O31—V—O2	114.9 (19)	O32—V—O32^{iv}	125.2 (19)
O31^{iv}—V—O2	114.9 (19)	O32^{iv}—V—O1	110.7 (15)
O31—V—O31^{iv}	83 (2)		

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

The heavy-atom positions were obtained from Patterson analysis and the O atoms were obtained from Fourier syntheses. It appeared that, compared with the apatite structure, the Pb atom situated in site II (6*h*) must be shifted out of the site. According to this shift, the O3 atoms had to be split into two positions. Meanwhile, a difference Fourier synthesis revealed that I must be displaced from the 2*b* site occupied by Cl in chlorapatite (Hendricks *et al.*, 1932). Optimization of the Pb and I occupation factors was undertaken considering a PbI_2 deficit. All atoms, except the disordered I atoms, were refined with anisotropic displacement parameters. Although an absorption correction was performed using a numerical method (Coppens *et al.*, 1965), the high absorption of the material leads to large $\Delta\rho$ residues. The highest value is situated 1.40 Å from Pb2, and the lowest one at 1.40 Å from O31 and 1.39 Å from V.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1992). Cell refinement: *CAD*-4 *EXPRESS*. Data reduction: *CADAK* (Savariault, 1991). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *MOLVIEW* (Cense, 1989). Software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1208). Services for accessing these data are described at the back of the journal.

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$Cs_2Mo_3O_{10}$

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Abstract

Single crystals of dicaesium trimolybdate have been grown by solid-state reaction. The structure is built up of infinite molybdate chains interleaved by Cs atoms. The Mo atoms exhibit two coordination modes towards O atoms, namely, CN6 and CN5 as distorted octahedral and trigonal bipyramidal polyhedra, respectively, while Cs atoms, responsible for the cohesion of the network, sit in bicapped dodecahedra.

Comment

Within extended solid-state chemistry devoted to the system Cs–Nb–Mo–O, we grew single crystals of $Cs_2Mo_3O_{10}$. Such a compound has been synthesized as a microcrystalline powder, and rough cell dimensions have been reported by both Gatehouse & Leverett (1968) (a = 14.55, b = 8.43, c = 9.52 Å and β = 99°) and Foerster *et al.* (1985) (a = 14.47, b = 8.35, c = 9.31 Å and β = 99.1°). It was decided to carry out the present structure determination in order to examine, in particular, the coordination of molybdenum and its evolution in comparison with the potassium and rubidium homologous structures of this phase. To this end, we prepared single crystals of $Cs_2Mo_3O_{10}$ using caesium carbonate and molybdenum trioxide.

The projection of the title compound onto the (010) plane (Fig. 1) shows the infinite $[Mo_3O_{10}]_n$ molybdate chains running along the [001] direction associated by Cs atoms. Within the chain, the Mo atoms occupy two

