same composition $Ag_{0.37}Cr_{1.21}S_2$. We therefore accept the formula $Ag_{0.37}Cr_{1.21}S_2$. From the ionic description: $Ag_{0.37}^+Cr_{1.21}^{3+}S_2^{2-}$ it follows that $Cr^{3+}(d^3)$ only is present.

Preliminary measurements of the magnetic properties of $Ag_{0.37}Cr_{1.21}S_2$ show Curie–Weiss behaviour and antiferromagnetic order at low temperature. The asymptotic Curie temperature θ is about -750 K, also more in agreement with those of the two modifications of Cr_2S_3 [trigonal Cr_2S_3 -585 K, rh. Cr_2S_3 -670 K (van Bruggen, 1969)] than with that of $AgCrS_2$, -55 K (Engelsman et al., 1973).

Recently, we obtained a compound $Ag_xCr_ySe_2$ ($x \simeq 0.3, y \simeq 1.2$) with a hexagonal unit cell: $a = 3.628, c = 12.40$ Å; the compound was always contaminated by Cr_2Se_3. The structure, as derived from the powder intensities, consists of the same entities as found in $Ag_{0.37}Cr_{1.21}S_2$, but with hexagonal instead of rhombohedral stacking of the entities; the stacking of the Se layers is hexagonal.

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μ-Hyperoxo-bis[pentaamminecobalt(III)] Hydrogensulfate Bissulfate Trihydrate*

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Abstract. $[Co_2(NH_3)_{10}(O_2)](HSO_4)(SO_4)_2.3H_2O$, monoclinic, $P2_1/c$, $a = 13.392$ (3), $b = 9.742$ (3), $c = 17.709$ (7) Å, $\beta = 100.98$ (2)°, $Z = 4$, $D_c = 1.943$ g cm^{-3}, $R = 0.109$ for 3640 reflections with $I > 0$. The dicobalt pentacations are centrosymmetric with O–O bond lengths of 1.271 (7) Å, characteristic of a hyperoxo species. The sulfate, hydrogensulfate, and water moieties show various degrees of disorder.

Introduction. The dark-green, binuclear cation $[Co_2(NH_3)_{10}(O_2)]^{5+}$ crystallizes from 2 M H_2SO_4 in the form of orthorhombic crystals as a monosulfate tris(hydrogensulfate) salt. Both the structure (Schaefer

& Marsh, 1966; Schaefer, Ealick & Marsh, 1981; SEM hereafter) of this compound and its electronic spectrum (Lever & Gray, 1978) are consistent with the bridging group being hyperoxide, O_2^-. If this compound is recrystallized from 1 M H_2SO_4, monoclinic crystals form which contain only one hydrogensulfate and two sulfate groups per dicobalt cation. We have carried out X-ray diffraction studies of these monoclinic crystals; while crystal decay and disorder of the sulfate and hydrogensulfate groups have limited the accuracy of the studies, the dimensions of the cation are again consistent with a bridging hyperoxide group.

μ-Hyperoxo-bis[pentaamminecobalt(III)] monosulfate tris(hydrogensulfate) was prepared as described previously (Schaefer & Marsh, 1966). It was added to saturation to 50 ml of 1 M sulfuric acid at 373 K and

the solution was filtered into a small Dewar flask which was stoppered and placed in a refrigerator at 276 K. After 24 h the resulting green needles were filtered and air-dried. Nearly cubic pieces were cut from the needles with a razor blade and mounted on glass fibers using household cement. The crystal dimensions were all in the range 0·12–0·15 mm.

During a preliminary photographic survey using Fe $K\alpha$ radiation, the crystals showed very rapid decay. The decay was less severe in the Mo $K\alpha$ radiation used for intensity data; nevertheless, four crystals were needed for a complete data set. A preliminary rotation photograph (30 min, Co $K\alpha$ radiation) was taken of each crystal, and it was then mounted on a locally modified Syntex $P2_1$ diffractometer. Unit-cell dimensions and orientation matrices were calculated from the setting angles of 15 strong reflections; in all four cases the b axis was within 12° of the φ axis and the cell dimensions were within two e.s.d.'s of the averages we report here (see Abstract). Data were collected using graphite-monochromated Mo $K\alpha$ radiation and θ–2θ scans at a speed of 4° min⁻¹ in 2θ. The scan range was from 1° below $2\theta(K\alpha_1)$ to 1° above $2\theta(K\alpha_2)$; background was counted at each end of the scans, for $\frac{1}{4}$ the scan time. Four check reflections of low 2θ (10–15°) but widely different χ and φ values were monitored every 100 reflections. These check reflections indicated linear decay for each crystal, reaching about 3% in F before the crystal was replaced. The four data sets were scaled together using the check reflections, and corrections were made for Lorentz and polarization effects but not for absorption ($\mu r \simeq 0·13$).

