Acta Cryst. (1979). B35, 63–67

X-ray Crystal Structure of the Acetone Solvate of Tris(4,6-dimethylpyrimidine-2-thionato)cobalt(III): A Complex Involving Three Four-Membered Rings with Nitrogen and Sulphur as Donor Atoms

By Brian A. Cartwright, Paul O. Langguth Jr and Andrzej C. Skapski

Chemical Crystallography Laboratory, Imperial College, London SW7 2AY, England

(*Received* 21 *July* 1978; *accepted* 1 *September* 1978)

Abstract

$Co(C_6H_7N_2S)_3.(CH_3)_2CO$, $C_{18}H_{21}CoN_6S_3.C_3H_6O$, is monoclinic with $a = 8{\cdot}292$ (1), $b = 16{\cdot}604$ (1), $c = 18{\cdot}167$ (1) Å, $\beta = 90{\cdot}34$ (1)°, space group $P2_1/n$, $Z = 4$. Refinement with 3137 counter reflexions gave $R = 0{\cdot}044$. A chelate mode of binding *via* N and S atoms is found for the 4,6-dimethylpyrimidine-2-thionato ligands. These bidentate groups are arranged round the Co atom such that the three S atoms are *cis* to each other giving a facial octahedral complex of approximate C_3 point symmetry. A mean distance of 2·259 Å is found for Co—S, and the mean Co—N length is 1·979 Å. Distortion caused by the limited bite of the ligands is reflected in S—Co—N angles of *ca* 72·5°. The acetone molecules are neither coordinated nor hydrogen-bonded to the complex.

Introduction

While interest in S as a site for binding metals to naturally occurring substances containing thiolated chelates is well established (Eisenberg, 1970; Cox & Darken, 1971), as is that in S and N bidentate ligands (Ali & Livingstone, 1974), there is a paucity of structural information for the latter complexes (Fletcher & Skapski, 1972; Heitner & Lippard, 1974; Sletten & Apeland, 1975). An understanding of these interactions is important in work involving metal ions and complexes which are used as probes to study the conformation of such naturally occurring molecules in solution (Heitner & Lippard, 1974).

As part of a programme of structural studies on metal complexes with pyrimidine-based ligands (*e.g.* Cartwright, Reynolds & Skapski, 1977) we have studied the crystal structure of a Co complex with 4,6-dimethylpyrimidine-2-thionato ligands, especially as recent X-ray work on a Co complex of the parent ligand pyrimidine-2-thione, $Co(pym2S)_2Cl_2$, has revealed only a very weak Co—S interaction (McConway, 1975). We find the title compound to be a facial chelate complex with relatively strong Co—S and Co—N bonds. This is the first compound involving three four-membered rings with N and S as donor atoms, and preliminary details of the structure have been reported (Cartwright, Goodgame, Jeeves, Langguth & Skapski, 1977).

Experimental

Tris(4,6-dimethylpyrimidine-2-thionato)cobalt(III) was prepared from cobalt(II) perchlorate hexahydrate and 4,6-dimethylpyrimidine-2-thione (in a 1:3 molar ratio) in a warm acetone solution (Cartwright, Goodgame, Jeeves, Langguth & Skapski, 1977). Chemical analysis indicated that the dark-green prismatic crystals contained acetone of solvation in a Co:acetone ratio of 1:1.

Photographs showed the crystals to be monoclinic, with systematic absences $h0l$: $h + l = 2n + 1$, and $0k0$: $k = 2n + 1$. These absences uniquely determine the space group as $P2_1/n$. A crystal 0·19 × 0·13 × 0·05 mm was mounted with **a** parallel to the φ axis on a Siemens off-line four-circle automatic diffractometer, and measurement of 19 high-angle α_1 reflexions, followed by least squares, gave $a = 8{\cdot}292$ (1), $b = 16{\cdot}604$ (1), $c = 18{\cdot}167$ (1) Å, $\beta = 90{\cdot}34$ (1)°, $U = 2501{\cdot}2$ Å^3. Other crystal data are: $D_o = 1{\cdot}43$ (by flotation), $D_c = 1{\cdot}42$ Mg m^{-3} for $Z = 4$ and a formula of $C_{21}H_{27}CoN_6OS_3$, $M_r = 534{\cdot}6$, $F(000) = 1116$, $\mu(\mathrm{Cu}\ K\alpha) = 7{\cdot}70$ mm^{-1}.

