

*Acta Cryst.* (1975). B31, 2359**Tetrakis(thiourea)cobalt(II) Nitrate Hemihydrate; a Monoclinic Form**

BY R. F. BAGGIO, C. MANZANARES AND S. BAGGIO

*División Cristalografía, Área de Investigaciones, CNEA, Buenos Aires, Argentina and Escuela de Química, Universidad Central de Venezuela, Caracas, Venezuela*

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**Abstract.**  $\text{Co}[\text{SC}(\text{NH}_2)_2]_4(\text{NO}_3)_2 \cdot \frac{1}{2}\text{H}_2\text{O}$ , monoclinic,  $Pc$ ,  $a=17.40(4)$ ,  $b=11.90(3)$ ,  $c=9.81(2)$  Å,  $\beta=101.0(3)^\circ$ ,  $V=1990.7$  Å<sup>3</sup>,  $Z=4$  (two molecules in the asymmetric unit),  $D_m=1.58(1)$ ,  $D_x=1.59$  g cm<sup>-3</sup>,  $\mu(\text{Mo } K\alpha)=13.02$  cm<sup>-1</sup>,  $\lambda(\text{Mo } K\alpha)=0.7107$  Å, filtered with Zr. The structure consists of nitrate anions and distorted  $[\text{Co}(\text{tu})_4]^{2+}$  (tu=thiourea) cation layers parallel to (100), connected by ionic interactions and interlayer H bonds. The coordination symmetry about Co is nearly  $C_2$ , taking into account only nearest neighbours, and there is evidence of an interaction between a  $\text{Co}(sp^3)$  hybrid orbital, and a delocalized tu  $\pi$  molecular orbital.

**Introduction.** The crude material was kindly supplied by Dr R. Levitus. Crystals suitable for X-ray analysis were obtained by slow evaporation of an ethyl acetate solution at 0°C. They were blue-green needles elongated along  $c$ , and were mounted with this direction parallel to the spindle axis. Cell dimensions were taken from calibrated precession photographs (Mo  $K\alpha$  radiation). Intensity data were recorded with a crystal of approximate dimensions  $1.35 \times 0.19 \times 0.19$  mm. Levels  $hk0$  to  $hk7$  were recorded on a Weissenberg camera, and levels  $h0l$  and  $0kl$  on a precession camera, with the same Mo  $K\alpha$  radiation. Multiple film and multiple exposure techniques were used. 1863 reflexions were measured (82.5% of the Cu sphere) on mechanically integrated photographs with a microdensitometer. Of these, 330 were considered unobserved and given  $F_o=0$ . Absorption corrections were neglected. Reflexions from individual layers were cross-correlated and put on the same scale by the method of Hamilton, Rollett & Sparks (1960). Data were corrected for Lorentz and polarization factors, put on an absolute scale by a Wilson plot, and reduced to normalized structure factors 'E'.

A sharpened origin-removed Patterson map was computed using the  $|E^2-1|$  as coefficients. Resultant Co-Co peaks were successfully explained by both the possible space groups:  $Pc$  and  $P2/c$ . Co-S vectors, however, excluded the centrosymmetric group.

Successive Fourier syntheses in the non-centrosymmetric space group  $Pc$  (with a twofold multiplicity in the general position) developed the complete structure with two independent molecules in the asymmetric unit, as required by the fact that from density measurements  $Z$  was known to equal 4.

Atomic positions, temperature factors and scale factors were refined by full-matrix least-squares calculations with program *SFLS-5*. After several cycles with isotropic temperature factors the conventional residual  $R$  dropped to 0.129. At this stage those for Co and S were allowed to vary anisotropically and the refinement was continued minimizing the function  $\sum w| |F_o| - |F_c| |^2$ . Weights were chosen so as to make the average value of  $w\Delta^2$  constant, in ranges of  $\sin \theta$  and  $F_o$ . The weighting function used in the last few cycles was

$$\sigma^2 = \langle (126.086 - 2.1587F_o - 0.0144F_o^2 + 0.0011F_o^3) / \{1.04 - \exp(-10\sin^2 \theta)\} \rangle.$$

Scattering factors, including real and imaginary anomalous dispersion corrections were taken from *International Tables for X-ray Crystallography* (1968).

