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Tetraammonium Hexahydrogenhexamolybdozincate(II) Hexahydrate

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Abstract

The title compound, $(NH_4)_4(H_6ZnMo_6O_{24}).6H_2O$, exhibits a structure with six MoO_6 octahedral edge-sharing units surrounding a central ZnO_6 octahedron, with all metal atoms in a common plane. The average Zn—O distance is 2.081 (5) Å, while the average Mo—O distances are 2.240 (15), 1.946 (11) and 1.711 (12) Å for four-, two- and single-coordinate O atoms, respectively.

Comment

As part of our studies of the structures and types of heteroatoms found for heteropolymolybdates and tungstates, we have examined the structure of $(NH_4)_4(H_6ZnMo_6O_{24}).6H_2O$. The structure consists of an $(H_6ZnMo_6O_{24})^{4-}$ anion, NH_4^+ cations and water molecules. The anion has the standard Anderson structure (Anderson, 1937), with six MoO_6 octahedral edge-sharing units surrounding a central ZnO_6 octahedron and all metals in a common plane [the maximum deviation from the least-squares plane is 0.025 (1) Å]. The Zn atom is located at an inversion centre and the ZnO_6 octahedron is trigonally distorted, with Zn—O distances of 2.074 (7)–2.088 (7) Å [average 2.081 (5) Å]. Six non-acidic H atoms attached to the central O atoms surrounding the Zn atom are assumed to be present, as is typical of low oxidation state heteroatoms incorporated into the Anderson structure, such as $Na_3(H_6CrMo_6O_{24}).8H_2O$ (Perloff, 1970). All Mo—O distances are comparable with those found in other $(H_6XMo_6O_{24})^{n-}$ ions, where X = Co^{II} (Nolan, Burns & Lawrance, 1996), Cu^{II} (Ito, Ozeki, Ichida, Miyamae & Sasaki, 1989), Cr^{III} (Perloff, 1970), Co^{III} (Nagano, Lee, Ichida & Sasaki, 1990), Al^{III} (Lee, Park, Lee & Ichida, 1991) and Rh^{III} (Ozawa, Hayashi & Isobe, 1991). The sum of the bond valences around Mo1, Mo2 and Mo3 are 6.04, 6.06 and 5.96, respectively (Brown & Altermatt, 1985).

It should be noted that the choice of one ammonium N-atom position is different to that reported for the isomorphous Cu^{II} compound, $(NH_4)_4(H_6CuMo_6O_{24}).4H_2O$ (Ito *et al.*, 1989). In the latter, only four molecules of water were considered as being present, with two water O-atom sites having 0.5 occupancy. It is interesting, therefore, that one of the partly occupied water O-atom sites in the structure of the Cu^{II} compound corresponds to the location of an N atom in the present structure. Although some doubt must remain as to the location of the N atoms, it should be noted that the average N···O distance in the present structure is 2.96 Å, similar to the average N···O distance of 3.06 Å in $(NH_4)_6(Mo_7O_{24}).4H_2O$, for which the N and O atoms were unequivocally located (Evans, Gatehouse & Leverett, 1975).

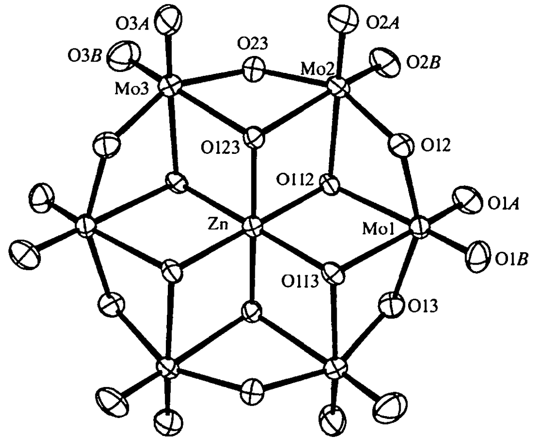

Fig. 1. The anion in $(NH_4)_4(H_6ZnMo_6O_{24}).6H_2O$, indicating the labelling of the non-H atoms. Displacement ellipsoids are shown at the 50% probability level.

Experimental

The title compound was prepared according to Nomiya, Takahashi, Shirai & Miwa (1987). The resulting solution was allowed to stand for several days and produced small colourless plate-shaped crystals.