Intensities were measured with Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å) at a take-off angle of 3°, a Ni β-filter, and a Na(Tl)I scintillation counter. The θ–2θ scan technique was employed with a five-value measuring procedure (Allen, Rogers & Troughton, 1971). 3142 independent reflexions were measured to $\theta = 55°$; of these, 901 were considered to be unobserved with $I < 2{\cdot}58\ \sigma(I)$. The 085 reflexion was monitored as a reference every 50 reflexions and its net count did not alter noticeably. This reflexion was used to scale the data, and Lorentz and polarization corrections were applied. At a later

0567-7408/79/010063-05$01.00

stage the data were corrected for absorption (Busing & Levy, 1957) with a 10 × 10 × 10 grid, and with crystal path lengths determined by the procedure of Coppens, Leiserowitz & Rabinovich (1965).

Solution and refinement of the structure

An origin-removed Patterson synthesis resulted in a solution for the Co atom to give $R = 0{\cdot}56$. Difference syntheses and isotropic refinement located the remaining non-hydrogen atoms and reduced R to 0·104. The data were now corrected for absorption and refinement as previously gave $R = 0{\cdot}090$. Inclusion of the anomalous-dispersion correction and refinement of all atoms with anisotropic temperature factors resulted in $R = 0{\cdot}066$. From a difference map all the H atoms were located. These were included as fixed-atom contributions with the isotropic temperature factors of their parent C atoms to give $R = 0{\cdot}046$. Introduction of a weighting scheme and the removal of five strong low-angle reflexions most affected by extinction reduced R to its final value of 0·044. The final difference synthesis was featureless. Table 1 lists the coordinates of the non-hydrogen atoms, while the unrefined positions of the H atoms are given in Table 2.†

Table 1. *Atomic coordinates with e.s.d.'s in parentheses*

	x	y	z
Co(1)	0·62213 (10)	0·70916 (5)	0·29437 (5)
S(10)*	0·70406 (18)	0·60369 (9)	0·22623 (8)
N(11)	0·7863 (5)	0·6497 (3)	0·3530 (3)
C(12)	0·8248 (7)	0·5927 (4)	0·3032 (3)
N(13)	0·9383 (6)	0·5364 (3)	0·3107 (3)
C(14)	1·0198 (7)	0·5376 (4)	0·3747 (4)
C(15)	0·9847 (7)	0·5926 (4)	0·4293 (3)
C(16)	0·8634 (7)	0·6494 (4)	0·4182 (3)
C(17)	1·1501 (7)	0·4754 (4)	0·3837 (4)
C(18)	0·8179 (8)	0·7104 (4)	0·4748 (3)
S(20)	0·41613 (18)	0·64278 (9)	0·34751 (9)
N(21)	0·5261 (5)	0·7819 (3)	0·3682 (3)
C(22)	0·4068 (7)	0·7335 (4)	0·3933 (3)
N(23)	0·2963 (6)	0·7534 (3)	0·4427 (3)
C(24)	0·3083 (7)	0·8286 (5)	0·4696 (3)
C(25)	0·4245 (8)	0·8820 (4)	0·4465 (4)
C(26)	0·5353 (7)	0·8578 (4)	0·3936 (3)
C(27)	0·1849 (9)	0·8521 (5)	0·5267 (4)
C(28)	0·6623 (9)	0·9132 (4)	0·3652 (4)
S(30)	0·47373 (16)	0·76438 (10)	0·20199 (8)
N(31)	0·7646 (5)	0·7822 (3)	0·2387 (2)
C(32)	0·6608 (7)	0·8074 (4)	0·1849 (3)
N(33)	0·6938 (5)	0·8537 (3)	0·1276 (3)
C(34)	0·8486 (7)	0·8797 (4)	0·1252 (3)
C(35)	0·9614 (7)	0·8579 (4)	0·1767 (4)
C(36)	0·9189 (7)	0·8084 (4)	0·2349 (3)
C(37)	0·8902 (8)	0·9336 (4)	0·0622 (4)
C(38)	1·0351 (7)	0·7833 (5)	0·2923 (4)
O(1)	0·2780 (9)	0·5745 (5)	0·0425 (4)
C(2)	0·2476 (11)	0·5757 (7)	0·1063 (6)
C(3)	0·1353 (13)	0·6334 (9)	0·1381 (7)
C(4)	0·3118 (18)	0·5173 (9)	0·1603 (8)

* Atoms of the ligands are numbered (*mn*) where *m* is the ligand number, and *n* is the atom number within each ligand.

