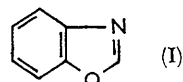


Oxazole Complexes. Part I. *N*-Bonded Complexes of Benzoxazole with Cobalt(II), Nickel(II), Copper(II), and Zinc(II)

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The preparation is described of some complexes of benzoxazole (L) with halides and nitrates of Co(II), Ni(II), Cu(II), and Zn(II) (M). With the exception of CuBr_2L , all halide complexes were of the type ML_2X_2 ; with the exception of CuCl_2L_2 , which was planar, the complexes had either tetrahedral or octahedral stereochemistry. The octahedral complexes all contained bridging halide atoms. Co(II) and Ni(II) nitrates formed the dihydrate, containing unidentate nitrate; heating to 140° dehydrated the complex, resulting in complexes containing bidentate nitrate groups.

BENZOXAZOLE (I) closely resembles benzimidazole in its properties; both compounds have a quinoline ring with one C=C group replaced by O in benzoxazole (I), and NH in benzimidazole. Complexes of quinoline^{1,2} and benzimidazole³⁻⁵ have recently been described.



Benzimidazole forms planar complexes with copper(II); with nickel(II), octahedral, tetrahedral, and planar complexes have been characterised. We are interested in the co-ordination behaviour of oxazoles in general; this paper presents our results for benzoxazole. This compound contains two potential donor atoms, but no evidence was found in this work for bidentate behaviour.

¹ D. M. L. Goodgame, M. Goodgame, M. A. Hitchman, and M. J. Weeks, *J. Chem. Soc. (A)*, 1966, 1769.

² D. M. L. Goodgame and M. Goodgame, *J. Chem. Soc.*, 1963, 207.

³ D. M. L. Goodgame, M. Goodgame, and M. J. Weeks, *J. Chem. Soc. (A)*, 1967, 1125.

EXPERIMENTAL

Infrared spectra in the region $4000\text{--}625\text{ cm}^{-1}$ were run as Nujol or hexachlorobutadiene mulls between sodium chloride supports on a Perkin Elmer 237 spectrophotometer, and between 667 and 222 cm^{-1} as Nujol mulls between stiff Polythene supports on a Grubb-Parsons DM4 spectrophotometer. Diffuse reflectance spectra were run on a Unicam SP 500 spectrometer. All spectra run in the solid state bear the usual reservations attached to such spectra. Solution spectra were run in *ca.* 10^{-2}M -solutions in dimethylformamide on a Unicam SP 700 spectrophotometer. Conductivities were measured on 10^{-3}M -solutions in dimethylformamide using a Doran E3924 conductivity bridge; magnetic moments were measured on a Gouy type balance, at room temperature.

The halide and nitrate complexes were prepared by mixing solutions of the metal salt and the ligand in ethanol and ethyl acetate respectively. Attempts to prepare analogous perchlorate complexes failed. Analytical results are in Table 1

⁴ D. M. L. Goodgame, M. Goodgame, and M. J. Weeks, *J. Chem. Soc. (A)*, 1967, 1676.

⁵ M. Goodgame and L. I. B. Haines, *J. Chem. Soc. (A)*, 1966, 174.

TABLE 1
Analytical data of complexes prepared

	Colour	Found (%)				Required (%)			
		C	H	N	H ₂ O	C	H	N	H ₂ O
ZnCl ₂ L ₂	White	43.7	2.5	7.4	—	43.9	2.9	7.5	—
ZnBr ₂ L ₂	White	36.0	2.1	6.0	—	36.3	2.15	6.0	—
CuCl ₂ L ₂	Pale blue	45.4	2.55	7.4	—	45.0	2.9	7.5	—
CuBr ₂ L	White	26.0	1.55	4.4	—	26.0	1.55	4.3	—
NiCl ₂ L ₂	Green	45.3	2.8	7.5	—	45.6	2.95	7.6	—
NiBr ₂ L ₂	Yellow	36.9	2.45	5.7	—	36.8	2.4	6.1	—
NiI ₂ L ₂	Greenish yellow	29.4	2.6	4.8	—	30.5	1.95	5.1	—
Ni(NO ₃) ₂ L ₂ .2H ₂ O	Greenish yellow	36.5	3.15	12.0	8.0	36.7	3.1	12.2	8.05
CoCl ₂ L ₂	Pink	46.0	2.6	7.05	—	46.2	2.95	7.7	—
CoBr ₂ L ₂	Blue	36.6	2.45	6.2	—	36.8	2.35	6.15	—
CoI ₂ L ₂	Green	30.0	1.85	5.0	—	30.5	1.95	5.1	—
Co(NO ₃) ₂ L ₂ .2H ₂ O	Pink	36.4	3.05	12.0	8.1	36.7	3.1	12.2	8.05

RESULTS AND DISCUSSION

The compounds prepared are shown in Table 1. Infrared spectra, conductivities in dimethylformamide, and magnetic moments at room temperature are in Table 2. Electronic spectra, in the solid state and in solution, are in Table 3. The far-infrared spectra of the

spectra in the 4000—625 cm.⁻¹ region are very complicated, and no attempt has been made to assign bands in this region except those arising from the nitrate group.

