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$\text{Ca}_2(\text{H}_3\text{O})_2[\text{V}_{10}\text{O}_{28}]\cdot 16\text{H}_2\text{O}$

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Abstract

The crystal structure of dicalcium bis(oxonium) decavanadate hexadecahydrate has been determined by X-ray analysis. The main feature of the structure is the $[\text{V}_{10}\text{O}_{28}]^{6-}$ anion, built up from ten distorted edge-sharing VO_6 octahedra with well established structures. Each Ca^{2+} ion is surrounded by seven water molecules in the form of a distorted pentagonal bipyramid. Water H atoms, as well as those of the H_3O^+ ions, participate in a complicated three-dimensional hydrogen-bonding system.

Comment

The $[\text{V}_{10}\text{O}_{28}]^{6-}$ decavanadate anion is one of the most investigated polyoxoanions of vanadium. The first identified salt, *i.e.* that of barium, $\text{Ba}_3[\text{V}_{10}\text{O}_{28}]\cdot 19\text{H}_2\text{O}$ (Norblad, 1875), was followed by others with alkaline, earth-alkaline and ammonium cations, for example, $\text{Na}_6[\text{V}_{10}\text{O}_{28}]\cdot 18\text{H}_2\text{O}$ (Durif *et al.*, 1980), $\text{Ca}_3[\text{V}_{10}\text{O}_{28}]\cdot 17\text{H}_2\text{O}$ (Swallow *et al.*, 1966), $\text{Sr}_3[\text{V}_{10}\text{O}_{28}]\cdot 22\text{H}_2\text{O}$ (Nieto *et al.*, 1993) and $\text{Ba}_3[\text{V}_{10}\text{O}_{28}]\cdot 19\text{H}_2\text{O}$ (Kamenar *et al.*, 1996), and by double salts such as $\text{K}_2\text{Zn}_2[\text{V}_{10}\text{O}_{28}]\cdot 16\text{H}_2\text{O}$ (Evans, 1966), $\text{K}_2\text{Mg}_2[\text{V}_{10}\text{O}_{28}]\cdot 16\text{H}_2\text{O}$, $\text{Rb}_2\text{Mg}_2[\text{V}_{10}\text{O}_{28}]\cdot 16\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{Mg}_2[\text{V}_{10}\text{O}_{28}]\cdot 16\text{H}_2\text{O}$ (Avtamonova *et al.*, 1990). It is interesting to note that the decavanadates are the

only polyoxometallates found as minerals, *e.g.* $\text{K}_2\text{Mg}_2[\text{V}_{10}\text{O}_{28}]\cdot 16\text{H}_2\text{O}$ is the mineral hummerite (Weeks *et al.*, 1951), which usually occurs together with pascoite, $\text{Ca}_3[\text{V}_{10}\text{O}_{28}]\cdot 17\text{H}_2\text{O}$.

As part of our research on vanadates, molybdates and mixed molybdovanadates, the title compound, $\text{Ca}_2(\text{H}_3\text{O})_2[\text{V}_{10}\text{O}_{28}]\cdot 16\text{H}_2\text{O}$, was prepared and studied. The centrosymmetrical decavanadate anion in this structure (Fig. 1) is built up of ten distorted VO_6 edge-sharing octahedra and is best described as a cubic close-packing of oxygen ions, with the octahedral holes filled by vanadium ions. Each VO_6 octahedron is considerably distorted, with bond angles at the V atoms ranging from 74.25 (5) to 106.46 (7)°. Accordingly, each vanadium ion is displaced from the centre of the polyhedron towards the exterior of the polyanion, causing variation of the V—O distances in the wide range 1.60–2.32 Å. The V—O distance depends upon the type of oxo ligand: V=O_t bond lengths to the terminal oxo O atoms vary from 1.6026 (17) to 1.6167 (16) Å, V—O_{2b} bond lengths to the O atoms bridging two V atoms vary from 1.6889 (15) to 2.0561 (16) Å, V—O_{3b} bond lengths to the O atoms bridging three V atoms vary from 1.9128 (14) to 2.0127 (15) Å and V—O_{6b} bond lengths to the O atoms shared between six V atoms range from 2.1100 (14) to 2.3219 (14) Å.

