

SHORT STRUCTURAL PAPERS

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Pentaammineaquacobalt(III) Dithionate Dihydrate

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Abstract. $[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5]_2(\text{S}_2\text{O}_6)_3 \cdot 2\text{H}_2\text{O}$, $M_r = 840$, $F(000) = 748$, monoclinic, $P2_1/a$, $a = 13.538$ (4), $b = 15.820$ (9), $c = 6.593$ (2) Å, $\beta = 95.99$ (3)°, $V = 1404$ (1) Å³, $Z = 2$, $D_m = 1.90$, $D_c = 1.99$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å. The structure was solved with *MULTAN* and refined by the block-diagonal least-squares method. The final R value is 0.039 for 2276 observed reflections. The ligands form nearly regular octahedra about the Co atoms; the two parts of one $\text{S}_2\text{O}_6^{2-}$ anion are related by a symmetry centre.

Introduction. Workers at the Department of Inorganic Chemistry of the University of Barcelona are studying the synthesis of coordination compounds with the dithionate ion as ligand (Coronas & Casabo, 1974; Ribas, Casabo & Coronas, 1976; Coronas, Ribas & Casabo, 1977). Pentaammineaquacobalt(III) dithionate was synthesized by Lozano (1969), as a first step towards preparing pentaamminedithionatocobalt(III) dithionate, $[\text{Co}(\text{NH}_3)_5(\text{S}_2\text{O}_6)]_2(\text{S}_2\text{O}_6)$. The characterization of these two compounds by electronic spectra (IR, UV, visible) was inconclusive, and for this reason it was decided to solve their structures by X-ray diffraction.

Red prismatic crystals of pentaammineaquacobalt(III) dithionate dihydrate, obtained by crystallization from ethanol, were kindly supplied by Dr J. Ribas.

A crystal $0.2 \times 0.2 \times 0.3$ mm was used for crystal-data and intensity measurements on a Syntex four-circle diffractometer. The unit cell was measured by automatically centring 15 independent reflections and

refining the orientation matrix and unit-cell parameters by least squares. Intensities were collected with Mo $K\alpha$ radiation using the ω -scan technique and a scan interval of -0.8° to $+0.8^\circ$. 2765 independent reflections were measured within the range $1 < \theta \leq 25^\circ$; 2276 of these were treated as 'observed' according to the condition $I \geq 2.5\sigma(I)$. Lorentz-polarization corrections were applied.

Table 1. *Nonhydrogen-atom coordinates* ($\times 10^5$) *with standard deviations in parentheses*

	<i>x</i>	<i>y</i>	<i>z</i>
Co(1)	74797 (1)	10982 (1)	51820 (1)
O(2)	71939 (3)	14204 (3)	23190 (6)
N(3)	61298 (4)	14453 (3)	56985 (9)
N(4)	77963 (4)	7489 (3)	80141 (8)
N(5)	88021 (4)	7792 (3)	45334 (9)
N(6)	70130 (4)	-451 (3)	44628 (8)
N(7)	79853 (4)	22433 (3)	58858 (9)
S(8)	59680 (1)	35115 (1)	-10826 (2)
S(9)	60273 (1)	36399 (1)	21519 (2)
O(10)	65488 (4)	27505 (3)	-13136 (8)
O(11)	49227 (3)	34151 (4)	-17696 (8)
O(12)	64130 (4)	42753 (3)	-17544 (9)
O(13)	70785 (3)	35825 (3)	28735 (8)
O(14)	56120 (4)	44690 (3)	24674 (9)
O(15)	54411 (4)	29465 (3)	28295 (8)
S(16)	47009 (1)	5118 (1)	7820 (2)
O(17)	36808 (3)	5893 (4)	-904 (9)
O(18)	53285 (4)	12249 (3)	3925 (9)
O(19)	48083 (4)	2529 (3)	29070 (7)
O(20)	34839 (4)	25311 (3)	10059 (11)

