to now the most comparable compound seems to be $Ag_6Si_2O_7$ (Jansen, 1977). In this salt, richer in silver than $Ag_4V_2O_7$, we also find a pseudo-hexagonal network of silver-metal-like structure, in which Si_2O_7 groups are inserted.

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Structure of Ammonium μ-Acetato-μ-amido-hexaammine-μ-hydroxo-dicobalt(III) Tetrakis(hydrogensulfate), NH₄.[Co₂(C₂H₃O₂)(NH₂)(NH₃)₆(OH)](HSO₄)₄*

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Abstract. $M_r = 718.44$, orthorhombic, *Pnma*, $a = 10.174$ (2), $b = 8.007$ (1), $c = 30.164$ (5), $V = 2457.3$ (7), $Z = 4$, $D_x = 1.941$, $D_m = 1.97$ (1) g cm⁻³, $\lambda(Mo K\alpha) = 0.71069$ Å, $\mu = 18.28$ cm⁻¹, $F(000) = 1480$, $T = 292$ K, $R = 0.063$ for 1882 reflections. This triply-bridged dicobalt cation crystallizes with the NH_2 and OH bridges disordered across a mirror plane in which the cobalt and acetate atoms lie. Bond distances and angles in the cation are normal. The hydrogensulfate ions show high apparent thermal motion; no significant hydrogen bonds are evident in the structure.

Introduction. Mandel, Marsh, Schaefer, Mandel & Wang (1977) described the structure of the μ-acetato-hexaammine-di-μ-hydroxo-dicobalt(III) cation. The bridging acetato group in that ion had C—O distances 1.316 (53) and 1.203 (53) Å, 0.113 Å different; although this is only 2.1σ, it is large enough to make us want to determine the structure of another compound with the same bridging group. I report here the structure of the μ-acetato-μ-amido-hexaammine-μ-hydroxo-dicobalt³⁺ cation, in which the bridging acetate group is nearly symmetric with C—O distances 1.269 (11) and 1.239 (11) Å.

Experimental. Compound synthesized as the iodide (Werner, 1910); treated with silver sulfate to give bright red crystalline material; good crystals by dissolving this material in ammonium bromide–nitric acid and evaporating; D_m by flotation; crystal 0.23 × 0.24 × 0.28 mm; Weissenberg photography, orthorhombic; Nicolet $P2_1$ diffractometer; unit cell: 15 forms of 4 reflections, $26 < 2\theta < 30°$, least-squares refinement; intensity measurements with graphite-monochromated Mo $K\alpha$ radiation, θ–2θ scans, 2° min⁻¹, backgrounds for one-half the scan time fore and aft, base width $2° + \alpha_1 - \alpha_2$ dispersion; 5625 reflections in $h, \pm k, l$ octants (h 0–12, k 0–9, l 0–35), $4 < 2\theta < 50°$, 2319 independent, used in structure solution and refinement (26 low h, k, high l deleted for overlap); three check reflections monitored every 100 reflections, linear decay of 0.6% in I, data corrected for decay, Lp factors; standard deviations of integrated intensities from counting statistics plus $(0.02\ I)^2$; systematic absences $hk0$, h odd and $0kl$, $k + l$ odd indicate $Pn2_1a$ or $Pnma$, statistics indicate centric $Pnma$ (No. 62), structure solution confirms; programs of *CRYM* system (Duchamp, 1964) used for all calculations, form factors from *International Tables for X-ray Crystallography* (1974), all S, O, N, C atoms located in Fourier maps phased initially on cobalt atoms, found in Patterson map, isotropic refinement based on F converged with $R = 0.145$; difference map indicated either high thermal motion or disorder in the oxygen atoms of the bisulfate groups; cobalt and sulfur atoms and oxygen atoms of bisulfate ions 2, 3 and 4 given anisotropic thermal parameters; bisulfate 1 treated as isotropic fourfold

disordered group; O(3) present for all four orientations; O(4A), O(4B) and O(4C) (and their mirror equivalents) comprise two orientations (26% each), O(5) and its mirror equivalent plus O(8) a third orientation (19%), and O(5A) plus O(6A) and its mirror equivalent the fourth (29%); hydrogen atoms ignored in refinement; population parameters for disordered atoms and secondary extinction parameter included in final full-matrix refinement, 169 parameters, $R = 0.072$ for 2181 reflections with $F_o > 0$, $R = 0.063$ for 1882 reflections with $F_o^2 > 3\sigma F_o^2$, $w = 1/\sigma^2(F^2)$, $S = [\sum w(F_o^2 - F_c^2)^2/(n-p)]^{1/2} = 4.42$ for 2319 reflections, 169 parameters, reflecting the disorder and/or high thermal motion in bisulfate groups; final difference Fourier map had maximum $\Delta\rho$ excursions of $+0.91$ [at O(11)] and $-0.60\,e\,\text{Å}^{-3}$ [at O(13)]; secondary extinction parameter (Larson, 1967) refined to 0.12 (4) $\times$ 10^{-6}; sum of populations of the four orientations of oxygen atoms about S(1) refined to 1.05 (6).