Experimental variances $\sigma^2(I)$ included counting statistics plus an additional term $(0·02 \times \text{scan counts})^2$. After averaging Laue-equivalent measurements, the final data set consisted of 4024 reflections of which 3640 had $F^2 > 0$.

The structure was solved by standard heavy-atom Patterson and Fourier methods. It was evident early on that the O atoms of the sulfate groups are disordered; groups S(1) and S(2) were satisfactorily represented in terms of two orientations having common sites for the S and one O atom, but group S(3) was more complicated and the O atoms were eventually represented by five sets of partially occupied tetrahedra. A difference map calculated when the R index was 0·15 showed three water molecules, one ordered and the other two disordered between two sites each. The final least-squares cycles had in a single matrix the positional parameters for the non-hydrogen atoms; anisotropic U's for the Co, S, and ordered O atoms on sulfate groups S(1) and S(2), and the ordered water molecule; isotropic B's for the O and N atoms of the cation, the disordered O atoms of the two partially ordered sulfate groups and the disordered water molecules; and population parameters for all the disordered atoms. The coordinates and B's of the 20

partial O atoms of sulfate group S(3) and of the 30 ammine H atoms were included as fixed contributions to the structure factors and were not refined. The population parameters for the pairs of sites of the disordered water molecules and for the two orientations of sulfate groups S(1) and S(2) were constrained to sum to 1·0. The population parameters for the five different orientations of sulfate group S(3) were chosen originally from peak heights on a difference map and were unconstrained; their sum at the end of refinement, 0·99 (2), brightened an otherwise dreary scene. The quantity minimized in the least squares was $\sum [(F_o^2 - F_c^2)/\sigma(F_o^2)]^2$, including reflections for which F_o^2 is less than zero. In the final cycle, all parameter shifts were

