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Complexes of Some 2-substituted Thiazoles

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The following complexes of 2-amino and 2-bromothiazole have been prepared and characterised by magnetic and spectroscopic techniques: $Co(atm)_4X_2$ $(X = Cl, Br)$; CoL_2X_2 $(L = amt, X = Cl, Br, I;$ $L = brt, X = Cl, Br)$; $Ni(amt)_4X_2$ $(X = Cl, Br\ NCS)$; $Ni(amt)Cl_2$; $Cu(amt)_4X_2$ $(X = Cl, Br)$; $Cu(amt)_2Cl_2$, *and* $Cu(brt)_2X_2$ $(X = Cl, Br)$.

Introduction

We have been engaged in the study of metal complexes of ligands containing the thiazole group,[1,2] and now report details of some complexes of 2-aminothiazole (amt) and 2-bromothiazole (brt) with cobalt, nickel and copper halides and thiocyanates.

Results and Discussion

All complexes prepared are listed in Table I with electronic spectra and magnetic moment data. Far infrared data for bromothiazole compounds are listed in Table II. It was a characteristic of 2-aminothiazole complexes that far infrared and low frequency Raman spectra were very ill defined.

Table II. Infrared Spectra (666-222 cm^{-1}).

Compound	Ligand modes	ν_{M-X}
$Co(brt)_2Cl_2$	358(s)	330(s), 300(s)
$Co(brt)_3Br_2$	354(w)	260(s)
$Cu(brt)_2Cl_2$	354(w)	335(s)
$Cu(brt)_2Br_2$	352(w)	258(s)

Cobalt Complexes. We have prepared the pink brown complexes $Co(amt)_4X_2$ $(X = Cl, Br)$ which have magnetic moments and reflectance spectra typical of distorted octahedral cobalt(II) complexes. These give non conducting blue solutions in nitromethane and acetone. The electronic spectra of these solutions, even in the presence of a large excess of ligand, were identical to the spectra of the tetrahedral complexes $Co(amt)_2X_2$ $(X = Cl, Br)$ which are described below. The infrared spectra of these and other complexes of amt showed a number of differences from the free ligand,[3] principally in regions associated with the $-NH_2$ group, where there was an increase in intensity and a shift to lower frequencies of the bands in the complexes. This phenomenon may result from the coordination of the amino group,[4] but

Table I. Electronic Spectra and Magnetic Moments.

Compound	μ_{eff}(B.M.)	Absorption Maxima (kK)
$Co(amt)_4Cl_2$	5.08	ca 28.6s,br; 20.8m; 19.1m; 17.6m. 8.3m.
$Co(amt)_4Br_2$	—	ca 26.6s,br; 21.2m,br; 18.8m; 17.4m; 8.0m.
$Co(amt)_2Cl_4$	4.71	16.7sh; 16.0sh; 15.4s; 8.4sh; 7.4m; 6.3m.
$Co(amt)_2Br_2$	4.62	26.5m,br; 16.3sh; 15.5sh; 15.0s; 8.0m; 7.0m; 6.0m.
$Co(amt)_2I_2$	4.58	26.1m,br; 16.4s; 15.0s; 13.9s; 8.4m; 6.5m; 5.8sh.
$Co(brt)_2Cl_2$	—	16.9sh; 16.1s; 15.8s; 8.4m; 7.0m; 6.1m.
$Co(brt)_2Br_2$	—	16.5sh; 15.6sh; 15.1s; 8.2m; 6.4m; 6.0m.
*Cot_2Cl_2(solution)		17.2s; 16.2s; 15.5s; 9.0m, 6.9m, 6.2sh.
*Cot_2Br_2(blue)		18.3w; 16.7sh; 15.3s; 14.9sh; 8.9m; 7.0m; 6.1m.
$Ni(amt)_4Cl_2$	2.97	24.9m; 15.1m; 12.6w; 10.8m; 7.0m.
$Ni(amt)_4Br_2$	3.30	ca 24.7sh; 14.9m; ca 12.0br,sh; 6.5m.
$Ni(amt)_4(NCS)_2$	3.27	26.3m; 16.3m; 9.7m.
$Ni(amt)Cl_2$	3.32	22.5m; ca 20.9sh; 12.4+11.6m; 7.4m.
$Ni(amt)Cl_2$(solvated)		ca 23.2sh; 13.5m; ca 12.6sh; 7.9m.
$Cu(amt)_4Cl_2$	1.88	20.0s,br; 16.1s.
$Cu(amt)_4Br_2$	1.79	21.0s,br; 17.0sh.
$Cu(amt)_2Cl_2$	1.81	ca 20.0s,br; 15.2s.
$Cu(brt)_2Cl_2$	1.84	22.4s,br; ca 12.0s,vbr.
$Cu(brt)_2Br_2$	1.82	22.4s,br; ca 13.0s,vbr.