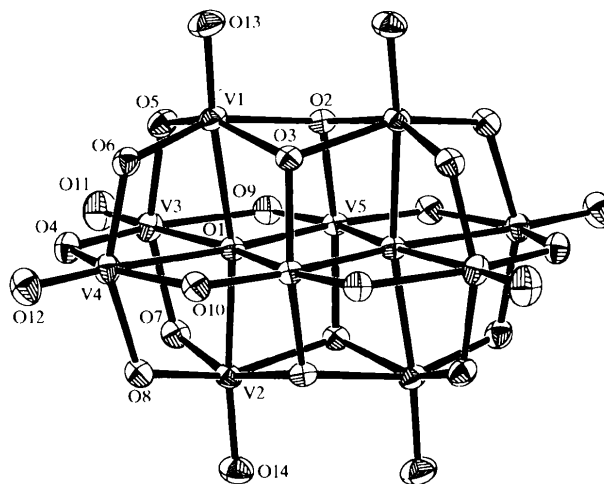


Fig. 1. The structure of the $[\text{V}_{10}\text{O}_{28}]^{6-}$ anion in $\text{Ca}_2(\text{H}_3\text{O})_2[\text{V}_{10}\text{O}_{28}]\cdot 16\text{H}_2\text{O}$. Displacement ellipsoids are drawn at the 50% probability level.

The decavanadate anions are interconnected with calcium and hydronium cations and water molecules. The Ca^{2+} ions are surrounded by seven water molecules in a distorted pentagonal bipyramidal arrangement, with distances ranging from 2.329 (2) to 2.475 (2) Å. The hydronium ion is hydrogen bonded to three O atoms from three different decavanadate anions, with $\text{O}\cdots\text{O}$

distances ranging from 2.785 (2) to 2.932 (2) Å. Water H atoms are also engaged in hydrogen bonding between decavanadate anions and water molecules, resulting in a rather complicated three-dimensional network.

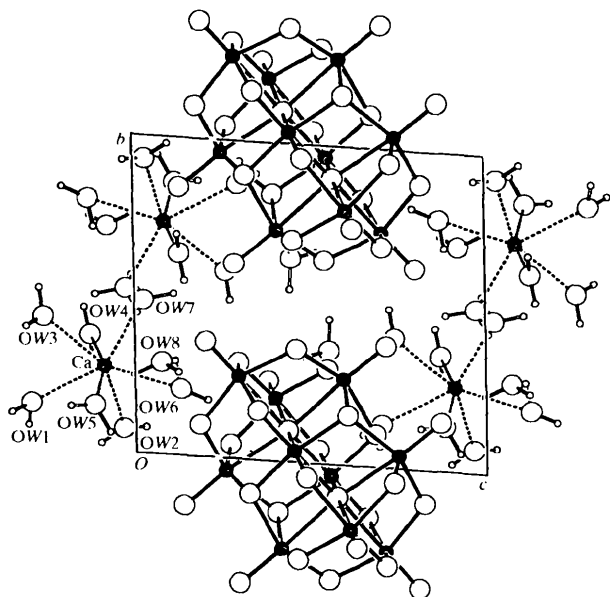


Fig. 2. The crystal structure of Ca₂(H₃O)₂[V₁₀O₂₈]·16H₂O, showing the coordination polyhedra around the calcium ions. The hydronium ions have been omitted for clarity.

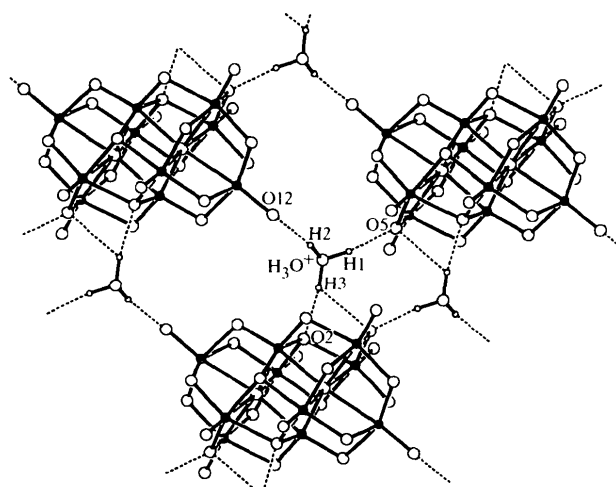


Fig. 3. The packing of polyoxovanadate anions, showing the hydrogen bonds between the hydronium and decavanadate ions.

