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Complexes of 4,6-Dimethylpyrimidine-2-thione with some Divalent Metal Ions

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Complexes of 4,6-dimethylpyrimidine-2-thione with divalent manganese, cobalt, nickel, zinc, cadmium and mercury have been isolated and their coordination geometries studied using infrared, e.p.r. and electronic spectroscopy. The usual mode of binding of the thione ligand involves the formation of four-membered chelate rings through sulphur and nitrogen coordination. The complexes CoL_2X_2 (X = Cl or Br) each exist in isomeric forms: blue, containing tetrahedral CoL_2 units involving N/S chelation, and green isomers in which the metal ion is in a distorted octahedral environment. Isomerism of this type was not found for the cobalt(II) halide complexes of 4,6-dimethylpyrimidine-2-one or 1-methylpyrimidine-2-one.

Introduction

Our studies of the metal complexes of pyrimidine-2-thione and its derivatives have shown that these ligands display quite varied coordination behaviour

TABLE I. Analytical Data for Some Complexes of 4,6-Dimethylpyrimidine-2-thione (= L), 4,6-Dimethylpyrimidine-2-one (= DMPO), and 1-Methylpyrimidine-2-one (= MPO).

Complex	Colour	Analysis (%)					
		Found			Calculated		
		C	H	N	C	H	N
MnL_2Cl_2	Yellow	35.04	3.80	13.65	35.48	3.97	13.79
MnL_2Br_2	Yellow	29.03	3.30	11.20	29.11	3.26	11.31
$NiL_2Cl_2\cdot 2H_2O$	Pale green	32.90	4.35	12.49	32.31	4.52	12.56
$NiL_2Br_2\cdot 2H_2O$	Pale green	26.72	3.60	10.52	26.94	3.77	10.47
$NiL_2(NO_3)_2$	Pale green	31.00	3.43	17.78	31.12	3.48	18.15
$Ni(L^-)_2$	Yellow/Brown	42.59	4.57	16.40	42.76	4.78	16.62
CoL_2Cl_2	Blue	35.34	4.04	13.52	35.13	3.93	13.66
CoL_2Br_2	Blue	28.98	3.26	11.14	28.87	3.23	11.22
CoL_2Cl_2	Green	34.97	4.06	13.49	35.13	3.93	13.66
CoL_2Br_2	Green	28.81	3.37	11.18	28.87	3.23	11.22
$CoL_2Cl_2\cdot 2H_2O$	Pink	32.43	4.33	12.49	32.30	4.52	12.55
$CoL_2Br_2\cdot 2H_2O$	Pink	27.09	3.63	10.38	26.93	3.77	10.47
ZnL_2Cl_2	White	34.65	3.73	13.28	34.59	3.87	13.45
ZnL_2Br_2	White	28.74	3.23	11.26	28.51	3.19	11.08
ZnL_2I_2	Yellow	25.61	2.93	9.13	24.04	2.69	9.34
$Zn(L^-)_2L$	White	44.11	4.73	17.83	44.67	4.58	17.36
CdL_2Cl_2	Pale Yellow	30.94	3.49	11.86	31.08	3.48	12.08
CdL_2Br_2	Pale Yellow	26.10	2.66	10.07	26.08	2.92	10.14
CdL_2I_2	Yellow	22.40	2.61	8.83	22.29	2.49	8.66
$Cd(L^-)_2$	Pale Yellow	35.38	3.54	13.64	36.88	3.61	14.34
HgL_2Cl_2	White	26.22	2.95	10.04	26.12	2.92	10.15
HgL_2Br_2	White	22.28	2.43	8.34	22.49	2.52	8.74
HgL_2I_2	Pale Yellow	20.11	2.17	7.46	19.61	2.19	7.62
$Hg(L^-)_2$	White	30.16	2.86	11.57	30.09	2.95	11.70
$Co(DMPO)_2Cl_2$	Blue	37.86	4.34	15.01	38.12	4.27	14.82
$Co(DMPO)_2Br_2$	Blue	31.02	3.54	12.13	30.86	3.45	12.00
$Co(MPO)_2Cl_2$	Blue	34.36	3.63	16.12	34.31	3.46	16.00
$Co(MPO)_2Br_2$	Blue	27.51	3.02	12.79	27.36	2.76	12.76

[1, 2]. As part of this work, we report here the isolation and characterization of the complexes formed by 4,6-dimethylpyrimidine-2-thione(=L) with the divalent ions of manganese cobalt, nickel, zinc, cadmium and mercury. Some copper (II) complexes of this ligand have recently been described by Battistuzzi and Peyonel [3] and we had previously reported the structure of the facial tris-chelate cobalt(III) complex $Co(L^-)_3$ (where L^- represents deprotonated L) [4].