* Taken from reference 1.

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(2) E.J. Duff, M.N. Hughes, and K.J. Rutt, *J. Chem. Soc. (A)*, 2101 (1969).
(3) J. Chouteau, G. Davidovics, J. Metzger, and A. Bonzom, *Spectrochim. Acta*, *22*, 719, (1966).
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it might also be due to electronic effects resulting from ring nitrogen coordination.

Complexes of the stoicheiometry CoL_2X_2 were prepared for L = amt, X = Cl, Br, I and L = brt, X = Cl, Br. These appear to have distorted tetrahedral structures on the basis of their electronic spectra, magnetic moments and, in the case of the brt complexes, by the positions[5] of their metal-halogen stretching frequencies. The electronic spectra are of interest. The lower energy transition ν_2 is split into three components as expected for C_{2v} symmetry. It is clear that the overall ν_2 band width of the corresponding thiazole complexes (Table I) is much greater than that of the complexes of the 2-substituted ligands. It appears[6] that a narrow band width for ν_2 is associated with sterically hindered donor sites, and we accordingly deduce ring nitrogen coordination for aminothiazole.

Nickel Complexes. These were only obtained for amt. Preparations using excess ligand produced the complexes $Ni(amt)_4X_2$ (X = Cl, Br, NCS), the magnetic moments and electronic spectra of which were characteristic of octahedral Ni^{II} compounds. In the electronic spectrum of the chloride the transitions to the ${}^3T_{2g}$ and ${}^3T_{1g}(F)$ states are clearly split into their components (in D_{4h}) ${}^3B_{2g}+{}^3E_g$ and ${}^3A_{2g}+{}^3E_g$, and the values of Ds and Dt obtained[7] are 500 cm^{-1} and 400 cm^{-1} respectively. These are rather high values and imply a large tetragonal distortion. Calculation of the in-plane and axial ligand fields[8] leads to values of 10,800 cm^{-1} and 3,800 cm^{-1} respectively. The axial ligand field is very much weaker than is normally observed for chloride ($\sim$7,000 cm^{-1}) and we attribute this to the severe steric restrictions imposed by the in-plane ligands resulting in a longer metal-chlorine bond. This, too, suggests that coordination takes place through the ring nitrogen, the steric restriction of the ligand then being associated with the 2-substituent.

The infrared spectrum of $Ni(amt)_4(NCS)_2$ indicated that the anion is N-bonded. However, the electronic spectrum showed no band splitting, and in view of the distortions brought about by steric effects in the halide complexes it may be that coordination occurs through a different atom in this case, although it should be noted that complexes NiL_2X_2 are often undistorted for X = SCN and distorted for X = Cl, Br. This may be explained[9] in terms of the π-acceptor properties of thiocyanate. We do not invoke this explanation in the present case in view of the fact that the distortion of the $Ni(amt)_4X_2$ complexes is much greater than normally found.

On heating $Ni(amt)_4Cl_2$ at 200° under vacuum for one hour, three moles of ligand are lost and the yellow complex $Ni(amt)Cl_2$ formed. We have attempted to prepare this complex from solution in a number of alcohols and obtained a number of yellow complexes whose analyses were dependent on the alcohol used. The ligand infrared spectrum was unchanged but it was not possible to remove the solvent by heating *in vacuo* for several hours.

