_2Cl_2$	i.r. 297s	282m, 272m, 261s, 242sh, 158s, 130w, 100w
$Zn(1,2DiMeim)_2Cl_2$	i.r. 294s	254m, 224s, 194w, 128s, 105m, vbr
	R 289s	255s, 238w, 202s, 113s
$Zn(1,2DiMeim)_2Br_2$	i.r. 180s	306w, sh, 274s, 239s, 225s, 209s, 154m, 139s
	R 184s	312w, 284m, 252m, 240sh, 214w.
$Zn(1,2DiMeim)_2I_2$	i.r. 195s	273s, 237m, 229s, 206s, 164m, 131s, vbr
	R	310w, 281w, 250m, 218w, 199w, 168s, 142s, 127w.

[a] Possibly component of ν(M-N)

Table 5.5

Vibrational Spectra 400 - 90 K of Other Complexes

$Cu(1,2DiMeim)_3Cl_2$	i.r.	310s, 274s, 267s, 258sh, 218s,br, ~ 200s, 154s, 135sh, 100m,br
$Co(1,2DiMeim)_2(NO_3)_2$	i.r.	~ 290sh, 274s,br, 243m, 143m, 93m
$Ni(1,2DiMeim)_2(NO_3)_2$	i.r.	302s,br, 279s, 261s, 238m, ~ 185w,br, 152m, 130w, 95w,br
$Cu(1,2DiMeim)_2(NO_3)_2$	i.r.	318s, 292s, 268m, 240sh, 213w, 187s, 170sh, 110m,vbr
$Zn(1,2DiMeim)_2(NO_3)_2$	i.r.	292sh, 280s, 254s, 236sh, 158m, 130m,br, 90m.

CHAPTER VI

COMPLEXES OF 2-METHYL BENZIMIDAZOLE

Introduction

2-Methyl benzimidazole has been patented as a herbicidal compound[11] and although some complexes have been reported, no comprehensive study has been undertaken. The preparations of $Cu(2Mebeim)_2X_2$ (X = Cl, Br, NO_3) and $Co(2Mebeim)_2X_2$ (X = Cl, Br) have been reported[84,148] and the complexes $Ni(2Mebeim)_2X_2$ (X = Cl, Br, I, NCS) have been studied in detail.[152]

The complexes $M(2Mebeim)_2X_2$ (M = Co, Ni, Zn; X = Cl, Br, I, NO_3; M = Cu, X = Cl, Br, NO_3) have been prepared and studied here. No complexes could be obtained with a ligand to metal ratio of greater than 2:1.

Electronic Spectra and Magnetic Properties (Tables 6.1 and 6.2)

As has been discussed, the nickel halide complexes must have very distorted pseudo tetrahedral structures in order to give a splitting of ν_3 of the order of 3kK, and yet even at about 90°K only a single band is observed in the region of ν_1[84,152] and dilution of the nickel chloride complex in the isomorphous zinc chloride complex which should provide even better resolution[30], gives an almost identical spectrum to the undiluted complex. Although it has been suggested that the components of ν_1 may fortuitously be very little split[152], from comparison with the complexes $Ni(NMeim)_2X_2$ (X = Cl, Br, I) (Chapter 3) it seems more likely that a component of ν_1 is within the ν_2 band envelope.

The copper halide complexes would appear to have weakly bridging octahedral structures on the bases of the electronic spectra, similar to those of the equivalent pyridine complexes[129,127]. The bands are at higher energy than in the equivalent benzimidazole complexes[156], which would indicate not that the ligand field is stronger, but that there is a greater tetragonal distortion[34]. In the bromide case, the width of the charge transfer band almost obscures the d-d transitions.

The cobalt halide complexes have pseudo tetrahedral structures and the nitrate complexes have the usual six coordinate structures.

Vibrational Spectra (Table 6.3)

The nitrate band positions would indicate the presence of bidentate nitrate groups. The ν_3 bands in the nickel case are considerably broader than those in the other complexes.

Vibrational Spectra 400-90K (Tables 6.4 and 6.5)

The low frequency spectrum of 2-methyl benzimidazole is listed below:-

I.r. 324w, 285m, 270sh, 261s, 197m,br, 132w.

R. 334w, 281w, 123s.

The profusion of ligand modes makes assignment of the bands in the complexes exceedingly difficult. In the case of the pseudo-tetrahedral complexes, tentative band assignments are given, however in no case could all four stretching vibrations be identified.

Table 6.1

Electronic Spectra (kK)

$Co(2Mebeim)_2Cl_2$	4.55s,br, 6.15s, 7.3s, 8.8s, 15.9vs, 16.2sh, 17.4vs, [a]
$Co(2Mebeim)_2Br_2$	4.17s,br, 5.65s, 6.9s, 8.7s, 15.3vs, 15.6vs, 17.2vs, [a]
$Co(2Mebeim)_2I_2$	~4.0s,br, 5.65s, 6.85s, 8.5s, 14.8vs, 15.1sh, 16.7vs, [a] 26.8vs.
$Co(2Mebeim)_2(NO_3)_2$	~4.0m,br, 7.45m, 8.7sh, 14.1m, 18.2s, ~21.3sh.
$Ni(2Mebeim)_2Cl_2$ (diluted 10% in $Zn(2Mebeim)_2Cl_2$)	6.6br, 10.1, 12.2sh, 15.0, 17.7.
$Ni(2Mebeim)_2(NO_3)_2$	9.1m, 13.3sh, 15.7m, 23.3sh, 24.6m.
$Cu(2Mebeim)_2Cl_2$	13.2s, ~17.0sh, 23.3s,br.
$Cu(2Mebeim)_2Br_2$	14.5sh, 16.4m, 23.8s,br.
$Cu(2Mebeim)_2(NO_3)_2$	~13.7sh, 17.2m, 26.8s.
at 95°K	13.9m, 17.9m, 26.5s.

[a] High energy spin forbidden bands omitted.

Table 6.2

Magnetic Moments (B.M.)

$Co(2Mebeim)_2Cl_2$	4.46	$Ni(2Mebeim)_2(NO_3)_2$	3.05
$Co(2Mebeim)_2Br_2$	4.57	$Cu(2Mebeim)_2Cl_2$	1.78
$Co(2Mebeim)_2I_2$	4.59	$Cu(2Mebeim)_2Br_2$	1.76
$Co(2Mebeim)_2(NO_3)_2$	4.47	$Cu(2Mebeim)_2(NO_3)_2$	1.75

Table 6.3

Nitrate Group Frequencies (K)

		ν_3	ν_1	ν_2	ν_4
$Co(2Mebeim)_2(NO_3)_2$	i.r.	1490s, 1270s	1014m	808m	Obscured by
$Ni(2Mebeim)_2(NO_3)_2$	i.r.	1480s,br, 1270s,br	1011m	805m	ligand ring
$Cu(2Mebeim)_2(NO_3)_2$	i.r.	1440s, 1290s	1026m	809m	breathing modes
$Zn(2Mebeim)_2(NO_3)_2$	i.r.	1475s, 1280s	1017m	812m	
	R.	-	1018s	-	

Table 6.4

Vibrational Spectra 400 - 90 K of Pseudotetrahedral Complexes

		ν(M-L)	ν(M-X)	Other bands
$Co(2Mebeim)_2Cl_2$	i.r.	229w, 210w	311s, [a]	326m, 297sh, 280m, 178m, 150s, 130s, 106m.
$Co(2Mebeim)_2Br_2$	i.r.	210m	249s, 236s[b]	329w, 321w, 302s, 287m, 279m, 170s, 129s, 100m, br.
$Co(2Mebeim)_2I_2$	i.r.	218sh	208s	329m, 299s, 282s, 174w, 120m.
$Ni(2Mebeim)_2Cl_2$	i.r.	211m	315s, [a]	330sh, 305s, 282m, 177m, 167m, 154m, 125m, 109w.
$Ni(2Mebeim)_2Br_2$	i.r.	202w	246s, 238m[b]	329m, 322m, 304s, 291w, 280m, 174m, 128m, 100m, br.
$Ni(2Mebeim)_2I_2$	i.r.	226m, 200m	216m	330m, 323m, 302s, 283m, 279m, 174w, 153m, 112s.
$Zn(2Mebeim)_2Cl_2$	i.r.	197s	[a]	330w, 322w, 303s, 287s, 280w, 176w, 152s, 125s.
	R	-	-	309w, 290m, 184w, 144s, 104m.
$Zn(2Mebeim)_2Br_2$	i.r.	189s	229s, 218s	329w, 321w, 297m, 286m, 278w, 170m, 131m, 100w, br.
	R	-	226m	171m, 139s, 98sh

Table 6.4 (continued)

		ν(M-L)	ν(M-X)	Other bands.
$Zn(2Mebeim)_2I_2$	i.r.	187s	195vs	328m, 323m, 297s, 277s, 160wm 97m.
	R	-	-	285w, 167sh, 159m, 97m.

[a] Ligand band obscuring ν(M-X)

[b] Possibly ν(M-N)

Table 6.5

Vibrational Spectra 400 - 90 K of Other Complexes

$Co(2Mebeim)_2(NO_3)_2$	i.r. 326m, 307s, 285m, 268sh, 220m, 165s
$Ni(2Mebeim)_2(NO_3)_2$	i.r. 332s, 309s, 291s, 262s,br, 240sh, ~160s,vbr, ~100s,vbr
$Cu(2Mebeim)_2(NO_3)_2$	i.r. 343s, 327s, 300s,br, 257m, 185s, 132s, 102m
$Zn(2Mebeim)_2(NO_3)_2$	i.r. 323w, 307m, 280m, 260sh, ~200w,vbr, ~170m,br, ~100m,vbr
$Cu(2Mebeim)_2Cl_2$	i.r. 331w, 290m, 276s, 270s, 220w, 181s, 160s
$Cu(2Mebeim)_2Br_2$	i.r. 343s, 326s, 292s, 240m, 214s, 175s, 124s.

CHAPTER VII

COMPLEXES OF SOME OTHER SUBSTITUTED BENZIMIDAZOLES

Introduction

As has been mentioned in Chapter 1, 2 trifluoromethyl substituted benzimidazoles were the first benzimidazoles shown to exhibit herbicidal activity and a series of these (2 trifluoromethyl benzimidazole, 5 chloro and 5 nitro 2 trifluoromethyl benzimidazole, 5,6 dichloro 2 trifluoromethyl benzimidazole, 4 chloro 6 nitro 2 trifluoromethyl benzimidazole and 4,6,7 tribromo 2 trifluoromethyl benzimidazole) was prepared to investigate their behaviour towards metal ions. In order to distinguish electronic effects of the trifluoromethyl group from steric effects, 2 tert butyl benzimidazole was also prepared and studied. Attempts were made to prepare complexes with the following metal ions:-

VO^{2+}, Cr^{3+}, Mn^{2+}, Fe^{3+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+},

but although evidence was obtained in the case of 2 trifluoromethyl benzimidazole from infrared spectroscopy of the formation of complexes with Fe^{3+}, Co^{2+}, Ni^{2+} and Cu^{2+}, only with Cu^{2+} could pure solids be isolated. Cu^{2+} complexes could be obtained also with the 5 chloro and 5 nitro substituted compounds and 2 tert butyl benzimidazole. The hydrochlorides of 2 trifluoromethyl benzimidazole and 5 chloro 2 trifluoromethyl benzimidazole were prepared, but no complexes of these could be obtained. The inner complexes of Cu^{2+} and Ag^{+} with 2 trifluoromethyl benzimidazole were isolated, but only the latter gave an acceptable analysis.