Results and Discussion

The complexes we have isolated are listed in Table I.

Cobalt Complexes

Cobalt(II) chloride and bromide each gave two isomeric anhydrous complexes CoL_2X_2, as well as the corresponding dihydrates $CoL_2X_2 \cdot 2H_2O$, depending upon the reaction conditions. When anhydrous cobalt halides were used in dry acetone blue complexes CoL_2X_2 were formed. These were converted into pink dihydrates by exposure to moisture. The dihydrates were obtained directly from acetone when hydrated cobalt halides were employed. When the pink dihydrates were heated *in vacuo* at 80 °C green anhydrates were formed. These could not be converted back to dihydrates by exposure to a damp atmosphere or by addition of a damp solvent, nor were they directly interconvertible with their blue isomers.

The electronic reflectance spectra of the isomeric anhydrates are shown in Fig. 1, and the band energies are listed in Table II. The spectra of the blue complexes have band intensities consistent with a non-centrosymmetric coordination sphere. Apart from a better resolution of the components forming the very strong band at *ca.* 16,000 cm^{-1} in the case of the chloride, there is virtually no change on replacing Cl by Br. A characteristic feature of these spectra is the pair of well-resolved bands at *ca.* 5000 and *ca.* 9600 cm^{-1}. Such near i.r. spectra are unlike those found for pseudotetrahedral CoN_2X_2 chromophores [5], nor do they resemble the spectrum of Co(pyrimidine-2-thione)$_2$Cl$_2$ in which there is a $CoN_2S_2Cl_2$ arrangement, but with long Co–S bonds, leading to very distorted six-coordinate geometry [6].

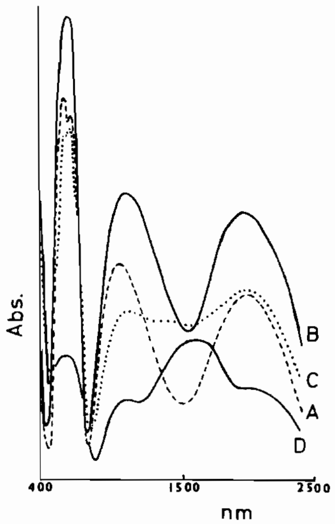

Fig. 1. Reflectance spectra of: (A) Blue CoL_2Cl_2; (B) Blue CoL_2Br_2; (C) Green CoL_2Cl_2; (D) Green CoL_2Br_2 (L = 4,6-dimethylpyrimidine-2-thione).

The electronic spectra of the pink dihydrates obtained from the blue CoL_2X_2 complexes are typical of centrosymmetric six-coordinate complexes with respect to both band intensity and band energies (Table II), and, again, replacement of Cl by Br leads to no significant change in the spectrum.

TABLE II. Electronic Spectral Band Energies (cm^{-1}) of Some Complexes of 4,6-Dimethylpyrimidine-2-thione (= L), 4,6-Dimethylpyrimidine-2-one (= DMPO), and 1-Methylpyrimidine-2-one (= MPO).

CoL_2Cl_2 (blue)	5000	9750	15,400sh	16,650	
CoL_2Br_2 (blue)	5025	9500	16,100		
CoL_2Cl_2 (green)	5000	~6900sh	9300	15,400	16,400sh
CoL_2Br_2 (green)	~5000sh	6250	9500	16,650br	
$CoL_2Cl_2 \cdot 2H_2O$	7900^a	20,600			
$CoL_2Br_2 \cdot 2H_2O$	7900^a	20,600			
$NiL_2Cl_2 \cdot 2H_2O$	9750	14,400	16,800^b		
$NiL_2Br_2 \cdot 2H_2O$	9700	14,300	16,700^b		
$NiL_2(NO_3)_2$	9600	15,400^b			
$Ni(L^-)_2$	7650	10,750	15,750sh^b		
$Co(DMPO)_2Cl_2$	6250sh	6900	9600	17,200	
$Co(DMPO)_2Br_2$	6150sh	6900	9100sh	16,650	
$Co(MPO)_2Cl_2$	6500br	16,700			
$Co(MPO)_2Br_2$	6900br	16,100			

^{a}Asymmetric to lower energy. $^b\nu_3(^3A_{2g} \rightarrow {}^3T_{1g}(P))$ band obscured by intense U.V. absorption.

