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Tris-Chelate Complexes of 1,4,6-Trimethylpyrimidine-2-thione with Divalent Transition Metal Ions

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Studies of N/S chelating systems show there to be very few examples of octahedral, tris-chelate complexes [1, 2], particularly where the chelate ring would be four-membered, and hence highly strained. Where such chelates do occur, they are usually of the inner complex type [3].

As a complement to part of our research programme concerning studies on the coordination behaviour of sulphur-containing components of nucleic acids we have investigated several pyrimidinethione derivatives. We report here some results for 1,4,6-trimethylpyrimidine-2-thione (= L).

Experimental

The ligand was prepared by the method of Hale and Williams [4].

The complexes, with the exception of the iodides, were prepared by reacting a solution of the metal salt (1 mmol in 10 ml ethanol) with a solution of the ligand (3 mmol in 60 ml of hot propan-1-ol). In most cases, the solid complex precipitated out almost immediately or for the remainder after standing for a few days in a refrigerator.

The iodides were prepared by mixing a solution of the metal chloride (1 mmol in 10 ml acetone) with potassium iodide (2 mmol in 10 ml acetone), filtering off the sodium chloride and reacting the fresh iodide solution with the ligand as above.

The products were filtered, washed well with ethanol, acetone and diethyl ether and dried *in vacuo* at room temperature.

Infrared spectra were run on Perkin–Elmer 457 (4000–250 cm^{-1}) and 325 (450–200 cm^{-1}) spectrophotometers. The samples were prepared as nujol mulls supported between CsI plates and as vaseline mulls between rigid polythylene plates respectively. EPR measurements were made on a Varian 14 X-Band spectrometer. Diffuse electronic reflectance spectra were run using a Beckman DK2 spectrophotometer. X-ray powder patterns were obtained using a Guinier camera employing Gu(Kα) radiation.

Microanalyses were carried out by the Microanalytical Laboratory, Imperial College.

Results and Discussion

The complexes isolated were all of the stoichiometry ML_3X_2 (their analyses are given in Table I). The main structural feature of interest in these complexes centres on the question as to whether the sulphur atoms are coordinated as well as the non-methylated ring nitrogen, or whether, at least in the case of the iodide and nitrate complexes, the anions are acting as ligands. The infrared spectra of the perchlorates show that the anions in these compounds are not coordinated, as there is little or no splitting of the anion ν_3 and ν_4 modes (both F_2 in T_d). Reliable conclusions concerning the bonding of the anion in the nitrates could not be made from their infrared spectra as the main nitrate bonds were hidden by the organic ligand bands. However both nitrate complexes showed relatively strong $\nu_1 + \nu_4$ combination bands at 1738 cm^{-1} consistent [5] with ionic nitrate groups.

TABLE I. Analyses (L = 1,4,6-trimethylpyrimidine-2-thione).

Complex	Colour	Found %			Calculated %		
		C	H	N	C	H	N
$MnL_3(ClO_4)_2$	Yellow	35.64	4.29	11.92	35.20	4.23	11.73
$CoL_3(ClO_4)_2$	Pink/brown	35.09	4.16	11.81	35.00	4.19	11.66
$CuL_3(ClO_4)_2$	Dark brown	35.64	4.12	11.55	34.78	4.17	11.59
$ZnL_3(ClO_4)_2$	Off-white	34.72	4.03	11.87	34.70	4.16	11.56
MnL_3I_2	Yellow	32.93	3.98	10.86	32.70	3.92	10.89
CoL_3I_2	Pink/brown	32.42	3.77	10.39	32.53	3.90	10.84
ZnL_3I_2	Yellow	32.30	3.78	10.63	32.26	3.87	10.75
$CuL_3(BF_4)_2$	Brown	36.05	4.27	11.86	36.04	4.32	12.01
$CoL_3(NO_3)_2$	Brown	39.33	4.66	17.47	39.07	4.68	17 35
$NiL_3(NO_3)_2$	Green	38.95	4.79	17.47	39.08	4.69	17.36

TABLE II. Reflectance Spectra of the Cobalt and Nickel Complexes.

Complex	Band Energies (cm^{-1})		10 Dq	B	β
Co(II)	${}^4T_{2g} \leftarrow {}^4T_{1g}(F)$	${}^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$			
$CoL_3(ClO_4)_2$	8475	18,100	10,600	788	0.81
$CoL_3(NO_3)_2$	8660	18,350	10,800	777	0.80
CoL_3I_2	8330	17,900	10,400	774	0.80
Ni(II)	${}^3T_{2g} \leftarrow {}^3A_{2g}$	${}^3T_{1g}(F) \leftarrow {}^3A_{2g}$			
$NiL_3(NO_3)_2$	9800	15,630	9,800	[a]	[a]

[a] Not calculated as ${}^3T_{1g}(P) \leftarrow {}^3A_{2g}$ hidden by strong UV band.