The complexes reported here are:-

$Cu(2CF_3beim)_2X_2$ (X = Cl, Br, NO_3), $CuL_2(NO_3)_2.2$ acetone (L = 5Cl2CF_3 beim, 5NO_2 2CF_3beim), $Cu(2Bubeim)_2X_2$ (X = Cl, Br), $Ag^+(2CF_3beim)^-$.

Electronic Spectra (Table 7.1)

The highest possible symmetry of these complexes is D_{2h}, however the e.s.r. spectra obtained (Chapter 8) indicate that the three transitions to components of the T_{2g} level must be relatively unsplit. Further, as the intensity of the major component in the visible region would suggest the presence of a doubly degenerate level[156], the bands will be assigned on the basis of a D_{4h} symmetry unit, as has been adopted in the case of the equivalent pyridine complexes[34].

A reasonable Δ value of 6.0 kK can be obtained in the case of $Cu(2Bubeim)_2Cl_2$ by assigning the bands as $^2B_1 \rightarrow {}^2B_2$ at 13.5 kK, $^2B_1 \rightarrow {}^2E$ at 15.6 kK and $^2B_1 \rightarrow {}^2A_1$ at 17.7 kK, and a similar assignment can be made in the case of $Cu(2CF_3beim)_2Cl_2$. The charge transfer band intrudes into the visible region in the case of the bromides, making assignments difficult, however the band systems closely resemble those of the chloride complexes if it is assumed that the $^2B_1 \rightarrow {}^2A_1$ transition is obscured. The spectra of the four nitrates are almost identical and are very similar to the spectrum of $Cu(NH_3)_4(NO_2)_2$[35], and adopting their assignment of $^2B_1 \rightarrow {}^2A_1$ at 13.8 kK and $^2B_1 \rightarrow {}^2E$, $^2B_2$ at 17 kK gives a Δ value of 10 kK.

All these assignments must be considered speculative, as single crystal polarisation studies are essential for definitive assignments,

but the assignments quoted above are consistent with weak axial distortion in the cases of the nitrates, and very strong axial distortion (i.e. approximately a square planar environment) in the cases of the halides.[97]

Vibrational Spectra

The ν(C=O) band in the two complexes containing acetone is at 1688 K in $Cu(5NO_2 2CF_3 beim)_2(NO_3)_2 .2$acetone and at 1699 K in $Cu(5Cl2CF_3 beim)_2(NO_3)_2 .2$acetone. This is lower than the free acetone value of 1714 K[157] but not as low as the values ranging from 1580 to 1640 K observed in the cases of strong coordination[158,159]. The vibration is observed at 1670 K for the zinc bromide-acetone complex[160]. The similarity of the electronic spectra of these two compounds to that of $Cu(2CF_3 beim)_2(NO_3)_2$ would suggest that the shift of the ν(C=O) band is caused by hydrogen bonding effects[95], though it is difficult to understand why there should be such a significant difference in shifts between the two complexes.

Although the large number of ligand vibrations makes unambiguous assignment very difficult in the low energy region, the $\nu(M\text{-}X_{plane})$ (i.r.) may be assigned as follows:-

	Cl	Br
$2CF_3$beim	312	232
2Bubeim	288	225

The position and number of the C-F antisymmetric stretching modes was found to be a good indication of complex formation. It has been shown that CF_3 groups bonded to aromatic rings exhibit

two antisymmetric C-F stretches (1179 ± 7 and 1140 ± 9 K)[184], and that in the case of substituted 2 trifluoromethyl benzimidazoles, these vibrations couple with out-of-plane C-H deformation modes to give a total of 4 bands[194]. As can be seen from Table 7.3, these bands are further modified on coordination to metal ions, or on taking the compound into solution. The latter fact suggests that solid-state effects might well be one of the causes of the band splittings.

The heterocycle ring breathing mode[194] could also be used as a criterion of complex formation.

Impure Complexes

The complexes $Co(2CF_3beim)_2X_2$ (X = Br, I, NO_3), $Ni(2CF_3beim)_2(NO_3)_2$ and $Zn(2CF_3beim)_2(NO_3)_2$ could be obtained by azeotroping the stoichiometric ligand to metal ratios with acetone-benzene mixtures, however although analysis figures were sufficiently close to those predicted for the above formulae, the degree of impurity (~ 10 - 20%) was too high to make their detailed investigation worthwhile. The electronic spectra were obtained and were found to be very similar to the 2 methyl benzimidazole congeners.

Other complexes, such as the copper "inner" complex and a ferric nitrate complex gave completely unacceptable analysis results.

Table 7.1

Electronic Spectra (kK) and Magnetic Moments (B.M.)

$Cu(2CF_3beim)_2Cl_2$	15.7m, 18.1m, 25.6vs	1.80
$Cu(2CF_3beim)_2Br_2$	15.5m, 24.1s	1.79
$Cu(2CF_3beim)_2(NO_3)_2$	13.8sh, 16.1m, 26.2m	1.82
$Cu(5Cl2CF_3beim)_2(NO_3)_2.2acetone$	13.9sh, 17.2m, 28.3m	1.93
$Cu(5NO_2 2CF_3beim)_2(NO_3)_2.2acetone$	13.8m, 17.2m, 27.5m	1.86
$Cu(2Bubeim)_2Cl_2$	13.5sh, 15.6m, 17.7sh, 24.5s	1.81
$Cu(2Bubeim)_2Br_2$	13.5sh, 15.5m, 23.5s	1.82

Table 7.2

Vibrational Spectra 400 - 90 K (Infrared)

$2CF_3beim$	383w, 345w, 337w, 309s, 276w, 266w, 227w, 175w, 145w
$5Cl2CF_3beim$	398w, 365w,br, 327w, 312w, 280w, 247w, 158w.
$5NO_2 2CF_3beim$	399m, 390sh, 351w, 310w, 249vw, 131s.
2 Bubeim	399m, 309m, 264m, 221m, 197w, 168m, 100m.
$Cu(2CF_3beim)_2Cl_2$	392w, 352m, 312vs, 262s, 222m, 184vs, 160vs, 135w.
$Cu(2CF_3beim)_2Br_2$	391w, 354m, 310m, 303m, 267m, 232m, 194m, 177s, 142vs, 107m.
$Cu(2CF_3beim)_2(NO_3)_2$	388m, 355m, 324s, 310s, 277s, 227w, 202w, 171m, 152m, 128sm 108s,br.
$Cu(5Cl2CF_3beim)_2(NO_3)_2$ 2acetone.	395w, 380w, 351m, 338m,br, 272m,br, 240w, 173w, 136m,vbr.
$Cu(5NO_2 2CF_3beim)_2(NO_3)_2$ 2acetone.	395m, 348s,vbr, 299w, 265m, 252w, 223w, 175-100v,br.
$Cu(2Bubeim)_2Cl_2$	369w, 323sh, 304s, 288s,br, 243s, 187v.s, 168m. 139s, 100 br.
$Cu(2Bubeim)_2Br_2$	368w, 327m, 300m, 247m, 225s, 178s, 166m, 106s, 94m.

Table 7.3

Carbon-fluorine antisymmetric stretching vibrations (K)

$2CF_3$ beim (solid)	1192	1171	1146	1134
$2CF_3$ beim (Dimethyl formamide or Dimethyl sulphoxide solution)	1182	1156	1139	
Ag^+ $(2CF_3 beim)^-$	1195	1144	1127	
$Cu(2CF_3 beim)_2Cl_2$	1189	1166	1159	
$Cu(2CF_3 beim)_2Br_2$	1191	1161		
$Cu(2CF_3 beim)_2(NO_3)_2$	1198	1166		

CHAPTER VIII

E.S.R. SPECTRA OF THE COPPER SYSTEMS

(a) CuL_4X_2 Complexes

X-band spectra (9.3 GHz) were obtained on polycrystalline samples of the complexes $Cu(im)_4X_2$ (X = Cl, Br, I, NO_3), $Cu(im)_4X_2.2im$ (X = I, NO_3), $Cu(NMeim)_4X_2$ (X = Br, I, NO_3), $Cu(NMeim)_4Cl_2.2H_2O$, $Cu(2Meim)_4X_2$ (X = Cl, Br), and $Cu(1,2DiMeim)_4X_2$ (X = Br, NO_3). Only in five cases were resolved spectra obtained, and these are listed in Table 8.1. The spectra were analysed according to the method of Kneubühl[170], though as has been shown, computer fit line calculations are necessary to obtain accurate values of the g and A factors[63,64,171-3,177].

The other complexes showed only single line spectra at about g = 2.05. This could be due to the dynamic Jahn-Teller effect[174]; however as an isotropic signal was obtained from $Cu(im)_4I_2$ down to 36°K, this explanation seems unlikely. Spin-spin broadening would explain this effect as it is temperature independent.[175]

(b) The cupric iodide complexes

Cupric iodide complexes with ammonia and ethylene diamine have been known for a long time, namely, $Cu(NH_3)_6I_2$, $Cu(NH_3)_5I_2$, $Cu(NH_3)_4I_2.H_2O$, $3CuI_2.10NH_3$, $Cu(NH_3)_2I_2$[178-181], $Cu(en)_2I_2$ hydrates[181] and $[Cu(en)_2](CuI_4)$[182]. Since this initial work, apart from a revival of interest in the amine complexes[183] and the preparation and crystal structure of iodobis(2,2'bipyridyl)copperII iodide[86], little interest

has been shown in the preparation of cupric iodide complexes.

The cupric iodide complexes formed with imidazole and N-methyl imidazole are of special interest as copperI - copperII redox reactions are important in several biological systems[195] and as copperII - imidazole systems have been used as model complexes[187,189].

CopperII complexes may be prepared using copperI iodide: Addition of imidazole and elemental iodine to a suspension of copperI iodide in ethanol gives a blue solution from which $Cu(im)_4I_2.2im$ can be isolated ($Cu(en)_2I_2.2H_2O$ has been prepared similarly[185]). If this preparation is performed without the addition of iodine, a blue, paramagnetic solution is slowly formed from which a variety of complexes may be isolated. The colour appears more rapidly if air is bubbled through the solution. (Oxidation by atmospheric oxygen also occurs in the copperI perchlorate - imidazole system[186]). N-methyl imidazole exhibits similar behaviour.