A similar anion-independence is also found in the low frequency i.r. spectra (down to 200 cm^{-1}). The spectrum of 4,6-dimethylpyrimidine-2-thione in the region 200–400 cm^{-1} has bands at 228, 268 and 285 cm^{-1}. No additional halogen dependent bands were observed in this region for either blue CoL_2X_2 or pink $CoL_2X_2 \cdot 2H_2O$. The hydrates had a $\nu(Co{-}OH_2)$ band at 395 cm^{-1} (X = Cl) or at 388 cm^{-1} (X = Br) respectively. The blue anhydrates each had a pair of new bands at 250 and 315 cm^{-1} but their anion independence suggest that these bands are due to modes with appreciable $\nu(M{-}L)$ character or to activated ligand modes (complementary Raman spectra could not be obtained because of sample fluorescence).

These spectral results strongly suggest that the blue anhydrates should be formulated as $[CoL_2]X_2$ with cobalt surrounded tetrahedrally by two N and two S donors from chelating thione ligands. Any Co–X bonding appears to be sufficiently weak to ensure that (a) the electronic spectra show virtually no dependence on X, and (b) any $\nu(Co{-}Cl)$ is below 200 cm^{-1}. The uptake of two water molecules then results in the formation of pink $[CoL_2(OH_2)_2]X_2$ again involving N/S chelates, and, from the low electronic band intensity, of *trans*-structure.

Assignment of the near i.r. bands of blue $[CoL_2]X_2$ at *ca.* 5000 and *ca.* 9600 cm^{-1} as $\nu_1[{}^4A_2 \rightarrow {}^4T_2]$ and $\nu_2[{}^4A_2 \rightarrow {}^4T_1(F)]$ respectively, and use of the appropriate equations [7], leads to ligand field parameters for the $[CoL_2]^{2+}$ ion of: $\Delta = 5000$ cm^{-1} and $B' = 713$ cm^{-1}, values which are quite reasonable when compared with those for other tetrahedral cobalt(II) species and for octahedral tris-chelates of the related ligand 1,4,6-trimethylpyrimidine-2-thione [8].

The green chloride CoL_2Cl_2 obtained by heating $[CoL_2(OH_2)_2]Cl_2$ *in vacuo* has, from its electronic spectrum, a much more distorted coordination geometry than its blue isomer. This effect is even more marked in the green bromo-analogue (Fig. 1) and, for this, the spectral bands are much less intense. It appears likely that the thermal dehydration produces structures intermediate between octahedral and tetrahedral. Although the far i.r. spectra of these complexes differ from those of their blue isomers, again no anion dependent bands were observed above 200 cm^{-1} suggesting that any Co–X bonding leading to a quasi-six-coordination structure must be weaker than in *e.g.*, $Co(pyrimidine\text{-}2\text{-}thione)_2Cl_2$, for which Co–Cl bond lengths of 2.369 Å resulted in $\nu(Co{-}Cl)$ bands at 232 and 246 cm^{-1} [6].

Because of the isomerism found for the anhydrous CoL_2X_2 complexes with 4,6-dimethylpyrimidine-2-thione, attempts were made to obtain analogous pairs of compounds with 4,6-dimethylpyrimidine-2-one (= DMPO) and with 1-methylpyrimidine-2-one (= MPO). However, with each of these ligands cobalt chloride and bromide gave only blue complexes of 2:1 stoichiometry. In the case of $Co(MPO)_2X_2$ the electronic spectra (Table II) and the $\nu(Co{-}X)$ bands in the low frequency i.r. spectra (X = Cl, 330 and 300 cm^{-1}; X = Br, 264 and 243 cm^{-1}) are fully consistent with the presence of an essentially tetrahedral CoN_2X_2 arrangement. The electronic spectra of $Co(DMPO)_2X_2$ are also characteristic of a tetrahedral geometry but with a greater distortion. This is further shown by the lower $\nu(Co{-}X)$ bands in the DMPO complexes (X = Cl, 281 and 259 cm^{-1}; X = Br, 234 cm^{-1}). It seems probable that the exocyclic oxygen in 4,6-dimethylpyrimidine-2-one interacts with the metal ion so as to perturb the basic CoN_2X_2 coordination sphere, but such interaction is less than the exocyclic sulphur atom in related pyrimidine-2-thiones.