Table 1. Coordinates ($\times 10^4$) and isotropic B's

		x	y	z	B (Å²)	Pop.†
	Co(1)	486 (1)	1096 (1)	1137 (1)	1·67 (2)*	
	O(1)	271 (5)	−197 (7)	316 (3)	3·3 (1)	
	N(1)	735 (5)	2300 (8)	2024 (3)	2·2 (1)	
	N(2)	1680 (6)	9 (8)	1562 (4)	2·5 (2)	
	N(3)	1293 (6)	2280 (8)	595 (4)	2·8 (2)	
	N(4)	−711 (6)	2132 (9)	702 (4)	2·7 (2)	
	N(5)	−332 (6)	−149 (8)	1664 (4)	2·9 (2)	
	Co(2)	5412 (1)	1366 (1)	4078 (1)	1·71 (2)*	
	O(2)	4902 (6)	625 (6)	4916 (4)	3·5 (1)	
	N(6)	5913 (7)	2260 (8)	3232 (4)	2·9 (2)	
	N(7)	6207 (6)	2627 (9)	4798 (5)	3·3 (2)	
	N(8)	6545 (5)	62 (8)	4238 (4)	2·4 (1)	
	N(9)	4598 (6)	99 (8)	3355 (4)	2·6 (2)	
	N(10)	4260 (6)	2654 (8)	3988 (4)	2·8 (2)	
	S(1)	1944 (2)	100 (3)	3661 (1)	2·65 (5)*	
	O(3)	1123 (5)	−606 (7)	3166 (4)	3·48 (15)*	
A	O(4)	1564 (14)	1108 (34)	4244 (12)	5·0 (6) ⎫	
A	O(5)	2435 (13)	1037 (19)	3162 (10)	2·2 (4) ⎬	0·45 (4)
A	O(6)	2768 (13)	−655 (22)	4093 (12)	2·6 (4) ⎭	
B	O(4)	1485 (10)	408 (21)	4379 (8)	2·7 (4) ⎫	
B	O(5)	2239 (14)	1373 (21)	3330 (11)	3·6 (4) ⎬	0·55
B	O(6)	2746 (14)	−1027 (25)	3920 (12)	4·2 (4) ⎭	
	S(2)	8933 (2)	1323 (3)	3647 (1)	2·52 (4)*	
	O(7)	8131 (5)	2083 (7)	3926 (4)	3·68 (15)*	
A	O(8)	9788 (10)	1131 (18)	4347 (8)	4·3 (4) ⎫	
A	O(9)	9260 (12)	2001 (16)	3038 (9)	3·3 (3) ⎬	0·55 (2)
A	O(10)	8531 (13)	−51 (16)	3454 (10)	3·9 (4) ⎭	
B	O(8)	9931 (12)	1938 (20)	4078 (9)	3·5 (5) ⎫	
B	O(9)	8876 (16)	1653 (20)	2802 (12)	4·3 (5) ⎬	0·45
B	O(10)	8921 (16)	−92 (19)	3738 (11)	3·8 (4) ⎭	
	S(3)	4259 (2)	1298 (3)	1183 (1)	2·95 (5)*	
A	O(11)	4035	877	386	4·0 ⎫	
A	O(12)	3410	2040	1380	4·0 ⎬	0·17 (1)
A	O(13)	5100	2300	1310	4·0 ⎪	
A	O(14)	4520	120	1680	4·0 ⎭	
B	O(11)	3660	1860	480	4·0 ⎫	
B	O(12)	4390	−160	1160	4·0 ⎬	0·34 (1)
B	O(13)	5217	2032	1353	4·0 ⎪	
B	O(14)	3560	1650	1760	4·0 ⎭	
C	O(11)	3580	2070	600	4·0 ⎫	
C	O(12)	5020	640	780	4·0 ⎬	0·18 (1)
C	O(13)	3840	180	1560	4·0 ⎪	
C	O(14)	4960	2080	1740	4·0 ⎭	
D	O(11)	3530	1860	550	4·0 ⎫	
D	O(12)	5280	1060	980	4·0 ⎬	0·17 (1)
D	O(13)	3950	−20	1430	4·0 ⎪	
D	O(14)	4480	2270	1810	4·0 ⎭	
E	O(11)	4062	614	1870	4·0 ⎫	
E	O(12)	5040	2380	1340	4·0 ⎬	0·13 (1)
E	O(13)	3320	1960	810	4·0 ⎪	
E	O(14)	4500	259	657	4·0 ⎭	
	W(1)	7650 (5)	−159 (9)	528 (4)	4·87 (18)*	
A	W(2)	7057 (22)	831 (43)	1790 (11)	6·1 (8)	0·51 (7)
B	W(2)	7321 (26)	1468 (53)	1796 (14)	6·8 (10)	0·49
A	W(3)	6310 (19)	−857 (20)	2506 (10)	5·0 (7)	0·57 (6)
B	W(3)	6841 (49)	−1266 (50)	2667 (22)	11·8 (12)	0·43

* $B_{eq} = \frac{4}{3}\pi^2(U_{11} + U_{22} + U_{33})$ for atoms with anisotropic Gaussian coefficients.
† Site population factor, if other than 1·0.

less than their standard deviations. The final R index is 0·109 for the 3640 reflections with $F_o^2 > 0$ and 0·071 for the 2288 reflections with $F_o^2 > 3\sigma(F_o^2)$ [$R = (\sum |F_o - |F_c||/\sum F_o)$]; the goodness-of-fit for all 4024 reflections surveyed was 1·71.* Atomic parameters are given in Table 1.

In hopes of removing, or at least reducing, the disorder, we cooled a crystal to 17 K on an extensively modified Syntex $P\bar{1}$ diffractometer (Samson, Goldish & Dick, 1980). The resulting scan profiles were very irregular, perhaps due to crystal splitting or to a poor focal spot on the X-ray tube; nevertheless, there were clear violations of the space-group extinctions for $P2_1/c$ and the Laue symmetry appeared to be merely $\bar{1}$ rather than $2/m$. We were able to refine a $P\bar{1}$ model, very closely related to the room-temperature monoclinic structure, to an R of 0·106 for 4272 reflections with $F^2 > 0$, but the disorder problems remained and the goodness-of-fit was an unsatisfactory 3·7 (4368 total reflections). In view of the poor profiles, we did not carry out a systematic search for additional reciprocal-lattice points that might have signified a more ordered structure based on a larger unit cell.

