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Complexes of 1,4,6-Trimethylpyrimidine-2-thione with Some Divalent Metal Halides

D. M. L. GOODGAME and G. A. LEACH
Chemistry Department, Imperial College of Science and Technology, London SW7 2AY, U.K.

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The preparation of complexes of 1,4,6-trimethylpyrimidine-2-thione with divalent manganese, cobalt, nickel, copper, zinc, cadmium and mercury halides is reported, together with complexes of zinc, cadmium and mercury halides with 1-methylpyrimidine-2-thione. Their structures were investigated using various physical techniques, including infrared, e.p.r. and electronic spectroscopy. The trimethyl-ligand displays a strong chelating tendency whilst 1-methylpyrimidine-2-thione is more varied in its modes of coordination.

Introduction

We have recently shown [1] that 1,4,6-trimethylpyrimidine-2-thione (= L) forms four-membered chelate rings with some divalent metal ions of the first transition series in compounds of the type $[ML_3]X_2$, where X is an anion of low coordinating ability. Because of the possible strain in such chelate rings we have examined the coordination behaviour of L with these metals when it is in competition with anions of good coordinating power. We report here the results of this work and of studies of some zinc, cadmium, and mercury complexes of L and also of the related ligand 1-methylpyrimidine-2-thione (= L′).

Results and Discussion

The complexes isolated are listed in Tables I and II. We shall discuss first the results for the ligand L. With most of the metal halides studied the complexes had the stoichiometry ML_2X_2, but cobalt chloride and bromide formed compounds of composition $Co_2L_3X_4$, copper chloride and bromide yielded 1:1 complexes and nickel bromide also gave a 3:1 complex.

The electronic spectrum of NiL_3Br_2 (Table III) corresponds closely to that of the analogous nitrate [1], indicating the presence of the tris-chelate cation NiL_3^{2+}. This is further shown by the low frequency i.r. spectrum which contains no ν(Ni–Br) band, and is quite similar to the spectra of $[NiL_3]X_2$ (X = I, NO_3, and ClO_4). The i.r. spectra (430–200 cm^{-1}) of these last three complexes and of the other $[ML_3]X_2$ compounds described previously [1] are summarized

TABLE I. Analytical and Low Frequency Infrared (450–200 cm^{-1}) Data for Some Complexes of 1,4,6-Trimethylpyrimidine-2-thione (= L).

Complex	Colour	Analysis (%)						Infrared Bands (cm^{-1})	
		Found			Calculated			ν(M–X)	ν(M–L)^a
		C	H	N	C	H	N		
MnL_2Cl_2	Pale Yellow	38.63	4.30	12.96	38.72	4.64	12.90	263s, 254s	229w
MnL_2Br_2	Pale Yellow	32.39	3.80	10.55	32.14	3.85	10.71	–	225w
$Co_2L_3Cl_4$	Green	33.34	4.15	10.55	34.06	4.36	11.35	299s	232m, br
$Co_2L_3Br_4$	Green	27.39	3.14	9.30	27.47	3.51	9.15	229s	b
NiL_2Cl_2	Pale Green	38.20	4.50	12.40	38.38	4.60	12.79	229s	244ms
NiL_2Br_2	Pale Green	31.90	3.76	10.51	31.91	3.83	10.63	–	248s
NiL_3Br_2	Green	37.07	4.49	11.84	37.03	4.44	12.34	–	252s, 223mw
$CuLCl_2$	Green	29.32	3.51	9.41	29.12	3.49	9.70	325s	–
$CuLBr_2$	Brown	22.49	2.85	7.50	22.27	2.86	7.42	261s, 220s	–

^{a}See text for designation of ν(M–L). ^{b}Obscured by very strong ν(Co–Br) band.

TABLE II. Analytical and Infrared (300–100 cm^{-1}) Data for the Zinc, Cadmium, and Mercury Complexes of 1,4,6-Trimethylpyrimidine-2-thione (= L) and 1-Methylpyrimidine-2-thione (= L')