Although in the solid state the presence of a charge transfer band at relatively low energy (25.8 kK) in the complex $Cu(NMeim)_4I_2$ indicates a lower stability than that of the complex $Cu(im)_4I_2$, solution behaviour of the two complexes is very similar. The complexes are stable in aqueous solution and in other polar solvents, but reduction of the copperII ions occurs in ethanol solution unless the ligand to metal ratio is raised to approximately 6:1. In the latter solvent, the absorption in the visible region increases in intensity and the charge transfer band moves further into the ultraviolet region as the ratio of ligand to metal is increased or

the temperature is decreased. Rapid decomposition to copperI iodide occurs in such non polar solvents as nitrobenzene.

E.s.r. and electronic spectral studies in various environments are shown in Table 8.2.

In the case of $Cu(NMeim)_4I_2$, nitrogen superhyperfine structure is observed weakly on the $m_I = +\frac{3}{2}$ copper hyperfine component for room temperature aqueous solutions, with separations of about 11 x 10^{-4}K, similar to that observed for the $[Cu(pyridine)_4]^{2+}$ system[188]. If a small excess of ligand is present in the aqueous solution, the copper hyperfine components become better defined, whereas the superhyperfine structure (number of components $\geq$ 7) becomes less well resolved.

The spectra of the frozen solutions in ethanol of both complexes show nitrogen superhyperfine structure, the resolution of which depends on the quality of the glass formed. On $g_\perp$, up to 15 lines were observed with separations of about 14 x 10^{-4}K. Variations in the numbers and intensity ratios of the superhyperfine components with different samples made assignment difficult, however, it is probable that they are caused by the superimposition of the nine nitrogen superhyperfine components of each of the four copper hyperfine components of $g_\perp$. In support of this explanation, single crystal studies on a series of dilute 4:1 copper complexes with pyridine and substituted pyridines showed four copper hyperfine lines each having nine nitrogen superhyperfine components with the applied field along the z axis, but as the angle between the field

Table 8.1

X-band spectra of CuL_4X_2 complexes

	$g_{\|\|}$	$g_\perp$	$A_{\|\|}$ (K)	
$Cu(im)_4(NO_3)_2.2im$	2.35	2.03	0.0186	
$Cu(py)_4(NO_3)_2.2py$	2.25	2.05	0.0199	from Ref.176
$Cu(NMeim)_4Cl_2.2H_2O$	2.28	2.00	0.0175	
$Cu(NMeim)_4Br_2$	2.28	2.01	0.0175	
$Cu(NMeim)_4I_2$	2.27	2.00	0.0164	
$Cu(1,2DiMeim)_4(NO_3)_2$	2.25	2.00	0.0194	

Table 8.2

X-band spectra of CuL_4I_2 complexes in various environments

	$g_{\|\|}$	$g_\perp$	$A_{\|\|}$(K)	$A_\perp$(K)	ΔE(kK)
$Cu(im)_4I_2$		g_{av}= 2.07			18.2 14.5sh
$Cu(im)_4I_2.2im$		g_{av}= 2.06			16.8br
$Cu(im)_2I_2.2im$ in H_2O soln	2.26	2.09[a]	0.0174	0.002[c]	17.0
$Cu(im)_2I_2.2im$ in EtOH soln	2.27	2.07[a]	0.0179	0.002[c]	15.8
$Cu(im)_2I_2.2im$ diluted in $Co(im)_6I_2$	2.25	2.02[b]	0.0173	-	-
$Cu(im)_4(NO_3)_2$ in H_2O soln[d]	2.27	2.06(g_m)	0.018	-	16.8
$Cu(NMeim)_4I_2$	2.27	2.00[b]	0.0164	-	16.7 14.3sh
$Cu(NMeim)_4I_2$ in H_2O soln	2.27	2.07[a]	0.0165	0.003[c]	16.3
$Cu(NMeim)_4I_2$ in EtOH soln	2.27	2.06[a]	0.0170	>0.001[c]	15.5

[a] From $3g_o = g_{\|\|} + 2g_\perp$ (Ref.191)

[b] Using Kneubühl's method (Ref.170)

[c] From $3A_o = A_{\|\|} + 2A_\perp$ (Ref.192)

[d] From Ref.187.

and the four fold axis was increased, these four copper lines merged; and when the field is in the plane of the four nitrogens ($g_{\perp}$), only 14 lines in all were observed[207]. A further effect which must be considered is the possibility of superhyperfine structure due to delocalisation of the electron further into the ligand ring system[190]. It has been claimed that the 13 lines observed on $g_{\perp}$ at 100°K for polycrystalline samples of Zn[Cu](o-phenanthroline)$_3$(NO_3)$_2$ and Zn[Cu](bipyridyl)$_3$(NO_3)$_2$ decrease to 9 lines if pure isotopic ^{63}Cu is used[196], but considering the very small difference in values of the hyperfine splittings of the two isotopes[197], this seems very surprising.

For the imidazole frozen solutions in ethanol, on the lowest field copper hyperfine component of $g_{||}$, 5 weak but reproducible peaks of 8×10^{-4}K separation could be observed from the best glasses, which would suggest that at least in solution, there is weak axial interaction with the nitrogen atoms of two imidazole molecules.

Of interest is that the nitrogen superhyperfine structure on $g_{\perp}$ in the frozen solutions is centred near the point of maximum absorption (i.e. the point where the derivative signal crosses the baseline), and taking this position as $g_{\perp}$ gives values about 2.06, close to the values calculated using g_0 and $g_{||}$ (see Table 8.2).

(c) Cu(1,2 DiMeim)$_3$Cl$_2$

This green complex shows in the solid state a reversed spectrum with g_z = 2.06, g_y = 2.16 and g_z = 2.21 (X-band). This type of

spectrum is characteristic of trigonal bipyramid[193] or reversed tetragonal structures[183], and as has been discussed in Chapter 5, the former is more likely in this case. g_z is a considerable distance from 2.00, which would indicate that the structure is not strictly of D_{3h} symmetry[193].

The frozen acetone solution of the complex is blue and has a normal spectrum with $g_{||} = 2.26$, $g_{\perp} = 2.03$ and $A_{||} = 0.0191$ K, which would suggest an octahedral configuration, formed possibly either by dimerisation or by coordination of acetone.

(d) CuL_2X_2 pseudotetrahedral complexes

Pseudotetrahedral structures have been suggested for the complexes $Cu(NMeim)_2Cl_2$, $Cu(2Meim)_2Cl_2$, $Cu(2Meim)_2Br_2$ and $Cu(1,2\ DiMeim)_2Cl_2$. As tetrahedral copper environments are biologically important[193], spectra were also obtained from the complexes diluted in the equivalent zinc compound at between about 0.1 and 1% concentration.

In the cases of $Cu(2Meim)_2Cl_2$ and $Cu(2Meim)_2Br_2$ dilution only "smeared out" the $g_{||}$ signal, however the spectrum of $Cu(NMeim)_2Cl_2$ showed a considerable change with a shift of $g_{||}$ to lower field and the replacement of g_x and g_y by a single value. Both of these factors would indicate a decrease in the distortion of the copper environment, for as has been shown, $g_{||} = 2 + \frac{8\lambda'}{\Delta(B_2 \rightarrow E)}$, where $\Delta(B_2 \rightarrow E)$ is the splitting of the $^2T_2$ ground state term for the copper ion in a tetrahedral environment[198], thus as the distortion decreases, $g_{||}$ will increase in value. In the case here, dilution in the non isomorphous zinc complex has probably lead to a reduction in the "flattening" of the tetrahedron[199].

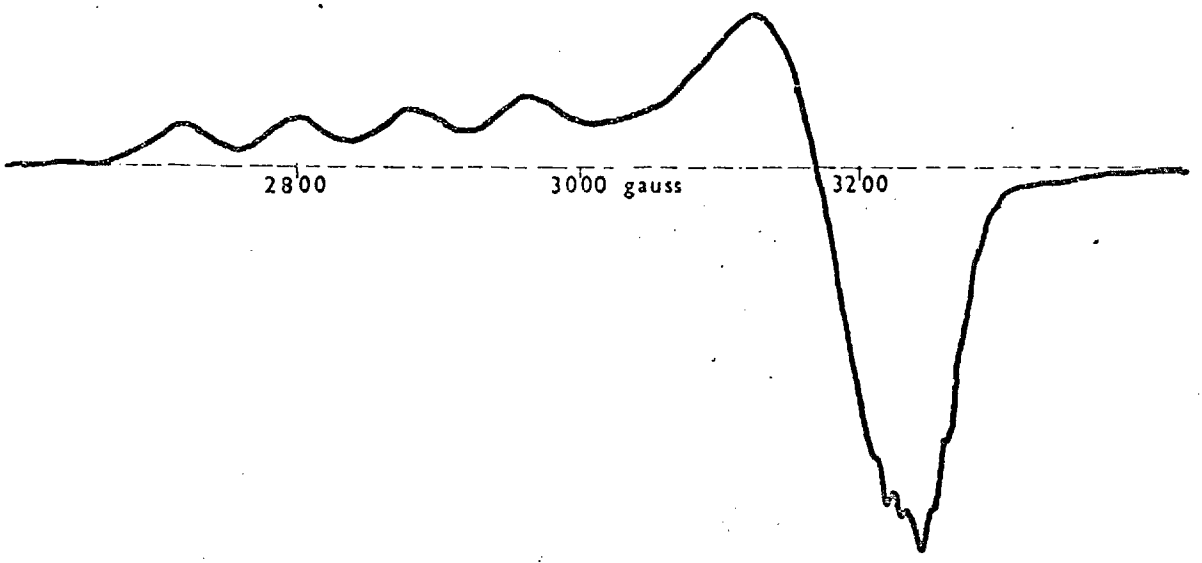
Copper hyperfine structure is observed on $g_{||}$ with $A_{||} = 70 \times 10^{-4}$K, which is a considerably smaller value than that observed for Zn[Cu](o-phenanthroline)Cl_2[200], but of similar order to that found for Zn[Cu]$Hg(SCN)_4$[201] and for some biological systems[202]. Weak superhyperfine structure is observed on $g_{\perp}$, the five components having about 1×10^{-4}K separation. This structure is probably nitrogen superhyperfine components, however it could also be due to the chlorine atoms.

The system of dilute $Cu(1,2DiMeim)_2Cl_2$ showed copper hyperfine structure on both g_z and g_x of 45×10^{-4}K (poorly resolved on g_z), which is as low as that observed for the $(CuCl_4)^{2-}$ ion in some environments[199].