Manganese and Nickel Complexes

The manganese(II) complexes MnL_2X_2 (X = Cl or Br) clearly show the effects of zeio-field splitting in their X-band e.p.r. spectra (Fig. 2). X-Band spectra of this type are not consistent with a halide-bridged polymeric structure and this conclusion is supported in the case of the chloride by the presence of a strong, terminal $\nu(Mn{-}Cl)$ band at 234 cm^{-1} (Mn–Cl bands for bridged species are well below 200 cm^{-1} [9]). The e.p.r. spectra are generally similar to those of the complexes $Mn(pyrimidine\text{-}2\text{-}thione)_2X_2$ (X = Cl or Br) [6], which are thought to have distorted octahedral $MnN_2S_2X_2$ coordination geometry.

The nickel complexes $NiL_2X_2 \cdot 2H_2O$ (X = Cl or Br) and $NiL_2(NO_3)_2$ also appear to be six-coordinate with N/S chelating thione ligands. Their electronic spectra (Table II) are typical of such species. The halides show no halogen dependent bands above 200 cm^{-1} in their low frequency i.r. spectra but had $\nu(Ni{-}OH_2)$ bands at 384 cm^{-1} (X = Cl) or at 380 cm^{-1} (X = Br). Accordingly, these compounds resemble their cobalt(II) analogues in being $[NiL_2(OH_2)_2]X_2$.

The nitrate fundamental vibrational bands in the spectrum of $NiL_2(NO_3)_2$ were too obscured by thione ligand bands to provide any firm information concerning nitrate coordination. However, the $\nu_1 + \nu_4$ combination band of NO_3 was observed as a weak, broad band at *ca.* 1730 cm^{-1}, consistent with nitrate coordination [10].

The reaction of nickel acetate with the thione ligand in propan-1-ol gave the inner complex $Ni(L^-)_2$, the electronic spectrum of which is consistent with a distorted octahedral, and presumably polymeric, structure.

Zinc, Cadmium and Mercury Complexes

The group IIB metals formed the following series of complexes with the thione ligand: ML_2X_2 (M = Zn, Cd, Hg; X = Cl, Br, I), $M(L^-)_2$ (M = Cd, Hg) and