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different crystallographic sites, Mo1 and Mo2. Mo1 sits on a twofold axis and is surrounded by six O atoms forming a distorted MoO_6 octahedron. Mo2, with a five-fold coordination, occupies a distorted triangular bipyramid (TBP), Mo_2O_5, formed by the O atoms O2, O3, O3^{i}, O4 and O5; the equatorial triangle is formed by O3, O4 and O5, with O2 and O3^{ii} at the apices [symmetry codes: (i) $1-x, y, \frac{1}{2}-z$; (ii) $1-x, 1-y, 1-z$]. A centre of symmetry situated on the O3–O3^{ii} edge repeats this TBP, forming an $[Mo_2O_8]$ group by the association of two TBP *via* edge sharing. This $[Mo_2O_8]$ group is linked on both symmetric sides to two $[\mathrm{Mo1O_6}]$ octahedra, developing this peculiar puckered $[Mo_3O_{10}]_n$ chain (Fig. 2). The puckering angle, measured by the angle Mo1—Mo1^{ii}—Mo1^{ix}, is 92.5 (2)° [symmetry code: (ix) $x, y, 1+z$]. Such unusual architectures infer some drastic distorsions. In the $[Mo_2O_8]$ TBP group, the O3···O3^{ii} distance is only 2.355 (3) Å (a normal distance is generally around 2.6 Å) due to the important repulsion of the heavily charged Mo^{6+} cations constraining this oxo bridge; the Mo2···Mo2^{ii} distance is 3.224 (3) Å. The TBP is then distorted towards a square pyramid (SP). In the equatorial plane, the sum of the three O—Mo—O angles is 359.9 (2)°, with bond distances varying from 1.707 (3) to 2.052 (3) Å. The other Mo—O distances are similar, with Mo2—O2 1.914 (3) and Mo2—O3^{ii} 1.938 (3) Å; on the other hand, a bending of the O3—Mo2—O2 and O3—Mo3—O3^{ii} angles is observed, *i.e.* 74.86 (12) and 72.27 (13)°, respectively. The distortion of the TBP has been inferred by comparison with the data of Muetterties & Guggenberger (1974) for idealized TBP and SP. The distortion (Δ = 28%) determined from the various dihedral angles of the faces of the polyhedra favours TBP (Δ = 0 and 100% correspond to perfect TBP and SP, respectively). It is worth noting that the same calculations performed on the compounds $K_2O_3O_{10}$ (Seleborg, 1966; Gatehouse & Leverett, 1968) and $Rb_2Mo_3O_{10}$ (Foerster *et al.*, 1985) give values of 21 and 25.5%, respectively. This indicates that the increasing size of alkali on going from K to Cs results in increasing stress on the $[Mo_2O_8]$ TBP group. The $\mathrm{Mo1O_6}$ octahedron is also distorted. The O1 atoms, which only interact with Cs atoms, exhibit short strong bonding to Mo1 [Mo1—O1 1.703 (3) Å], similar to the bonding of the O4 and O5 atoms with Mo2 [Mo2—O4 1.707 (3) and Mo2—O5 1.716 (3) Å]. $\mathrm{Mo1O_6}$ shares its O2–O3 and O2^{i}–O3^{i} edges with two $[Mo_2O_8]$ groups related by the twofold axis. The Mo1—O2 bond [1.956 (3) Å] is of a standard distance, whereas Mo1—O3 is greatly elongated at 2.206 (3) Å. The oxygenated environment of the Cs atom is composed of ten atoms forming a bicapped dodecahedron. The Cs···O interatomic distances range between 3.058 (4) and 3.566 (4) Å, with a mean distance of 3.250 (4) Å. Cs atoms are separated by 4.910 Å along the [001] direction, and by 4.853 and 4.889 Å along the [100] direction. The nature of the alkali also influences the puckering angle in the $[Mo_3O_{10}]_n$ chain. Since the *c* parameter increases along $K_2Mo_3O_{10}$, $Rb_2Mo_3O_{10}$ and $Cs_2Mo_3O_{10}$ [8.845 (Gatehouse & Leverett, 1968), 9.23 (Foerster *et al.*, 1985) and 9.4614 Å (this work), respectively] without modification of the Mo1···Mo1 homologous distances (6.54, 6.54 and 6.55 Å, respectively), the