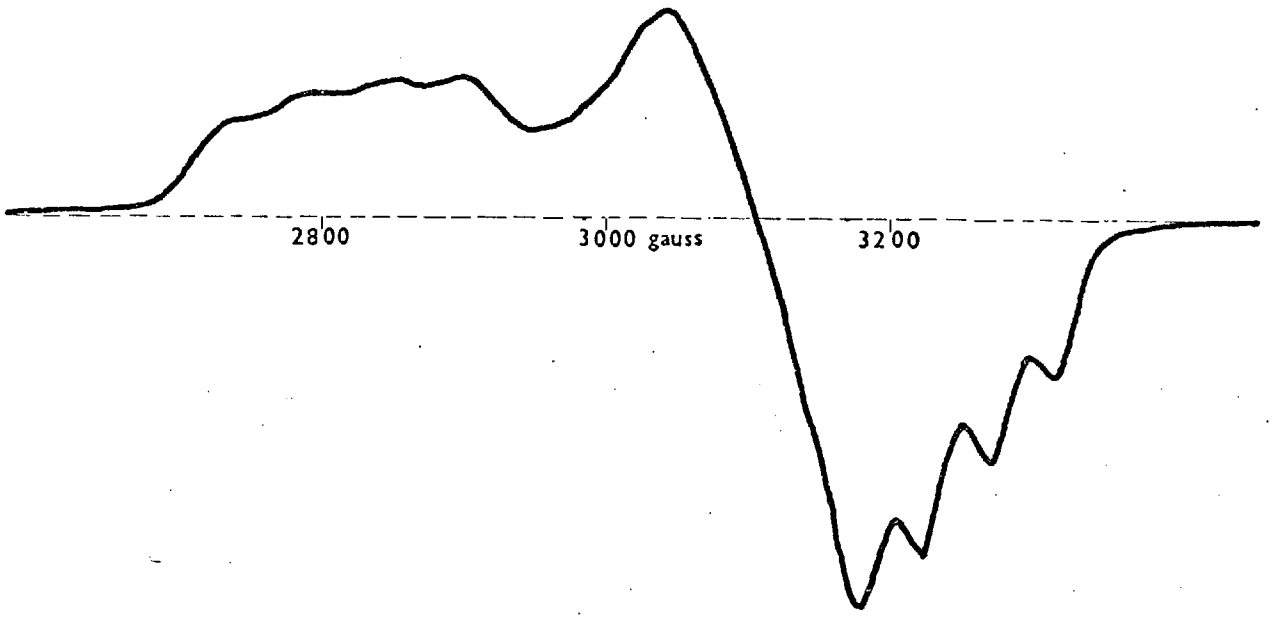
(e) Other CuL_2X_2 complexes

The complexes of the substituted benzimidazoles (and of benzimidazole itself[206]) were studied at both X band (9.3 GHz) and Q band (36.0 GHz) (Table 8.4), and in all cases, as one would expect, resolution was better at Q band. The spectra obtained are compatible with D_{2h} trans CuL_2X_2 structures with weak axial interactions[203] (this being the structure of $Cu(NMeim)_2Br_2$[128], but no patterns can be discerned from the results. Similar spectra have been obtained for substituted pyridine complexes[204,205].

In the case of $Cu(beim)_2Cl_2$, the broad X band spectrum ($\Delta H_{\frac{1}{2}}$, x component = 96 gauss, $\Delta H_{\frac{1}{2}}$, z component = 84 gauss) is replaced by a sharp spectrum at Q band ($\Delta H_{\frac{1}{2}}$, x component = 33 gauss, $\Delta H_{\frac{1}{2}}$, z component = 17 gauss).



e.s.r. X-band spectrum of $Zn[Cu](NMeim)_2Cl_2$



e.s.r. X-band spectrum of $Zn[Cu](12DiMeim)_2Cl_2$

The complexes $Cu(2CF_3beim)_2Cl_2$ and $Cu(2Bubeim)_2Cl_2$ show narrowing of all three transitions, both at X and Q band ($\Delta H_{\frac{1}{2}} \approx 5$ - 10 gauss). $Cu(beim)_2Br_2$ gives only a massively broadened isotropic signal centred on g = 2.20 ($\Delta H_{\frac{1}{2}}$ = 700 gauss), while $Cu(2Mebeim)_2Br_2$ and $Cu(2CF_3beim)_2Br_2$ show a two component spectrum at X band and three components at Q band, the g_x component being narrowed. $Cu(2Bubeim)_2Br_2$ also shows broadening, however the single line spectrum observed at X band is resolved into its components at Q band.

X band spectra of $Cu(NMeim)_2Br_2$, $Cu(1,2DiMeim)_2(NO_3)_2$, $Cu(5Cl\ 2CF_3beim)_2(NO_3)_2.2acetone$ and $Cu(5NO_2\ 2CF_3beim)_2(NO_3)_2.2acetone$ were all single line signals. The spectra of $Cu(im)_2(NO_3)_2$ and $Cu(NMeim)_2(NO_3)_2$ gave values of $g_{||}$ = 2.36, $g_\perp$ = 2.06 and $g_{||}$ = 2.27, $g_\perp$ = 2.05 respectively.

(f) Cu(NMeim)Cl_2

As might be expected, the X band spectrum showed only a broad derivative signal centred on g = 2.17.

Table 8.3

X-band spectra of CuL_2X_2 pseudotetrahedral complexes

	$g_{||}$	$g_\perp$
$Cu(NMeim)_2Cl_2$	2.28 (g_z)	2.10 (g_y) 2.05 (g_x)
$Zn[Cu](NMeim)_2Cl_2$	2.35	2.05
$Cu(2Meim)_2Cl_2$	2.32	2.08
$Cu(2Meim)_2Br_2$	2.31	2.07
$Cu(1,2DiMeim)_2Cl_2$	2.34	2.07
$Zn[Cu](1,2DiMeim)_2Cl_2$	2.36 (g_z)	2.14 (g_y) 2.04 (g_x)

Table 8.4

Spectra of some CuL_2X_2 complexes

	X-band				Q-band		
	$g_{\parallel}$, g_z	g_y	$g_{\perp}$	g_x	g_z	g_y	g_x
$Cu(beim)_2Cl_2$ [a]	2.27	2.14		2.07	2.23	2.14	2.06
$Cu(2Mebeim)_2Cl_2$	2.29		2.06		2.30	2.08	2.06
$Cu(2CF_3beim)_2Cl_2$	2.20	2.11		2.06	2.20	2.11	2.06
$Cu(2Bubeim)_2Cl_2$	2.19	2.13		2.06	2.20	2.14	2.06
$Cu(beim)_2Br_2$ [a]	-	-		-	-	-	-
$Cu(2Mebeim)_2Br_2$	2.21		2.05		2.22	2.07	2.06
$Cu(2CF_3beim)_2Br_2$	2.21		2.06		2.21	2.07	2.06
$Cu(2Bubeim)_2Br_2$	-	2.12	-		2.18	2.12	2.07
$Cu(beim)_2(NO_3)_2$ [a]	2.32		2.07		2.32	2.12	2.08
$Cu(2Mebeim)_2(NO_3)_2$	2.30	2.09		2.06	2.31	2.10	2.07
$Cu(2CF_3beim)_2(NO_3)_2$	2.18		2.07		2.25	2.15	2.08

[a] From Ref. 206.

CHAPTER IX

EXPERIMENTAL

(a) Preparation of Ligands

Imidazole (B.D.H.), N-methyl imidazole (K and K), 2-methyl imidazole (Koch Light) and 1,2-dimethyl imidazole (Fluka) were used without further purification.

2-methyl benzimidazole (Koch Light) was decolourised with charcoal and was recrystallised from water M.Pt 175-6 (176)°C.

2-t-butyl benzimidazole was prepared by the method of Davies et al.[146] The compound was decolourised with charcoal and was recrystallised from 95% ethanol. A poor yield (15%) was obtained. M.Pt 312 (315)°C.

2-trifluoromethyl benzimidazole was prepared according to the patented method,[11] and was decolourised and then recrystallised from an ethanol/water mixture. M.Pt 206 (208-9)°C.

5-chloro 2-trifluoromethyl benzimidazole was prepared similarly. M.Pt 204 (203)°C. C = 43.53(43.86)%, H = 1.60 (1.82)%.

5-nitro 2-trifluoromethyl benzimidazole was prepared according to the patented method[9] and was recrystallised from ethanol. M.Pt 151(156)°C.

4-chloro 6-nitro 2-trifluoromethyl benzimidazole, C = 36.13 (36.18)%, H = 1.10 (1.13)%, M.Pt 206 (206-208)°C, and

5,6-dichloro 2-trifluoromethyl benzimidazole, M.Pt 240 (244-5)°C

were prepared similarly.

4,6,7-tribromo 2-trifluoromethyl benzimidazole was prepared according to the patented method[4]. M. Pt 220 (227-30)°C.

The preparation of the following ligands was unsuccessful:-

2,5-bistrifluoromethyl benzimidazole[148,152] Reduction of the 4-amino 3-nitro benzotrifluoride gave very poor yields.

5-amino 2-trifluoromethyl benzimidazole. Very poor yields were obtained.

4,6,7-trichloro 2-trifluoromethyl benzimidazole[9] The majority of the product, even after extended periods of chlorination, appeared to be the monochloro substituted compound.

(b) Preparation of Complexes

Chapter 1

$Co(im)_6X_2$ (X = Cl, Br, I, NO_3)

Solutions of the hydrated cobalt salt and imidazole in 1:8 mole ratio in ethanol were evaporated to small volume and allowed to cool. The pink crystalline solid was filtered and washed with ether.

$Co(im)_6Cl_2$	C = 40.29 (40.14)	N = 31.45 (31.19)	H = 5.04(4.46)
$Co(im)_6Br_2$	C = 34.74 (34.43)	N = 26.44 (26.78)	H = 3.78(3.83)
$Co(im)_6I_2$	C = 30.38 (29.96)	N = 23.30 (23.28)	H = 3.45(3.33)
$Co(im)_6(NO_3)_2$	C = 36.80 (36.53)	N = 35.17 (33.13)	H = 4.04(4.06)

$Co(im)_2X_2$ (X = Cl, Br, I, NO_3)

Solutions of the hydrated cobalt salt and imidazole in 1:1.9 mole ratio in ethanol (nitromethane for X = NO_3) were evaporated to small volume, a little dichloromethane was added, and the solutions were stored at 0^oC for several days. The crystals formed (from an oil in the case of the nitrate) were filtered and washed with ether.

The nitrate was very hygroscopic.

$Co(im)_2Cl_2$ C = 27.27 (27.08) N = 21.41 (21.04) H = 3.00 (3.01)

$Co(im)_2Br_2$ C = 20.72 (20.28) N = - (-) H = 2.39 (2.25)

$Co(im)_2I_2$ C = 16.56 (16.04) N = 12.22 (12.47) H = 1.75 (1.78)

$Co(im)_2(NO_3)_2$ C = 22.35 (22.57) N = 25.81 (26.33) H = 2.13 (2.51)

Ni im_6X_2 (X = Cl, Br, I, NO_3)

Solutions of the hydrated nickel salt and imidazole in a 1:6.6 mole ratio in ethanol were evaporated down and allowed to cool. The pale violet-blue crystals formed were filtered and washed with acetone and ether.

Ni im_6Cl_2 C = 40.05 (40.15) N = 31.32 (31.20) H = 4.23 (4.46)

Ni im_6Br_2 C = 34.84 (34.46) N = 26.98 (26.79) H = 3.58 (3.83)

Ni im_6I_2 C = 30.31 (29.96) N = 24.64 (23.30) H = 3.33 (3.33)

Ni $im_6(NO_3)_2$ C = 36.67 (36.55) N = 35.46 (33.14) H = 4.02 (4.06)

Ni $im_4X_2, 2H_2O$ (X = Cl, Br, I)

A concentrated ethanol solution of imidazole and the hydrated nickel halide in a 4:1 mole ratio gave pale blue crystals which were filtered and washed with a little ice cold acetone. These compounds were air dried. The iodide spontaneously lost water to form yellow-orange Ni im_4I_2.

