

Chemical Preparation and Crystal Structure of Silver Pyrovanadate, $\text{Ag}_4\text{V}_2\text{O}_7$

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(Received 20 January 1983; accepted 30 August 1983)

Abstract. $M_r = 645.4$, orthorhombic, $Pbca$, $a = 18.820(4)$, $b = 10.89(3)$, $c = 13.925(3)$ Å, $V = 2853.9$ Å³, $Z = 16$, $D_x = 6.00$ g cm⁻³, $\lambda(\text{Ag K}\alpha) = 0.5608$ Å, $\mu = 6.76$ cm⁻¹, $F(000) = 4640$, room temperature. $R = 0.048$ for 2028 independent reflexions. This structure may be described as the c.c.p. silver-metal structure in which some silver atoms are replaced by V_2O_7 groups and others are shifted. This is supported by the Ag–Ag distances in their distorted hexagonal network: $2.989 < d(\text{Å}) < 3.206$.

Introduction. The metallic character of numerous silver-rich compounds is now well established by physical measurements and crystal structure determinations.

The common feature of all these compounds is the existence of fragments of the c.c.p. silver-metal structure within their atomic arrangement. Jansen (1980) summarized the important properties of silver-rich oxides. The title compound $\text{Ag}_4\text{V}_2\text{O}_7$ belongs to this class.

Experimental. Incongruent melting of $\text{Ag}_4\text{V}_2\text{O}_7$ at 663 K has been pointed out by Fleury & Kohlmüller (1966) during the investigation of the Ag_2O – V_2O_5 phase-equilibrium diagram. Crystals were obtained by introducing V_2O_5 into a flux of molten silver nitrate at 573 K ($\text{V}_2\text{O}_5/\text{AgNO}_3 = 1/20$ to $1/5$). After three days, large orange pseudo-hexagonal $\text{Ag}_4\text{V}_2\text{O}_7$ crystals were formed. A crystal of cubic shape ($0.18 \times 0.18 \times 0.18$ mm) was used for X-ray investigations. Using a compact pellet of $\text{Ag}_4\text{V}_2\text{O}_7$, an approximate value of the density (5.9 g cm⁻³) was determined leading to 16 formula units per cell. Apparatus: Philips PW 1100, graphite-plate monochromator. Ω scan mode, maximum number of scans 3, θ range 3 to 26°, scan width 1.20° (θ), scan speed 0.03° s⁻¹, reference reflexions 10,6,0 and $10,6,0$, background measuring time 20 s, 2563 reflexions collected ($0 \leq h \leq 29$, $0 \leq k \leq 16$, $0 \leq l \leq 21$); unit cell refined from 18 high-angle reflexions; Lorentz and polarization corrections, no absorption correction. Structure solved by three-dimensional Patterson function and successive Fourier syntheses, $\sum w(\Delta F)^2$ minimized, $w = 1$. Final $R = 0.048$ for 2028 independent reflexions with $F_o > 2\sigma_F$ ($R_w = 0.057$, $S = 9.95$). $\Delta/\sigma = 0$ for all parameters, final $\Delta\rho$

excursions ≤ 10.8 e Å⁻³. Scattering factors from Cromer & Waber (1965). Computer programs: *Enraf-Nonius Structure Determination Package* (1979).

Discussion. Table 1 reports the positional parameters while Tables 2 and 3 give the most significant interatomic distances and bond angles.* The ab projection of the Ag atoms (Fig. 1) shows an almost hexagonal net. If we examine the Ag–Ag distances in a hexagonal sheet (2.989 to 3.206 Å) and the distance between two sheets (3.48 Å) we find the values observed in the c.c.p. silver-metal structure, with only a small increase. If we consider the cubic edge (4.086 Å) of the unit cell of metal silver (Swanson & Tatge, 1953), the value of the close-packing period $ABCA$ is