	Found (%)			Calculated (%)			Infrared bands (cm^{-1})	
	C	H	N	C	H	N	ν(M–X)	ν(M–L)
ZnL_2Cl_2	37.90	4.33	12.43	37.81	4.53	12.60	269s, br	–
ZnL_2Br_2	31.96	3.74	10.70	31.51	3.78	10.50	205s	–
CdL_2Cl_2	33.93	4.03	11.19	34.19	4.10	11.39	246s	219m, 149mw
CdL_2Br_2	28.93	3.39	9.47	28.96	3.47	9.65	176s	222m, 156s
CdL_2I_2	24.89	3.02	8.05	24.92	2.99	8.30	145s	–, 164ms
HgL_2Cl_2	28.18	3.41	9.17	28.99	3.48	9.66	225s	–
HgL_2Br_2	25.26	2.95	8.26	25.14	3.01	8.38	154s	–
HgL_2I_2	22.16	2.61	7.46	22.04	2.64	7.34	125s	–
ZnL'_2Cl_2	30.63	3.08	14.77	30.91	3.11	14.42	294s, 269s	205ms
ZnL'_2Br_2	25.92	2.48	11.32	25.15	2.53	11.73	200s	a
ZnL'_2I_2	21.19	2.05	9.46	21.02	2.12	9.80	171s	212ms
$CdL'Cl_2$	19.98	2.07	9.07	19.40	1.95	9.05	236s, 210s	154ms
$CdL'Br_2$	15.26	1.50	7.17	15.07	1.52	7.03	168s, 154s	a
CdL'_2Br_2	22.71	2.43	10.77	22.90	2.31	10.68	190s, 178s	151s
CdL'_2I_2	19.81	2.06	9.02	19.42	1.96	9.06	134s, 122s	149s
$Hg_2L'_3Cl_4$	20.58	2.03	9.36	19.55	1.97	9.12	238s	200ms
$Hg_2L'_3Br_4$	16.66	1.61	7.62	16.39	1.65	7.64	164s	–
$HgL'I_2$	10.54	0.99	4.71	10.34	1.04	4.83	154s	190m

[a] Obscured by intense ν(M–X) band.

TABLE III. Reflectance Spectra (cm^{-1}). L = 1,4,6-Trimethylpyrimidine-2-thione.

$[CoL_3][CoCl_4]$	5,200br[a,b]	8,300[c]	14,900[a]	18,500[c]	
$[CoL_3][CoBr_4]$	5,000br[a,b]	8,300[c]	14,300[a]	18,700[c]	
NiL_2Cl_2	6,850	9,350	13,350	15,750	d
NiL_2Br_2	6,650	9,150	13,350	15,750	d
$[NiL_3]Br_2$	9,700	15,600	d		
$CuLCl_2$	13,600				
$CuLBr_2$	13,600				

[a] Due to CoX_4^{2-}. [b] Centre of multicomponent band. [c] Due to CoL_3^{2+}. [d] ν_3, or components thereof, hidden by intense absorption in near U.V.

in Table IV. Upon chelation, the weak ligand bands at 415 and 387 cm^{-1} are replaced by a single, though rather broad, band in the range 390–413 cm^{-1}. A medium intensity ligand band at 310 cm^{-1} is little changed on complexation, but the band at 274 cm^{-1} is raised to 290–300 cm^{-1}, and a new weak band appears at 329–338 cm^{-1} (unfortunately the ligand and its complexes fluoresce too strongly to obtain complementary Raman data).

The free ligand has no i.r. bands in the range 200–270 cm^{-1} but most of the $[ML_3]X_2$ complexes show two bands in that region, the positions of which are metal sensitive in the order Zn < Mn ~ Co < Ni ~ Cu (only one band was observed for the zinc complexes but there was the onset of strong absorption at the limit of our range, 200 cm^{-1}, indicating that there was a second band just below 200 cm^{-1}). Although we have designated these bands as ν(M–L) we fully recognize that the modes concerned will be complex and that they will possess only partial metal–donor atom stretching character.

The spectral properties of the compounds of composition $Co_2L_3X_4$ (X = Cl or Br) show that their correct formulation is $[CoL_3][CoX_4]$. Their electronic spectra (Table III) are, in each case, a composite of the spectra of the $[CoL_3]^{2+}$ ion [1] and of the respective $[CoX_4]^{2-}$ ions [2]. In the case of the chloride supporting evidence is provided by

TABLE IV. I.R. Spectra (430–200 cm^{-1}) of 1,4,6-Trimethylpyrimidine-2-thione (= L) and of Some [ML_3]X_2 Complexes.

