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Spectroscopic Studies of Substituted Imidazole Complexes. III. 2-Methylbenzimidazole Complexes of Divalent Cobalt, Nickel, Copper, and Zinc

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The preparations are reported of the 2-methylbenzimidazole (= L) complexes ML_2X_2 (M = Co, Ni, Cu, or Zn, X = Cl, Br, or NO_3) and ML_2I_2 (M = Co, Ni, or Zn). 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

Benzimidazoles with a wide variety of 2-substituents have interesting and useful biological properties. For example, 2-trifluoromethylbenzimidazole derivatives have been patented as herbicides,[1] and 2-α-hydroxybenzylbenzimidazole has anti-virus activity.[2] As part of a study of the coordination behaviour of molecules of this general type we have investigated metal complexes of 2-methylbenzimidazole (= L), since it is both useful itself as a herbicide,[3] and is also the simplest member of the class. We report here the results for divalent cobalt, nickel, copper, and zinc.

Experimental Section

Preparation of Complexes. All complexes were dried in vacuum over P_2O_5. Analyses (C, H, and N) for all compounds were good.

CoL_2X_2 and ZnL_2X_2 (X = Cl, Br, or I). Solutions of the metal salt and 2-methylbenzimidazole in acetone were mixed in 1:2 mole ratio. The mixture was evaporated to small bulk and a little benzene was added. The crystals formed were filtered off, washed with benzene, and recrystallised from acetone/carbon tetrachloride.

CuL_2X_2 (X = Cl, Br, or NO_3). Solutions of the copper salt and 2-methylbenzimidazole in ethanol were mixed in 1:2 mole ratio. On standing, crystalline solids were formed, and were filtered off, and washed with ethanol and ether.

$ML_2(NO_3)_2$ (M = Co, Ni, or Zn). The metal nitrate was dissolved in 2,2-dimethoxypropane, and a 2:1 mole ratio of 2-methylbenzimidazole was added. The solution was evaporated to small volume and was allowed to crystallise (addition of benzene was necessary for the zinc complex). The compounds were recrystallised from acetone/carbon tetrachloride, and were washed with carbon tetrachloride.

NiL_2X_2 (X = Cl, Br, or I). These were prepared as described previously.[4]

Physical Measurements. These were made as described previously[5]

Results and Discussion

All the compounds isolated have the stoichiometry ML_2X_2; the steric requirements of 2-methylbenzimidazole presumably preclude the formation of complexes with a higher ligand: metal ratio. With the cobalt halides, complexes of essentially tetrahedral geometry are formed. Their magnetic moments and intense reflectance spectra (Table I) agree well with those expected for this stereochemistry, with Δ values of 4000 (X = I) to 4500 cm^{-1} (X = Cl).

Although the compound $CoL_2(NO_3)_2$ has a relatively low magnetic moment (4.47 B.M. at room temperature) its electronic spectrum does not resemble those of distorted tetrahedral cobalt(II) compounds. It is probably six coordinate, with chelating nitrate groups.

All the cobalt(II) nitrate complexes which are known, or may be reasonably supposed, to be of this type have rather similar electronic spectra (Table II). In each case, in addition to the strong, broad, or multiple, band in the 17,500-21,500 cm^{-1} region expected for the ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transition for an octahedral cobalt(II) complex and bands in the near infrared region, there is a weak to medium intensity band at 12,000-14,500 cm^{-1}. The exact position of this extra band depends on the type of neutral ligand present, being near 12,000 cm^{-1} for oxygen donors[6] and at 13,400-14,500 cm^{-1} for nitrogen donors.[7-9] This de-

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(1) See, for example, D.E. Burton, A.H. Lambie, J.C.L. Ludgate, G.T. Newbold, A. Percival, and D.T. Saggers. *Nature, 208*. 1166 (1965).

(2) A.C. Hollinshead and P.K. Smith, *J. Pharm. Exp. Therapeuticus, 123*, 54 (1958).

(3) U.S. Borax and Chemical Corp., Brit, pat. 1, 015, 937 (1966).

(4) M. Goodgame and M.J. Weeks, *J. Chem. Soc. (A)*, 1156, (1966).

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

(6) F.A. Cotton, D.M.L. Goodgame, and R.H. Soderberg, *Inorg. Chem.*, *2*, 1162 (1963).

Table I. Reflectance Spectra and Room Temperature Magnetic Moments of the Complexes.

