Contribution from the Department of Chemistry, Imperial College of Science and Technology, London S.W. 7, United Kingdom

Spectroscopic Studies of Substituted Imidazole Complexes. II. N-methylimidazole Complexes of Divalent Cobalt, Nickel, Copper and Zinc

D. M. L. Goodgame, M. Goodgame, and G. W. Rayner-Canham

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The preparations are reported of various 6:1, 4:1, 2:1 and 1:1 complexes of N-methylimidazole with divalent cobalt through zinc. The results of electronic and low frequency vibrational spectral and magnetic susceptibility measurements are presented and are used to assign coordination geometries. E.p.r. data are also given for the copper complexes.

Introduction

As part of our program to investigate the coordination behavior of ligands containing the imidazole ring we recently described[1] some complexes of cobalt(II) through zinc(II) with 2-methylimidazole, The steric influence of the methyl group in the 2-position was sufficient to prevent the isolation of 6:1 complexes and also led to the formation of an unusual coordination geometry in the case of the compounds Ni(2–methylimidazole)$_4$X$_2$ (X = Cl or Br).[2] We report here an extension of this work to the ligand N–methylimidazole (=L). As well as a reduction in the steric factor mentioned above the alkylation of one of the ring nitrogens would be expected to diminish considerably the hydrogen bonding capability of the ligand.

Experimental Section

Unless stated otherwise the compounds were dried in vacuum over P_2O_5. Analytical results (C, H, and N by the Microanalytical Laboratory, Imperial College) for all the compounds were good.

$ML_6X_2 . 2H_2O$ (X = Cl, Br; M = Co, Ni), ML_6X_2 (X = I, NO$_3$; M = Co, Ni). The appropriate hydrated metal salt and N-methylimidazole were mixed in 1:10 mole ratio in hot acetone (for Co) or ethanol (for Ni). The complexes crystallised on cooling and were washed with CCl_4. The chlorides and bromides were air-dried. The cobalt compounds are pink and the nickel complexes are mauve (when prepared under strictly anhydrous conditions NiL_6I_2 is yellow — see Discussion section).

ZnL_6I_2. A hot acetone solution of zinc iodide and N–methylimidazole in 1:6.6 mole ratio gave white crystals on cooling. These were washed with acetone and ether.

NiL_4Cl_2. Hydrated nickel chloride was dissolved in an ethanol 2,2-dimethoxypropane mixture and the calculated quantity of N-methylimidazole was added, followed by ether until a cloudiness was observed. On storage green crystals formed which were collected and washed with ether.

CuL_4X_2 (X = Cl, Br, NO$_3$). The cupric salt and N-methylimidazole were mixed in 1:4.4 mole ratio in acetone (X = Cl, NO$_3$) or ethanol (X = Br). The chloride and nitrate separated as blue crystals, which were washed with acetone and ether. In the case of the bromide it was necessary to evaporate the solution to small bulk before the dark blue complex crystallized. The bromide was recrystallized from ethanol. The chloride was hygroscopic and formed a dihydrate on exposure to air.

CuL_4I_2. Cupric perchlorate and N-methylimidazole were mixed in 1:6 mole ratio in ethanol. A warm solution of KI was stirred into the resulting slurry. After filtering and allowing to stand, grey crystals formed, which were collected and washed with ethanol and ether.

ML_2X_2 (M = Co, Zn; X = Cl, Br, I) NiL_2X_2 (X = Cl, Br). The appropriate metal halide and N-methylimidazole were mixed in 1:2 mole ratio in hot acetone (for Co or Zn) or in ethanol/2,2-dimethoxypropane (for Ni). The solutions were evaporated to small volume. The cobalt chloride, zinc chloride, and zinc bromide complexes crystallized spontaneously, but it was necessary to add benzene to cause precipitation of the other compounds. The cobalt chloride and bromide complexes and their nickel analogs are blue. They were recrystallized from acetone/benzene; blue-green CoL_2I_2 was recrystallized from CH_2Cl_2/CCl_4 and ZnL_2Cl_2 from nitromethane.