Discussion. The structure (at room temperature) consists of two independent, centrosymmetric $[(NH_3)_5CoO_2Co(NH_3)_5]^{5+}$ cations, with two sulfate ions, one hydrogensulfate ion, and three water molecules per cation. A view of the structure is shown in Fig. 1.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36791 (30 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
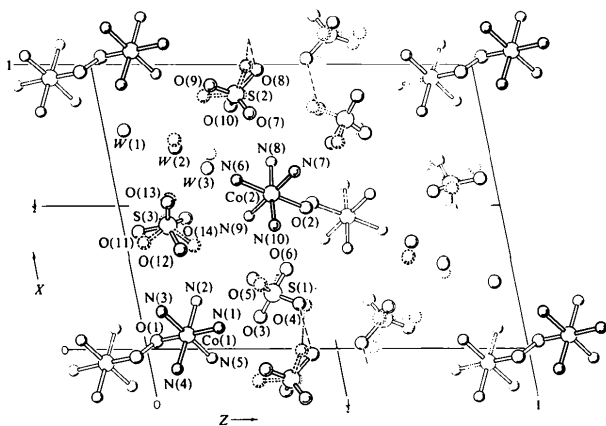

Fig. 1. The portion of the structure lying approximately between $y = -\frac{1}{4}$ and $y = \frac{1}{4}$, as viewed down **b**. For the disordered waters and sulfate groups, atoms with solid lines correspond to orientation A and those with dashed lines to orientation B (Table 1). The dashed (dotted) lines represent the hydrogen bond $O(4)\cdots O(8)$ (see text).

Table 2. *Bond lengths (Å) and some interbond angles (°) in the cation*

Co(1)–O(1)	1·904 (7)	Co(2)–O(2)	1·890 (7)
–N(1)	1·937 (7)	–N(6)	1·959 (8)
–N(2)	1·946 (8)	–N(7)	1·937 (8)
–N(3)	1·953 (8)	–N(8)	1·959 (7)
–N(4)	1·926 (8)	–N(9)	1·954 (8)
–N(5)	1·983 (8)	–N(10)	1·971 (8)
O(1)–O(1)′	1·272 (9)	O(2)–O(2)′	1·270 (10)
O(1)–Co(1)–N(1)	175·8 (3)	O(2)–Co(2)–N(6)	176·0 (3)
–N(2)	85·9 (3)	–N(7)	87·8 (3)
–N(3)	91·9 (3)	–N(8)	91·4 (3)
–N(4)	92·8 (3)	–N(9)	91·9 (3)
–N(5)	86·5 (3)	–N(10)	85·0 (3)
Co(1)–O(1)–O(1)′	116·7 (4)	Co(2)–O(2)–O(2)′	117·5 (4)

The bond distances and angles (Table 2) in the cations are normal, with the averages of the Co–O [1·897 (5) Å], Co–N [1·953 (5) Å], and O–O [1·271 (7) Å] distances in statistical agreement with the corresponding averages in the orthorhombic modification (SEM). The Co–O–O–Co groupings are planar (by symmetry), characteristic of hyperoxide links. There is no apparent *trans* effect on the Co–N distances; however, the scatter of the Co–N distances is considerably greater than the assigned e.s.d.'s would predict – perhaps due to hydrogen-bonding effects which we cannot sort out because of the disorder in the sulfate groups.