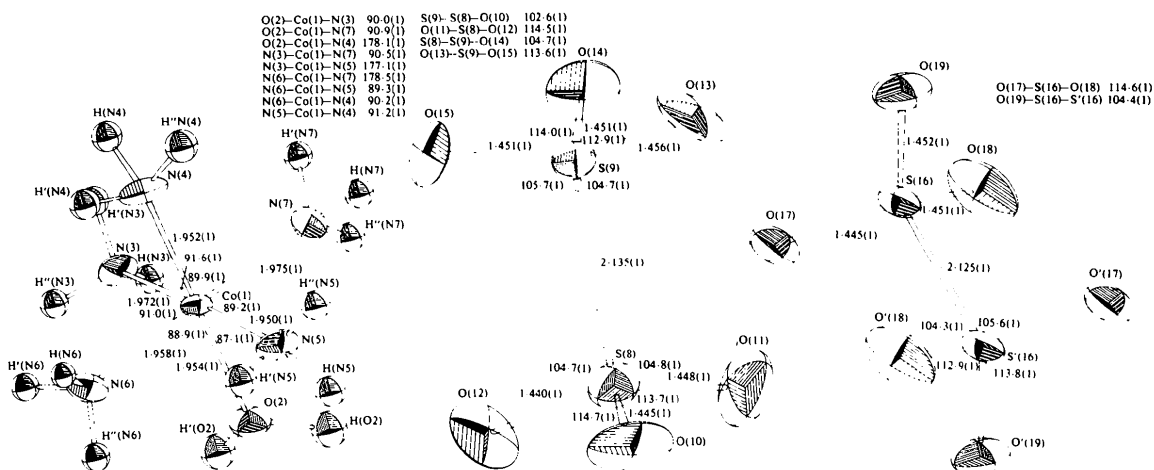


Fig. 1. Views of the ions showing thermal ellipsoids, the numbering of the atoms, and the bond lengths (Å) and angles (°) involving the non-hydrogen atoms.

The structure was solved with the *MULTAN* system of computer programs (Main, Woolfson, Lessinger, Germain & Declercq, 1977). 200 reflections and 2000 Σ_2 relationships were used in the phase-determining procedure. An *E* map computed with the phases from the set with the highest combined figure of merit revealed peaks for all non-hydrogen atoms. The structure was isotropically and anisotropically refined by means of block-diagonal least squares with the modified version of *SFLS* (Ahmed, Hall, Pippy & Huber, 1966) written by Solans. The function minimized was $\sum w|F_o| - |F_c|^2$, with the weights of Cruickshank (1966), i.e. $w = (2F_{\min} + |F_o| + 2|F_o|^2/F_{\max})$ with $F_{\min} = 4.18$ and $F_{\max} = 187$. A difference synthesis revealed positions for the H atoms, which were refined isotropically together with the non-hydrogen atoms (anisotropically). The refinement was terminated at $R = 0.039$ for all observed reflections, where R is defined as $\sum ||F_o| - |F_c||^2 / \sum |F_o|^2$.

The final atomic parameters are listed in Table 1; Fig. 1 (ORTEP, Johnson, 1965) shows a view of the molecule, the bond distances and angles, and the numbering of the atoms. The molecular-geometry calculations were performed with the computer program *CGMC* (Solans & Font-Altaba, 1975).

Discussion. Our results confirm that the dithionate ions are the anions in this first compound of the series.

* Lists of structure factors, anisotropic thermal parameters, atomic coordinates of the H atoms, and bond distances and angles involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34373 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

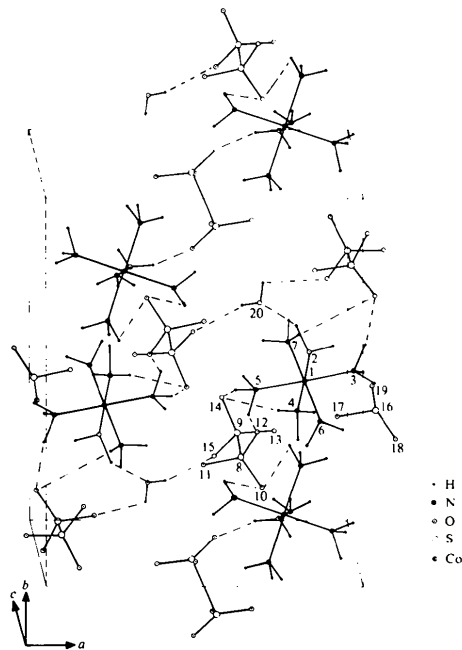


Fig. 2. A view of the unit-cell contents showing the hydrogen bonds.

The five independent Co-N bond distances [ranging from 1.950 (1) to 1.975 (1) Å, average 1.961 Å] agree well with those found in cobalt(III) hexammines (Epstein & Bernal, 1971; Barnett, Craven, Freeman, Kime & Ibers, 1966), and cobalt(III) pentaammines (Freeman & Robinson, 1965; Schaefer, 1968; Cristoph, Marsh & Schaefer, 1969; Wang, Schaefer & Marsh, 1971). The Co-O bond distance [1.954 (1) Å] is similar to those obtained by Freeman & Robinson