Table 2. *Fractional coordinates of the* H *atoms*

Each atom has a number which corresponds, except for the last digit, to that of the parent C atom.

	x	y	z
H(151)	1·060	0·603	0·476
H(171)	1·100	0·428	0·378
H(172)	1·200	0·475	0·444
H(173)	1·235	0·500	0·356
H(181)	0·840	0·773	0·456
H(182)	0·710	0·703	0·500
H(183)	0·900	0·703	0·524
H(251)	0·435	0·935	0·473
H(271)	0·250	0·908	0·553
H(272)	0·080	0·873	0·498
H(273)	0·160	0·810	0·578
H(281)	0·650	0·970	0·378
H(282)	0·770	0·885	0·364
H(283)	0·640	0·923	0·316
H(351)	1·085	0·873	0·173
H(371)	0·875	0·905	0·016
H(372)	1·025	0·953	0·078
H(373)	0·800	0·983	0·067
H(381)	1·050	0·728	0·289
H(382)	1·005	0·785	0·340
H(383)	1·130	0·810	0·280
H(31)	0·100	0·675	0·089
H(32)	0·025	0·613	0·156
H(33)	0·190	0·675	0·184
H(41)	0·425	0·518	0·138
H(42)	0·350	0·540	0·211
H(43)	0·270	0·458	0·160

The weighting scheme was that suggested by Hughes (1941) where $w = 1$ for $F < F^*$, $w^{1/2} = F^*/F$ for $F \geq F^*$, with $F^* = 58$ as the optimum value. Its introduction appreciably improved the e.s.d.'s of atomic parameters. Scattering factors of Cromer & Waber (1965), and for H of Stewart, Davidson & Simpson (1965), were used; the anomalous-dispersion corrections for Co and S were from Cromer & Liberman (1970). The July 1974 update of the XRAY 72 system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) was used, least-squares refinement being carried out by means of *CRYLSQ*. Most of the calculations were performed on the University of London CDC 7600 computer; steering-tape generation, data processing and structural illustrations were performed on the Imperial College CDC 6400 machine.

Description of the structure and discussion

The crystal structure consists of molecules of tris(4,6-dimethylpyrimidine-2-thionato)cobalt(III) and acetone.

---

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33885 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Fig. 1 shows the structure of the complex, and the thermal ellipsoids of the non-hydrogen atoms (Johnson, 1965). The more important bond lengths and angles in both molecules are given in Table 3.

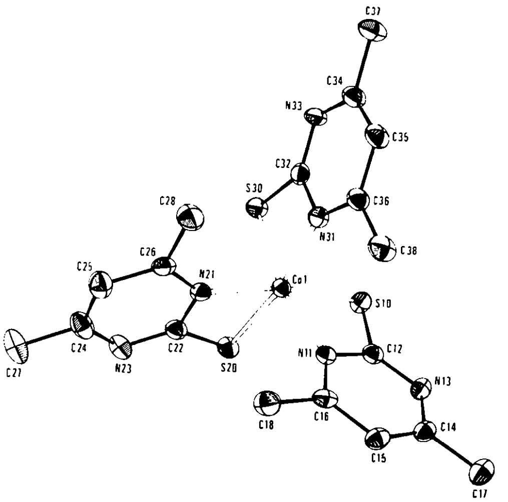

Fig. 1. Molecular structure of tris(4,6-dimethylpyrimidine-2-thionato)cobalt(III). Thermal-vibration ellipsoids are scaled to enclose 30% probability.

A distorted octahedral coordination is found for Co, with the three 4,6-dimethylpyrimidine-2-thionato ligands binding in a chelating mode *via* N and S atoms. The three S atoms are *cis* to each other giving a facial complex, with the plane of the S atoms nearly parallel to that of the N donor atoms, the angle between the two planes being 0·8°. A *cis* configuration of the S atoms can be rationalized on the grounds that it allows maximum π back-bonding to S, because the orbitals of the three S atoms can overlap different metal orbitals. The energy difference between *cis* and *trans* forms, however, is small and steric factors often cause the *trans* variant to be formed (Heitner & Lippard, 1974).

As can be seen from Fig. 1, the complex has approximate C_3 point symmetry, and the three bidentate ligands give it a propeller-like shape with a blade angle of incidence of *ca* 54°, this being the mean angle between the ring planes and the planes of the S and the N atoms.