* Lists of observed and calculated structure factors, of thermal parameters and interatomic angles in AgO_6 and AgO_3 groups have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38802 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic positions and B_{eq} with their standard deviations*

$$B_{\text{eq}} = \frac{4}{3} \sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	$B_{\text{eq}}(\text{Å}^2)$
Ag(1)	0.91764 (8)	0.0091 (1)	0.8854 (1)	2.03 (4)
Ag(2)	0.91647 (8)	0.0018 (1)	0.1235 (1)	1.90 (3)
Ag(3)	0.17329 (8)	0.2228 (1)	0.8989 (1)	1.75 (3)
Ag(4)	0.17061 (7)	0.7515 (1)	0.1221 (7)	1.62 (3)
Ag(5)	0.83549 (8)	0.2493 (2)	0.6295 (1)	2.14 (3)
Ag(6)	0.33895 (8)	0.7488 (2)	0.6576 (1)	2.03 (3)
Ag(7)	0.08983 (8)	0.4991 (1)	0.1409 (1)	2.04 (4)
Ag(8)	0.08592 (8)	0.5090 (1)	0.8697 (1)	2.41 (4)
V(1)	0.2570 (1)	0.9858 (2)	0.7507 (2)	1.40 (7)
V(2)	0.2579 (2)	-0.0174 (2)	0.0166 (2)	1.18 (7)
V(3)	-0.0012 (2)	0.7554 (2)	0.7291 (2)	1.02 (6)
V(4)	0.4981 (2)	0.2549 (3)	0.4968 (2)	1.08 (5)
O(L12)	0.2105 (6)	0.468 (1)	0.6220 (9)	1.40 (3)
O(E11)	0.3240 (7)	0.415 (1)	0.7400 (8)	1.4 (3)
O(E12)	0.1786 (7)	0.095 (1)	0.3055 (9)	1.7 (3)
O(E13)	0.2584 (7)	0.356 (1)	0.2619 (9)	1.3 (3)
O(E21)	0.1653 (7)	0.565 (1)	0.0067 (9)	2.08 (4)
O(E22)	0.2729 (7)	0.828 (1)	0.0289 (9)	1.6 (3)
O(E43)	0.4175 (6)	0.321 (1)	-0.0078 (9)	1.5 (3)
O(L34)	0.0003 (7)	0.168 (1)	0.3886 (8)	1.3 (3)
O(E31)	0.0749 (7)	0.832 (1)	0.2320 (8)	1.5 (3)
O(E32)	-0.0009 (9)	0.873 (1)	0.8074 (9)	2.1 (4)
O(E33)	0.4217 (7)	0.672 (1)	0.7667 (8)	1.5 (3)
O(E41)	0.4306 (7)	0.841 (1)	0.5031 (10)	1.8 (3)
O(E42)	0.0049 (8)	0.368 (1)	0.0846 (10)	2.0 (3)
O(E23)	0.2911 (8)	0.990 (1)	0.4182 (10)	2.2 (4)

$c_{Ag} = 7.077 \text{ \AA}$, so $2c_{Ag}$ may be compared to the c value (13.925 \AA) of the $Ag_4V_2O_7$ orthorhombic unit cell. It is then easy to imagine the relation between silver metal and silver pyrovanadate: in the $ABCABCA \dots$ package, two silver sheets, C for instance, are eliminated while the remaining ones are shifted and superposed on A so as to obtain a periodic sequence $AAAA \dots$. In such a network

Table 2. Interatomic distances (\AA) and angles ($^\circ$) in the two pyrovanadate anions

V(1)	O(L12)	O(E11)	O(E12)	O(E13)
O(L12)	1.902 (4)	2.758 (6)	2.712 (6)	2.789 (5)
O(E11)	99.2 (2)	1.715 (4)	2.885 (6)	2.951 (6)
O(E12)	98.3 (2)	116.4 (2)	1.678 (4)	2.915 (6)
O(E13)	100.4 (2)	118.1 (2)	117.8 (2)	1.726 (4)

V(2)	O(L12)	O(E21)	O(E22)	O(E23)
O(L12)	1.799 (4)	2.860 (6)	2.823 (5)	2.849 (6)
O(E21)	109.2 (2)	1.709 (5)	2.849 (6)	2.738 (7)
O(E22)	106.9 (2)	112.7 (2)	1.713 (4)	2.779 (6)
O(E23)	110.0 (2)	107.9 (2)	110.1 (2)	1.678 (5)

$$V(1)-V(2) = 3.289 (2)$$

$$V(1)-O(L12)-V(2) = 125.4 (2)$$

V(3)	O(L34)	O(E31)	O(E32)	O(E33)
O(L34)	1.838 (4)	2.828 (6)	2.767 (6)	2.835 (6)
O(E31)	105.2 (2)	1.721 (5)	2.853 (7)	2.884 (6)
O(E32)	103.5 (2)	113.8 (2)	1.684 (4)	2.823 (6)
O(E33)	106.0 (2)	114.4 (2)	112.5 (2)	1.710 (5)