Table 2. *Hydrogen bonds*

A	B	C	A-C	$\angle A-B-C$
O(2)-H(O2)...	O(20) ⁱ		2.620 (1) Å	145.1 (10)°
O(2)-H'(O2)...	O(18) ⁱⁱ		2.723 (1)	163.1 (10)
O(20)-H(O20)...	O(13) ⁱⁱⁱ		2.955 (1)	117.6 (11)
O(20)-H'(O20)...	O(15) ⁱⁱ		2.869 (1)	161.1 (13)
N(3)-H'(N3)...	O(10) ^{iv}		2.869 (1)	122.8 (8)
N(4)-H(N4)...	O(14) ^v		2.998 (1)	108.7 (7)
N(5)-H(N5)...	O(14) ⁱ		2.951 (1)	127.1 (8)
N(5)-H'(N5)...	O(14) ^v		2.917 (1)	111.7 (7)
N(5)-H'(N5)...	O(12) ^{vi}		2.998 (1)	124.7 (7)
N(6)-H(N6)...	O(13) ^v		2.976 (1)	165.4 (9)
N(7)-H'(N7)...	O(10) ^{iv}		2.930 (1)	142.8 (9)

Symmetry code

- | | | | |
|-------|---------------------------------------|------|---|
| (i) | $x + \frac{1}{2}, \frac{1}{2} - y, z$ | (iv) | $x, y, z + 1$ |
| (ii) | x, y, z | (v) | $\frac{1}{2} - x, y + \frac{1}{2}, 1 - z$ |
| (iii) | $x - \frac{1}{2}, \frac{1}{2} - y, z$ | (vi) | $\frac{1}{2} - x, y + \frac{1}{2}, \bar{z}$ |

(1965) in pentaamminecarbonatocobalt(III) bromide hydrate (1.93 Å).

The pentaammineaquacobalt(III) cation octahedron is slightly distorted, with a compression that tends to preserve the 'threefold' axis determined by N(6), N(5) and N(4); this produces the lengthening of Co(1)-N(7), Co(1)-N(3) and Co(1)-O(2) and the shortening of Co(1)-N(4), Co(1)-N(5) and Co(1)-N(6), and also reduces the N(4)-Co(1)-N(7), N(5)-Co(1)-N(7), N(6)-Co(1)-O(2) and N(5)-Co(1)-O(2) angles below 90°. This distortion may be produced by anion-cation packing (Fig. 2), because the two S(8)-S(9) anions, surrounding each pentaammineaquacobalt(III) cation, are in different relative orientations with respect to the octahedra.

The S-S (mean value = 2.130 Å) and S-O (1.450 Å) bond distances and the O-S-S (104.6°) and O-S-O (113.8°) angles are similar to those in disodium dithionate dihydrate (2.141, 1.452 Å and 104.6, 114.1° respectively) (Kiers, Piepenbroek & Vos, 1978).

The details of the hydrogen-bond system are shown in Fig. 2 and listed in Table 2. The O-H...O hydrogen bonds from the coordinated water molecule are relatively short, but those from the hydrate water molecules are long (2.96 and 2.87 Å), and hence rather weak. The N-H...O hydrogen bonds are relatively long and therefore weak.

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References

- AHMED, F. R., HALL, S. R., PIPPY, M. E. & HUBER, C. P. (1966). NRC Crystallographic Programs for the IBM/360 System. National Research Council, Ottawa, Canada.
- BARNETT, M. R., CRAVEN, B. M., FREEMAN, H. C., KIME, N. E. & IBERS, J. A. (1966). *Chem. Commun.* pp. 307-308.
- CORONAS, J. M. & CASABO, J. (1974). *An. Quím.* **70**, 335-341.
- CORONAS, J. M., RIBAS, J. & CASABO, J. (1977). *An. Quím.* **73**, 481-484.
- CRISTOPH, C. G., MARSH, R. E. & SCHAEFER, W. P. (1969). *Inorg. Chem.* **8**, 291-297.
- CRUICKSHANK, D. W. J. (1966). *Computing Methods in Crystallography*, edited by J. S. ROLLETT, pp. 112-116. Oxford: Pergamon Press.
- EPSTEIN, E. F. & BERNAL, I. (1971). *J. Chem. Soc. A*, pp. 3628-3631.
- FREEMAN, H. C. & ROBINSON, G. (1965). *J. Chem. Soc.* pp. 3194-3200.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- KIERS, C. T., PIEPENBROEK, A. & VOS, A. (1978). *Acta Cryst.* **B34**, 888-890.
- LOZANO, A. (1969). PhD thesis, Univ. de Barcelona.
- MAIN, P., WOOLFSON, M. M., LESSINGER, L., GERMAIN, G. & DECLERCQ, J. P. (1977). *MULTAN. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain-la-Neuve, Belgium.
- RIBAS, J., CASABO, J. & CORONAS, J. M. (1976). *Rev. Chim. Minér.* **13**, 229-236.
- SCHAEFER, W. P. (1968). *Inorg. Chem.* **7**, 725-731.
- SOLANS, X. & FONT-ALTABA, M. (1975). *Acta Geol. Hisp.* **3**, 116-117.
- WANG, B. C., SCHAEFER, W. P. & MARSH, R. E. (1971). *Inorg. Chem.* **10**, 1492-1497.