Ni $im_4Cl_2.2H_2O$ C = 33.21 (32.88) N = 25.34 (25.56) H = 4.43 (4.56)

Ni $im_4Br_2.2H_2O$ C = 26.88 (27.33) N = 21:49 (21.26) H = 4.23 (3.79)

Ni im_4X_2 (X = Cl, Br)

These were obtained by heating the corresponding dihydrates at 120°C for 24 hours.

Ni im_4Cl_2 C = 36.21 (35.83) N = 27.80 (27.86) H = 4.21 (3.98)

Ni im_4Br_2 C = 29.51 (29.34) N = 22.74 (22.02) H = 3.18 (3.26)

Ni im_4I_2

This could be prepared either by heating the dihydrate or as follows. A 4:1 mole ratio of imidazole and nickel iodide hexahydrate in acetone solution was evaporated down to small bulk and a little benzene was added. The green oil initially formed crystallised to a dark yellow-brown solid. This was filtered off and recrystallised from an ethanol-benzene mixture.

Ni im_4I_2 C = 24.75 (24.63) N = 19.09 (19.16) H = 2.89 (2.74)

Ni $im_4X_2.2D_2O$ (X = Cl, Br)

The anhydrous compounds were placed in an atmosphere of D_2O for 5 hours.

Ni $im_4Cl_2.2D_2O$ C = 32.47 (32.64) N = 25.31 (25.38) H = 4.87 (4.65)

Ni $im_4Br_2.2D_2O$ C = 26.83 (27.14) N = 21.11 (21.09) H = 4.19 (3.86)

(D content expressed as H equivalent)

Ni imX_2 (X = Cl, Br)

These compounds were prepared by Dr N.J. Weeks.[84]

Cu im_4X_2 (X = Cl, Br, NO_3)

Solutions of imidazole and the appropriate, hydrated copper salt in ethanol were mixed in a 4.4:1 mole ratio. Dark blue-purple crystals separated which were washed with acetone and ether.

$Cu\ im_4Cl_2$ C = 35.43 (35.39) N = 27.53 (27.52) H = 3.85 (3.93)

$Cu\ im_4Br_2$ C = 29.07 (29.06) N = 22.95 (22.60) H = 3.07 (3.23)

$Cu\ im_4(NO_3)_2$ C = 31.51 (31.32) N = 30.27 (30.44) H = 3.42 (3.48)

$Cu\ im_4I_2$

The calculated quantity of potassium iodide in hot ethanol was added to a hot ethanol solution of imidazole and cupric perchlorate (6:1 mole ratio) and the precipitate of potassium perchlorate was filtered off. The dark green-blue solution was evaporated to a small volume and was allowed to cool. The dark purple crystals were filtered off and washed with ether.

$Cu\ im_4I_2$ C = 24.60 (24.43) N = 18.95 (19.00) H = 2.74 (2.71)

$Cu\ im_4I_2.2im$

$Cu\ im_4I_2$ was dissolved in the minimum quantity of ethanol containing a 3:1 mole excess of imidazole. Dark blue crystals formed on storing at 0°C for 12 hours. These were filtered off and washed with ether.

$Cu\ im_4I_2\ 2im$ C = 30.84 (29.77) N = 23.56 (23.14) H = 3.76 (3.31)

$Cu\ im_4(NO_3)_2.2im$

A 3:1 mole excess of imidazole was added to a suspension of $Cu\ im_4(NO_3)_2$ in nitromethane. A little dichloromethane was added to the resulting blue solution and after storing at 0°C for 12 hours, the dark blue crystals formed were filtered.

$Cu\ im_4(NO_3)_2\ 2im$. C = 36.61 (36.25) N = 32.68 (32.88) H = 4.58 (4.03)

Cu $im_2(NO_3)_2$

Solutions of imidazole and hydrated cupric nitrate in hot 2,2-dimethoxypropane were mixed in a 2:1 mole ratio. The blue oil initially formed, crystallised overnight. The hygroscopic solid was filtered and washed with 2,2-dimethoxypropane and ether.

Cu $im_2(NO_3)_2$ C = 22.12 (22.24) N = 25.67 (25.95) H = 2.62 (2.47)

Zn im_6X_2 (X = Cl, NO_3)

An acetone solution of imidazole was added in a 6.6:1 mole ratio to an acetone suspension of the appropriate zinc salt. The resulting solution was evaporated to a small volume and a little dichloromethane was added. The solution was stored at 0°C until the oil which initially formed, had crystallised. The solid was filtered and washed with ether. The chloride was hygroscopic.

Zn im_6Cl_2 C = 39.79 (39.66) N = 30.09 (30.84) H = 4.77 (4.41)

Zn $im_6(NO_3)_2$ C = 35.92 (36.13) N = 32.54 (32.78) H = 4.18 (4.01)

Zn $im_4(NO_3)_2$

Solutions of imidazole and zinc nitrate hexahydrate in hot ethanol were mixed in a 4:1 mole ratio. The white solid formed on cooling was filtered and washed with acetone and ether.

Zn $im_4(NO_3)_2$ C = 31.30 (31.24) N = 30.36 (30.36) H = 3.56 (3.47)

Zn im_2X_2 (X = Cl, Br, I, NO_3)

A hot nitromethane solution of imidazole was added in a 2:1 mole ratio to a suspension of the appropriate zinc salt in the same solvent. The resulting solution was concentrated, and dichloromethane

was added until a faint cloudiness appeared. Storing at 0°C for several days gave white crystals, which were filtered and washed with ether. The nitrate was hygroscopic.

$Znim_2Cl_2$ C = 26.76 (26.43) N = 20.38 (20.54) H = 3.03 (2.93)

$Znim_2Br_2$ C = 20.04 (19.93) N = 15.46 (15.50) H = 2.19 (2.21)

$Znim_2I_2$ C = 16.03 (15.81) N = 12.40 (12.29) H = 1.70 (1.76)

$Znim_2(NO_3)_2$ C = 21.79 (22.11) N = 26.21 (25.80) H = 2.53 (2.46)

$Co(NMeim)_6X_2.2H_2O$ (X = Cl, Br) $Co(NMeim)_6X_2$ (X = I, NO_3) (Chapter III)

A hot acetone solution of the appropriate hydrated cobalt salt and N methyl imidazole were mixed in a 1:10 mole ratio. On cooling, pink crystals formed which were filtered and washed with carbon tetrachloride. The chloride and bromide complexes were air dried.

$Co(NMeim)_6Cl_2.2H_2O$ C = 43.68 (43.78) N = 25.47 (25.53) H = 5.82 (6.08)

$Co(NMeim)_6Br_2.2H_2O$ C = 39.01 (38.57) N = 22.37 (22.49) H = 5.29 (5.36)

$Co(NMeim)_6I_2$ C = 36.49 (35.81) N = 21.26 (20.86) H = 4.92 (4.47)

$Co(NMeim)_6(NO_3)_2$ C = 42.97 (42.67) N = 29.30 (29.02) H = 5.45 (5.33)

$Co(NMeim)_2X_2$ (X = Cl, Br, I)

A hot acetone solution of the appropriate hydrated cobalt halide and N methyl imidazole were mixed in a 1:2 mole ratio. The solution was evaporated down to a small bulk. Upon cooling, the chloride crystallised spontaneously whereas addition of benzene was necessary to cause precipitation of the bromide and iodide. The chloride and bromide were recrystallised from acetone/benzene and the iodide from dichloromethane/carbon tetrachloride.

$Co(NMeim)_2Cl_2$ C = 32.75 (32.68) N = 19.21 (19.04) H = 3.83 (4.08)

$Co(Nmeim)_2Br_2$ C = 25.45 (25.08) N = 15.09 (14.62) H = 3.10 (3.13)

$Co(NMeim)_2I_2$ C = 20.00 (20.13) N = 11.61 (11.74) H = 2.60 (2.52)

$Ni(NMeim)_6X_2$ $2H_2O$ (X = Cl, Br) $Ni(NMeim)_6X_2$ (X = I, NO_3)

These were prepared similarly to the equivalent cobalt complexes utilising ethanol as the solvent.

$Ni(NMeim)_6Cl_2.2H_2O$ C=44.42 (43.77) N=25.42 (25.53) H=5.99 (6.08)

$Ni(NMeim)_6Br_2.2H_2O$ C=38.80 (38.61) N=22.91 (22.48) H=4.94 (5.36)

$Ni(NMeim)_6I_2$ C=35.78 (35.82) N=20.76 (20.86) H=4.42 (4.47)

$Ni(NMeim)_6(NO_3)_2$ C=42.77 (42.68) N=29.16 (29.02) H=5.00 (5.33)

$Ni(NMeim)_4Cl_2$

Hydrated nickel chloride was dissolved in an ethanol/2,2 dimethoxypropane mixture, and N methyl imidazole was added in a 1:4 mole ratio. Ether was added until a cloudiness developed and upon standing, green crystals formed which were filtered and washed with ether.

$Ni(NMeim)_4Cl_2$ C = 42.24 (41.97) N = 25.07 (24.46) H = 5.40 (5.25)

$Ni(NMeim)_2X_2$ (X = Cl, Br)

The appropriate nickel halide was dissolved in an ethanol/2,2-dimethoxypropane mixture and N methyl imidazole was added in a 1:2 mole ratio. The solution was evaporated to small bulk and benzene was added. The blue solid isolated was recrystallised from acetone/benzene.

$Ni(NMeim)_2Cl_2$ C = 32.29 (32.66) N = 18.92 (19.05) H = 4.52 (4.08)

$Ni(NMeim)_2Br_2$ C = 25.23 (25.10) N = 14.99 (14.63) H = 3.60 (3.13)

$Ni(NMeim)_2I_2$

This was obtained by heating $Ni(NMeim)_6I_2$ at 120°C under vacuum until no further weight loss occurred.

$Ni(NMeim)_2I_2$ C = 20.64 (20.16) N = 11.99 (11.76) H = 2.50 (2.54)

$Ni(NMeim)X_2$ (X = Cl, Br)

The appropriate nickel halide was dissolved in an ethanol/2,2-dimethoxypropane mixture and the solution was evaporated to a small volume. A 1:1 mole ratio of N-methyl imidazole was stirred into the solution. The solid formed was filtered and washed with the solvent and then ether.

$Ni(NMeim)Cl_2$ C = 22.92 (22.68) N = 12.92 (13.23) H = 3.51 (2.84)

$Ni(NMeim)Br_2$ C = 16.02 (15.99) N = 9.19 (9.32) H = 2.13 (2.01)

$Cu(NMeim)_4X_2$ (X = Cl, NO_3)

An acetone solution of the cupric salt and N methyl imidazole were mixed in a 1:4.4 mole ratio.. The blue crystals which formed were filtered off and washed with acetone and ether.