It seems apparent that the hydrogensulfate proton is associated with sulfate groups S(1) and S(2), and is involved in a hydrogen bond $O(4)\cdots O(8)$ between them (see Fig. 1). This hydrogen bond must key the disordered orientations A and B (Table 1) of these two sulfate groups to one another: the distances $O(4A)\cdots O(8A)$ and $O(4B)\cdots O(8B)$ are, at 2·43 (2) and 2·53 (2) Å, reasonably close to the shortest hydrogensulfate–sulfate $O\cdots O$ distances of 2·51–2·55 Å found in the orthorhombic form (SEM), whereas the alternative distances $O(4A)\cdots O(8B)$ and $O(4B)\cdots O(8A)$ would be prohibitively short at 2·30 and 2·37 Å. The S(1)–O(4) and S(2)–O(8) bond lengths are, on the average, the longest in these sulfate groups, at 1·55 (1) Å; the other S–O distances in these groups, including the ordered S(1)–O(3) and S(2)–O(7) bonds, average at 1·46 (1) Å. The corresponding averages of the S–O(H) and S–O distances in the orthorhombic form are 1·57 (1) and 1·45 (1) Å (SEM).

The $O(4)\cdots O(8)$ distances of 2·43 (2) and 2·53 (2) Å are characteristic of symmetric hydrogen bonds (Hamilton & Ibers, 1968), so the hydrogensulfate proton may be shared equally by groups S(1) and S(2). Group S(3), which shows more extensive disorder and comes no closer than 3·2 Å to another SO_4 group, must be entirely sulfate in character. In view of the disorder involving the SO_4 groups and two

of the three water molecules, there is no profit in attempting to unravel a detailed hydrogen-bonding scheme. There are many $N\cdots O$ and $H_2O\cdots O$ distances in the range 2·8–3·1 Å; the shortest, at 2·64 Å, is to an O atom of group S(3) and hence has a large and unspecified uncertainty.

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Ca₂Cu with Trigonal-Prismatic Coordination of the Copper Atoms Forming Infinite Chains

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Abstract. Ca₂Cu, orthorhombic, *Pnma*, $a = 6·126$ (2), $b = 4·161$ (4), $c = 14·53$ (1) Å, $Z = 4$, $D_c = 2·58$ Mg m⁻³, μ(Mo $K\alpha$) = 8·4 mm⁻¹. The structure was solved by direct methods and refined isotropically to an *R* value of 0·082 for 118 reflexions. The structure of Ca₂Cu is built up by stacking Cu-centered trigonal prisms of Ca atoms in such a way that they share two rectangular faces. This arrangement allows infinite zigzag chains of Cu atoms to be formed, giving a close relationship with the FeB-type structure.

Introduction. In the phase diagram studied by Bruzzone (1971) three phases exist: CaCu₅ with its own well known structure, CaCu present in two modifications [both stacking variants of the FeB–CrB types (Merlo & Fornasini, 1981)], and Ca₂Cu with unknown structure. The purpose of this work was to determine the crystal structure of this last phase.

In order to avoid the formation of the more stable compound CaCu, an alloy of nominal composition 7Ca:3Cu was prepared by melting the two metals (Ca 99·9, Cu 99·999% purity) in an iron crucible and annealing at 723 K for two months.

The softness and oxidizability of the alloy prevented good crystals being easily found; their diffraction spots were in every case elongated and intensities dropped at high θ values. After many trials a plate-like single crystal of acceptable quality and dimensions 0·02 × 0·06 × 0·17 mm was chosen for the X-ray analysis.

Precession photographs showed orthorhombic symmetry with $0kl$ reflexions present only for $k + l = 2n$ and $hk0$ present only for $h = 2n$, indicating space groups $Pn2_1a$ and $Pnma$.

The crystal was then mounted on an Enraf–Nonius CAD-4 automatic diffractometer and 1212 hkl and $\bar{h}kl$ reflexions were measured with graphite-monochromated Mo $K\alpha$ radiation in the ω–2θ scan mode ($3 \leq \theta \leq 30°$). A check reflexion was employed to test the stability of the crystal; this faded at the end of the data collection. A decay correction, as a function of the elapsed time, was then applied, together with Lorentz and polarization corrections. Absorption was taken into account using the semi-empirical method of North, Phillips & Mathews (1968) with 18 ψ-scan data of a strong reflexion. Finally, averaging gave 609 independent reflexions.

The lattice constants were obtained from a least-squares refinement of 24 diffractometer-measured reflexions, and by comparing the cell volume with that calculated using the elemental atomic volumes, four Ca₂Cu formulae per cell could be assigned.

For the structure resolution and refinement the *SHELX* 76 program (Sheldrick, 1976) was used, taking atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974). Direct methods in the space group *Pnma* gave a solution compatible with both cell content and geometrical requirements. An