NiL_2I_2. This dark green complex was obtained by heating NiL_6I_2 to constant weight at 120°C in vacuum.

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(1) D. M. L. Goodgame, M. Goodgame, and G. W. Rayner-Canham, *Inorg. Chim. Acta*, 3, 399 (1969).

CuL_2X_2 ($X = Cl, NO_3$). These were prepared as for the corresponding 4:1 complexes but using a 2:1 mole ratio of ligand to metal salt. They were recrystallized from acetone. The chloride is green and the nitrate is blue.

CuL_2Br_2. Cupric bromide was stirred into a hot acetone solution of the calculated quantity of N-methylimidazole. The solution was filtered and allowed to cool, when green crystals separated. These were collected and washed with acetone and ether.

$NiLX_2$ ($X = Cl, Br$). The nickel halide was dissolved in an ethanol/2,2-dimethoxypropane mixture. After concentration, the calculated amount of N-methylimidazole was stirred into the hot solution. The solid which formed was collected, washed with ethanol/2,2-dimethoxypropane, and then with ether. The chloride is yellow and the bromide orange-pink.

$CuLCl_2$ Equimolar proportions of cupric chloride and N-methylimidazole were mixed in acetone and filtered. Concentration of the filtrate caused the separation of the khaki-coloured complex.

Physical Measurements. These were carried out as described previously.[1,3]

Results and Discussion

We have isolated the compounds ZnL_6I_2 and ZnL_2X_2 ($X = Cl, Br, I$) and the cobalt, nickel, and copper complexes listed in Table I. The formation of 6:1 complexes by N-methylimidazole contrasts with the behavior of its 2-methyl-analog which did not form complexes of that stoichiometry with these metal ions.[1,4] This, presumably, reflects the decrease in the steric hindrance on moving the methyl group from the carbon atom adjacent to the coordinating nitrogen. However, the hexakis-N-methylimidazole compounds are formed less readily than their imidazole analogs[3,5] and are also less stable towards loss of ligand after isolation.

The preparation of $CoL_6Cl_2 . 2H_2O$, for example, required a large excess of N-methylimidazole and the solid compound had to be air-dried at room-temperature to avoid loss of the ligand. Even so the *finely powdered* solid tended to change to CoL_2Cl_2 on prolonged exposure to the atmosphere. The ease of removal of ligand from the hexakis-compounds was in the order $Cl > Br > I \sim NO_3$ for the anion, and $Co > Ni$ (for nickel, the solid compounds appeared to be quite air stable, but attempts to dehydrate the chloride and bromide under vacuum, or thermally, led to ligand loss here, also).

The compound NiL_6I_2 could be obtained in either of two colours, mauve or yellow, the latter being formed when strictly anhydrous conditions were maintained during the preparation. However both forms had identical X-ray powder patterns, magnetic moments and low frequency infrared spectra, and neither showed the presence of lattice water either by their infrared spectra or by the analytical results (Found for yellow form C, 35.78; H, 4.42; N, 20.76. Found for mauve form C, 35.94; H, 4.35; N, 20.92. Calcd. for NiL_6I_2, C, 35.82; H, 4.47; N, 20.86%). The difference in colour arises from

Table I. Room temperature magnetic moments and diffuse reflectance spectral band energies of the complexes