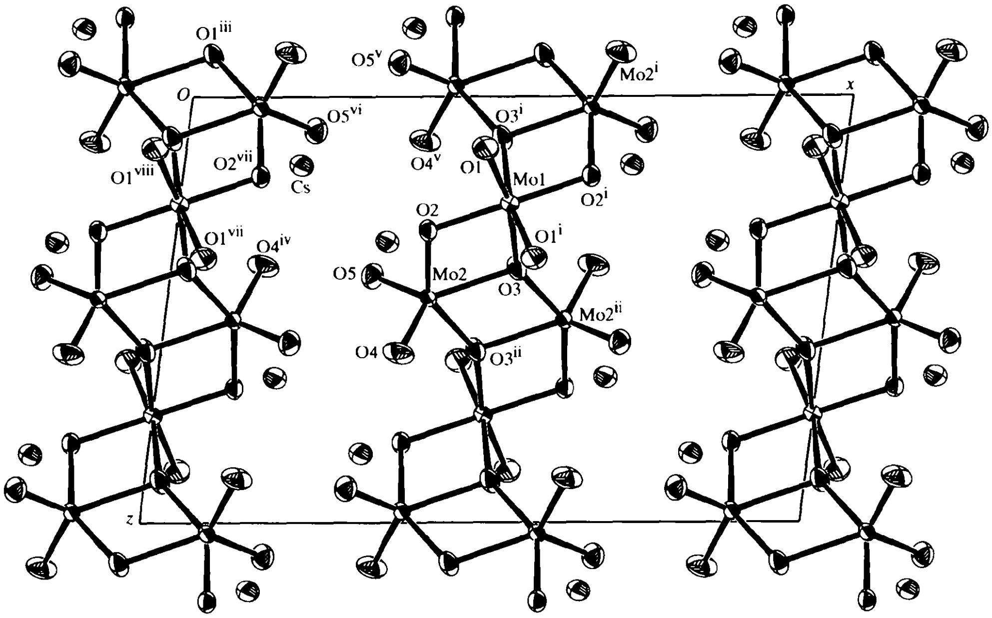

Fig. 1. Projection of the $Cs_2Mo_3O_{10}$ structure onto the (010) plane. Displacement ellipsoids are plotted at the 50% probability level. Symmetry codes are as in Table 2.

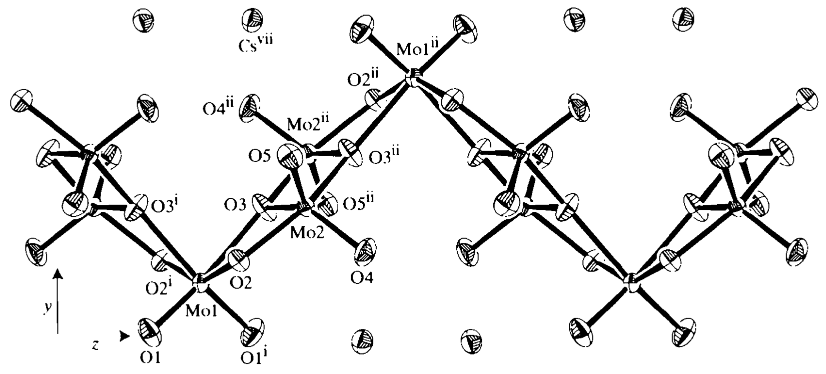

Fig. 2. Projection of one $[Mo_3O_{10}]_n$ chain onto the (100) plane. Displacement ellipsoids are plotted at the 50% probability level. Symmetry codes are as in Table 2.

puckering angle also increases (85.2, 88.9 and 92.5°, respectively).

Experimental

Single crystals of $Cs_2Mo_3O_{10}$ were obtained from a mixture of Cs_2CO_3 and MoO_3 in a molar ratio of 1:3. The mixture was ground in an agate mortar, placed in an alumina crucible and heated at 1073 K for 10 h. After grinding, the mixture was heated at 803 K for 24 h, following by slow cooling (60 K h^{-1}) to 723 K and finally furnace cooling to room temperature.

Crystal data

$Cs_2Mo_3O_{10}$
$M_r = 713.64$
Monoclinic
$C2/c$
$a = 14.465\,(1)$ Å
$b = 8.3997\,(4)$ Å
$c = 9.4614\,(4)$ Å
$\beta = 97.74\,(1)°$
$V = 1139.10\,(11)$ Å^3
$Z = 4$
$D_x = 4.161$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 5.89$–$22.23°$
$\mu = 9.581$ mm^{-1}
$T = 293\,(2)$ K
Parallelepiped
$0.225 \times 0.095 \times 0.052$ mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.374$, $T_{max} = 0.608$
2452 measured reflections
2452 independent reflections

