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# X-Ray Molecular Structure of the Facial Chelate Complex Tris(4,6-dimethylpyrimidine-2-thionato)cobalt(III)

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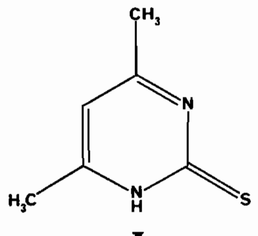
Although there has been appreciable interest in the coordination chemistry of chelating ligands containing one or more sulphur atoms as donors [1–5], there has been relatively little work carried out with heterocyclic amine ligands with substituted sulphur atoms.

During our studies involving 4,6-dimethylpyrimidine-2-thione (I, shown in the predominant thione form) we attempted to prepare a cobalt(II) perchlorate complex by the following method. A warm solution of I (0.420 g, 3 mmol) in acetone (15 ml) was added, with stirring, to one of cobalt perchlorate hexahydrate (0.366 g, 1 mmol) in acetone (15 ml). This solution was heated and stirred until its volume had been reduced to one third. On cooling to 0 °C for *ca.* 24 hours, a dark green crystalline solid deposited. This was filtered, washed with cold acetone and air dried. Its analysis (C, 47.28; H, 4.98; N, 15.99; and S, 17.51%) corresponded to an inner complex of formula $Co^{II}(L - H)_2L$·acetone or $Co^{III}(L - H)_3$·acetone.



I

Of the two formulae proposed, physical properties strongly suggested the complex to be $Co^{III}(L–H)_3$·acetone. It was found to be diamagnetic and the infrared spectrum showed that all three ligand molecules were deprotonated; no ν(N–H) [or ν(N–D)] vibrations were observed. The infrared spectrum also confirmed the presence of acetone in the complex with a ν(C=O) band at 1707 $cm^{-1}$.

Because of the paucity [6–8] of structural information for complexes with these types of ligands, a single-crystal X-ray study was undertaken, especially as recent work on a cobalt complex of the parent ligand pyrimidine-2-thione, $Co(pym2S)_2Cl_2$, has revealed only a very weak metal–sulphur interaction [9].

Dark green prisms of the acetone solvate of stoichiometry $Co(L - H)_3$·acetone are monoclinic, with unit-cell dimensions $a = 8.292(1)$, $b = 16.604(1)$, $c = 18.167(1)$ Å, $\beta = 90.34(1)^\circ$, space group is $P2_1/n$ and $Z = 4$. A total of 3142 independent reflections were measured (to $\theta = 55^\circ$) on a Siemens four-circle automatic diffractometer. The structure was solved by Patterson and Fourier methods, and least-squares refinement has reached $R = 0.044$.

Figure 1 shows the molecular structure, in which each 4,6-dimethylpyrimidine-2-thionato ligand acts as a chelate bonding to cobalt via nitrogen and sulphur atoms. The arrangement of the chelate ligands is such that all three sulphur atoms are *cis* to each other, giving a facial complex. As can be clearly seen from the Figure the molecule conforms quite closely to $C_3$ point symmetry. It has a propeller-like shape with the three ligands forming the blades, with a blade angle of incidence of *ca.* 54°.

Because of the limited 'bite' of the ligands the coordination about cobalt is appreciably distorted from regular octahedral with S–Co–N chelate angles of *ca.* 72°, N–Co–N angles in the range 100–103°, and S–Co–S angles of 94–96°. The three Co–S bond lengths are in the range 2.252–2.269 Å, with a mean of 2.259 Å, while equivalent figures for Co–N are 1.975–1.986° with a mean of 1.979 Å. These distances correspond to fairly strong bonds given the strain implicit in a four-membered chelate ring system. The Co–S bond lengths are very similar to those found in the tris chelate complex of N,N-diethyldithiocarbamate, $Co(dtc)_3$ (mean distances of 2.258 [10] and 2.267 Å [11]), despite a somewhat smaller 'bite' of I as compared to the dtc ligand (S–Co–S chelate angles of *ca.* 76°).

The acetone molecules simply fill gaps in the crystal structure and are held by van der Waals forces. As the non-donor nitrogen atoms on the chelate ligands are not protonated there is no opportunity to form hydrogen bonds between the complex molecules and acetone.

To our knowledge, this is the first complex involving three four-membered rings with nitrogen and sulphur as the donor atoms. Full crystallographic details will be published separately.

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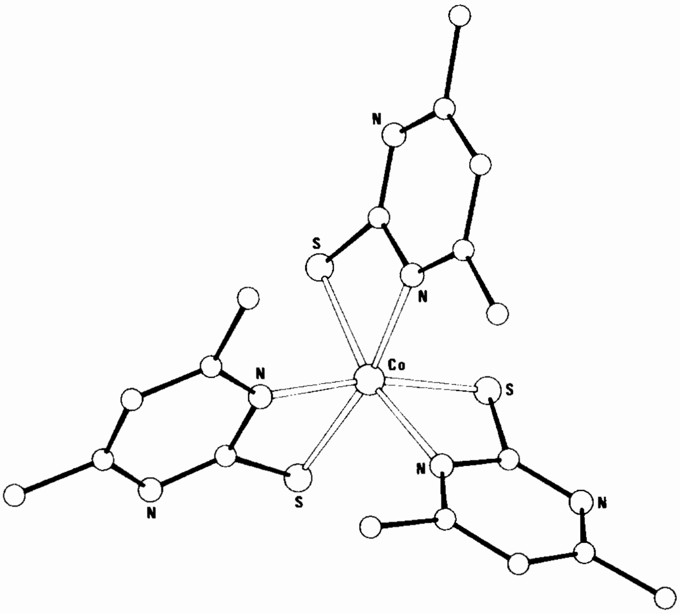

Figure 1. The molecular structure of the complex.

## References

1 R. Eisenberg, *Prog. Inorg. Chem., 12,* 295 (1970).
2 M. Cox and J. Darken, *Coord. Chem. Rev., 7,* 29 (1971).
3 S. E. Livingstone, *Coord. Chem. Rev., 7,* 59 (1971).
4 M. A. Ali and S. E. Livingstone, *Coord. Chem. Rev., 13,* 101 (1974).
5 M. J. M. Campbell, *Coord. Chem. Rev., 15,* 279 (1975).
6 S. R. Fletcher and A. C. Skapski, *J. Chem. Soc. Dalton,* 635 (1972).
7 H. I. Heitner and S. J. Lippard, *Inorg. Chem., 13,* 815 (1974).
8 E. Sletten and A. Apeland, *Acta Cryst., B31,* 2019 (1975).
9 J. C. McConway and D. Rogers, personal communication; J. C. McConway, *Ph. D. Thesis,* University of London (1975).
10 S. Merlino, *Acta Cryst., B24,* 1441 (1968).
11 T. Brennan and I. Bernal, *J. Phys. Chem., 73,* 443 (1969).