Discussion. Final parameters are given in Table 1, with selected distances and angles in Table 2.*

The cation is shown in Fig. 1. A mirror plane passing through the cobalt atoms, N(1) and N(3), O(1), O(2), C(1) and C(2) relates N(2) to N(2'), N(4) to N(4') and NO to NO'. The —OH and —NH$_2$ bridges cannot be distinguished because of their presumed disorder across this plane; they were represented as a single atom with form factor one-half N and one-half O. The Co—N and Co—O distances are normal and the acetate group is nearly symmetric: the C—O distances, 1.269 (11) and 1.239 (11) Å, are 2σ apart but the difference, 0.030 Å, is only one-fourth as large as the difference in the μ-acetato-di-μ-hydroxo complex (Mandel et al., 1977). Thus, we conclude that the acetate bridge in these dicobalt cations is symmetric (at least to X-rays).

Details of the four bisulfate groups are not of real interest. The S—O bond distances range from 1.287 (15) [S(3)—O(11)] to 1.50 (5) Å [S(1)—O(6A)] and the 'tetrahedral' angles from 99.9 (12) to 125.9 (13)°. Each sulfate ion must bear a proton, but the bond distances are so distorted by the disorder or high thermal motion that they do not differentiate between S—O and S—OH bonds. No overall hydrogen-bonding scheme was discernible that would identify S—OH bonds. The shortest O···O contact is 3.12 (2) Å, suggesting at best a weak interaction. The shortest N···O distance is 2.85 (4) Å, again too long to be a good bond, and the nitrogen atoms have as many as five sulfate oxygen atoms about 3 Å from them [seven for the ammonium nitrogen, N(5)]. The con-

clusion is that there are a large number of hydrogen-bonding patterns of nearly equal energy available and the observed structure is simply an average of them all.

Table 1. Atomic parameters ($\times$ 10^4; U_{eq} in Å^2 $\times$ 10^4; B in Å^2)

	x	y	z	B or U_{eq}	Number of atoms in the cell
Co(1)	2202 (1)	2500	659.0 (0.4)	299 (2)*	4
Co(2)	1196 (1)	2500	1536.0 (0.4)	263 (2)*	4
N(1)	4111 (8)	2500	755 (3)	3.3 (2)	4
N(2)	2336 (5)	732 (7)	200 (2)	3.3 (1)	8
N(3)	2775 (8)	2500	1903 (3)	3.0 (2)	4
N(4)	406 (5)	717 (7)	1900 (2)	3.1 (1)	8
NO	1982 (4)	938 (6)	1133 (1)	2.5 (1)	8
O(1)	359 (6)	2500	527 (2)	2.7 (1)	4
O(2)	−422 (6)	2500	1215 (2)	2.8 (1)	4
C(1)	−572 (9)	2500	807 (3)	2.5 (2)	4
C(2)	−1974 (10)	2500	631 (3)	3.2 (2)	4
S(1)	1519 (3)	2500	3126 (1)	375 (5)*	4
O(3)	588 (9)	2500	2791 (3)	1045 (37)*	4
O(4A)	884 (24)	1434 (22)	3444 (7)	3.2 (7)	
O(4B)	2534 (25)	1550 (40)	2916 (10)	4.3 (7)	2.2 (2)
O(4C)	2171 (31)	1062 (32)	3300 (11)	4.7 (8)	
O(5)	1554 (42)	1118 (45)	3409 (11)	5.1 (11)	1.6 (2)
O(6)	2781 (47)	2500	2920 (15)	4.7 (13)	0.8
O(5A)	802 (54)	2500	3493 (19)	11.2 (20)	1.2
O(6A)	2418 (39)	1043 (58)	3045 (16)	9.6 (14)	2.4 (3)
S(2)	343 (3)	2500	5613 (1)	466 (6)*	4
O(7)	−161 (9)	1123 (9)	5822 (4)	1522 (35)*	8
O(8)	−10 (13)	2500	5200 (4)	2650 (100)*	4
O(9)	1772 (8)	2500	5623 (3)	806 (27)*	4
S(3)	590 (3)	2500	9155 (1)	405 (6)*	4
O(10)	141 (8)	1083 (9)	9387 (3)	1161 (26)*	8
O(11)	175 (17)	2500	8752 (4)	1629 (56)*	4
O(12)	1949 (10)	2500	9212 (4)	1510 (53)*	4
S(4)	1651 (3)	2500	7233 (1)	539 (7)*	4
O(13)	1116 (9)	1147 (10)	7029 (3)	1465 (33)*	8
O(14)	1241 (14)	2500	7681 (5)	1583 (54)*	4
O(15)	2962 (12)	2500	7215 (6)	1758 (62)*	4
N(5)	3454 (9)	2500	8324 (3)	4.4 (2)	4

* $U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$; $\sigma(U_{eq}) = 1/\sqrt{6}\,\langle \sigma U_{ii}/U_{ii}\rangle\,U_{eq}$.