	Ligand Bands (cm^{-1})				ν(M–L)[a] (cm^{-1})	
L	415w	387w	310m	274mw	–	
MnL_3I_2	401w	331w	314m	292mw	220s	210sh
$MnL_3(ClO_4)_2$	413w	336w	312m	290mw	223s	211sh
CoL_3I_2	397w	332w	309m	293mw	226s	210sh
$CoL_3(NO_3)_2$	396w	332w	310m	293sh	223s,br	
$CoL_3(ClO_4)_2$	397w	337w	308m	292mw	230s	214s
$CoL_3(BF_4)_2$	396w	336w	308m	292mw	229s	214s[b]
NiL_3Br_2	396w	330w	309m	296sh	252s	223mw
NiL_3I_2	390w	332w	310m	296mw	243s	220w
$NiL_3(NO_3)_2$	393w	334w	310m	298mw	250s	224m
$NiL_3(BF_4)_2$	394w	338w	309m	295m	245s	223mw[b]
$CuL_3(NO_3)_2$	397w	329m	309m	300sh	251m	240m
$CuL_3(ClO_4)_2$	403w	330mw	311m	297sh	249m	236m
$CuL_3(BF_4)_2$	400w	330mw	310m	297sh	248m	236m[b]
ZnL_3I_2	402w	330sh	315ms	294sh	216s	
$ZnL_3(ClO_4)_2$	408w	336w	314ms	296mw	218s	
$ZnL_3(BF_4)_2$	401w	336sh	314m	295mw	219s[b]	

[a] See text for description of ν(M–L). [b] $\nu_2(BF_4^-)$ at ~353 cm^{-1}.

the very strong ν_3(Co–Cl) band of $CoCl_4^{2-}$ at 299 cm^{-1} (lit. [3] 297 cm^{-1}). The bromide has a very strong band at 229 cm^{-1} in the region expected [3] for $CoBr_4^{2-}$, and this band obscures the weaker ν(Co–L) bands of the CoL_3^{2+} ion.

It appears, therefore, that the tendency of the thione ligand L to form the tris-chelate cations ML_3^{2+} is very strong and can occur even in the presence of chloride or bromide ions.

Turning to the complexes of stoichiometry ML_2X_2 we find more varied coordination behaviour. The X-band e.p.r. spectra of the manganese complexes (Figure 1) clearly show the effects of zero-field splitting, implying that halide bridges are absent, as polymerisation of that type results in a collapse of such fine structure for undiluted samples [4]. The spectra are also quite unlike those observed for manganese(II) complexes containing a distorted tetrahedral MnN_2X_2 (X = Cl or Br) coordination sphere [5]. We conclude that the thione ligand L also chelates in the MnL_2X_2 complexes, which thus have distorted octahedral geometry. The observation of two ν(Mn–Cl) bands for MnL_2Cl_2 (Table I) indicates a *cis*-ligand arrangement, corresponding to that shown by X-ray diffraction studies [6] for the complex $Co(Hpymt)_2Cl_2$ (Hpymt = pyrimidine-2-thione) [7]. No ν(Mn–Br) bands were observed above 200 cm^{-1} for the bromide but, from the values of ν(Mn–Cl), they would be expected to be below this limit.

In contrast, the complexes NiL_2X_2 (X = Cl or Br) appear to be halogen bridged polymers with the ligand L coordinated only by the ring nitrogen. Their ν_1 and ν_2 electronic bands (Table III) show the pronounced splitting and low intensity characteristic of such structures, as in $Nipy_2Cl_2$, though their band energies are slightly higher than for the pyridine compounds. The low frequency i.r. spectrum of the chloride has one ν(Ni–Cl) band at 229 cm^{-1}, very slightly above the upper end of the range reported by Goldstein and Unsworth [9] for nickel compounds of this type. The other expected ν(Ni–Cl) band and both ν(Ni–Br) bands would be below 200 cm^{-1} [9]. Both complexes showed a strong or medium strong band at 244–248 cm^{-1}, which we assign as ν(M–L). Unlike the NiL_3^{2+} complexes, there is no band at 220–225 cm^{-1}, but insufficient results are available to check whether this is a consistent observation for unidentate N-bonding as compared with chelation.

The electronic spectra of the compounds $CuLX_2$ (X = Cl or Br) are similar to those observed by Livingstone and co-workers [10] for the complexes Cu(N-SMe)X_2 formed by the chelating ligand 2-(2-methylthioethyl)pyridine (= N–SMe). We conclude that the thione ligand L chelates in the compounds $CuLX_2$ to give a *cis*-planar geometry, perhaps with additional, weaker Cu–X bonds of the types frequently present in copper(II) halide complexes. The e.p.r. spectra of the two complexes differ. That of the chloride was an axial type spectrum with $g_{\parallel}$ = 2.214 and $g_{\perp}$ = 2.052, whilst the bromide merely showed a single, broad signal at g = 2.10.

