Table 2. *Geometric parameters* (Å, °)

Ag(1)—Te	2.8765 (7)	Ag(2)—Te$^{\rm ix}$	2.8415 (7)
Ag(1)—Te$^{\rm i}$	2.8947 (7)	Ag(2)—Te$^{\rm x}$	2.9050 (8)
Ag(1)—Te$^{\rm ii}$	2.9648 (8)	Ag(2)—Te$^{\rm i}$	3.0114 (9)
Ag(1)—Te$^{\rm iii}$	3.0163 (8)	Ag(2)—Te$^{\rm xi}$	3.034 (1)
Ag(1)—Ag(1$^{\rm iv}$)	2.841 (1)	Te—Te$^{\rm xii}$	4.2331 (8)
Ag(1)—Ag(1$^{\rm ii}$)	3.0091 (7)	Te—Te$^{\rm xiii}$	4.2811 (7)
Ag(1)—Ag(2$^{\rm v}$)	2.9093 (8)	Te—Te$^{\rm xiv}$	4.3534 (8)
Ag(1)—Ag(2$^{\rm vi}$)	3.061 (1)		
Ag(1)—Ag(2$^{\rm vii}$)	3.133 (1)		
Ag(2)—Ag(2$^{\rm viii}$)	3.053 (2)		
Te—Ag(1)—Te$^{\rm ii}$	119.17 (3)	Te$^{\rm i}$—Ag(2)—Te$^{\rm x}$	155.79 (3)
Te—Ag(1)—Te$^{\rm iii}$	117.47 (3)	Te$^{\rm i}$—Ag(2)—Te$^{\rm ix}$	92.60 (2)
Te—Ag(1)—Te$^{\rm i}$	104.48 (2)	Te$^{\rm i}$—Ag(2)—Te$^{\rm xi}$	95.32 (2)
Te$^{\rm ii}$—Ag(1)—Te$^{\rm iii}$	96.66 (2)	Te$^{\rm x}$—Ag(2)—Te$^{\rm ix}$	96.31 (2)
Te$^{\rm ii}$—Ag(1)—Te$^{\rm i}$	122.01 (2)	Te$^{\rm x}$—Ag(2)—Te$^{\rm xi}$	100.38 (2)
Te$^{\rm iii}$—Ag(1)—Te$^{\rm i}$	94.85 (2)	Te$^{\rm ix}$—Ag(2)—Te$^{\rm xi}$	117.49 (3)

Symmetry code: (i) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (ii) $-x, y - \frac{1}{2}, \frac{1}{2} - z$; (iii) $-x, \frac{1}{2} + y, \frac{1}{2} - z$; (iv) $-x, -y, 1 - z$; (v) $-x, 1 - y, 1 - z$; (vi) $x, \frac{1}{2} - y, z - \frac{1}{2}$; (vii) $x, \frac{3}{2} - y, z - \frac{1}{2}$; (viii) $1 - x, 2 - y, 2 - z$; (ix) $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$; (x) $x, 1 + y, 1 + z$; (xi) $x, \frac{3}{2} - y, \frac{1}{2} + z$; (xii) $1 - x, -y, 1 - z$; (xiii) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$; (xiv) $-x, -y, -z$.

The unit-cell dimensions and their e.s.d.'s were determined according to de Boer & Duisenberg (1984). We wanted to choose the same unit cell as Frueh (1959) in order to compare the atomic coordinates. The parameters a, c and β are very similar in the two alternative settings (both with space group $P2_1/c$) for this crystal. Frueh reported values (without e.s.d.'s) of $a = 8.09$, $b = 4.46$, $c = 8.97$ Å and $\beta = 123.33°$ which can be transformed ($a' = -a-c$, $b' = -b$, $c' = c$) to $a = 8.13$, $b = 4.46$, $c = 8.97$ Å, $\beta = 123.74°$. Our unit cell corresponds to the former setting, despite appearing to be the latter; this became unambiguously clear on initiating refinements in both settings using Frueh's atomic coordinates as starting values. Examination of the final atomic coordinates of the structure did not yield extra metric symmetry elements (Le Page, 1987, 1988).

All calculations were carried out on the CDC-Cyber 962-31 computer of the University of Groningen with the program system *PROMETHEUS* (Zucker, Perenthaler, Kuhs, Bachmann & Schulz, 1983).