	μ_{eff}(B.M.)	ν (cm^{-1})
$CoL_6Cl_2 . 2H_2O$	5.06	9,430, ~16,000 wsh, ~19,100 sh, 20,400
$CoL_6Br_2 . 2H_2O$	5.05	9,520, ~15,300 wsh, ~16,100 wsh, ~19,100 sh, 20,500
CoL_6I_2	5.00	9,750, ~14,300 wsh, ~16,200 wsh, ~19,100 sh, 20,600
$CoL_6(NO_3)_2$	5.16	9,700, ~16,000 wsh, ~19,100 sh, 20,500
CoL_2Cl_2	4.66	6,400 sh, 7,050, 9,090, 15,900, 16,500, 17,200 sh, [b]
CoL_2Br_2	4.69	6,200 sh, 6770, 8700, 15,100, 16,300, 16,900 sh [b]
CoL_2I_2	4.67	6,100 sh, 6670, 8200, 14,600, 15,800, 16,600 sh, [b]
$NiL_6Cl_2 . 2H_2O$	3.16	10,600, ~13,500 wsh, 17,200, ~23,200 wsh, 26,900
$NiL_6Br_2 . 2H_2O$	3.11	10,700, ~13,300 wsh, 17,300, ~23,500 wsh, 26,900
NiL_6I_2 [c]	3.12	10,900, ~13,300 wsh, 17,700, 26,300 vs
$NiL_6(NO_3)_2$	3.01	10,900, ~13,300 wsh, 17,500, ~23,800 wsh, 27,200
NiL_4Cl_2	3.18	7,870, 11,200, 13,200, 16,100, 20,500 vw, 25,600
NiL_2Cl_2	3.29	~5700 br, ~9000 sh, 10,900, ~12,500 sh, 17,400, ~18,500 sh, 24,400 w
NiL_2Br_2	3.43	~5550 br, 8770, 10,900, ~12,000 sh, 16,400, ~17,400 sh, 23,900 w
NiL_2I_2	3.44	~5700 br, 8150, 10,200, ~11,000 sh, 15,200, ~18,400 sh
$NiLCl_2$	3.47	7600 [d], 12,100, 13,100, ~18,500 wsh, 22,200
$NiLBr_2$	3.39	7250 [d], ~11,400 sh, 12,400, ~18,000 wsh, 21,400
$CuL_4Cl_2 . 2H_2O$	1.84	~14,300 sh, 17,200
CuL_4Br_2	1.87	16,700
CuL_4I_2	1.88	16,700, 25,800
$CuL_4(NO_3)_2$	1.91	17,200
CuL_2Cl_2	1.91	12,200
CuL_2Br_2	1.88	14,600, 24,400
$CuL_2(NO_3)_2$	1.85	~13,800 sh, 15,400
$CuLCl_2$	1.84	~6000 vbr, w, sh, 12,500, ~21,000 sh

[a] Low energy absorptions obscured by vibrational bands. [b] High energy spin-forbidden bands omitted for conciseness. [c] Yellow form. [d] Asymmetric to lower energy.

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(2) F. Akhtar, D. M. L. Goodgame, M. Goodgame, G. W. Rayner-Canham, and A. C. Skapski, to be published.

(3) D. M. L. Goodgame, M. Goodgame, P. J. Hayward, and G. W. Rayner-Canham, *Inorg. Chem.*, *7*, 2447 (1968).

(4) W. J. Eilbeck, F. Holmes, C. E. Taylor, and A. E. Underhill, *J. Chem. Soc. (A)*, 128 (1968).

(5) W. J. Eilbeck, F. Holmes, and A. E. Underhill, *ibid.*, 757 (1967).

an appreciable enhancement of the spectral intensity in the region of the $^3A_{2g}\rightarrow{}^3T_{1g}$ (P) transition for the yellow form, but the energies of the d-d bands for the two forms are the same.

Electronic Spectra and Coordination Geometries. The room-temperature magnetic moments and diffuse reflectance spectral band energies are listed in Table I. The near identity of the spectra of the hydrated 6: 1 complexes of cobalt and nickel with those of the related anhydrous compounds indicates that the water molecules are not coordinated. The Dq value of N-methylimidazole is ~ 1080 cm^{-1} and is thus very close to that of imidazole itself.[5]

In contrast to the behavior of 2-methylimidazole only one 4: 1 complex could be obtained with the nickel halides, NiL_4Cl_2. The electronic spectrum of this compound shows the pronounced splittings of the $^3T_{1g}$(F) and $^3T_{2g}$ levels typical[6,7] of *trans*-distorted octahedral (D_{4h}) nickel compounds. The spectrum of NiL_4Cl_2 is, in fact, very similar to that[8] of Ni(pyrazole)$_4$Cl$_2$, which is known[9] to have this type of configuration with Ni–N = 2.09 and 2.10 Å, and Ni–Cl = 2.51 Å.