Table 3 shows that the distortion of the coordination from octahedral is quite severe. The S—Co—N angles of 72·4–72·6° show the greatest deviations, with N—Co—N angles of 99·8–102·5° and S—Co—N *trans* angles of 164·7–167·4°. A similar, though slightly smaller, degree of strain can be seen in tris(*O*-ethyl

Table 3. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

						Mean	
Co(1)—S(10)	2·252 (2)	Co(1)—S(20)	2·255 (2)	Co(1)—S(30)	2·269 (2)	Co(1)—S(*m*0)	2·259
Co(1)—N(11)	1·986 (5)	Co(1)—N(21)	1·976 (5)	Co(1)—N(31)	1·975 (5)	Co(1)—N(*m*1)	1·979
S(10)—C(12)	1·724 (6)	S(20)—C(22)	1·723 (6)	S(30)—C(32)	1·738 (6)	S(*m*0)—C(*m*2)	1·728
N(11)—C(12)	1·351 (7)	N(21)—C(22)	1·356 (7)	N(31)—C(32)	1·365 (7)	N(*m*1)—C(*m*2)	1·357
C(12)—N(13)	1·333 (7)	C(22)—N(23)	1·328 (8)	C(32)—N(33)	1·320 (8)	C(*m*2)—N(*m*3)	1·327
N(13)—C(14)	1·342 (8)	N(23)—C(24)	1·344 (9)	N(33)—C(34)	1·355 (8)	N(*m*3)—C(*m*4)	1·347
C(14)—C(15)	1·381 (9)	C(24)—C(25)	1·377 (10)	C(34)—C(35)	1·369 (9)	C(*m*4)—C(*m*5)	1·376
C(15)—C(16)	1·392 (8)	C(25)—C(26)	1·393 (9)	C(35)—C(36)	1·386 (9)	C(*m*5)—C(*m*6)	1·390
C(16)—N(11)	1·342 (7)	C(26)—N(21)	1·344 (7)	C(36)—N(31)	1·354 (7)	C(*m*6)—N(*m*1)	1·347
C(14)—C(17)	1·502 (8)	C(24)—C(27)	1·513 (10)	C(34)—C(37)	1·495 (9)	C(*m*4)—C(*m*7)	1·503
C(16)—C(18)	1·494 (9)	C(26)—C(28)	1·493 (9)	C(36)—C(38)	1·476 (9)	C(*m*6)—C(*m*8)	1·488
O(1)—C(2)	1·188 (13)	C(2)—C(3)	1·459 (16)	C(2)—C(4)	1·477 (18)		