$Cu(NMeim)_4Cl_2$ C = 41.87 (41.48) N = 23.87 (24.20) H = 5.83 (5.19)

$Cu(NMeim)_4(NO_3)_2$ C=37.40 (37.26)N = 27.13 (27.16) H = 4.56 (4.65)

$Cu(NMeim)_4Br_2$

Ethanol solutions of cupric bromide and N methyl imidazole were mixed in a 1:4.4 mole ratio. The solution was evaporated to small bulk, and upon standing dark blue crystals formed. The complex was recrystallised from ethanol and washed with acetone and ether.

$Cu(NMeim)_4Br_2$ C = 35.03 (34.81) N = 20.22 (20.30) H = 4.30 (4.35)

$Cu(NMeim)_4I_2$

An ethanol solution of cupric perchlorate and N methyl imidazole were mixed in a 1:6 mole ratio. A warm solution of potassium iodide was stirred into the slurry that formed, and the solution was filtered. Upon standing, grey crystals formed which were separated and washed with ethanol and ether. Evaporation of the filtrate gave a further yield.

$Cu(NMeim)_4I_2$ C = 29.74 (29.77) N = 17.41 (17.36) H = 3.78 (3.75)

$Cu(NMeim)_2X_2$ (X = Cl, NO_3)

This was prepared as for the appropriate 4:1 complex but using a 2:1 mole ratio of ligand to metal. The complexes were recrystallised from acetone.

$Cu(NMeim)_2Cl_2$ C = 32.17 (32.17) N = 18.93 (18.75) H = 3.91 (4.05)

$Cu(NMeim)_2(NO_3)_2$ C=27.10(27.33) N = 23.63 (23.88) H = 3.36 (3.41)

$Cu(NMeim)_2Br_2$

Solid cupric bromide was stirred into a solution of N methyl imidazole in acetone in a 1:2 mole ratio. The heated solution was filtered and allowed to cool. The green crystals formed were filtered off and washed with acetone and ether.

$Cu(NMeim)_2Br_2$ C = 24.82 (24.81) N = 14.42 (14.44) H = 3.04 (3.12)

$Cu(NMeim)Cl_2$

A 1:1 mole ratio of N methyl imidazole and cupric chloride were mixed in acetone. The solution was filtered, and the filtrate was evaporated to a small volume. The khaki coloured solid which

precipitated was filtered off and washed with acetone and ether.

$Cu(NMeim)Cl_2$ C = 22.20 (22.19) N = 12.75 (12.94) H = 2.84 (2.77)

$Zn(NMeim)_6I_2$

A hot acetone solution of zinc iodide and N methyl imidazole were mixed in a 1:6.6 mole ratio. On cooling, white crystals formed which were filtered off and washed with acetone and ether.

$Zn(NMeim)_6I_2$ C = 35.71 (35.55) N = 21.16 (20.70) H = 4.07 (4.47)

$Zn(NMeim)_2X_2$ (X = Cl, Br, I)

These were prepared as for the equivalent cobalt complexes, however the chloride was recrystallised from nitromethane.

$Zn(NMeim)_2Cl_2$ C = 32.01 (31.95) N = 18.70 (18.64) H = 3.68 (3.99)

$Zn(NMeim)_2Br_2$ C = 24.92 (24.85) N = 14.52 (14.39) H = 3.15 (3.08)

$Zn(NMeim)_2I_2$ C = 20.52 (20.68) N = 11.55 (11.58) H = 2.99 (2.48)

$Co(2\ Meim)_4I_2$ (Chapter IV)

Ethanol solutions of cobalt iodide and 2 methyl imidazole were mixed in a 1:4 mole ratio. The solution was filtered, evaporated to small bulk and benzene was added until a cloudiness was observed. From the blue solution, intense purple crystals were filtered, washed with benzene, and kept under vacuum for 2 days to remove occluded benzene.

$Co(2\ Meim)_4I_2$ C = 30.26 (29.94) N = 17.61 (17.47) H = 3.79 (3.74)

$Co(2\ Meim)_4(NO_3)_2$ Form A

Hot ethanol solutions of cobalt nitrate and 2 methyl imidazole were mixed in a 1:4 mole ratio and filtered. On cooling, pink crystals

formed from a dark red solution. The solid was filtered off and washed with acetone and ether.

Form B.

Hot ethanol solutions of cobalt nitrate and 2 methyl imidazole were mixed in a 1:4 mole ratio and filtered. A large quantity of dichloromethane was added, and the dark red oil formed was allowed to crystallise at 0°C. The crystals obtained were treated as above. This preparation was successful only twice, form [A] or mixtures of the two forms being obtained on subsequent occasions.

$Co(2\ Meim)_4(NO_3)_2$ form A

C = 37.44 (37.57) N = 27.31 (27.39) H = 4.75 (4.69)

form B

C = 37.96 (37.57) N = 27.31 (27.39) H = 5.12 (4.69)

$Co(2\ Meim)_2X_2$ (X = Cl, Br, I)

Hot acetone solutions of the appropriate cobalt halide, and 2 methyl imidazole were mixed in a 1:2 mole ratio and filtered. Dichloromethane (X = Cl, Br) or benzene (X = I) were added until a cloudiness developed. The solutions were stored at 0°C for 24 hours. The dark blue crystals formed were filtered and washed with acetone/dichloromethane mixture (X = Cl, Br) or acetone/benzene (X = I).

$Co(2\ Meim)_2Cl_2$ C = 32.97 (32.66) N = 19.21 (19.04) H = 4.26 (4.08)

$Co(2\ Meim)_2Br_2$ C = 25.35 (25.08) N = 14.78 (14.62) H = 3.24 (3.13)

$Co(2\ Meim)_2I_2$ C = 20.45 (20.13) N = 11.51 (11.74) H = 2.50 (2.52)

$Co(2\ Meim)_2(NO_3)_2$

A solution of cobalt nitrate in 2,2 dimethoxypropane was allowed to stand for 2 hours. A solution of 2 methyl imidazole in acetone was added to give a 1:1.9 mole ratio. The mixture was filtered and the excess solvent distilled off until an oil formed. This was separated and left under benzene until crystallised. The solid was filtered off and washed with benzene and ether.

$Co(2\ Meim)_2(NO_3)_2$ C = 28.07 (27.67) N = 23.77 (24.17) H = 3.52 (3.46)

$Ni(2\ Meim_4X_2$ (X = Cl, Br)

Hot ethanol solutions of the appropriate nickel halide and 2 methyl imidazole were mixed in a 1:4.4 ratio. Upon cooling, green crystals formed, together with a small quantity of a yellow compound (identified as the nickel "inner" complex). The solid was filtered and washed with ethanol and ether. The complex was then recrystallised from ethanol.

$Ni(2\ Meim)_4Cl_2$ C = 42.10 (41.91) N = 24.66 (24.44) H = 5.01 (5.24)

$Ni(2\ Meim)_4Br_2$ C = 35.43 (35.10) N = 20.42 (20.48) H = 4.39 (4.39)

$Ni(2\ Meim)_4I_2$

Anhydrous nickel iodide was dissolved in hot ethanol and a solution of 2 methyl imidazole was added to give a 1:4.4 mole ratio. Ether was added, giving a yellow precipitate. This was filtered off and recrystallised from acetone.

$Ni(2\ Meim)_4I_2$ C = 30.09 (29.94) N = 17.76 (17.47) H = 3.55 (3.74)

$Ni(2\ Meim)_4(NO_3)_2$

Ethanol solutions of nickel nitrate and 2 methyl imidazole were mixed in a 1:4.4 mole ratio. A pale blue precipitate slowly formed, which was filtered and washed with acetone and ether.

$Ni(2\ Meim)_4(NO_3)_2$ C = 37.91 (37.57) N = 27.68 (27.39) H = 4.96 (4.69)

$Ni(2\ Meim)_{3.5}I_2$

$Ni(2\ Meim)_4I_2$ was heated in vacuo at 75°C until no further weight loss occurred, giving a purple product. This preparation was not always reproducible, but if the green 2:1 complex started forming, cessation of heating for a few hours caused conversion of the green areas to purple and subsequently only the purple complex would form.

$Ni(2\ Meim)_{3.5}I_2$ C = 27.89 (28.04) N = 16.19 (16.35) H = 3.42 (3.50)

This analysis figure was reproducible, and weight loss studies also confirmed this stoichiometry.

$Ni(2\ Meim)_2Cl_2$

Solid hydrated nickel chloride was added to an acetone solution of 2 methyl imidazole to give a 1:2 mole ratio. The blue solution was boiled and filtered hot. Benzene was added until a cloudiness developed, which upon cooling gave a purple oil. This crystallised over 24 hours to give a yellow solid, which was filtered and washed with a little acetone and ether.

$Ni(2\ Meim)_2Cl_2$ C = 32.38 (32.66) N = 18.80 (19.05) H = 4.31 (4.08)

$Ni(2\ Meim)_2X_2$ (X = Br, I)

The appropriate 4:1 complex was heated at 120°C in vacuo until no further weight loss occurred. The blue bromide and dark green iodide were both very hygroscopic.

$Ni(2\ Meim)_2Br_2$ C = 25.18 (25.10) N = 14.26 (14.63) H = 3.46 (3.13)

$Ni(2\ Meim)_2I_2$ C = 20.55 (20.14) N = 11.61 (11.74) H = 2.72 (2.52)

$Ni(2\ Meim)_2(NO_3)_2$

This was prepared similarly to the equivalent cobalt complex

$Ni(2\ Meim)_2(NO_3)_2$ C = 27.96 (27.67) N = 23.95 (24.21) H = 3.14 (3.46)

$Ni(2\ Meim)Cl_2$

Nickel chloride was dissolved in an ethanol - 2,2-dimethoxypropane mixture and refluxed for 15 minutes. 2 methyl imidazole in a 1:1.1 mole ratio was added, and the solution was evaporated to dryness. Successive portions of acetone were added (to dissolve the small quantity of $Ni(2\ Meim)_2Cl_2$ formed) until colourless washings were obtained.

$Ni(2\ Meim)Cl_2$ C = 22.41 (22.66) N = 12.99 (13.23) H = 3.01 (2.84)

$Cu(2\ Meim)_4X_2$ (X = Cl, Br)

These were prepared similarly to the equivalent nickel complexes.

$Cu(2\ Meim)_4Cl_2$ C = 42.09 (41.48) N = 23.47 (24.20) H = 5.27 (5.19)

$Cu(2\ Meim)_4Br_2$ C = 34.87 (34.81) N = 20.14 (20.30) H = 4.31 (4.35)

$Cu(2\ Meim)_2X_2$ (X = Cl, Br)

Solutions of the appropriate copper salt and 2 methyl imidazole in acetone (chloride) or ethanol (bromide) were mixed in a 1:2 mole ratio. Crystals slowly separated (yellow-green, chloride and red brown, bromide) which were filtered and washed with the appropriate solvent and then ether.