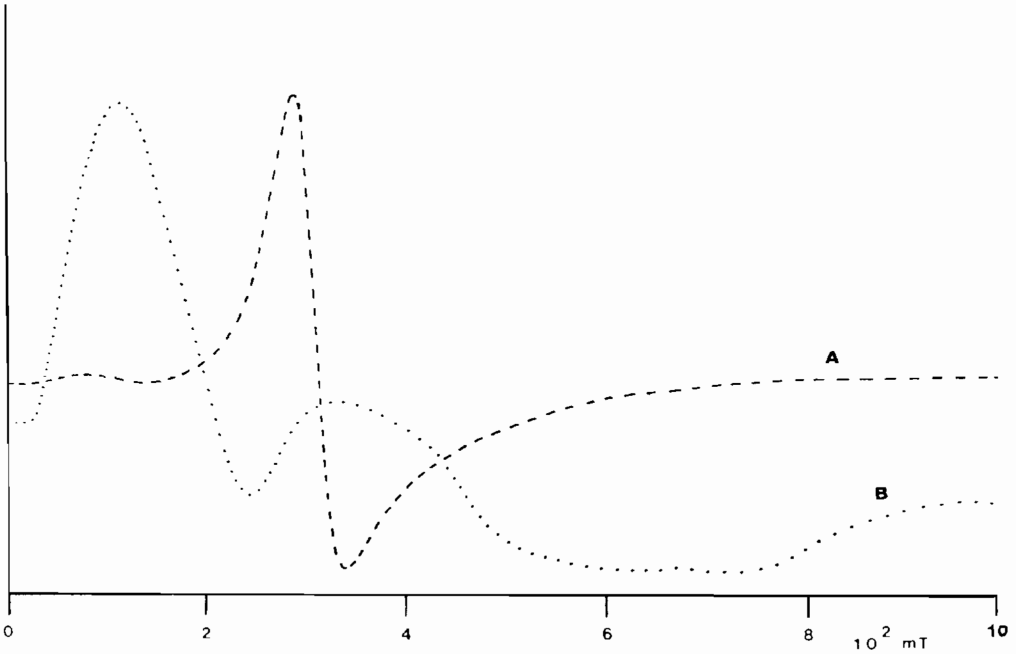

Fig. 2. X-band e.p.r. spectra of polycrystalline Mn(4,6-dimethylpyrimidine-2-thione)$_2$X$_2$: A, X = Cl; B, X = Br.

Zn(L$^-$)$_2$L. The metal–halide stretching frequencies observed in the far i.r. spectra (400–90 cm^{-1}) are given in Table III.

The zinc–halide and mercury–halide stretching frequencies are in the same ranges as those found for the corresponding 1-methyl- and 1,4,6-trimethylpyrimidine-2-thione complexes [2] and a similar geometry is implied, namely a tetrahedral MN$_2$X$_2$ structure distorted towards octahedral by weaker metal–sulphur bonding.

TABLE III. Metal–Halogen Stretching Frequencies (cm^{-1}) for the Zinc, Cadmium and Mercury Complexes.^{a}

M	ML$_2$Cl$_2$	ML$_2$Br$_2$	ML$_2$I$_2$
Zn	272,250^b	198	169
Cd	213^c	149	127
Hg	222	146	98

^{a}All bands are of strong intensity. $^b\delta$(Cl–Zn–Cl) at 158 cm^{-1}. $^c\delta$(Cl–Cd–Cl) at 120 cm^{-1}.

The bands assigned as ν(Cd–X), however, lie at lower frequencies than those of complexes of other methylated pyrimidinethione ligands but not so low as to suggest a halogen bridged polymer [11, 12]. A bis- N/S chelate with terminal halides completing an octahedral coordination sphere seems the most probable structure.

Experimental

Preparations

4,6-Dimethylpyrimidine-2-thione was prepared by the method of Hale and Williams [13] but via the hydrochloride salt, and 4,6-dimethylpyrimidine-2-one was similarly obtained using urea. 1-Methylpyrimidine-2-one was prepared by the method of Fox and Van Praag [14].

Except where state below, the complexes were prepared by reacting the required stoichiometric amounts of the pyrimidine derivative and the appropriate metal salt in ethanol or propan-1-ol. The resulting mixture was heated at 60 °C for 15 min and the solids which formed either immediately or on cooling in a refrigerator for several days were filtered off, washed with a little ethanol and then diethyl ether and dried *in vacuo* at room temperature for 2 hours. Microanalyses (Table I) were by the Microanalytical Laboratory, Imperial College.

The complexes M(L$^-$)$_2$ (M = Ni, Cd, Hg) and Zn(L$^-$)$_2$L were prepared from the appropriate metal acetate. Attempts to isolate a complex from manganese(II) acetate proved unsuccessful.

The cadmium complexes were prepared by dissolving the appropriate cadmium salt in water (1 mmol in 4–5 cm^3), increasing the volume to 15 cm^3 with ethanol and then adding a solution of the thione ligand. The solids isolated were dried *in vacuo* at 100 °C for 2 hours.

$CoL_2X_2 \cdot 2H_2O$ (X = Cl or Br)

A solution of $CoX_2 \cdot 6H_2O$ in acetone (2 mmol in 10 cm^3) was added to a warm solution of the ligand (4 mmol in 15 cm^3). After heating and stirring for 15 min, the pink solids were filtered off, washed with a little acetone and dried *in vacuo* over silica gel.

CoL_2X_2 (X = Cl, Br) [*blue form*]

These were prepared as for the dihydrates but using the anhydrous cobalt(II) halide.

CoL_2X_2 (X = Cl, Br) [*green form*]

These were obtained by heating the dihydrates at 80 °C for 4 hours.

Physical Measurements

The far infrared spectra of the zinc, cadmium and mercury halide complexes were run on a Beckmann FS-720 Interferometer, with the sample mounted as a vaseline mull supported between rigid polyethylene plates. The other physical measurements were made as described previously [8].

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