S(10)—Co(1)—N(11)	72·58 (14)	S(20)—Co(1)—N(21)	72·47 (14)	S(30)—Co(1)—N(31)	72·35 (13)
S(10)—Co(1)—S(20)	94·99 (7)	S(10)—Co(1)—S(30)	94·12 (7)	S(20)—Co(1)—S(30)	96·05 (6)
S(10)—Co(1)—N(31)	90·72 (14)	S(20)—Co(1)—N(11)	92·63 (14)	S(30)—Co(1)—N(21)	92·06 (14)
N(11)—Co(1)—N(21)	102·54 (19)	N(11)—Co(1)—N(31)	99·76 (18)	N(21)—Co(1)—N(31)	102·53 (19)
S(10)—Co(1)—N(21)	166·56 (15)	S(20)—Co(1)—N(31)	167·44 (14)	S(30)—Co(1)—N(11)	164·73 (14)
Co(1)—S(10)—C(12)	79·2 (2)	Co(1)—S(20)—C(22)	79·4 (2)	Co(1)—S(30)—C(32)	79·5 (2)
Co(1)—N(11)—C(12)	98·8 (3)	Co(1)—N(21)—C(22)	99·4 (4)	Co(1)—N(31)—C(32)	100·3 (3)
Co(1)—N(11)—C(16)	142·8 (4)	Co(1)—N(21)—C(26)	141·6 (4)	Co(1)—N(31)—C(36)	142·4 (4)
C(12)—N(11)—C(16)	118·4 (5)	C(22)—N(21)—C(26)	118·7 (5)	C(32)—N(31)—C(36)	117·1 (5)
S(10)—C(12)—N(11)	109·3 (4)	S(20)—C(22)—N(21)	108·7 (4)	S(30)—C(32)—N(31)	107·8 (4)
S(10)—C(12)—N(13)	124·3 (5)	S(20)—C(22)—N(23)	125·2 (5)	S(30)—C(32)—N(33)	124·7 (4)
N(11)—C(12)—N(13)	126·4 (5)	N(21)—C(22)—N(23)	126·0 (5)	N(31)—C(32)—N(33)	127·5 (5)
C(12)—N(13)—C(14)	115·5 (5)	C(22)—N(23)—C(24)	115·3 (5)	C(32)—N(33)—C(34)	114·5 (5)
N(13)—C(14)—C(15)	121·6 (5)	N(23)—C(24)—C(25)	122·6 (6)	N(33)—C(34)—C(35)	122·3 (6)
N(13)—C(14)—C(17)	116·3 (5)	N(23)—C(24)—C(27)	116·1 (6)	N(33)—C(34)—C(37)	116·2 (5)
C(15)—C(14)—C(17)	122·1 (6)	C(25)—C(24)—C(27)	121·3 (7)	C(35)—C(34)—C(37)	121·5 (6)
C(14)—C(15)—C(16)	119·9 (5)	C(24)—C(25)—C(26)	119·3 (6)	C(34)—C(35)—C(36)	120·2 (5)
C(15)—C(16)—N(11)	118·1 (5)	C(25)—C(26)—N(21)	118·1 (5)	C(35)—C(36)—N(31)	118·4 (5)
C(15)—C(16)—C(18)	122·9 (5)	C(25)—C(26)—C(28)	122·0 (6)	C(35)—C(36)—C(38)	122·6 (5)
N(11)—C(16)—C(18)	118·9 (5)	N(21)—C(26)—C(28)	119·9 (5)	N(31)—C(36)—C(38)	119·1 (5)
O(1)—C(2)—C(3)	122·6 (10)	O(1)—C(2)—C(4)	124·0 (10)	C(3)—C(2)—C(4)	113·4 (10)

dithiocarbonato)cobalt(III) where the corresponding angles are *ca* 76, 96 and 165° (Merlino, 1969). The relatively acute chelate angles are due to the strain involved in having a four-membered ring with the metal, and the difference between the two arises from the somewhat smaller bite of the thionato ligand as against that of the thiocarbonato.

The Co—S lengths are in the range 2·252–2·269 Å (mean 2·259 Å), in good agreement with means of 2·277 Å in tris(*O*-ethyl dithiocarbonato)cobalt(III) (Merlino, 1969), and 2·258 Å (Merlino, 1968) and 2·267 Å (Brennan & Bernal, 1969) in [Co(dtc)$_3$] (dtc = *N*,*N*-diethyldithiocarbamato). Co—N distances are in the range 1·975–1·986 Å (mean 1·979 Å). As expected, this is appreciably shorter than the 2·098 Å in [Co(pyrimidine-2-thione)$_2$Cl$_2$] (McConway & Rogers, 1975; McConway, 1975), as the latter is a Co^{II} complex. Although no Co^{III}–N (pyrimidine) distance is available for comparison, the value is similar to the 1·979 Å in [Co(TPP)(piperidine)$_2$]$^+$ and the 1·983 Å in [Co(TPP)(imidazole)$_2$]$^+$ (Ibers, Lauher & Little, 1974), where TPP = $\alpha,\beta,\gamma,\delta$-tetraphenylporphyrin dianion. Given the strain necessarily present in a four-membered chelate ring both the Co—S and Co—N distances correspond to quite strong bonds.

The S—C length is also an indication of the strength of the Co—S bond. Its values range from 1·723–1·738 Å (mean 1·728 Å). Fig. 2 shows a comparison of four related pyrimidine-2-thione and pyridine-2-thione systems, and it can be seen that in (*a*) and (*b*) where chelate bonding takes place the C—S length is 1·73–1·74 Å, while in [Co(pyrimidine-2-thione)$_2$Cl$_2$] where the Co—S interaction is at best weak and also in free pyridine-2-thione this length is *ca* 1·68 Å. In the tetrahedral complex [Zn(1-methylpyrimidine-2-thione)$_4$](ClO$_4$)$_2$ (Skapski & Woode, 1979) C—S is 1·659 Å, again with insignificant *M*—S interaction. Another indication of the strength of metal—ligand bonding in these systems is the distortion from *ca* 120° of the S—C(*m*2)—N(*m*1) and Co—N(*m*1)—C(*m*2) angles. In Fig. 2(*c*) this distortion is relatively small, especially for the more rigid S—C(*m*2)—N(*m*1) angle, while it is much greater for the title compound with a mean S—C(*m*2)—N(*m*1) angle of 108·6°. Here the strain seems to be taken up by the whole four-membered ring rather than at one atom, although, as expected, the distortion is greatest at the donor N atom with a mean Co—N(*m*1)—C(*m*2) angle of 99·5°.