The spectra of the 2: 1 cobalt and nickel complexes, and the magnetic moments of the former, suggest that they have pseudo-tetrahedral configurations. The nickel compounds have two d-d bands below 10,000 cm^{-1} which are presumably components of the $^3T_{1g}$(F) level split in a very distorted ligand field. The compounds Ni(di-2-pyridyl-amine)X$_2$ (X = Br, I) also show two bands in this region,[10] whereas usually only one broad band is observed.[1,11] The relatively small orbital contribution to the magnetic moments of the nickel complexes is typical of those found for distorted tetrahedral geometries. The tetrahedral structure of NiL_2Cl_2 contrasts with the octahedral, polymeric configuration of its analog with 2-methylimidazole[1] in the solid state (the latter was tetrahedral in acetone[1]).

The spectral and magnetic properties of the polymeric 1: 1 nickel halide complexes are very similar to those of their benzimidazole[12] and imidazole[3] analogs.

The reflectance spectra of the CuL_4X_2 compounds each showed a broad band with its maximum in the region 16,500-17,500 cm^{-1}. Despite the fact that no anion-dependent vibrational bands were observed in the 400-200 cm^{-1} region (see below) the electronic band energies and contours varied with X suggesting that the anions, or possibly the water molecules for $CuL_4Cl_2 . 2H_2O$, are weakly coordinated as in Cu en$_2$X$_2$ and related compounds.[13] The e.p.r. spectra of polycrystalline samples of the 4: 1 cupric halide complexes are also typical of tetragonal copper(II) systems. The g-values, measured by Kneubühl's procedure,[14] are listed in Table II.

Table II. E.p.r. parameters for some N-methylimidazole complexes of copper(II)

	$g_{\parallel}$	$g_{\perp}$	A,, (cm^{-1})
$CuL_4Cl_2 . 2H_2O$	2.28	2.00	0.0175
CuL_4Br_2	2.28	2.01	0.0175
CuL_4I_2	2.27	2.00	0.0164
$CuL_4(NO_3)_2$	[a]	2.00	—
CuL_2Cl_2	2.28	2.10, 2.05	—
$CuL_2(NO_3)_2$	2.27	2.05	—

[a] Poorly resolved.

In each case the g,, signal showed hyperfine components with A,, close to 0.017 cm^{-1}. The spectrum of $CuL_4(NO_3)_2$ was also of the two g-value type but here line broadening was sufficient to prevent an accurate measurement of g,,. This effect was even more pronounced for polycrystalline samples of CuL_2Br_2 and $CuLCl_2$ and for these only a very broad derivative signal was observed. The powder pattern of CuL_2Br_2 showed that it was not isomorphous with its cobalt and zinc analogs and its electronic and far infrared spectra suggest that it has a tetragonal, halide-bridged structure. Halide bridges are also probable in $CuLCl_2$, the electronic spectrum of which resembles those of some reversed tetragonal copper(II) complexes, such as β–Cu(NH$_3$)$_2$Br$_2$,[15] when allowance is made for the weaker total ligand field in the 1: 1 N–methylimidazole complex. The 1: 1 copper chloride compound was not isomorphous with its nickel analog.

In contrast to the results for CuL_2Br_2 the e.p.r. spectrum of the corresponding nitrate showed both $g_{\parallel}$ and $g_{\perp}$ bands and for CuL_2Cl_2 a three g-value spectrum was observed. The 2: 1 cupric halide complexes differ not only in their e.p.r. spectra but also in their electronic and far infrared spectra. The d-d band of the chloride (Table I) is at distinctly *lower* energy than that of the bromide and those of some other halide bridged copper(II) complexes.[16] Although X-ray powder photographs show that CuL_2Cl_2 is not isomorphous with its cobalt and zinc analogs[17] the close similarity of the low frequency infrared spectra of the series of compounds ML_2Cl_2 (M = Co, Ni, Cu, Zn) (Table III) suggests that CuL_2Cl_2 has a distorted tetrahedral configuration. The electronic band energy of 12,200 cm^{-1} is comparable to those of other copper(II) compounds thought to have this geometry[1,18,19] but there is not the band splitting observed[1,18] for some of these compounds.