Compound	μ_{eff}(B.M.)	ν_{max} (cm^{-1})
CoL_2Cl_2	4.46	4550 br, 6150, 7300, 8800, 15,900, ~16,200 sh, 17,400 [a]
CoL_2Br_2	4.57	4170 br, 5650, 6900, 8700, 15,300, 15,600, 17,200 [a]
CoL_2I_2	4.59	~4000 br, 5650, 6850, 8500, 14,800, ~15,100 sh, 16,700, [a] 26,800
$CoL_2(NO_3)_2$	4.47	7450, ~8700 sh, 14,100, 18,200, ~21,300 sh
NiL_2Cl_2 [b]	3.60	6750, 10,000, ~12,100 sh, 15,500, 18,300
$Zn(Ni)L_2Cl_2$	—	6600, 10,100, ~12,200 sh, 15,000, 17,700
$NiL_2(NO_3)_2$	3.05	9100, ~13,300 sh, 15,700, ~23,300 sh, 24,600
CuL_2Cl_2	1.78	13,200, ~17,000 sh; 24,400 br
CuL_2Br_2	1.76	~14,500 sh, 16,400, 23,800 br
$CuL_2(NO_3)_2$	1.75	~13,700 sh, 17,200, 26,800
» (95°K)	—	13,900, 17,900, 26,500

[a] Spin-forbidden bands above 17,000 cm^{-1} omitted. [b] From. ref. 4.

Table II. Electronic spectra of some complexes $CoL_2(NO_3)_2$.

L	ν, cm^{1-}					Ref.
Me_3PO	5660	7800	11,900	17,850	19,050	6
Ph_3PO		7580	11,900	17,920	~19,000 sh	6
Ph_3AsO	~6700 sh	7810	~11,800 sh	17,450	~18,700 sh ~20,600 sh	6
benzimidazole	7840	9010	13,790	17,860	~20,000 sh	7
2-methylimidazole	7870	9500	14,500		18,600	8
1,2-dimethylimidazole	7900	8800	13,400		18,500	9
2-methylbenzimidazole	7450	~8700 sh	14,100	18,200	~21,300 sh	[a]

[a] This work

Table III. Vibrational Spectra (400-90 cm^{-1}) of 2-methylbenzimidazole and some of its complexes.

Compound	ν_{max} (cm^{-1})
L	324w, 285m, ~270sh, 261s, 197mbr, 132w
L (R) [a]	334w, 281w, 123s.
$CoL_2(NO_3)_2$	326m, 307s, 285m, ~268sh, 220m, 165s
$NiL_2(NO_3)_2$	332s, 309s, 291s, 262sbr, ~240sh, ~160s, vbr, ~100s, vbr.
$ZnL_2(NO_3)_2$	323w, 307m, 280m, ~260sh, ~200w, vbr, ~170mbr, ~100m, vbr.
$CuL_2(NO_3)_2$	343s, 327s, 300s, br, 257m, 185s, 132s, 102m
CuL_2Cl_2	331w, 290m, 276s, 270s, 220w, 181s, 160s.
CuL_2Br_2	343s, 326s, 292s, 240m, 214s, 175s, 124s.

[a] (R) indicates Raman Spectrum

pendence of the band position on the ligand field strength and its intensity suggest that the upper level of the transition concerned originates from the ^4F free ion term and not from ^2G. It is probably a component of ν_1 ($^4T_{1g}(F) \rightarrow {}^4T_{2g}$ in O_h), the pronounced splitting reflecting the very low symmetry in this class of compound, as is further shown by the relatively low magnetic moment.

Pseudotetrahedral structures have been assigned[4] to the complexes NiL_2X_2 (X = Cl, Br, or I) on the basis of their electronic spectra and magnetic moments. The $^3T_1 \rightarrow {}^3T_2$ transition (ν_1) appears as a symmetrical band near 7000 cm^{-1}, and shows no sign of splitting either at low temperature, or, in the case of the chloride, on dilution in the isomorphous zinc complex. However, other components of this transition may be hidden by the $^3T_1 \rightarrow {}^3A_2$ transition, or be below the range of our measurements.

All the copper compounds appear to have distorted six-coordinate structures. They each have a pair of *d–d* bands at 13,000-18,000 cm^{-1}, plus an intense band at high energy (Table I). This last moves to higher energy in the sequence $Br^- < Cl^- < NO_3^-$, and presumably arises from anion→metal electron transfer.

Vibrational Spectra. For the compounds $ML_2(NO_3)_2$ (M = Co, Ni, or Zn), the internal vibrations of the nitrate group are similar to those found[10] for complexes of the type $Mpy_2(NO_3)_2$, where py is pyridine or a substituted pyridine, which were considered to contain chelating nitrate groups, though the positions of ν_1 for our compounds (1475-1490 cm^{-1}) are at the low end of the reported range.

For $CuL_2(NO_3)_2$, the ν_1 frequency (1440 cm^{-1}) is distinctly lower than for the cobalt, nickel and zinc compounds and is closer to, though still above, the values quoted[10] for monodentate nitrate groups. Since copper nitrato-complexes usually have ν_1 towards

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(7) M. Goodgame and F.A. Cotton, *J. Amer. Chem. Soc.*, *84*, 1543 (1962).

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

(9) D.M.L. Goodgame, M. Goodgame, and G.W. Rayner Canham, *J. Chem. Soc. (A)*, 1923 (1971).