Zinc, Cadmium, and Mercury Complexes

As the results with the transition metal ions showed that the thione ligand L apparently had a greater tendency to chelate than did the related

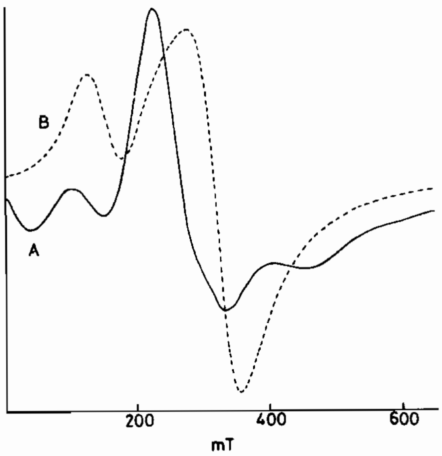

Figure 1. X-Band e.p.r. spectrum of polycrystalline Mn(1,4,6-trimethylpyrimidine-2-thione)$_2$X$_2$: A, X = Cl; B, X = Br.

ligand 1-methylpyrimidine-2-thione (= L′) [11] it seemed worthwhile to compare the behaviour of the two ligands with the halides of zinc, cadmium, and mercury.

The ligand L formed 2:1 complexes, except with zinc iodide, which gave $[ZnL_3]I_2$, [1], but L′ showed more varied coordination behaviour (Table II). Although, in principle, information about the coordination of the S-atom could be obtained from the mid-i.r. spectra, the ν(C=S) modes are extensively coupled with the pyrimidine ring vibrations and the resulting 'thioamide bands' are difficult to identify reliably and show no consistent frequency shift on coordination.

However the low frequency i.r. spectra are more informative, at least for the zinc and mercury complexes. The ν(Zn–X) bands for ZnL_2X_2 and ZnL'_2X_2 are rather low for tetrahedral complexes [12–14], but are high for octahedral halogen bridged polymers [15]. A similar set of intermediate ν(M–X) values was observed for the compounds M(Hpymt)$_2$X$_2$ in which the metal ions have a coordination geometry between tetrahedral and octahedral because of the presence of long M–S bonds in addition to M–N and M–X bonds [6, 7]. It appears likely, therefore that the zinc halide complexes reported here have a similar type of structure.

X-ray powder photographs show that the compounds HgL_2X_2 (X = Cl and Br) are isomorphous with their zinc analogues. Bearing in mind the affinity of mercury(II) for sulphur donor atoms the formation of a chelate by the thione ligand with this metal ion is expected. Indeed we observe that mercuric nitrate forms tris-chelate complexes $[HgL_3](NO_3)_2$ and $[HgL'_3](NO_3)_2$. Moreover when 1-methylpyrimidine-2-thione (L′) was reacted with mercuric chloride or bromide, complexes of stoichiometry $Hg_2L'_3X_4$ resulted. These complexes are probably of the type $[HgL'_3][HgX_4]$ as their low frequency i.r. spectra have strong ν(Hg–X) bands at 238 cm^{-1} (X = Cl) and 164 cm^{-1} (X = Br) respectively, close to those reported [16–18] for the HgX_4^{2-} ions, and the thione ligand bands are identical for the series $[HgL'_3]X_2$, where $X_2 = (NO_3^-)_2$, $HgCl_4^{2-}$, and $HgBr_4^{2-}$.

The mercuric iodide complex of L′ has, however, a stoichiometry $HgL'I_2$ and a ν(Hg–I) band (154 cm^{-1}) in the region expected for terminal, rather than bridging, iodide [17]. This suggests a tetrahedral structure involving N–S chelation by the thione ligand.

The results reported here demonstrate that the chelating behaviour of N1-methylated pyrimidine-2-thiones is not limited to metal salts with poorly coordinating anions, but that it also frequently occurs with chlorides and bromides to yield compounds of a variety of structural types.

Experimental

The thione ligands were prepared as reported previously [1, 11]. The complexes were prepared by mixing warm solutions of the metal salt (1 mmol) in ethanol (10 cm^3) with the required stoichiometric amount of thione ligand in acetone, ethanol, or propan-1-ol (40–50 cm^3). The mixtures were then heated at *ca.* 60 °C for 10 min. The complexes either precipitated immediately or during several days storage in a refrigerator. The products were washed with acetone and then diethyl ether and dried *in vacuo* at 80 °C. For the nickel halide complexes a small amount of 2,2-dimethoxypropane was added to the reaction mixture to remove water, and the products were dried *in vacuo* at 100 °C.

Microanalyses were by the Microanalytical Laboratory, Imperial College.

Physical measurements were made as described previously [1, 7].

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