The material used in this investigation was kindly placed at our disposal by Dr R. O. Felius (Instituut voor Aardwetenschappen, University of Utrecht, The Netherlands). We thank the Romanian Embassy in the Hague for help in tracing the exact finding place of the mineral.

Lists of structure factors, anisotropic thermal parameters and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71038 (24 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA1058]

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Structure of $Na_3[VMo_{12}O_{40}].19H_2O$

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Abstract

The crystal structure of $Na_3[VMo_{12}O_{40}].19H_2O$, trisodium tetracontaoxo(dodecamolybdo)vanadate nonadecahydrate, has been determined by X-ray structure analysis. The polyanion centre sits on a special position with $\bar{4}3m$ symmetry. The VO_4 tetrahedron is at the centre, with three MoO_6 octahedra linking together, through shared edges, to form an Mo_3O_{13} unit. The O(1) atom common to these three octahedra is coordinated to the central V atom and four Mo_3O_{13} groups share O atoms to form the structure known as the Keggin anion. The V—O distance is 1.628 (15) Å, V—Mo is 3.501 (1) Å, and the Mo—O distances range from 1.665 (9) to 2.318 (8) Å.

Comment

Crystallization experiments yielded a number of different compounds containing discrete molybdovanadate anions, of which $[Mo_{57}V_6O_{183}(NO)_6(H_2O)_{18}]^{6-}$ is the largest polymetalate and shows the largest degree of aggregation of molybdate (Zhang, Huang, Shao & Tang, 1993). In solutions containing P^{v} or Si^{iv}, as well as Mo and W, Keggin-type anions are readily formed (Weakley, 1974). Owing to the similarity in behaviour between P^{v} and V^{v} in aqueous solution, a Keggin anion (Keggin, 1934) with V^{v} as the central atom was considered as a species likely to be found in the solution investigated. Crystal structures have been reported for two other Keggin-type $XM_{12}O_{40}$ anions with V^{v} at the centre,

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$K_7V_5W_8O_{40}.12H_2O$ (Nishikawa, Kobayashi & Sasaki, 1975) and $K_6(V_2Mo_{10})VO_4O_{36}.13H_2O$ (Björnberg & Hedman, 1980), but in both of these, V and Mo (or W) are randomly distributed over the other 12 sites. The present study concerns the phase $Na_3[VMo_{12}O_{40}].19H_2O$, a third example of the Keggin structure containing one V atom in the centre as V^v.

The MoO_6 octahedron resembles that found in all Mo Keggin anions, such as $[PMo_{12}O_{40}]^{3-}$ (Strandberg, 1975), $[GeMo_{12}O_{40}]^{4-}$ (Strandberg, 1977) and $[SiMo_{12}O_{40}]^{4-}$ (Ichida, Kobayashi & Sasaki, 1980). In this octahedron, the Mo is bound to one terminal oxygen at 1.665 (9) Å, one oxygen shared with three other Mo atoms, at 2.318 (8) Å, and four oxygens each shared with two Mo atoms, at 1.902 (9)–1.928 (5) Å. The Mo···Mo distance is 3.324 Å when the MoO_6 octahedra share edges and this increases to 3.674 Å when they share corners. These distances are comparable to those found in similar structures (Strandberg, 1975, 1977; Hedman, 1977).

The Na^+ ions coordinate to six water molecules at distances from 3.194 to 3.316 Å. There are six crystallographically diffent water molecules, most of them being not very tightly bonded; hydrogen bonded distances between them range from 2.804 (2) to 3.40 (3) Å. O(*W*6) has no neighbouring atoms closer than 3.998 Å; O(*W*3) is surrounded by six Na atoms with an O···Na distance of 3.194 Å.

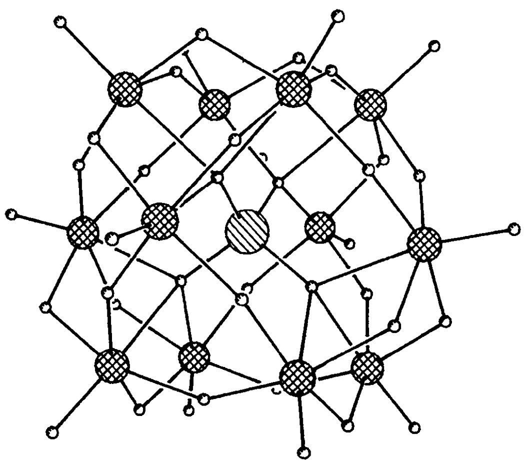

Fig. 1. View of the title compound with the V atom represented by a large lined sphere, Mo atoms by crosshatched spheres and O atoms by small unshaded spheres.