When shifts in atom parameters were less than  $\frac{1}{3}$  e.s.d., refinement was stopped with a conventional residual  $R=0.076$  (hydrogen atoms were included in their expected positions). No extraneous peaks were found in a Fourier difference map. Final atomic coordinates and temperature factors are given in Table 1. Calculated atomic positions for the H atoms are listed in Table 2.\*

**Discussion.** The structure of  $\text{Co}(\text{tu})_4(\text{NO}_3)_2$  has been the subject of controversy since the compound was first prepared by Cotton, Faut & Mague (1963).

Magnetic and electronic spectra of this compound did not permit a clear distinction between octahedral and tetrahedral stereochemistry. Thus, while the electronic spectrum is quite consistent with the postulate of a tetrahedral  $\text{Co}(\text{tu})_4^{2+}$  ion, magnetic data seem to be decidedly against this, the measured magnetic moment favouring the occurrence of an octahedral coordination (Cotton *et al.*, 1963).

Several authors (Flint & Goodgame, 1967; Basso & Levitus, 1968) later reported the existence of several forms of the compound. The present study seems to correspond to the 'C' form reported by Flint *et al.*, as suggested by the agreement between their measured

\* A list of structure factors and a table containing bond distances and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30992 (12 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Positional ( $\times 10^4$ ) and thermal parameters of the non-hydrogen atoms* $B_{ij}$ 's defining anisotropic temperature factors as  $\exp[-(h^2B_{11} + \dots + hkB_{12} + \dots)]$  are multiplied by  $10^4$ .

	$x/a$	$y/b$	$z/c$	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
Co(1)	2470 (2)	2699 (2)	687 (4)	25 (1)	25 (4)	19 (8)	7 (2)	13 (2)	20 (6)
Co(2)	7534 (2)	2504 (2)	4196 (4)	20 (1)	32 (3)	35 (7)	1 (1)	14 (1)	7 (4)
S(1)	1838 (3)	4063 (5)	1776 (7)	21 (2)	50 (9)	62 (17)	3 (4)	22 (5)	6 (14)
S(2)	3176 (4)	3438 (5)	9166 (8)	30 (3)	54 (10)	91 (20)	7 (4)	41 (6)	1 (15)
S(3)	2964 (4)	1711 (6)	2741 (7)	25 (2)	83 (11)	32 (17)	1 (4)	16 (5)	4 (15)
S(4)	1851 (4)	1447 (6)	-950 (8)	29 (3)	75 (10)	71 (16)	-4 (4)	27 (5)	-12 (14)
S(5)	8113 (4)	3837 (5)	3052 (7)	33 (3)	61 (9)	36 (14)	-1 (4)	13 (5)	0 (13)
S(6)	7231 (4)	3073 (5)	6273 (7)	33 (3)	60 (9)	34 (15)	4 (4)	21 (5)	7 (12)
S(7)	6585 (4)	2151 (5)	2323 (7)	33 (3)	67 (10)	78 (18)	2 (5)	2 (5)	-16 (15)
S(8)	8105 (4)	871 (5)	5237 (7)	38 (3)	49 (8)	21 (15)	4 (4)	25 (5)	29 (12)