Table 2. Selected distances (Å) and angles (°)

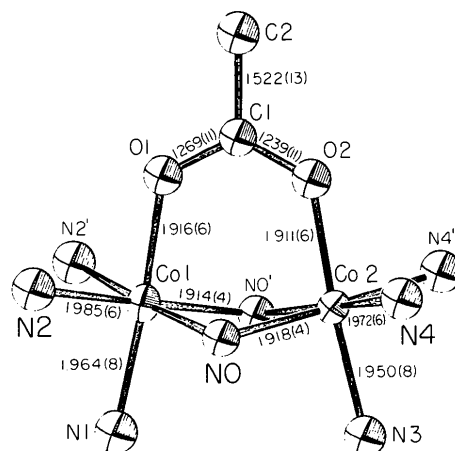|			
Co(1)···Co(2)	2.837 (2)	Co(1)—NO—Co(2)	95.5 (2)
		C(2) C(1)—O(1)	117.9 (8)
		C(2)—C(1)—O(2)	117.5 (8)
		O(1)—C(1)—O(2)	124.6 (8)

Fig. 1. An ORTEP (Johnson, 1965) drawing of the cation with 50% probability thermal ellipsoids, showing the numbering system and selected distances (Å).

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Affinement de la Structure du Tétramétaphosphate d'Ammonium et de Cérium, CeNH₄P₄O₁₂. Relation Entre la Forme Cubique des Composés du Type LnM^IP₄O₁₂ et le Tétramétaphosphate d'Aluminium Al₄(P₄O₁₂)₃

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Abstract. $M_r = 474 \cdot 04$, cubic, $I\bar{4}3d$, $a = 15 \cdot 23$ (1), $V = 3532 \cdot 6$ Å³, $Z = 12$, $D_x = 2 \cdot 674$ Mg m⁻³, Ag $K\alpha$, $\lambda = 0 \cdot 5608$ Å, $\mu = 23 \cdot 43$ cm⁻¹, $F(000) = 2700$, 295 K, $R = 0 \cdot 030$ for 459 independent reflexions. The packing of the P_4O_{12} ring anions is found to be similar to the one already observed in $Al_4(P_4O_{12})_3$ and in some derived structures.

Introduction. Un certain nombre de phosphates du type $LnM^I(PO_3)_4$ sont polymorphes et possèdent une forme cubique. Dans ce dernier cas l'anion phosphorique est un cycle P_4O_{12}. La structure de β-$CsNdP_4O_{12}$ a été déterminée par Soldato, Kuz'min, Ilyakhim & Belov (1981). Certains aspects de ce travail [occupation statistique d'un site 16(c) par 12 atomes de césium, affinement isotrope du facteur thermique de l'atome le plus lourd] montraient l'intérêt d'une révision de la structure cristalline de cette classe de composés. Cet intérêt fut encore accru lorsqu'un examen préliminaire de l'arrangement atomique proposé, nous a montré une analogie très poussée avec la structure cristalline du tétramétaphosphate d'aluminium: $Al_4(P_4O_{12})_3$, analogie non signalée par les auteurs. La présente étude a été réalisée à l'aide du sel de cérium–ammonium: $CeNH_4P_4O_{12}$ dont la préparation chimique a été décrite par l'un de nous (Rzaigui, 1983).

Partie expérimentale. Le cristal présentait la forme d'un tétraèdre régulier de 0,24 mm d'arête; appareillage: Enraf–Nonius; monochromateur: graphite; les paramètres de la maille calculés avec 18 réflexions d'angle haut; domaine des mesures: 3 à 20° (θ); type de balayage: ω; domaine de balayage: 1–40° θ; vitesse de balayage: de 0,01 à 0,03° s⁻¹ suivant l'intensité de la réflexion; temps de mesure du fond continu: 23 à 70 s; réflexions de référence: 800 et $\bar{8}00$; nombre de réflexions mesurées: 3026 (*hkl*; *h,k,l* 0–18); 588 réflexions indépendantes ont été extraites; correction de Lorentz–polarisation, aucune correction d'absorption. Structure résolue par des méthodes classiques: exploitation de la fonction de Patterson puis synthèses de Fourier, après quelques cycles d'affinement, basé sur F, utilisant des facteurs de températures anisotropes, $R = 0,030$, $R_w = 0,036$, $S = 2,785$, pour 459 réflexions telles que $F_o > 3\sigma(F)$;* schéma de pondération unitaire; $\Delta_{max}/\sigma = 0,01$ (β_{23} de N), 0,00 ailleurs; $\Delta\rho_{max}$ 0,4, $\Delta\rho_{min}$ 0,0 e Å⁻³; facteurs de diffusion ceux des atomes neutres (*International Tables for X-ray Crystallography*, 1974); les programmes *SDP* (Enraf–Nonius, 1979) ont été utilisés.

Discussion. Le Tableau 1 rassemble les coordonnées atomiques finales. Comme nous l'avons signalé au début de ce travail il existe une analogie très prononcée

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* Les listes des facteurs de structure et des paramètres thermiques anisotropes ont été déposées au dépôt d'archives de la British Library Lending Division (Supplementary Publication No. SUP 38798: 6 pp.). On peut en obtenir des copies en s'adressant à: The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, Angleterre.