Experimental

Crystal data

$Na_3[VMo_{12}O_{40}].19H_2O$
$M_r = 2253.5$
Cubic
$Fm\bar{3}m$
$a = 22.334$ (2) Å
$V = 11\,140$ (2) Å^3
$Z = 8$
$D_x = 2.687$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å

Cell parameters from 25 reflections
$\theta = 7.5$- 12.5°
$\mu = 2.841$ mm^{-1}
$T = 299$ K
Cubic
0.5 × 0.5 × 0.4 mm
Dark green

Data collection

Siemens *R*3*m*/*V* diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2455 measured reflections
449 independent reflections
405 observed reflections
$[F > 5.0\sigma(F)]$

$R_{\text{int}} = 0.0424$
$\theta_{\text{max}} = 23°$
$h = 0 \rightarrow 24$
$k = 0 \rightarrow 24$
$l = 0 \rightarrow 24$
2 standard reflections monitored every 100 reflections
intensity variation: <1%

Refinement

Refinement on F^2
Final $R = 0.0547$
$wR = 0.0556$
$S = 26.65$
405 reflections
51 parameters
H-atom parameters not refined

Unit weights applied
$(\Delta/\sigma)_{\text{max}} = 2.071$
$\Delta\rho_{\text{max}} = 2.071$ e Å^{-3}
$\Delta\rho_{\text{min}} = -2.99$ e Å^{-3}
Atomic scattering factors from *SHELXTL-Plus* (Sheldrick, 1990)

Table 1. *Fractional atomic coordinates, equivalent isotropic thermal parameters* (Å^2) *and site symmetries*

$$U_{\text{eq}} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	Site symmetry	x	y	z	U_{eq}
Mo	$\underline{m}$	0.1392 (1)	0.2444 (1)	0.1392 (1)	0.023 (1)
V(1)	$\bar{4}3m$	0.2500	0.2500	0.2500	0.048 (2)
Na	4*mm*	0.0	0.3570 (5)	0.0	0.013 (2)
O(1)	3*m*	0.2079 (4)	0.2079 (4)	0.2079 (4)	0.007 (2)
O(2)	*m*	0.1997 (3)	0.8003 (3)	0.6174 (4)	0.013 (2)
O(3)	*m*	0.1825 (3)	0.1825 (3)	0.0975 (4)	0.016 (2)
O(4)	*m*	0.0874 (3)	0.2584 (5)	0.0874 (3)	0.023 (3)
O(*W*1)	*mm*2	0.5000	0.1484 (7)	0.1484 (7)	0.064 (6)
O(*W*2)	*mm*2	0.1266 (7)	0.1266 (7)	0.0	0.071 (6)
O(*W*3)	4*mm*	0.5000	0.0	0.0	0.041 (10)
O(*W*4)	4*mm*	0.0	0.2109 (12)	0.0	0.042 (8)
O(*W*5)	*mmm*	0.2500	0.0	0.2500	0.096 (11)
O(*W*6)	*m*3*m*	0.0	0.0	0.0	0.118 (14)

Table 2. *Bond lengths* (Å) *and angles* (°)