	$x/a$	$y/b$	$z/c$	$B$		$x/a$	$y/b$	$z/c$	$B$
C(1)	1280 (16)	4789 (22)	413 (31)	5.5 (5)	C(2)	3517 (13)	4782 (19)	9666 (26)	2.6 (5)
C(3)	3489 (16)	677 (23)	2201 (31)	3.9 (5)	C(4)	1354 (13)	529 (19)	9887 (25)	2.5 (4)
C(5)	8714 (12)	4697 (18)	4235 (25)	2.3 (4)	C(6)	6578 (12)	4197 (17)	5924 (23)	1.8 (4)
C(7)	6309 (14)	778 (21)	2682 (27)	2.9 (5)	C(8)	8674 (14)	295 (20)	4187 (28)	3.0 (5)
N(11)	952 (15)	4322 (23)	9285 (29)	5.1 (6)	N(12)	1193 (17)	5918 (24)	624 (34)	6.3 (6)
N(21)	3309 (13)	5433 (20)	599 (27)	4.2 (5)	N(22)	4028 (12)	5262 (18)	8905 (25)	4.0 (5)
N(31)	3465 (13)	-432 (19)	2571 (26)	4.3 (5)	N(32)	3988 (15)	886 (22)	1368 (29)	5.3 (6)
N(41)	925 (13)	825 (18)	784 (24)	3.8 (4)	N(42)	1432 (14)	-638 (20)	9610 (26)	4.4 (5)
N(51)	9115 (13)	4278 (19)	5361 (26)	4.2 (5)	N(52)	8759 (14)	5750 (21)	4039 (27)	4.7 (5)
N(61)	6600 (14)	4963 (21)	4979 (29)	4.9 (5)	N(62)	6088 (15)	4253 (22)	6755 (24)	5.3 (5)
N(71)	5810 (14)	611 (20)	3505 (26)	4.4 (5)	N(72)	6564 (12)	-55 (18)	2056 (24)	3.9 (5)
N(81)	8988 (12)	850 (18)	3327 (23)	3.5 (4)	N(82)	8760 (19)	-897 (28)	4148 (36)	6.9 (7)
N(A)	33 (11)	1630 (17)	6918 (22)	3.2 (4)	N(B)	30 (12)	3152 (16)	2197 (23)	3.0 (4)
N(C)	5422 (10)	2407 (15)	8998 (22)	2.7 (4)	N(D)	4628 (11)	2003 (17)	5413 (23)	3.0 (4)
O(A1)	55 (10)	622 (13)	7163 (18)	3.2 (3)	O(A2)	272 (13)	2057 (19)	5971 (26)	5.6 (5)
O(A3)	9743 (13)	2356 (19)	7723 (26)	5.7 (5)	O(B1)	9830 (13)	2783 (19)	1148 (27)	5.8 (5)
O(B2)	416 (12)	2601 (18)	3187 (25)	5.2 (4)	O(B3)	9990 (11)	4241 (13)	2398 (21)	3.7 (3)
O(C1)	5314 (11)	3398 (14)	9294 (20)	4.0 (4)	O(C2)	5098 (11)	1606 (17)	9507 (22)	4.8 (4)
O(C3)	5959 (12)	2161 (18)	8382 (24)	5.3 (5)	O(D1)	4895 (13)	2607 (18)	4712 (25)	5.4 (4)
O(D2)	4170 (10)	2384 (15)	6150 (21)	4.0 (4)	O(D3)	4857 (12)	1013 (17)	5578 (22)	5.0 (4)
W	4936 (11)	3846 (16)	1911 (20)	4.4 (4)					

Table 2. *Calculated positions of the hydrogen atoms ( $\times 10^4$ )*

	$x/a$	$y/b$	$z/c$		$x/a$	$y/b$	$z/c$
H(111)	741	3523	-698	H(121)	901	4746	-1625
H(121)	671	6224	794	H(122)	1652	6452	625
H(211)	2841	5223	1055	H(212)	3614	6152	916
H(221)	4027	5000	-2060	H(222)	4405	5877	-638
H(311)	2949	-862	2381	H(312)	3963	-826	3081
H(321)	3794	927	345	H(322)	4567	1006	1799
H(411)	373	511	709	H(412)	1142	1371	1570
H(421)	969	-1167	-396	H(422)	1950	-944	-563
H(511)	8866	3704	5972	H(512)	9682	4522	5756
H(521)	8265	6200	3719	H(522)	9289	6145	4312
H(611)	6148	5033	4192	H(612)	7068	5491	5110
H(621)	5530	3963	6481	H(622)	6257	4586	7762
H(711)	5226	550	3136	H(712)	6004	543	4587
H(721)	6178	-599	1527	H(722)	7151	-170	2172
H(811)	8647	1206	2532	H(812)	9582	938	3546
H(821)	8278	-1396	3939	H(822)	9303	-1249	4437

Table 3. *Comparison between experimental interplanar spacings of the C form (Flint et al.) and those calculated with our cell constants*

Exp.	Calc.	$h k l$	Exp.	Calc.	$h k l$	Exp.	Calc.	$h k l$
7.23	7.26	1 1 $\bar{1}$	4.50	4.52	1 1 $\bar{2}$	3.72	{ 3.74	0 2 2
6.49	6.51	1 1 1		4.28	2 1 $\bar{2}$		{ 3.70	2 1 2
6.10	6.10	2 1 $\bar{1}$	4.27	{ 4.27	4 0 0	3.60	{ 3.61	3 2 1
5.60	5.62	1 2 0		{ 4.27	3 1 1	3.51	{ 3.53	1 3 1
	{ 4.89	3 1 $\bar{1}$		{ 4.08	3 0 2	3.46	{ 3.47	4 2 0
4.91	{ 4.88	1 0 $\bar{2}$	4.05	{ 4.02	4 1 0		{ 3.46	2 3 $\bar{1}$
	{ 4.88	2 2 0	3.90	{ 3.89	2 0 2	3.26	{ 3.27	1 0 $\bar{3}$
4.82	4.81	0 0 2					{ 3.26	2 2 2