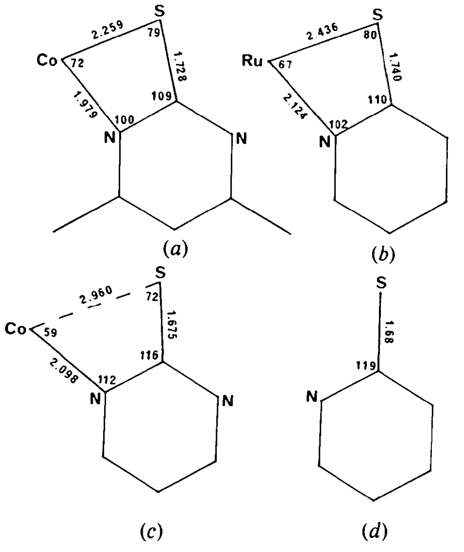

Fig. 2. A comparison of some average bond lengths (Å) and bond angles (°) in four related ligand systems: (*a*) title complex, (*b*) Ru(pyridine-2-thionato)$_2$(PPh$_3$)$_2$ (Fletcher & Skapski, 1972), (*c*) Co(pyrimidine-2-thione)$_2$Cl$_2$ (McConway & Rogers, 1975; McConway, 1975), (*d*) pyridine-2-thione (Penfold, 1953).

Although the crystal structure of the free ligand is not known, the C—N and C—C bonds are typical of those found in heterocyclic rings. In all three ligands the

Table 4. *Planarity of groups of atoms in the structure and distances* (Å) *from the least-squares planes*

Equations of the planes are expressed as $Px + Qy + Rz = S$ in direct space. Atoms not defining planes are marked with asterisks.

Ring(1*n*): $5·62x + 10·39y - 7·07z = 8·66$					
N(11)	0·017	C(12)	−0·007	N(13)	−0·007
C(14)	0·011	C(15)	−0·001	C(16)	−0·013
		Co(1)*	0·126	S(10)*	−0·027
		C(17)*	0·033	C(18)*	−0·036
Ring(2*n*): $5·02x - 5·30y + 13·19z = 3·34$					
N(21)	0·010	C(22)	0·000	N(23)	−0·009
C(24)	0·007	C(25)	0·003	C(26)	−0·011
		Co(1)*	−0·096	S(20)*	−0·076
		C(27)*	0·016	C(28)*	−0·042
Ring(3*n*): $-2·00x + 13·34y + 9·92z = 11·28$					
N(31)	−0·003	C(32)	0·007	N(33)	−0·007
C(34)	0·005	C(35)	−0·001	C(36)	0·000
		Co(1)*	−0·140	S(30)*	−0·024
		C(37)*	0·015	C(38)*	0·003
Acetone: $6·35x + 10·26y + 3·17z = 7·80$					
O(1)	−0·006	C(2)	0·016	C(3)	−0·005
C(4)	−0·005				

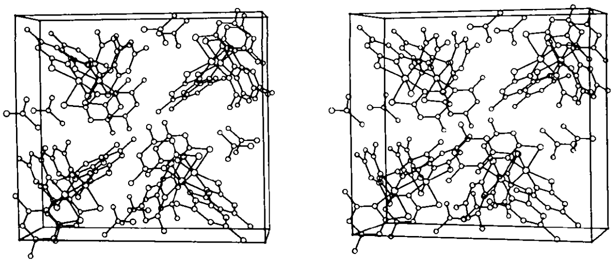

Fig. 3. Stereoscopic drawing showing packing of the complex and the acetone solvate molecules. The *b* axis is vertical, *c* is to the right and *a* is into the page, from an origin in the bottom left-hand corner.

shortest bond is C(m2)—N(m3). This is consistent with a lessening of double-bond character in the C—S bonds, and with the direction of bending of the C—S bonds out of their normal positions.

Table 4 shows that the pyrimidine rings are satisfactorily planar, while some of the exocyclic atoms, *e.g.* S(20), show a slight departure from the plane. The maximum distance of the Co atom from a ring plane is 0·14 Å.