Experimental

The title compound was prepared by mixing a hot water solution of MoO₃ and Ca(OH)₂ with a suspension of NH₄VO₃ in water, using hydrochloric acid to adjust the pH to 6. The resulting mixture was filtered and to the yellow solution

obtained, solid CaCl₂·H₂O was added. After 4 d at room temperature, transparent orange crystals were isolated. The water content was determined by thermogravimetric analysis.

Crystal data

Ca₂(H₃O)₂[V₁₀O₂₈]·16H₂O
M_r = 1363.848
 Triclinic
P $\bar{1}$
a = 9.7172 (6) Å
b = 10.2638 (5) Å
c = 10.5991 (4) Å
 α = 89.996 (4)°
 β = 102.938 (4)°
 γ = 110.121 (4)°
V = 963.92 (9) Å³
Z = 1
D_s = 2.35 Mg m⁻³
D_m not measured

Mo *K*α radiation
 λ = 0.7107 Å
 Cell parameters from 35 reflections
 θ = 11.4–18.0°
 μ = 2.708 mm⁻¹
T = 293 (2) K
 Prism
 0.38 × 0.36 × 0.35 mm
 Orange

Data collection

Philips PW1100 diffractometer updated by Stoe
 $\theta/2\theta$ scans
 Absorption correction: none
 5861 measured reflections
 5585 independent reflections
 4302 reflections with $I > 2\sigma(I)$

*R*_{int} = 0.034
 θ_{\max} = 30.04°
h = -13 → 13
k = -14 → 14
l = 0 → 14
 3 standard reflections
 frequency: 120 min
 intensity decay: 2.3%

Refinement

Refinement on *F*²
R(*F*) = 0.030
 $wR(F^2)$ = 0.081
S = 1.006
 5585 reflections
 262 parameters
 H atoms not refined
 $w = 1/[\sigma^2(F_o^2) + (0.0427P)^2 + 0.3079P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max}$ = 0.002
 $\Delta\rho_{\max}$ = 0.577 e Å⁻³
 $\Delta\rho_{\min}$ = -0.587 e Å⁻³
 Extinction correction: none
 Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. Selected bond lengths (Å)

V1—O13	1.6063 (16)	V3—O5'	1.8795 (16)
V1—O5	1.8267 (15)	V3—O9	2.0538 (15)
V1—O6	1.8299 (16)	V3—O1	2.3182 (14)
V1—O3	1.9971 (15)	V4—O12	1.6055 (16)
V1—O2'	2.0095 (15)	V4—O4'	1.8321 (16)
V1—O1'	2.2587 (14)	V4—O6	1.8593 (16)
V2—O14	1.6167 (16)	V4—O8'	1.9110 (15)
V2—O8	1.8179 (15)	V4—O10	2.0561 (16)
V2—O7	1.8209 (15)	V4—O1'	2.3219 (14)
V2—O3	2.0127 (15)	V5—O10	1.6889 (15)
V2—O2'	2.0119 (14)	V5—O9	1.6937 (15)
V2—O1	2.2242 (14)	V5—O2	1.9128 (14)
V3—O11	1.6026 (17)	V5—O3	1.9280 (14)
V3—O4	1.8448 (16)	V5—O1'	2.1100 (14)
V3—O7	1.8637 (16)	V5—O1	2.1326 (14)

Symmetry code: (i) 2 - *x*, -*y*, 1 - *z*.