Cobalt(II) Complexes.—The complexes CoX₂L₂ (X = Br, I) have magnetic moments (*ca.* 4.6 B.M.) and reflectance spectra typical of tetrahedral cobalt(II) complexes. Both are non-electrolytes in dimethylformamide, but the iodo-complex gives a pink solution, and has an electronic solution spectrum typical of an octahedral cobalt(II) complex, presumably by co-ordination of two molecules of solvent. Evaporation of this solution resulted in the recovery of the green, tetrahedral complex. The pink CoCl₂L₂ complex differs from the bromo- and iodo-complexes; the reflectance spectrum and magnetic moment are typical of octahedral cobalt(II) complexes. On solution in a number of solvents, a deep-blue solution was formed, having an electronic spectrum typical of a tetrahedral cobalt(II) complex. On evaporation of the solvent, the pink complex was recovered. This suggests a polymeric structure for the compound in the solid state, with bridging chlorine; the bridges breaking down in solution to give a tetrahedral species. The cobalt(II) nitrate complex has the stoichiometry, when isolated, of CoL₂(NO₃)₂.2H₂O. The infrared spectrum suggests the presence of co-ordinated water and unidentate nitrate groups.⁶ This is consistent with the suggested octahedral structure (from the electronic spectrum and the magnetic moment at room temperature). Heating this complex for 2 hours at 140° resulted in the loss of both molecules of water (shown by the infrared spectrum and the weight loss), and the formation of a complex containing bidentate nitrate groups. The nature of this complex will be discussed fully in a later paper,⁷ but the infrared spectrum showed the nitrate modes to be similar to those of other bidentate nitrates.⁸

Nickel Complexes.—The 1 : 2 nickel halide complexes prepared had magnetic moments at room temperature and electronic spectra in both solid state and solution typical of octahedral complexes of this metal. The magnetic moments were near the upper limit of the

TABLE 2

	μ_{eff} (B.M.) *	Λ_{M} (ohm ⁻¹)	M-X (cm. ⁻¹)	M-N (cm. ⁻¹)	N-O (cm. ⁻¹)
ZnCl ₂ L ₂	—	4.17	327 308 294	233	
ZnBr ₂ L ₂	—	5.96	237 318		
CuCl ₂ L ₂	1.57	16.37	314 301sh		
CuBr ₂ L	~0	8.73	—	234	
NiCl ₂ L ₂	3.40	14.83	265	232	
NiBr ₂ L ₂	3.29	8.37	—	227	
NiI ₂ L ₂	3.40	12.41	—	226	
Ni(NO ₃) ₂ L ₂ .2H ₂ O	3.31	9.08	—	229	1422vs 1320vs 853m
CoCl ₂ L ₂	5.31	24.28	254	232	
CoBr ₂ L ₂	4.59	17.67	256	238	
CoI ₂ L ₂	4.56	12.30	233	241	1420vs 1325vs 860m
Co(NO ₃) ₂ L ₂ .2H ₂ O	5.37	11.67	—	228	

* At room temperature.

TABLE 3

Electronic spectra (kK), against MgCO₃

	Solid	Solution
ZnCl ₂ L ₂	19.10, 20.80	28.00
ZnBr ₂ L ₂	19.23, 20.80	27.45
CuCl ₂ L ₂	14.40, 16.64sh, dis- torted	8.20sh, 10.70, 15.95, 20.35, 23.20
CuBr ₂ L		15.42, 20.41
NiCl ₂ L ₂	12.82sh, 14.20, 24.75	8.18, 13.40sh, 14.49, 24.00, 32.00
NiBr ₂ L ₂	12.51sh, 13.79, 24.00	8.20, 14.00, 24.30, 32.00
NiI ₂ L ₂	14.60, 17.60sh	14.52, 27.15
Ni(NO ₃) ₂ L ₂ .2H ₂ O	15.75, 21.05sh, 25.97	13.35sh, 14.80
CoCl ₂ L ₂	17.10, 18.18	14.38sh, 14.75, 16.47
CoBr ₂ L ₂	15.76, 16.93sh, 18.32	14.45, 14.90sh, 15.50, 16.00
CoI ₂ L ₂	15.19, 16.21sh, 24.10	19.18, 20.90sh, 30.50
Co(NO ₃) ₂ L ₂ .2H ₂ O	19.23, 21.98sh	19.28, 21.10sh, 31.46

complexes are discussed separately, but support the suggested formulations given below. The infrared

⁶ B. M. Gatehouse, S. E. Livingstone, and R. S. Nyholm, *J. Chem. Soc.*, 1957, 4222.