1940 reflections with $I > 2\sigma(I)$
$\theta_{max} = 34.88°$
$h = -23 \rightarrow 23$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 15$
2 standard reflections every 250 reflections intensity decay: 0.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.079$
$S = 1.079$

$\Delta\rho_{max} = 2.23$ e Å^{-3} (0.78 Å from Cs)
$\Delta\rho_{min} = -1.50$ e Å^{-3} (0.71 Å from Mo2)

2452 reflections
70 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0409P)^2 + 6.8260P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$

Extinction correction: *SHELXL*96
Extinction coefficient: 0.00043 (9)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coördinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Mo1	1/2	0.23042 (5)	1/4	0.01704 (9)
Mo2	0.39525 (2)	0.43035 (4)	0.47440 (3)	0.01693 (8)
Cs	0.17805 (2)	0.42166 (3)	0.16034 (3)	0.02644 (8)
O1	0.4529 (3)	0.1018 (4)	0.1209 (4)	0.0345 (7)
O2	0.3816 (2)	0.2889 (3)	0.3144 (3)	0.0220 (5)
O3	0.5233 (2)	0.4284 (4)	0.4038 (4)	0.0296 (7)
O4	0.3606 (3)	0.3105 (5)	0.6032 (4)	0.0384 (8)
O5	0.3065 (2)	0.5617 (4)	0.4209 (4)	0.0308 (7)

Table 2. *Selected geometric parameters* (Å, °)

Mo1—O1	1.703 (3)	Cs—O4^{iv}	3.076 (3)
Mo1—O2	1.956 (3)	Cs—O5	3.112 (4)
Mo1—O3	2.206 (3)	Cs—O5^{v}	3.121 (4)
Mo2—O4	1.707 (3)	Cs—O5^{vi}	3.135 (4)
Mo2—O5	1.716 (3)	Cs—O2^{vii}	3.220 (3)
Mo2—O2	1.914 (3)	Cs—O2	3.299 (3)
Mo2—O3^{ii}	1.938 (3)	Cs—O1^{vii}	3.349 (4)
Mo2—O3	2.052 (3)	Cs—O1^{viii}	3.565 (4)
Cs—O1^{iii}	3.058 (4)	Cs—O4^{v}	3.566 (4)
O1—Mo1—O1^{i}	101.2 (3)	O4—Mo2—O5	108.07 (19)
O1—Mo1—O2^{i}	102.63 (15)	O4—Mo2—O2	100.93 (16)
O1—Mo1—O2	95.74 (15)	O5—Mo2—O2	99.94 (15)
O1^{i}—Mo1—O2	102.63 (15)	O4—Mo2—O3^{ii}	98.61 (17)
O2^{i}—Mo1—O2	150.92 (17)	O5—Mo2—O3^{ii}	98.76 (16)
O1—Mo1—O3	164.27 (16)	O2—Mo2—O3^{ii}	147.13 (12)
O1^{i}—Mo1—O3	89.70 (16)	O4—Mo2—O3	126.32 (19)
O2^{i}—Mo1—O3	87.34 (12)	O5—Mo2—O3	125.51 (16)
O2—Mo1—O3	70.60 (11)	O2—Mo2—O3	74.86 (12)
O3—Mo1—O3^{i}	82.1 (2)	O3^{i}—Mo2—O3	72.27 (13)

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

The Mo and Cs atoms were located by Patterson methods (Sheldrick, 1996). The five independent O atoms were located from difference Fourier synthesis. The calculations were performed with anisotropic displacement parameters for all atoms. The residual maximum and minimum electron densities are located at 0.78 and 0.71 Å from the Cs and Mo2 atoms, respectively.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1993). Cell refinement: *CAD*-4 *EXPRESS*. Data reduction: *CADAK* (Savariault, 1991). Program(s) used to solve structure: *SHELXS*96 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*96 (Sheldrick, 1996). Molecular graphics: *ORTEP*III (Burnett & Johnson, 1996). Software used to prepare material for publication: *SHELXL*96.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1225). Services for accessing these data are described at the back of the journal.