(10) A.B.P. Lever, *Inorg. Chem.*, *4*, 1042 (1965).

Table IV. Vibrational Spectra (400-90 cm^{-1}) of Pseudotetrahedral Complexes of 2-methylbenzimidazole

Compound	Ligand Bands	ν(M-L)	ν(M-X)	Other Bands
CoL_2Cl_2	326m, 297sh, 280m, 178m	229w, 210w	311s[a]	150s, 130s, 106m
CoL_2Br_2	329m, 321m, 302s, 287m, 279m, 170s	210m	249s, 236s	129s, 100m, br
CoL_2I_2	329m, 299s, 282s, 174w	(218sh, 208s)[b]		120m
NiL_2Cl_2	330sh, 305s, 282m, 177m	211m	315s[a]	167m, 154m, 125m, 109w
NiL_2Br_2	329m, 322m, 304s, 291w, 280m, 174 m	202w	246s, 238m	128m. 100m, br
NiL_2I_2	330m, 323m, 302s, 283m, 279m, 174w	(226m, 216m, 200m)		153m, 112s
ZnL_2Cl_2	330w, 322w, 303s, 287s, 280w, 176w	197s	[a]	152s, 125s
» (R)[c]	309w, 290m, 184w			144s, 104m
ZnL_2Br_2	329w, 321w, 297m, 286m, 278w, 170m	189s	229s, 218s	131m, 100w, br
» (R)	171m		226m	139s, 98sh
ZnL_2I_2	328m, 323m, 297s, 277s	(195vs, 187s)		160wm, 97m
» (R)	285w, 167sh			159m, 97m

[a] One or more components of ν(M-Cl) obscured by ligand bands. [b] Bands in parentheses due to ν(M-L) and ν(M-X). [c] (R) indicates Raman spectrum.

Table V. Observed g-values for some Cu(2-methylbenzimidazole)$_2$X$_2$ Complexes

	X-band			Q-band		
X	g_1	g_2	g_3	g_1	g_2	g_3
NO_3	2.06	2.09	2.30	2.07	2.10	2.31
Cl	2.06		2.29	2.06	2.08	2.30
Br	2.05		2.21	2.06	2.07	2.22

the low end of the range,[10] it seems unlikely that these are genuinely monodentate, but that unsymmetrical chelation is present in this complex.

The low-frequency vibrational bands of 2-methylbenzimidazole are given in Table III and those of some of its complexes in Tables III and IV. The ligand band at 324 cm^{-1} generally moves to higher energy in the complexes, and is somewhat enhanced in intensity, and the band-system at 261-285 cm^{-1} also moves to higher energy. One of the bands in this region may be related to the strong band at 265 cm^{-1} in 2-methylimidazole, which also moves to higher energy on complex formation.[8] This band is probably due to a bending mode of the H_3C-ring grouping

The profusion of ligand bands makes the identification of metal-ligand stretches difficult. However, for the pseudotetrahedral complexes most of the metal-anion stretching frequencies were observed (Table IV). There is also a metal-sensitive band, or pair of bands, at 210-230 cm^{-1} for cobalt, 200-226 cm^{-1} for nickel and 187-197 cm^{-1} for zinc, which may have appreciable metal-nitrogen stretching character. This is very close to the region associated with metal-iodine stretching frequencies, and for the iodides it is likely that appreciable interaction occurs between the ν(M-N) and ν(M-I) modes.

Below 180 cm^{-1}, the spectra are more dependent on the anion than the metal. A band at 170-180 cm^{-1}, which may be the 197 cm^{-1} ligand band shifted to lower energy, appears in nearly all of the compounds, while the band at about 130 cm^{-1} has much greater intensity in the complexes. In addition, all the chlorides have a band near 150 cm^{-1} which is absent from the other complexes, except NL_2I_2, where it may be due to a Ni–I stretching mode.

E.P.R. Spectra. Polycrystalline samples of CuL_2X_2 (X = Cl, Br, or NO_3) were studied at both X-band (~9.3 GHz) and Q-band (~36.0 GHz) frequencies and the g-values were determined by the method of Kneubühl,[12] (Table V).

In the absence of X-ray structural information the observed g-values cannot be taken as the accurate molecular g-values. However in the case of the nitrate at X-band frequency and all three compounds at Q-band frequency, which provides better resolution, the $g_\perp$ absorption is split. This indication of a rhombic distortion for the compounds is in agreement with the conclusions from the infrared spectrum of the nitrate, and, by analogy with the known structure of Cu(N-methylimidazole)$_2$Br$_2$,[13] with the probable structures of the halide complexes.

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(11) C.C. Addison and W.B. Simpson, *J. Chem. Soc.*, 598 (1965).
(12) F.K. Kneubühl, *J. Chem. Phys.*, 33, 1074 (1960).
(13) B.D. Ludbrook, D. Rogers, and D.J. Williams, to be published.