The electronic spectrum of $Ni(amt)Cl_2$ was similar but not identical to those of the solvates in that the bands were at slightly lower energies and showed greater splitting. The spectra were consistent with polymeric octahedral structures.[10] We conclude that the organic ligand and chloride are both bridging.

Copper Complexes. The complexes $Cu(amt)_4X_2$ (X = Cl, Br) were formed with 2-aminothiazole. Their electronic spectra are consistent with octahedral stereochemistry, probably with *trans* halide groups. A 1:2 complex was also formed with $CuCl_2$. This again probably has an octahedral stereochemistry, with a polymeric halogen bridged structure.

The reflectance spectra of $Cu(brt)_2X_2$ (X = Cl, Br) were indicative of distorted stereochemistries. Strong bands at 335 and 260 cm^{-1} in the far infrared spectra of these complexes have been assigned to ν_{Cu-Cl} and ν_{Cu-Br}. These values are high[10] for bridging ν_{Cu-X} modes and would be more consistent with a structure approximating to *trans* square planar.

Comparison of 2-bromothiazole and 2-aminothiazole. When these two ligands form complexes of the same stoicheiometry their behaviour is similar Bromothiazole does, however, have a low affinity for nickel and there is no evidence for the formation of 1:4 complexes of this ligand. This latter fact may result from aminothiazole being a better π-acceptor than bromothiazole and so more effectively maintaining electroneutrality in a 1:4 complex.

The Donor Atom in Aminothiazole. It is often difficult to distinguish between heterocyclic ring and amino nitrogen coordination. In our report[2] on complexes of 2-aminobenzothiazole we suggested that the ligand was amino-nitrogen bonded in the yellow form of $Ni(ambt)_2Cl_2$ and ring nitrogen bonded to other metals. In the present case the ligand appears to be coordinated *via* the ring nitrogen to cobalt, as is suggested by the near infrared spectrum and by the similarity with the complexes of 2-bromothiazole. The situation is not as clear-cut for nickel. It appears that the ligand is ring-nitrogen bonded to nickel. except possibly in the isothiocyanato complex.

Experimental Section

2-Bromothiazole (Kodak) was used as supplied. 2-Aminothiazole (Koch-Light) was recrystallised from ethanol and ether. The complexes were prepared as follows. $Co(brt)_2X_2$ (X = Cl, Br), $Cu(brt)_2X_2$ (X = Cl, Br) and $Cu(amt)_2X_2$: On mixing stoichiometric amounts of the appropriate hydrated metal salt and ligand in ethanol, the complexes crystallised out over 30 mins, were filtered and washed with ethanol and ether. $Co(amt)_2X_2$ (X = Cl, Br, I), $Ni(amt)_4X_2$ (X = Cl, Br), $Ni(amt)Cl_2\,.\,x$ alcohol $Cu(amt)_4X_2$ (X =

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(7) C.J. Ballhausen and W. Moffit, *J. Inorg. Nucl. Chem.*, 3, 178 (1956).

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(9) S.M. Nelson and T.M. Shepherd, *J. Chem. Soc.*, 3276 (1965).

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Cl, Br) were prepared as above except that the mixed solutions were refluxed for 1 hour.

Co(amt)₄X₂ (X = Cl, Br) were obtained by mixing a solution of the hydrated metal salt in ethanol with an 8 fold excess of amt in ethanol and evaporating to small bulk. The products were filtered and washed with ethanol and ether.

Ni(amt)₄(NCS)₂. Equimolar quantities of hydrated nickel nitrate and KNCS in ethanol were mixed and filtered into an ethanol solution of a four-fold excess of amt. The complex, prepitating on standing, was washed with ethanol and ether. *Analyses* (C, H, N, metal and halide) for all complexes were good. Instrumentation was as described in earlier papers.[1,2]

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