Table 2. Contact distances (Å)

Ca...OW5	2.3291 (19)	Ca...OW3	2.4621 (18)
Ca...OW7	2.357 (2)	Ca...OW1	2.4762 (18)
Ca...OW4	2.3774 (19)	Ca...OW6	2.475 (2)
Ca...OW2	2.4195 (17)		

Table 3. Hydrogen-bonding geometry (\AA , $^\circ$)

D—H...A	D—H	H...A	D...A	D—H...A
OH3O—H1...O5	0.964	1.833	2.785 (3)	168.9
OH3O—H2...O12 ⁱ	0.971	1.993	2.932 (3)	162.3
OH3O—H3...O2 ⁱⁱ	1.001	1.910	2.902 (2)	170.5
OW1—H11...O10 ⁱⁱⁱ	0.869	2.011	2.875 (2)	172.7
OW1—H12...O8 ^{iv}	0.806	2.097	2.828 (2)	150.8
OW2—H21...O7	0.891	1.814	2.690 (2)	167.1
OW2—H22...O8 ^v	0.940	1.970	2.885 (2)	163.9
OW3—H31...O4 ^{vi}	0.897	2.026	2.917 (2)	172.1
OW3—H32...O6 ^{vii}	0.819	1.971	2.785 (2)	171.9
OW4—H41...O11 ^{viii}	0.886	1.945	2.815 (3)	167.0
OW4—H42...O14 ^{ix}	0.944	1.899	2.829 (2)	167.8
OW5—H51...O2 ^x	0.964	1.966	2.892 (2)	160.3
OW5—H52...O3 ^{xi}	0.818	1.835	2.639 (2)	167.2
OW6—H61...O9	0.981	1.953	2.913 (2)	165.4
OW6—H62...O7	0.879	2.129	2.892 (3)	155.5
OW7—H71...O8 ^{xii}	0.838	1.909	2.715 (3)	161.1
OW7—H72...O13 ^{xiii}	0.917	1.998	2.889 (3)	163.4
OW8—H81...O4	0.918	2.016	2.799 (3)	142.3
OW8—H82...O5 ^{xiv}	0.958	1.944	2.868 (3)	161.4

Symmetry codes: (i) $1-x, -1-y, 1-z$; (ii) $x, y-1, z$; (iii) $1-x, -y, -z$; (iv) $2-x, -y, -z$; (v) $2-x, 1-y, -z$; (vi) $x, 1+y, z$; (vii) $1+x, y, z$.

Water H atoms were found in a final difference Fourier map and included in the structure-factor calculations.

Data collection: *STAD14* (Stoe & Cie, 1996a). Cell refinement: *STAD14*. Data reduction: *X-RED* (Stoe & Cie, 1996b). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997a). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997b). Molecular graphics: *EUCLID* (Spek, 1982) and *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1295). Services for accessing these data are described at the back of the journal.

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Ag₂[Pd(NH₃)₂(SO₃)₂] powder

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Abstract

The water-insoluble title compound, disilver(I) diamminedisulfitopalladium(II), Ag₂[Pd(SO₃)₂(NH₃)₂], was obtained from Na₂[Pd(NH₃)₂(SO₃)₂] as a pale-green powder. *Ab initio* crystal structure determination was carried out using X-ray powder diffraction techniques. Patterson and Fourier syntheses were used for atom location, and Rietveld fitting was used for the final refinement. The structure consists of isolated flat *trans*-[Pd(NH₃)₂(SO₃)₂] complexes, with SO₃ and Pd bonded through S. The Ag⁺ cations are coordinated by distorted tetrahedra of O atoms from the SO₃ groups. Pd...Ag contacts of 3.296 (1) Å supplement the coordination of the Pd to octahedral, according to the (4 + 2) scheme. The substance is stable in air up to 448 K, after which it decomposes, yielding an Ag–Pd alloy of a solid solution and metallic Ag and Pd.

Comment

Heteronuclear complex compounds with a low decomposition temperature are often regarded as potential precursors for obtaining metal alloys. As there was some interest in Ag–Pd alloys, the available data on Ag–Pd complex compounds were investigated. The literature search revealed rather limited information on these compounds. References to syntheses of Ag₂[Pd(NO₂)₄] (Chernyaev, 1964) and Ag₂[Pd(C₂O₄)₂] (Gmelin, 1942), and to crystal structure data on Ag₂PdCl₄ (Schroder & Keller, 1988) were found.

The crystal structure of *trans*-Ag₂[Pd(NH₃)₂(SO₃)₂], (I), is presented in Fig. 2. The structure can be defined as ionic, with separately located [Pd(NH₃)₂(SO₃)₂]²⁻ anions. Complex ions are arranged in layers parallel to the *ab* plane, keeping an identical orientation. The