Packing of the two molecular species in the unit cell is shown in Fig. 3 (Johnson, 1965). Solvate acetone molecules are only loosely held as indicated by temperature parameters which are much higher than those of atoms in the complex. The whole structure is held together by van der Waals forces. There is no possibility of hydrogen bonding between acetone and the ligands since the only potential sites on the rings, N(m3), are deprotonated.

We thank Drs D. M. L. Goodgame and I. Jeeves for providing the crystals and for discussions, Professor D. Rogers for the use of a diffractometer, and the Science Research Council for a Research Studentship (to BAC).

References

ALI, M. A. & LIVINGSTONE, S. E. (1974). *Coord. Chem. Rev.* **13**, 101–132.
ALLEN, F. H., ROGERS, D. & TROUGHTON, P. G. H. (1971). *Acta Cryst.* B**27**, 1325–1337.
BRENNAN, T. & BERNAL, I. (1969). *J. Phys. Chem.* **73**, 443–445.
BUSING, W. R. & LEVY, H. A. (1957). *Acta Cryst.* **10**, 180–182.
CARTWRIGHT, B. A., GOODGAME, D. M. L., JEEVES, I., LANGGUTH, P. O. JR & SKAPSKI, A. C. (1977). *Inorg. Chim. Acta*, **24**, L45–L46.
CARTWRIGHT, B. A., REYNOLDS, C. D. & SKAPSKI, A. C. (1977). *Acta Cryst.* B**33**, 1883–1887.
COPPENS, P., LEISEROWITZ, L. & RABINOVICH, D. (1965). *Acta Cryst.* **18**, 1035–1038.
COX, M. & DARKEN, J. (1971). *Coord. Chem. Rev.* **7**, 29–58.
CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.
EISENBERG, R. (1970). *Prog. Inorg. Chem.* **12**, 295–369.
FLETCHER, S. R. & SKAPSKI, A. C. (1972). *J. Chem. Soc. Dalton Trans.* pp. 635–639.
HEITNER, H. I. & LIPPARD, S. J. (1974). *Inorg. Chem.* **13**, 815–822.
HUGHES, E. W. (1941). *J. Am. Chem. Soc.* **63**, 1737–1752.
IBERS, J. A., LAUHER, J. W. & LITTLE, R. G. (1974). *Acta Cryst.* B**30**, 268–272.
JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
MCCONWAY, J. C. (1975). PhD thesis, Univ. of London.
MCCONWAY, J. C. & ROGERS, D. (1975). Unpublished work.
MERLINO, S. (1968). *Acta Cryst.* B**24**, 1441–1448.
MERLINO, S. (1969). *Acta Cryst.* B**25**, 2270–2276.
PENFOLD, B. R. (1953). *Acta Cryst.* **6**, 707–713.
SKAPSKI, A. C. & WOODE, K. A. (1979). *Acta Cryst.* B**35**, 59–62.
SLETTEN, E. & APELAND, A. (1975). *Acta Cryst.* B**31**, 2019–2022.
STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. & HALL, S. R. (1972). The XRAY system – version of June 1972. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Acta Cryst. (1979). B**35**, 67–71

The Structure of (1,2,3-Triamino-1,3-diimino-2-methylpropane)triamminecobalt(III) Tribromide $\frac{2}{3}$-Hydrate

BY P. A. TUCKER

Research School of Chemistry, The Australian National University, PO Box 4, *Canberra, ACT* 2600, *Australia*

(*Received* 26 *July* 1978; *accepted* 6 *September* 1978)

Abstract

$[C_4H_{20}CoN_8]^{3+}[Br^-]_3.\frac{2}{3}H_2O$, hexagonal, space group $P6_3/m$, $a = 14{\cdot}455$ (1), $c = 13{\cdot}300$ (1) Å, $U = 2406{\cdot}7$ Å^3, $D_m = 2{\cdot}05$ (1) by flotation, $Z = 6$, $D_c = 2{\cdot}03$ Mg m^{-3}. $R = 0{\cdot}036$ for 1661 reflections. The cation contains a tridentate bis(amidine)aminomethylmalonate cap coordinated to Co *via* two imine and one amine function.

Introduction and experimental

Acetonitrile coordinated to Co in pentaammineacetonitrilecobalt(III) ions is attacked by CN^- at the

0567-7408/79/010067-05$01.00