V(4)	O(L34)	O(E41)	O(E42)	O(E43)
O(L34)	1.801 (4)	2.789 (6)	2.759 (6)	2.821 (6)
O(E41)	105.5 (2)	1.703 (4)	2.825 (6)	2.867 (6)
O(E42)	104.7 (2)	113.1 (2)	1.682 (4)	2.850 (6)
O(E43)	106.0 (2)	113.2 (2)	113.3 (2)	1.731 (4)

$$V(3)-V(4) = 3.235 (1)$$

$$V(1)-O(L34)-V(4) = 125.6 (2)$$

Table 3. Interatomic distances (\AA) in AgO_6 and AgO_5 groups

Ag(1)—O(L12)	2.453 (4)	Ag(5)—O(E11)	2.569 (4)
Ag(1)—O(E43)	2.512 (4)	Ag(5)—O(E13)	2.390 (4)
Ag(1)—O(E31)	2.384 (4)	Ag(5)—O(E21)	2.759 (5)
Ag(1)—O(E32)	2.391 (4)	Ag(5)—O(E43)	2.423 (4)
Ag(1)—O(E41)	2.410 (4)	Ag(6)—O(E31)	2.711 (4)
Ag(2)—O(E11)	2.733 (4)	Ag(6)—O(L12)	2.613 (3)
Ag(2)—O(E43)	2.510 (4)	Ag(6)—O(E12)	2.694 (4)
Ag(2)—O(E32)	2.303 (5)	Ag(6)—O(E13)	2.605 (4)
Ag(2)—O(E33)	2.439 (4)	Ag(6)—O(E22)	2.337 (4)
Ag(2)—O(E41)	2.496 (5)	Ag(6)—O(E33)	2.329 (4)
Ag(2)—O(E23)	2.432 (5)	Ag(6)—O(E41)	2.936 (5)
Ag(3)—O(E12)	2.378 (4)	Ag(7)—O(E11)	2.328 (4)
Ag(3)—O(E13)	2.637 (4)	Ag(7)—O(E21)	2.455 (5)
Ag(3)—O(E22)	2.370 (4)	Ag(7)—O(L34)	2.540 (4)
Ag(3)—O(E33)	2.624 (4)	Ag(7)—O(E33)	2.570 (4)
Ag(3)—O(E41)	2.533 (5)	Ag(7)—O(E42)	2.278 (4)
Ag(3)—O(E23)	2.432 (4)	Ag(8)—O(E12)	2.262 (4)
Ag(4)—O(E11)	2.445 (4)	Ag(8)—O(E21)	2.499 (4)
Ag(4)—O(E13)	2.623 (4)	Ag(8)—O(L34)	2.530 (4)
Ag(4)—O(E21)	2.589 (4)	Ag(8)—O(E31)	2.592 (4)
Ag(4)—O(E22)	2.468 (4)	Ag(8)—O(E42)	2.261 (5)
Ag(4)—O(E43)	2.570 (4)		
Ag(4)—O(E31)	2.520 (4)		
Ag(1)—Ag(2)	3.127 (1)	Ag(3)—Ag(5)	3.091 (1)
Ag(1)—Ag(4)	3.093 (1)	Ag(4)—Ag(7)	3.152 (1)
Ag(1)—Ag(6)	3.254 (1)	Ag(5)—Ag(8)	3.006 (1)
Ag(2)—Ag(3)	2.989 (1)	Ag(6)—Ag(7)	3.023 (1)
Ag(2)—Ag(5)	3.111 (1)	Ag(6)—Ag(4)	3.206 (1)

four Ag atoms are exchanged with two V_2O_7 groups so as to form $Ag_4V_2O_7$ (Fig. 2).