Mo—O(1)	2.318 (8)	O(2)—O(3)	2.694 (10)
Mo—O(3) ×2	1.928 (5)	O(2)—O(4)	2.759 (12)
Mo—O(4)	1.665 (9)	O(3)—O(3$^{\text{iii}}$)	2.686 (15)
Mo—O(2) ×2	1.902 (9)	O(3)—O(4)	2.727 (9)
V(1)—O(1) ×4	1.628 (15)	O(*W*2)—O(3)	2.804 (16)
O(1)—O(1$^{\text{i}}$)	2.659 (24)	O(*W*4)—O(4)	2.959 (16)
O(1)—O(2)	2.894 (7)	V(1)—Mo	3.501 (1)
O(1)—O(3)	2.593 (15)	Mo—Mo$^{\text{iv}}$ (edge)	3.324 (2)
O(2)—O(2$^{\text{ii}}$)	2.602 (12)	Mo—Mo$^{\text{v}}$ (corner)	3.674 (2)
O(1)—Mo—O(3)	74.7 (3)	O(2)—Mo—O(3)	89.4 (3)
O(1)—Mo—O(4)	170.2 (5)	O(2)—Mo—O(3$^{\text{iii}}$)	160.4 (3)
O(1)—Mo—O(2)	86.0 (3)	O(2)—Mo—O(4)	101.1 (3)
O(1)—V—O(1$^{\text{i}}$)	109.5 (3)	O(3)—Mo—Mo(3$^{\text{iii}}$)	88.3 (5)
O(2)—Mo—O(2$^{\text{iii}}$)	86.3 (4)	O(3)—Mo—Mo(4)	98.5 (3)

Symmetry code: (i) $x, \frac{1}{2} - y, \frac{1}{2} - z$; (ii) $x, \frac{3}{2} - z, \frac{3}{2} - y$; (iii) z, y, x; (iv) x, z, y; (v) $x, \frac{1}{2} - z, \frac{1}{2} - y$.

The structure was refined by full-matrix least squares using *SHELXTL-Plus* (Sheldrick, 1990). All non-H atoms were assigned anisotropic displacement parameters in the refinement. Data collection, all calculations and graphics were carried out using *SHELXTL-Plus*.

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Lists of structure factors, anisotropic thermal parameters and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71057 (6 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA1022]

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Single-Crystal Structure Refinement of Spinel-Type $CuCr_2Se_4$

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Abstract

Chromium copper selenide $CuCr_2Se_4$ crystallizes in the normal spinel structure (space group $Fd\bar{3}m$). Copper and chromium are tetrahedrally and octahedrally coordinated in the cubic close packing of selenium atoms, respectively.

Comment

Hitherto structure determinations of spinel-type copper chromium selenide $CuCr_2Se_4$ have been performed by neutron powder diffraction studies (Colominas, 1967; Robbins, Lehmann & White, 1967). The phase relationships of the system $CuSe–Ga_2Se_3–Cr_2Se_3$ were investigated by Okońska-Kozlowska (1989). The growth of single crystals of spinel-type $CuCr_2Se_4$ and $(Cu,Ga)Cr_2Se_4$ and their electrical properties have been described (Okońska-Kozlowska, Kopyczok, Wokulska & Kammel, 1992). In order to compare the cation distribution of this compound with that of spinel-type copper gallium chromium selenide solid solutions we redetermined the crystal structure of $CuCr_2Se_4$ on the basis of single-crystal X-ray measurements.

The structure determination of $CuCr_2Se_4$ confirms the literature data. The standard deviations of the atomic coordinates and bond lengths are improved by an order of magnitude. Deviation from normal spinel cation distribution has not been observed.

Experimental

Crystal data

Cr_2CuSe_4
$M_r = 483.38$
Cubic
$Fd\bar{3}m$
$a = 10.337\ (6)$ Å
$V = 1104.4$ Å^3
$Z = 8$
$D_x = 5.81$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.7093$ Å

Cell parameters from 25 reflections
$\theta = 17.9\text{–}22.8°$
$\mu = 33.58$ mm^{-1}
$T = 293$ K
Pyramid-like
$0.20 \times 0.14 \times 0.14$ mm
Black
Crystal source: chemical vapor transport of the elements

Data collection

Enraf-Nonius CAD-4 diffractometer
ω-2θ scans
Absorption correction: empirical
$T_{min} = 0.709$, $T_{max} = 0.979$
862 measured reflections
197 independent reflections
186 observed reflections [$I>3\sigma(I)$]

$R_{int} = 0.081$
$\theta_{max} = 39.75°$
$h = 0 \rightarrow 18$
$k = 0 \rightarrow 18$
$l = 0 \rightarrow 18$
3 standard reflections monitored every 200 reflections
frequency: 300 min
intensity variation: <1%

Refinement

Refinement on F
Final $R = 0.027$
$wR = 0.033$
$S = 0.91$

$\Delta\rho_{min} = -1.60$ e Å^{-3}
Extinction correction: Zachariasen (1967); Larson (1969)

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