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(6) D. M. L. Goodgame, M. Goodgame, M. A. Hitchman, and M. J. Weeks, *ibid.*, 1769 (1966).

(7) D. A. Rowley and R. S. Drago, *Inorg. Chem.*, *6*, 1092 (1967).

(8) The reflectance spectrum of Ni(pyrazole)$_4$Cl$_2$ has been partially described by Daugherty and Swisher (*Inorg. Chem.*, *7*, 1651 (1968)). The complete list of d-d bands is: 8,150, 11,800, 13,300, 16,500, $\sim$21,300 vwsh, 26,000 cm^{-1}.

(9) C. W. Reimann, A. D. Mighell, and F. A. Mauer, *Acta Cryst.*, *23*, 135 (1967).

(10) C. D. Burbridge and D. M. L. Goodgame, *J. Chem. Soc.* (*A*), 237 (1968).

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(13) B. J. Hathaway, D. E. Billing, P. Nicholls, and I. M. Procter, *ibid.*, (A) 319 (1969) and refs. therein.

(14) F. K. Kneubühl, *J. Chem. Phys.*, *33*, 1074 (1960).

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(16) D. E. Billing and A. E. Underhill, *J. Inorg. Nucl. Chem.*, *30*, 2147 (1968).

(17) CoL_2Cl_2 and ZnL_2Cl_2 are isomorphous.

(18) L. Sacconi and M. Ciampolini, *J. Chem. Soc.*, 276 (1964).

(19) D. Forster and D. M. L. Goodgame, *ibid.*, 262 (1965).

Table III. Vibrational Spectra (80-400 cm^{-1}) of some tetrahedral M(N-methylimidazole)$_2$X$_2$ complexes

		Ligand band	ν(M—X)	ν(M—N)	Other bands
CoL_2Cl_2	IR[a]	368 mw	323 s, 296 s	267 ms	240 w, 219 w, 160 w, 142 s, ~105 mbr
CoL_2Br_2	IR	367 m	259 s, 184 s	271 sh	248 m, ~222 wsh, 158 s, 137 s
CoL_2I_2	IR	365 w	219 s	270 ms	242 mw. 162 s, 145 s
NiL_2Cl_2	IR	370 w	323 s, 288 s	269 m	~238 wsh, 227 wbr, 175 mbr, 145 s, 114 mw
NiL_2Br_2	IR	368 m	259 s[c] 182 s	[d]	~240 wsh, 161 m, 140 m, ~90 wbr
NiL_2I_2	IR	366 m	228 s	266 m, 258 ms	175 s, 154 w, 137 s, 89 w
CuL_2Cl_2	IR	382 m	311 s, 279 s	262 m	230 w, 208 m, 188 s, 167 s, 104 m
ZnL_2Cl_2	IR	368 m	306 s, 285 s	235 s	216 m, 183 w, 160 ms, 144 s, 112 m
	R	371 m	289 s	—	246 w, 223 w, 189 w, 163 w, 149 w
ZnL_2Br_2	IR	366 m	234 s[c] 187 s	[d]	~223 wsh, 159 m, 137 m
	R	371 m	190 s	—	244 s, 175 w, 157 w, 150 s
	R[b]	394 s	187 w	—	—
ZnL_2I_2	IR	364 m	206 s	225 m	169 s, 140 m
	R	371 m	206 w	—	254 ms, 170 m, 142 s
	R[b]	395 s	—	—	144 vs pol.

[a] IR = infrared; R = Raman; solids unless stated otherwise. [b] In acetone. [c] Probably also contains ν(M—N) absorption. [d] ν(M—Br) in same region.