⁷ E. J. Duff, M. N. Hughes, and K. J. Rutt, to be published.

⁸ A. P. B. Lever, *Inorg. Chem.*, 1965, 1042.

range normally accepted for octahedral nickel(II) complexes (2.8—3.4 B.M.); similar high moments have been found in some analogous nickel-quinoline complexes.² All complexes were non-electrolytes in dimethylformamide. The structure of these complexes in the solid state is considered to involve halide bridges, in a similar manner to the CoCl_2L_2 complex; this is unexpected for the NiI_2 complex, since analogous complexes of other nitrogen heterocyclic ligands tend to be tetrahedral.

The nickel(II) nitrate complex isolated was exactly analogous to that of cobalt(II) nitrate.

Copper Complexes.—Complexes of formula CuL_2X_2 ($\text{X} = \text{Cl}, \text{NO}_3$) and CuBr_2L were obtained. All attempts to prepare cupric bromide complexes containing greater than 1 mol. of ligand were unsuccessful. All the complexes were non-electrolytes in dimethylformamide. The magnetic moment for the nitrate complex is near the lower limit of the range normally accepted for copper(II) complexes (1.7—2.1 B.M.); that of the chloride complex is below the lower limit, whilst the bromide is diamagnetic. This suggests that the cupric bromide complex is dimeric with the possible pairing of the single d -electron on each copper atom to form a copper-copper bond. There is also the possibility of the presence of cuprous copper in the compound; this was ruled out on examination of the electronic spectrum. Whilst electronic spectra of copper(II) complexes must be interpreted with caution, the spectrum of this complex appears to indicate the presence of a tetrahedral copper(II) species. A further possibility for the structure of this compound is the presence of bridging benzoxazole groups, with magnetic superexchange through the conjugated ring system.⁹ No bands could be assigned in the far-infrared spectrum to copper-oxygen modes. The frequency of any copper-copper band present would be below the range of the instrument used.

The electronic spectrum of the copper chloride complex was consistent with a square-planar structure.

Zinc Complexes.—These complexes, by comparison of

⁹ W. J. Eilbeck, F. Holmes, C. E. Taylor, and A. E. Underhill, *J. Chem. Soc. (A)*, 1968, 128.

their infrared spectra with those of the tetrahedral cobalt(II) complexes, are tetrahedral. The electronic spectra indicate a ligand band at 19.6 kK in the solid state, which shifts to *ca.* 28 kK in solution. (These ligand bands have not been removed from the electronic spectra listed for the complexes.)

Far-infrared Spectra.—These are shown in Table 2, together with assignments. In most cases, the existence of analogous halogen complexes has enabled the unequivocal assignment of metal-halogen frequencies. The tetrahedral ZnCl_2L_2 complex shows characteristic metal-chlorine stretching frequencies at 327 and 308 (split) cm^{-1} , while the ZnBr_2L_2 complex shows a zinc-bromine band at 237 cm^{-1} , the second band occurring beyond the range of the instrument used. The octahedral polymeric CoCl_2L_2 and NiCl_2L_2 complexes show single bands at 254 and 265 cm^{-1} , respectively, which we assign to bridging metal-chlorine, and which are consistent with values obtained in other octahedral chlorine bridged systems. The spectra of the aquo-nitrato-complexes were poor, and no assignments could be effected. The anhydrous nitrates showed two bands at *ca.* 250 and 280 cm^{-1} which we have assigned to metal-(nitrate) oxygen stretching frequencies, although it is doubtful whether these frequencies can be regarded as pure.

All complexes had a strong band in the region 241—227 cm^{-1} , which we have assigned to metal-ligand. We consider, by comparison with the spectra of the corresponding benzothiazole complexes,¹⁰ that the nitrogen heteroatom in the ligand molecule is acting as the donor; this band is therefore assigned as a metal-nitrogen stretching mode. This vibration occurs at the higher end of the range quoted, for tetrahedral complexes; octahedral complexes all had this vibration near 230 cm^{-1} . The frequency at which this vibration occurs drops, as expected, with increasing atomic weight of the metal atom.

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¹⁰ E. J. Duff, M. N. Hughes, and K. J. Rutt, *J. Chem. Soc. (A)*, 1968, in the press.