The electronic spectra of the solid cobalt and nickel complexes (Table II) are typical of octahedral stereochemistries [6]. The great similarity of the spectra of the three cobalt complexes demonstrates that the octahedral coordination is formed from only the pyrimidine-2-thione ligands and that the anions are not bonded. In the case of the nickel nitrate complex the ν_3 transition (${}^3T_{1g}(P) \leftarrow {}^3A_{2g}$ in O_h) was hidden under intense parity allowed absorption in the UV region, and, as is frequently the case, ν_2 was not resolved for the cobalt complexes.

In contrast to the case of $Ni(TSC)_3Cl_2$ (TSC = thiosemicarbazide), which showed a splitting of $\nu_1({}^3T_{2g} \leftarrow {}^3A_{2g})$ attributed [7] to a *mer*-configuration of an N/S tris-chelate (later confirmed by X-ray studies [8]), the spectrum of $NiL_3(NO_3)_2$ shows no significant splitting of ν_1. This is consistent with a *fac*-structure, analogous to that recently reported [3] for tris-(4,6-dimethylpyrimidine-2-thionato)cobalt (III).

X-ray powder photographs showed the following series to be isomorphous: (a) $ML_3(ClO_4)_2$, M = Mn, Co, Cu, and Zn; (b) ML_3I_2, M = Mn, Co and Zn; (c) $ML_3(NO_3)_2$, M = Co and Ni.

The X-band epr spectrum of a polycrystalline sample of $MnL_3(ClO_4)_2$ is shown in Figure 1. Spectra of the manganese iodide analogue and of samples of manganese doped into the compounds $ML_3(ClO_4)_2$ (M = Co and Zn) and ZnL_3I_2 were very similar, with the addition of manganese hyperfine structure in the case of the cobalt and zinc lattices. In each case, the effects of the low symmetry components of the ligand fields can be observed by the presence of bands in addition to that in the g ≈ 2 region. The zero-field splitting parameters have been calculated using the programme ESRS [9] and the values for the perchlorate: D = 0.055 cm^{-1}, λ (= E/D) = 0.05 were checked by computer simulation [10] of the spectrum (Fig. 1).

These values are quite small and, in fact, are similar to those found [11] for the octahedrally coordinated manganese(II) ions in host lattices of $[M(4\text{-}Me\text{-}pyO)_6](ClO_4)_2$ (where M = Zn, Cd or Hg;

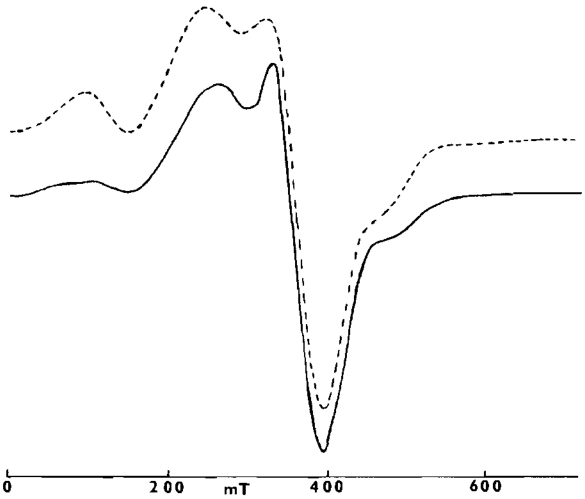

Fig. 1. X-Band epr spectrum of polycrystalline Mn(1,4,6-trimethylpyrimidine-2-thione)$_3(ClO_4)_2$: —— experimental, – – – – simulation with D = 0.055 cm^{-1}, λ = 0.05.

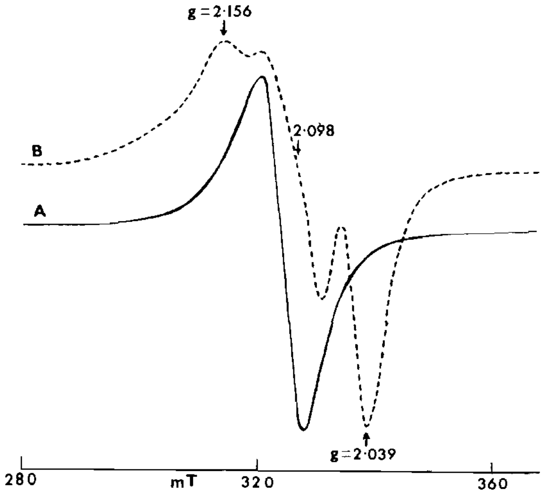

Fig. 2. X-Band epr spectra of polycrystalline: A, $CuL_3(ClO_4)_2$ (L = 1,4,6-trimethylpyrimidine-2-thione); B, Zn[Cu]$L_3(ClO_4)_2$.

4-Me-PyO = 4-methylpyridine-N-oxide). It appears therefore that despite the geometric constraints imposed by the four-membered chelate rings, the ligand fields in the ML_3^{2+} cation are not severely distorted from cubic symmetry. This, again, indicates a *fac*-arrangement.

Further evidence for the ligand field distortions is provided by the epr spectra of the copper complexes. Both the pure copper perchlorate and fluoroborate compounds have a single band in the g = 2.1 region (Fig. 2). On doping the perchlorate in the isomorphous zinc analogue the increased magnetic dilution permitted the observation of a three g-value signal (Fig. 2), an observation in accord with the finite E values for the isomorphous Mn(II) complexes.

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