Table IV. Vibrational spectra (80-400 cm^{-1}) of N-methylimidazole(L) and some of its complexes

L	IR	351 mw, 222 wbr
	IR[a b]	355 s, 223 s, 80
	R	358 m, 225 ms
	R[b]	353, 220
CoL_6I_2	IR	371 m, 245 m, 220 s, 180 s, 170 m, 150 w, ~80 m
	R	376 m, 247 m
$CoL_6(NO_3)_2$	IR	372 m, 242 m, 220 s, 180 sbr, 151 w
	R	378 m, 246 m
NiL_6I_2	IR	374 w, 259 s, 230 s, 181 s, 161 m
$NiL_6(NO_3)_2$	IR	378 w, 261 s, 231 s, 188 s, 163 mw
ZnL_6I_2	IR	368 w, ~239 wsh, 188 vs
	R	373 s, 247 s, 190 sh, 105 sh
NiL_4Cl_2	IR	377 w, 366 w, 254 s, 226 s, 177 s, 150 w, 117 wbr
$CuL_4Cl_2 . 2H_2O$	IR	366 w, 280 s, 271 s, 248 m, 207 m, 191 s, 110 s, vbr
CuL_4Br_2	IR	381 w, 374 w, 288 s, 280 s, 256 s, ~246 sh, 213 s, 197 s, 95 svbr
CuL_4I_2	IR	383 w, 372 w, 282 s, 260 m, ~ 245 wsh, 204 s, 195 s, 88 s
$CuL_4(NO_3)_2$	IR	384 w, 372 w, 296 s, 282 m, 255 s, 220 s, 206 s, 197 s, 95 s
CuL_2Br_2	IR	370 m, 299 s, 218 s, 198 s, 179 s, 127 s, 87 m
$CuL_2(NO_3)_2$	IR	377 w, 303 sbr, 222 w, 195 m, 170 w, 137 w, 88 w
$NiLCl_2$	IR	372 w, 264 sh, 247 s, 200 s, 148 m, 83 m
$NiLBr_2$	IR	370 w, 243 m, 216 m, 183 s, 158 s, 146 s, 132 m
$CuLCl_2$	IR	380 w, 351 w, 325 m, 284 s, vbr, 215 w, 187 m, 167 s, 157 sh, 142 w, 116 s, 93 s

[a] From ref. 20. [b] From: C. Perchard and A. Novak, *Spectrochim. Acta, 23 A*, 1953 (1967).

Vibrational Spectra (80-400 cm^{-1}). The low-frequency vibrational bands of N-methylimidazole are listed in Table IV. Upon complexing the band at ~355 cm^{-1} is raised in frequency. It is split into two in the anhydrous tetragonal 4:1 complexes but not in the other compounds.

Results for the anhydrous 6:1 compounds are given in Table IV (the hydrates gave poorly resolved spectra below 200 cm^{-1} and are not listed). Assignment of the bands is complicated by two factors. First, it is uncertain how the frequency and intensity of the free ligand 223 cm^{-1} band (assigned[20] as an out-of-plane skeletal (γ-CH$_3$–N) mode) are modified upon coordination, and, second, there is an appreciable difference between the spectra of ZnL_6I_2 and those of ML_6X_2 (M = Co, Ni; X = Br, I) although the three iodides are isomorphous.

The fact that the Raman bands at ~247 cm^{-1} are significantly higher in frequency than the bands assigned[3] as ν_1 (O_h notation) for the hexakis-imidazole complexes suggests that this may correspond to the 225 cm^{-1} band in the free ligand rather than to ν_1. However neither of the 6:1 cobalt complexes had Raman bands at lower frequency, whereas ZnL_6I_2 had a weak Raman band at ~190 cm^{-1} (*cf.* ν_1 at 192 cm^{-1} for Zn(imidazole)$_6^{2+}$).[3] The i.r. spectra of CoL_6^{2+} and ZnL_6^{2+} also have a band close to 240 cm^{-1}, but in NiL_6^{2+} this, and the band at 220 cm^{-1} for CoL_6^{2+}, are replaced by a pair of bands at 230 and 260 cm^{-1}, and for some of the other N-methylimidazole complexes (*e.g.* CuL_2X_2, X = Cl, Br) there are no i.r. bands between 220 and 280 cm^{-1}. It appears, then, that the ~223 cm^{-1} free ligand band is either quite variable in its frequency in metal complexes or has a comparatively low intensity and is thus frequently masked by metal-nitrogen, or metal-halogen, modes. If the latter alternative is correct, then the pair of bands between 200 and 300 cm^{-1} for CoL_6^{2+} and NiL_6^{2+} may be assigned as components of ν_3 the F_{1u} M–N stretch,[21] split because

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(20) C. Perchard and A. Novak, *J. Chem. Phys.*, *48*, 3079 (1968).