$Cu(2\ Meim)_2Cl_2$ C = 32.64 (32.17) N = 18.58 (18.75) H = 4.10 (4.05)

$Cu(2\ Meim)_2Br_2$ C = 24.89 (24.81) N = 14.48 (14.44) H = 3.28 (3.12)

$Zn\ (2\ Meim)_4(NO_3)_2$

Hot acetone solutions of zinc nitrate and 2 methyl imidazole were mixed in a 1:4.4 mole ratio. A little benzene was added to give a cloudy solution. Upon standing, colourless crystals formed, which were filtered, washed with ether and recrystallised from an ethanol-benzene mixture.

$Zn(2\ Meim)_4(NO_3)_2$ C = 36.98 (37.08) N = 27.30 (27.04) H = 4.57 (4.63)

$Zn(2\ Meim)_2X_2$ (X = Cl, Br, I, NO_3)

These were prepared similarly to the equivalent cobalt complexes.

$Zn(2\ Meim)_2Cl_2$ C = 31.87 (31.95) N = 18.64 (18.64) H = 3.87 (3.99)

$Zn(2\ Meim)_2Br_2$ C = 24.85 (24.73) N = 14.65 (14.39) H = 3.00 (3.08)

$Zn(2\ Meim)_2I_2$ C = 20.77 (20.68) N = 10.53 (11.58) H = 2.55 (2.48)

$Zn(2\ Meim)_2(NO_3)_2$ C = 27.40 (27.23) N = 23.76 (23.88) H = 3.36 (3.41)

$Co(1,2DiMeim)_4I_2$ (Chapter V)

Dilute acetone solutions of 1,2 dimethyl imidazole and hydrated cobalt iodide were mixed in a 4.2:1 mole ratio. The solution was filtered and evaporated down until crystallisation occurred. The purple crystals were filtered off and washed with acetone.

$Co(1,2DiMeim)_4I_2$ C = 34.46 (33.97) N = 16.07 (15.85) H = 4.86 (4.55)

$Co(1,2DiMeim)_4(NO_3)_2$

An acetone solution of 1,2 dimethyl imidazole and a 2,2 dimethoxypropane solution of cobalt nitrate were mixed in a 4:1 mole ratio. Purple crystals formed which were washed with 2,2 dimethoxypropane and ether.

$Co(1,2DiMeim)_4(NO_3)_2$ C = 42.16 (42.33) N = 24.74 (24.71) H = 5.79 (5.69)

$Co(1,2DiMeim)_2X_2$ (X = Cl, Br, I)

Acetone solutions of 1,2 dimethylimidazole and the appropriate cobalt salt were mixed in a 2:1 mole ratio. The solution was evaporated to a small volume and allowed to cool (benzene was added in the case of the iodide). The crystals formed were filtered off and washed with ether.

$Co(1,2DiMeim)_2Cl_2$ C = 37.28 (37.30) N = 17.53 (17.40) H = 4.91 (5.01)

$Co(1,2DiMeim)_2Br_2$ C = 29.30 (29.22) N = 13.57 (13.64) H = 3.70 (3.93)

$Co(1,2DiMeim)_2I_2$ C = 23.88 (23.79) N = 11.16 (11.10) H = 3.40 (3.19)

$Co(1,2DiMeim)_2(NO_3)_2$

Hot 2,2 dimethoxypropane solutions of 1,2 dimethyl imidazole and cobalt nitrate were mixed in a 2:1 mole ratio. Upon cooling,

an oil is formed. The supernatant liquid was replaced by an equal volume of ether and the mixture was left overnight. The purple crystals formed were filtered off and washed with ether.

$Co(1,2DiMeim)_2(NO_3)_2$ C = 32.11 (32.00) N = 22.35 (22.40) H = 4.17 (4.30)

$Ni(1,2DiMeim)_4Cl_2$

$Ni(1,2DiMeim)_2Cl_2$ (see below) was stirred at 60°C with 1,2 dimethyl imidazole in a 1:6 mole ratio for 5 hours. After cooling, benzene was added, and the yellow solid was filtered off and washed with ether.

$Ni(1,2DiMeim)_4Cl_2$ C = 47.09 (46.75) N = 21.73 (21.80) H = 6.31 (6.28)

$Ni(1,2DiMeim)_4Br_2$

A solution of hydrated nickel bromide in ethanol/2,2 dimethoxypropane was filtered into a rapidly stirred solution of a sixfold mole excess of 1,2 dimethyl imidazole in 2,2 dimethoxypropane. The mixture was left overnight, filtered and the yellow product washed with ether.

$Ni(1,2DiMeim)_4Br_2$ C = 39.69 (39.85) N = 19.23 (18.62) H = 5.74 (5.36)

$Ni(1,2DiMeim)_4I_2$

Hydrated nickel iodide was dissolved in acetone and filtered into an acetone solution of 1,2 dimethyl imidazole in a 1:4 mole ratio. A red solid formed which was filtered off and washed with acetone and ether.

$Ni(1,2DiMeim)_4I_2$ C = 34.27 (34.46) N = 15.95 (16.08) H = 4.57 (4.63)

$Ni(1,2DiMeim)_4(NO_3)_2\ CCl_4$

Acetone solutions of 1,2 dimethyl imidazole and nickel nitrate were mixed in a 4:1 mole ratio. The solution was evaporated to small volume and carbon tetrachloride was added until a cloudiness appeared. Upon cooling, green blue crystals formed which were filtered off and washed with carbon tetrachloride.

This complex could only be isolated with solvent in the lattice (e.g. acetone or 2,2 dimethoxypropane) but only carbon tetrachloride appeared to give a stoichiometric adduct.

$Ni(1,2DiMeim)_4(NO_3)_2\ CCl_4$

C = 35.59 (34.97) N = 19.97 (19.44) H = 4.94 (4.47)

The analysis was reproducible on several samples.

$Ni(1,2DiMeim)_2X_2$ (X = Cl, Br)

Hot ethanol/2,2 dimethoxypropane solutions of the hydrated nickel halide and 1,2 dimethyl imidazole were mixed in a 1:2 mole ratio. The blue crystalline solid formed on cooling was recrystallised from acetone/2,2 dimethoxypropane and washed with ether.

$Ni(1,2DiMeim)_2Cl_2$ C = 37.30 (37.32) N = 17.60 (17.40) H = 4.90 (5.01)

$Ni(1,2DiMeim)_2Br_2$ C = 29.13 (29.25) N = 13.83 (13.64) H = 4.01 (3.93)

$Ni(1,2DiMeim_2I_2$

$Ni(1,2DiMeim)_4I_2$ was heated at 120°C to constant weight.

$Ni(1,2DiMeim)_2I_2$ C = 23.85 (23.81) N = 11.13 (11.10) H = 3.37 (3.19)

$Ni(1,2DiMeim)_2(NO_3)_2$

This was prepared similarly to the equivalent cobalt complex.

$Ni(1,2DiMeim)_2(NO_3)_2$ C = 31.75 (32.03) N = 22.12 (22.42) H = 4.42 (4.30)

$Cu(1,2DiMeim)_4Br_2$

Cupric bromide was dissolved in ethanol and 1,2 dimethyl imidazole was added in a 1:10 mole ratio. The solution was evaporated to a small volume and benzene was added. After leaving overnight, the blue crystals formed were filtered off and washed with benzene.

$Cu(1,2DiMeim)_4Br_2$ C = 40.04 (39.55) N = 18.47 (18.45) H = 5.29 (5.31)

$Cu(1,2DiMeim)_4(NO_3)_2$

A hot solution of cupric nitrate in ethanol/2,2 dimethoxypropanate and 1,2 dimethyl imidazole were mixed in a 1:4 mole ratio. The blue oil formed gave purple crystals on cooling which were isolated and washed with 2,2 dimethoxypropane and ether.

$Cu(1,2DiMeim)_4(NO_3)_2$ C = 42.03 (42.00) N = 24.42 (24.62) H = 5.69 (5.64)

$Cu(1,2DiMeim)_3Cl_2$

An acetone solution of cupric chloride was added slowly to a rapidly stirred acetone solution of 1,2 dimethyl imidazole in a 1:3 mole ratio. The solution was filtered and evaporated to a small volume. Upon cooling, pale green crystals formed which were filtered off and washed with ether.

$Cu(1,2DiMeim)_3Cl_2$ C = 42.69 (42.63) N = 19.88 (19.90) H = 5.65 (5.73)

$Cu(1,2DiMeim)_2Cl_2$

This was prepared as for the preceding complex but using a metal to ligand mole ratio of 1:2.

$Cu(1,2DiMeim)_2Cl_2$ C = 36.79 (36.78) N = 17.10 (17.16) H = 4.85 (4.94)

$Cu(1,2DiMeim)_2(NO_3)_2$

Acetone solutions of cupric nitrate and 1,2 dimethyl imidazole were mixed in a 1:2 mole ratio. The solution was evaporated to a small volume and ether was added until a cloudiness developed. The blue crystals isolated were washed with ether.

$Cu(1,2DiMeim)_2(NO_3)_2$ C = 31.26 (31.61) N = 21.96 (22.14) H = 4.25 (4.10)

$Zn(1,2DiMeim)_4(NO_3)_2.H_2O$

Hot acetone solutions of zinc nitrate and 1,2 dimethyl imidazole were mixed in a 1:4.4 mole ratio. The white crystals obtained on cooling were washed with carbon tetrachloride.

$Zn(1,2DiMeim)_4(NO_3)_2.H_2O$ C = 40.64 (40.60) N = 23.66 (23.67) H = 5.39 (5.80)

$Zn(1,2DiMeim)_2X_2$ (X = Cl, Br, I, NO_3)

The halides were prepared as for the equivalent cobalt complexes. The nitrate was prepared similarly to the equivalent copper complex.

$Zn(1,2DiMeim)_2Cl_2$ C = 36.49 (36.55) N = 17.02 (17.05) H = 4.81 (4.91)

$Zn(1,2DiMeim)_2Br_2$ C = 28.99 (28.78) N = 13.31 (13.42) H = 3.78 (3.87)

$Zn(1,2DiMeim)_2I_2$ C = 23.68 (23.48) N = 11.09 (10.95) H = 3.27 (3.15)

$Zn(1,2DiMeim)_2(NO_3)_2$ C = 31.52 (31.47) N = 21.93 (22.04) H = 4.56 (4.23)

$Co(2Mebeim)_2X_2$ (X = Cl, Br, I) (Chapter VI)

The appropriate cobalt salt and 2 methyl benzimidazole were mixed in a 1:2 mole ratio in acetone. The mixture was evaporated down and a little benzene was added. The crystals formed were filtered, washed with benzene and recrystallised from acetone/carbon tetrachloride.

$Co(2Mebeim)_2Cl_2$ C = 49.00 (48.77) N = 14.11 (14.22) H = 4.05 (4.07)

$Co(2Mebeim)_2Br_2$ C = 40.55 (39.78) N = 11.60 (11.28) H = 3.52 (3.32)

$Co(2Mebeim)_2I_2$ C = 33.33 (33.31) N = 9.50 (9.71) H = 2.61 (2.77)

$M(2Mebeim)_2(NO_3)_2$ (M = Co, Ni, Zn)

The metal nitrate was dissolved in 2,2 dimethoxypropane and a 2:1 mole ratio of 2-methyl benzimidazole in ethanol was added. The solution was evaporated to a small volume and was allowed to crystallise (addition of benzene being necessary for the zinc complex). The complexes were recrystallised from acetone/carbon tetrachloride, and were washed with carbon tetrachloride.