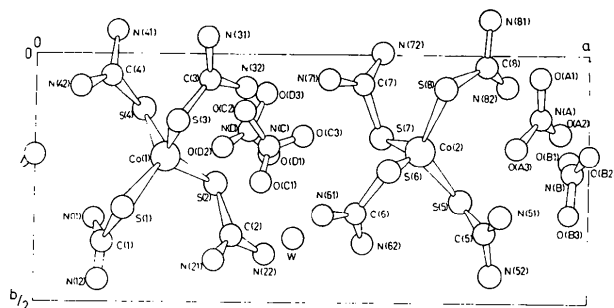


Fig. 1. Projection of the structure down  $c \sin \beta$ .

powder diagram and the calculated one based on our cell constants (Table 3).

More recently, the crystal structure of an orthorhombic form of the compound was reported (Spofford, Boldrini, Amma, Carfagno & Gentile, 1970), where the metal atom is surrounded by four sulphur atoms from tu molecules. The structure has the unusual feature that Co is bonded to one of the tu molecules through the ligand  $\pi$  molecular orbital.

Our present investigation gives results analogous to those of the orthorhombic form in the coordination around the metal atoms (Fig. 1). The two tetrahedral cations in the asymmetric unit are bonded to tu molecules through sulphur atoms, with an average Co-S distance of 2.305 Å. This suggests some Co-S  $\pi$  bonding, since it is shorter than 2.36 Å, the expected value based on the sum of their covalent radii (Pauling, 1960). Distortion gives the coordination about Co almost a  $C_2$  character.

Table 4. Orientation of the tu molecules

The first column gives the Co-S-C angle, the second column the dihedral angle between the tu plane, and that determined by Co, S and C. Angles are in degrees, with e.s.d.'s in parentheses.

tu(1)	103.8 (1.0)	35 (1)
tu(2)	111.5 (1.0)	10 (1)
tu(3)	103.3 (1.0)	46 (1)
tu(4)	107.0 (1.0)	46 (1)
tu(5)	110.3 (1.0)	38 (1)
tu(6)	107.6 (0.9)	33 (1)
tu(7)	101.2 (0.9)	81 (1)
tu(8)	108.6 (0.9)	33 (1)

The eight thiourea molecules are planar to within experimental error. Mean values for S-C (1.725 Å) and N-C (1.326 Å) agree with those found in the free ligand and other metal thiourea complexes. The orientation of the tu molecules is best described by Co-S-C angles and dihedral angles between Co-S-C and S-C-N planes. Table 4 shows that the tu(7) orientation is quite different from that of the rest. In this case the Co(2)-S(7)-C(7) angle is significantly smaller than the average, while the dihedral angle between planes is greater and close to 90°. This had already been found by Spofford *et al.* in the orthorhombic form of the compound, and the bond was interpreted as an overlap of an  $sp^3$  Co hybrid orbital and the thiourea delocalized  $\pi$  molecular orbital. A striking feature of this structure is that this type of bonding seems to be present in only one of the independent  $\text{Co}(\text{tu})_4^{2+}$  moieties in the cell.

Packing is best described as layers of nitrate anions and  $\text{Co}(\text{tu})_4^{2+}$  cations parallel to (100). Apart from ionic interactions between layers some H bonds suggested by short contacts satisfying the angular criterion (Fuller, 1959) (Table 5) hold layers together.

Table 5. Probable hydrogen bonds

Primes indicate atoms related by a  $c$  glide plane.

N(B1)-S(1)	3.41 Å	N(B1)-H...S(1)	159°
N(B1)-O(D2')	2.99	N(B1)-H...O(D2')	169
N(B2)-O(D1')	2.98	N(B2)-H...O(D1')	159
N(D2)-O(B2)	3.09	N(D2)-H...O(B2)	144

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