(21) The terms « M—N stretch » and « N—M—N bend » used here and later are employed for convenience to describe modes which, although undoubtedly more complex, are thought to have appreciable M—N etc. stretching character.

of site or molecular symmetry lower than O_h. By analogy with the hexakisimidazole compounds[3] the corresponding absorption for ZnL_6^{2+} would be expected to be slightly below 200 cm^{-1}; only one strong band is found, at 188 cm^{-1} but this is quite broad (half-band width ~45 cm^{-1}). The pairs of bands at 150 and 180 cm^{-1} for CoL_6^{2+} and at ~160 and ~185 cm^{-1} for NiL_6^{2+} may be due to modes with predominantly N–M–N bending character, but no corresponding band was observed for ZnL_6I_2.

The spectrum of NiL_4Cl_2 below 300 cm^{-1} closely resembles that of its imidazole analog[3] but with better band resolution in the 150-180 cm^{-1} region, and similar assignments to those for the imidazole complex may be made here. The 4:1 cupric halide complexes show no bands assignable as copper-halogen stretches, but there is an extra band at 220 cm^{-1} for the nitrate, which we tentatively ascribe to ν(Cu–O) of relatively weakly coordinated nitrate groups. This may be compared with the very strong, broad band at 303 cm^{-1} for $CuL_2(NO_3)_2$ which probably contains both ν(Cu–N) and also ν(Cu–O) of the nitrate groups which would be more strongly coordinated in this compound. The spectra of the 4:1 copper complexes in this region are more complicated than that of NiL_4Cl_2. The chloride, bromide, and nitrate have a pair of bands in the 270-300 cm^{-1} region which are reasonably assigned as components of ν(Cu–N) (ν_6, E_u, in D_{4h}). The absence of anion independent bands between 100 and 180 cm^{-1} suggests that one or both of the bands near 200 cm^{-1} may be due to N–Cu–N bending modes derived from ν_7 (E_u) in D_{4h} symmetry.

Results and some assignments for the tetrahedral ML_2X_2 compounds are given in Table III. The ν(M–Cl) bands were readily identified, as were the asymmetric ν(M–Br) and ν(M–I) bands. The proposed assignments for the symmetric ν(M–Br) absorptions give larger separations between the two metal-halogen modes than for the chlorides, but for the nickel and zinc bromides there were no other strong bands in the correct region. Moreover the assignment of the 187 cm^{-1} band as ν_{sym}(Zn–Br) is supported by the observation of a Raman band at 190 cm^{-1} (*cf.* 285 cm^{-1} (IR) and 289 cm^{-1} (R) for ν_{sym}(Zn–Cl)). Assignment of ν_{sym}(M–I) is not unambiguous, the choice resting between the band at 160-170 cm^{-1} and that at ~140 cm^{-1}. A similar problem was encountered in the corresponding 2-methylimidazole complexes and the remarks made previously[1] apply here also.

For all the compounds except NiL_2Br_2 and ZnL_2Br_2, where ν_{as}(M–Br) interferes, at least one metal-nitrogen stretching band may be assigned. The lower frequency of this absorption for the zinc compounds compared with those of cobalt and nickel parallels the difference observed[22] for tetrahedral $M(pyridine)_2X_2$ compounds. Many of the compounds have weak bands in the 220 and/or 240 cm^{-1} regions (Table III) but, as discussed earlier, the uncertainty as to the position of the 223 cm^{-1} ligand band precludes any confident assignment of the other, expected ν(M–N) band.

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(22) R. J. H. Clark and C. S. Williams, *Inorg. Chem.*, *4*, 350 (1965).