A relatively small number of pyrovanadates are known: in $Cd_2V_2O_7$ (Au & Calvo, 1967), $Mn_2V_2O_7$ (Baglio & Dann, 1972) and $\beta\text{-Cu}_2V_2O_7$ (Mercurio-Lavaud & Frit, 1973b) the V_2O_7 groups are centrosymmetric. In $\alpha\text{-Cu}_2V_2O_7$ (Mercurio-Lavaud & Frit, 1973a) V—O distances are similar to those observed in the title compound but the V—O—V angles are very different: 145° ($\alpha\text{-Cu}_2V_2O_7$), 125.6 and 125.4° for $Ag_4V_2O_7$. Up

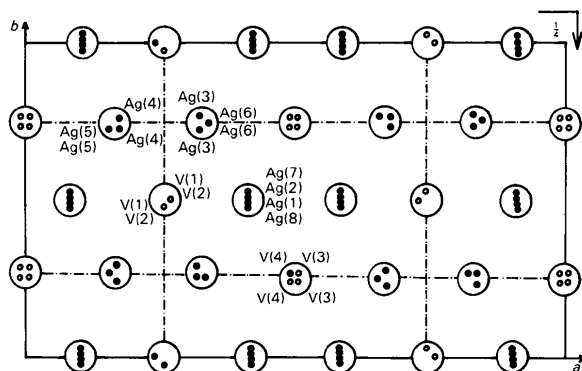


Fig. 1. Projection along $[001]$ of silver and vanadium atomic positions. Large empty circles give the limit within which the cations are projected. The main symmetry operators are drawn.

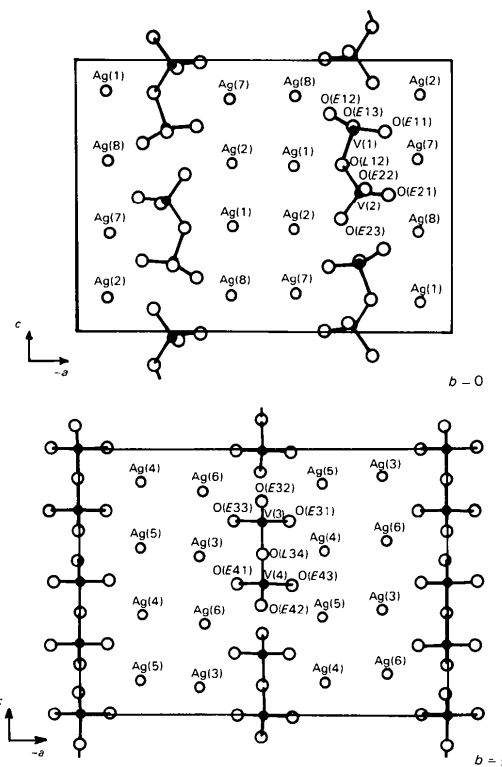


Fig. 2. View in planes $b = 0$ and $b = \frac{1}{4}$ of columns of Ag atoms and pyrovanadate anions.

to now the most comparable compound seems to be $\text{Ag}_6\text{Si}_2\text{O}_7$ (Jansen, 1977). In this salt, richer in silver than $\text{Ag}_4\text{V}_2\text{O}_7$, 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), $\text{NH}_4\cdot[\text{Co}_2(\text{C}_2\text{H}_3\text{O}_2)(\text{NH}_2)(\text{NH}_3)_6(\text{OH})](\text{HSO}_4)_4^*$

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(Received 5 July 1983; accepted 17 August 1983)

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} , $\lambda(\text{Mo } K\alpha) = 0.71069$ 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 $0.23 \times 0.24 \times 0.28$ mm; Weissenberg photography, orthorhombic; Nicolet $P2_1$ diffractometer; unit cell: 15 forms of 4 reflections, $26 < 2\theta < 30^\circ$, 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 $2^\circ + \alpha_1 - \alpha_2$ dispersion; 5625 reflections in $h, \pm k, l$ octants (h 0–12, k 0–9, l 0–35), $4 < 2\theta < 50^\circ$, 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, L_p 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

* Contribution No. 6864 from the A. A. Noyes Laboratory of Chemical Physics.