$Co(2Mebeim)_2(NO_3)_2$ C = 42.51 (42.95) N = 17.83 (18.77) H = 4.35 (3.58)

$Ni(2Mebeim)_2(NO_3)_2$ C = 43.27 (42.98) N = 18.01 (18.78) H = 4.34 (3.58)

$Zn(2Mebeim)_2(NO_3)_2$ C = 42.09 (42.35) N = 17.88 (18.51) H = 4.02 (3.53)

(The nitrogen analysis is reproducibly low, with no infrared evidence for the presence of solvent).

$Ni(2Mebeim)_2X_2$ (X = Cl, Br, I)

The solid hydrated nickel salt was added in a 1:2 mole ratio to an acetone solution of 2-methyl benzimidazole. The mixture was warmed, filtered and evaporated to small volume. Benzene was added, and the oil formed was separated, dissolved in acetone and filtered. Addition of benzene and evaporation led to crystallisation of the complex, which was filtered and washed with benzene.

$Ni(2Mebeim)_2Cl_2$ Cl = 18.22 (18.04) $Ni(2Mebeim)_2Br_2$ Br = 32.61 (33.09)

$Ni(2Mebeim)_2I_2$ I = 43.64 (44.00).

$Cu(2Mebeim)_2X_2$ (X = Cl, Br, NO_3)

2-methyl benzimidazole and the copper salt were mixed in a 2:1 mole ratio in ethanol. Upon standing, crystalline solids formed which were filtered and washed with ethanol and ether.

$Cu(2Mebeim)_2Cl_2$ C = 47.92 (48.19) N = 13.90 (14.04) H = 3.95 (4.04)

$Cu(2Mebeim)_2Br$ C = 39.29 (39.21) N = 11.67 (11.49) H = 3.21 (3.29)

$Cu(2Mebeim)_2(NO_3)_2$ C=43.05 (42.53) N = 18.32 (18.59) H = 4.01 (3.54)

$Zn(2Mebeim)_2X_2$ (X = Cl, Br, I)

These were prepared similarly to the cobalt complexes.

$Zn(2Mebeim)_2Cl_2$ C = 47.37 (48.02) N = 14.11 (14.06) H = 3.78 (4.02)

$Zn(2Mebeim)_2Br$ C = 39.22 (39.27) N = 11.24 (11.44) H = 3.24 (3.27)

$Zn(2Mebeim)_2I_2$ C = 32.51 (32.92) N = 9.32 (9.60) H = 3.23 (2.73)

$Cu(2CF_3beim)_2Cl_2$ (Chapter VII)

Solid hydrated cupric chloride was added slowly to a rapidly stirred, concentrated acetone solution of 2 trifluoromethyl benzimidazole to give a 1:2 mole ratio. A dark green solid formed which was filtered off and washed with a little acetone.

$Cu(2CF_3beim)_2Cl_2$ C = 38.08 (37.95) N = 11.17 (11.06) H = 2.09 (1.97)

$Cu(2CF_3beim)_2Br_2$

Ethanol solutions of cupric bromide and 2 trifluoromethyl benzimidazole were mixed in a 1:2.1 mole ratio and evaporated under vacuum to a small volume. The yellow green crystalline solid formed was filtered off and washed with ethanol and ether.

$Cu(2CF_3beim)_2Br_2$ C = 32.10 (32.27) N = 9.50 (9.40) H = 2.31 (2.35)

$Cu(2CF_3beim)_2(NO_3)_2$

Acetone solutions of hydrated cupric nitrate and 2 trifluoromethyl benzimidazole were mixed in a 1:2.1 mole ratio and allowed to stand. A blue grey crystalline solid formed which was filtered off and washed with a little acetone.

$Cu(2CF_3beim)_2(NO_3)_2$ C = 34.70 (34.35) N = 15.05 (15.01) H = 1.80 (1.81)

$Ag^+(2CF_3beim)^-$

Aqueous ethanol solutions of silver nitrate and 2 trifluoromethyl benzimidazole were mixed in a 1:3 mole ratio and heated. The white solid formed was filtered off and washed with aqueous ethanol and ether.

$Ag^+(2CF_3beim)^-$ C = 33.02 (32.77) N = 9.85 (9.56) H = 1.50 (1.37).

$CuL_2(NO_3)_2.2$ acetone (L = ($5Cl2CF_3$beim) or ($5NO_2 2CF_3$beim))

The blue crystals were prepared similarly to $Cu(2CF_3beim)_2(NO_3)_2$.

$Cu(5NO_2 2CF_3beim)_2(NO_3)_2.2$ acetone

C = 34.76 (34.48) N = 14.91 (14.63) H = 2.44 (2.35)

$Cu(5Cl\ 2CF_3beim)_2(NO_3)_2.2$ acetone

C = 35.62 (35.46) N = 11.04 (11.38) H = 2.77 (2.42)

$Cu(2Bubeim)_2X_2$ (X = Cl, Br)

Solutions of the hydrated cupric halide and 2 tert butyl benzimidazole in 1:2 mole ratio in acetone (chloride) and ethanol (bromide) were mixed, evaporated to a small volume and allowed to cool. The green crystals formed were filtered off and washed with acetone and ether.

$Cu(2Bubeim)_2Cl_2$ C = 54.28 (54.74) N = 11.27 (11.59) H = 5.81 (5.84)

$Cu(2Bubeim)_2Br_2$ C = 46.82 (46.20) N = - - H = 5.12 (4.94)

(c) Physical Techniques

Electronic Spectra were obtained by diffuse reflectance over the range 28 to 4 kK on a Beckman DK2. The low temperature spectra were recorded using an attachment designed by Dr D.M.L. Goodgame. Using liquid nitrogen coolant, this was shown to equilibrate at about $95^{o}K$. A white tile (11572 H. and R. Johnson Ltd) was used as reference. Solution spectra were obtained over the range 28 to 7 kK on a Perkin Elmer 350.

Magnetic Measurements were made by the Gouy method using both permanent and electro magnets. The variable temperature unit was constructed

by Dr D. Forster to the design of Figgis and Nyholm[161]. Mercury tetrathiocyanato cobaltate was used as calibrant[162,163].

Infrared Spectra were recorded on Grubb Parsons Spectromaster (4000-400 K), DM4 Mark II (500 - 200 K) and GM3 (200 - 66 K) instruments. Both the DM4 and GM3 were dried by a McGraw Edison Co. Lectrodryer. The poor transmission of the DM4 between 500 and 400 K and between 240 and 200 K, and the sensitivity of the GM3 to traces of water vapour, were two of the several unwelcome aspects of these instruments. Although silicon is the preferred window material for the low energy region[164], 1 mm polythene was found to be satisfactory. Vaseline was used as the mulling agent. Mercuric oxide is the best calibrant,[165] however the GM3 spectra were readily calibrated using the water vapour absorptions[166].

Raman Spectra were obtained on a Cary 81 instrument with a Spectra Physics 125 He-Ne laser using 180° collection. No results could be obtained on a Cary 81 using Toronto arc or 300 mW Argon ion laser sources employing 90° collection (King's College, Physics Department, instrument). Polarisation measurements on solutions were performed using carbon tetrachloride as an internal standard[167].

E.s.r. Spectra were obtained on a Varian V 4500-15 spectrometer using the appropriate X band and Q band accessories. Spectra were calibrated using Mn^{2+} in MgO[168,169].

X-ray powder photographs were taken by Miss Osborne of the X-ray Crystallography Department on an Erraf-Nonius Guinier-De Wolff II camera using iron radiation.

Analyses: Carbon, hydrogen and nitrogen analyses were performed by the Microanalytical Department. Classical techniques were used for other elements.

CHAPTER X

CONCLUSIONS

Biological

It has recently been shown that a series of chelating 2-thiazolyl benzimidazoles, which exhibit anthelmintic and fungicidal activity, readily form metal complexes, and that the metal complexes isolated showed in some cases increased activity over that of the parent ligand[208,209]. In the case of the benzimidazole ligands studied here however, the small number of complexes formed and their instability towards water would indicate that metal complexation is not involved in the mode of action of the herbicides, nor would metal complexes appear to be of any interest as a way of improving the activity of the organic moiety. It is interesting to note though, the preference for coordination to copper ions in the few cases where complexation occurred.

The imidazole, and many of the substituted imidazole complexes, are quite stable in water, and may well be biologically significant. Investigations are currently in progress as to the potential of these complexes and their parent ligands as fungicides and acaricides[210].

Chemical

Variations in stereochemistry of the imidazole and substituted imidazole complexes could not always be coordinated with basicity, or with steric or electronic effects. Steric effects can in part explain the formation of the almost five coordinate complexes $Ni(2Meim)_4Cl_2$ and Br_2,

though they do not explain the fact that $Ni(2Meim)_2Cl_2$ has a polymeric octahedral structure whereas the less sterically hindered complex $Ni(NMeim)_2Cl_2$ has a pseudotetrahedral structure. This is the opposite to what is expected from steric effects (cf. the equivalent 2- and 3-methyl pyridine complexes[211]) and from basicity changes[212] (NMeim pK_a = 7.33, 2Meim pK_a = 7.86). The existence of $Ni(2Meim)_2Cl_2$ as a pseudotetrahedral species in solution would indicate that the comparative lattice energies of the two environments are the most important factor in deciding the stereochemistry of the solid state species.

The difference in structure between the complexes $Cu(NMeim)_2Cl_2$ and Br_2 would also seem to be due to comparative lattice energies as the chloride does not have a pseudotetrahedral environment in solution, and a similar case occurs for the complex $Co(2Meim)_4(NO_3)_2$, which is tetrahedral in solution, whereas the most stable solid form is octahedral. The compound $Ni(2Meim)_{3.5}I_2$ is most clearly an example of a complex whose existence is due to packing effects. Slightly different is $Ni(1,2DiMeim)_4(NO_3)_2$, which appears to require the presence of solvent molecules to stabilize the lattice.

The formation of the substituted benzimidazole complexes appears to be governed by electronic effects, the presence of electron withdrawing groups such as CF_3, Cl and NO_2 on the rings causing a reduction in the coordinating ability, as might be expected. It was possible that the 2-trifluoromethyl group caused steric hindrance, but since complexes could be obtained even with a tert-butyl group substituted in the 2 position, the major effect would appear to be electronic.

(To confirm that the presence of the 2-trifluoromethyl group was the main cause of the reluctance of the ligands to coordinate, it has been shown that 5 nitro 2 methyl benzimidazole readily forms complexes analogous to those isolated with 2 methyl benzimidazole[213]). Though the 2-trifluoromethyl group would appear to be the most influential on bonding ability, the inability to obtain any complexes using ligands with more than one electron withdrawing substituent in the benzene ring indicates that the influence from these groups is far from negligible.

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