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The vanadium oxide bronze η-$Na_xV_2O_5$ ($x = 1.286$)

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Abstract

The vanadium oxide bronze η-$Na_xV_2O_5$ ($x = 1.286$) crystallizes in the monoclinic system with an original structure built up of layers formed by VO_5 square pyramids and VO_4 tetrahedra parallel to the (010) plane, with the Na atoms lying between these layers. To form the layer, the V atoms are distributed on seven different crystallographic sites: V1 and V2 are in oxygen tetrahedra connected in the layer *via* their corners to V3, V4, V5, V6 and V7 in oxygen square pyramids which share corners and edges. The general formula of the layer, with vanadium exhibiting mixed V^{5+}/V^{4+} valency, is $[V_{14}O_{35}]_n^{9n-}$, the electrical balance being assumed by $9n$ interleaved Na^+ cations.

Comment

Following the pioneer work by Wadsley (1955), with the synthesis and crystal structure determination of the β-$Na_xV_2O_5$ phase ($x \sim 0.3$), an original vanadium bronze with typical non-stoichiometry in sodium and mixed valency (V^{5+} and V^{4+}) of the vanadiums, an investigation was reported for the first time (Hardy *et al.*, 1965) of the $Na_xV_2O_5$ system with $0 \leq x \leq 1$. This study was then completed for x up to 2 (Pouchard *et al.*, 1967) and five phases were evidenced: (i) $0 \leq x \leq 0.02$, an α-$Na_xV_2O_5$ phase with an orthorhombic crystal structure analogous to V_2O_5, few Na atoms being intercalated between the layers; (ii) $0.22 \leq x \leq 0.40$, a β-$Na_xV_2O_5$ monoclinic phase with sodium inserted in tunnels as described by Wadsley (1955); (iii) $0.70 \leq x \leq 1$, an α'-$Na_xV_2O_5$ orthorhombic phase and an α-like phase with a high sodium concentration (Carpy & Galy, 1975); (iv) $1.28 \leq x \leq 1.45$, an η-$Na_xV_2O_5$ phase solely characterized by its powder pattern; (v) $1 \leq x \leq 2$, a χ-$Na_xV_2O_5$ phase crystallizing in the rhombohedral system [cell parameters $a = 6.99\,(1)$ Å and $\alpha = 101.7\,(1)°$] with eight formula units per unit cell ($\rho_{\rm exp} = 3.05\ {\rm g\,cm^{-3}}$). Recently, another sodium vanadium bronze, τ-$Na_xV_2O_5$ with $x = 0.64$, has been isolated and characterized (Savariault *et al.*, 1996). Its layered monoclinic structure is constituted by a balanced packing of DZ and D4 $(V_2O_5)_n$ layers separated by a plane of Na atoms. D4 depicts $(V_2O_5)_n$ double layers built up by infinite quadruple chains of VO_6 octahedra sharing equatorial-plane edges and associated along the short b axis (*i.e.* 3.6 Å) by edges. D2 depicts a $(V_2O_5)_n$ layer obtained from a crosslinked double string of VO_6 octahedra sharing edges and corners.

Up to now, it had been impossible to obtain single crystals of the η-$Na_xV_2O_5$ phase due to its easy decomposition. New crystal-growth methods which will be reported in a forthcoming paper have been developed. They allowed us to isolate blue–black crystals of the η phase. Single-crystal X-ray analysis shows that η-$Na_xV_2O_5$ crystallizes in the monoclinic system and exhibits a typical layer structure with alternating $[V_{14}O_{35}]_n^{9n-}$ and sodium layers. Within the mixed-valence vanadium layers, V^{5+} and V^{4+} are clearly evidenced. For example, V1 sits in a $V1O_4$ tetrahedron of O atoms similar to V2, but this last $V2O_4$ tetrahedron shares an oxygen, on a twofold axis, with its symmetry equivalent resulting in a $[V2_2O_7]$ group. All the inter-

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