Crystal data

$(NH_4)_4(H_6ZnMo_6O_{24}).6H_2O$
M_r = 1211.32
Cu $K\alpha$ radiation
λ = 1.54178 Å

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Monoclinic
$P2_1/c$
$a = 11.428\,(3)$ Å
$b = 11.171\,(3)$ Å
$c = 11.956\,(3)$ Å
$\beta = 106.86\,(2)°$
$V = 1460.7\,(7)$ Å^3
$Z = 2$
$D_x = 2.754$ Mg m^{-3}
$D_m = 2.73$ Mg m^{-3}
D_m measured by pycnometry (1,2-dibromoethane)

Cell parameters from 25 reflections
$\theta = 56.94–59.65°$
$\mu = 22.365$ mm^{-1}
$T = 294\,(1)$ K
Plate
0.25 × 0.23 × 0.02 mm
Colourless

Data collection

Rigaku AFC-7*R* direct-drive rotating-anode diffractometer
$\omega/2\theta$ scans
Absorption correction: analytical
$T_{\min} = 0.0533$, $T_{\max} = 0.6425$
1896 measured reflections
1675 independent reflections

1504 observed reflections $[I > 2\sigma(I)]$
$R_{\rm int} = 0.0414$
$\theta_{\max} = 59.93°$
$h = 0 \rightarrow 12$
$k = -9 \rightarrow 12$
$l = -13 \rightarrow 12$
3 standard reflections monitored every 150 reflections
intensity decay: 1.443%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0449$
$wR(F^2) = 0.1499$
$S = 1.136$
1673 reflections
188 parameters
H atoms not located
$w = 1/[\sigma^2(F_o^2) + (0.0775P)^2 + 16.0584P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.002$

$\Delta\rho_{\max} = 0.731$ e Å^{-3}
$\Delta\rho_{\min} = -0.976$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.00044 (7)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Zn	1/2	0	0	0.0216 (5)
Mo1	0.34746 (8)	0.23639 (8)	0.05281 (8)	0.0221 (3)
Mo2	0.65017 (8)	0.24077 (8)	0.13360 (8)	0.0233 (3)
Mo3	0.80389 (8)	0.00580 (8)	0.07477 (8)	0.0256 (3)
O112	0.5006 (6)	0.1141 (6)	0.1370 (6)	0.0203 (15)
O113	0.3534 (6)	0.1076 (6)	−0.0898 (6)	0.020 (2)
O123	0.6388 (6)	0.1133 (6)	−0.0163 (6)	0.022 (2)
O12	0.4967 (6)	0.3063 (6)	0.0335 (7)	0.026 (2)
O13	0.2417 (6)	0.1002 (7)	0.0583 (6)	0.028 (2)
O23	0.7612 (6)	0.1089 (7)	0.1890 (6)	0.029 (2)
O1*A*	0.3448 (8)	0.2966 (7)	0.1839 (7)	0.034 (2)
O1*B*	0.2525 (7)	0.3270 (7)	−0.0475 (7)	0.032 (2)
O2*A*	0.7436 (7)	0.3373 (7)	0.0869 (7)	0.036 (2)
O2*B*	0.6522 (8)	0.2958 (8)	0.2659 (7)	0.037 (2)
O3*A*	0.8953 (8)	0.0990 (8)	0.0228 (8)	0.043 (2)
O3*B*	0.9067 (7)	−0.0786 (8)	0.1789 (7)	0.044 (2)
OH1	0.8388 (10)	0.5254 (10)	0.2611 (9)	0.065 (3)
OH2	0.5118 (12)	0.0445 (9)	0.3563 (8)	0.067 (4)
OH3	0.0146 (12)	0.1711 (11)	0.5423 (17)	0.118 (6)
N1	0.8099 (12)	0.0258 (10)	0.4107 (10)	0.051 (3)
N2	0.0021 (14)	0.1994 (15)	0.2935 (16)	0.099 (6)

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

Zn—O112	2.074 (7)	Mo2—O23	1.932 (7)
Zn—O123	2.082 (7)	Mo2—O12	1.957 (7)
Zn—O113	2.088 (7)	Mo2—O112	2.228 (7)
Mo1—O1*B*	1.699 (7)	Mo2—O123	2.263 (7)
Mo1—O1*A*	1.714 (8)	Mo3—O3*A*	1.714 (8)
Mo1—O12	1.949 (7)	Mo3—O3*B*	1.724 (8)
Mo1—O13	1.956 (7)	Mo3—O13$^{\rm i}$	1.930 (7)
Mo1—O112	2.218 (7)	Mo3—O23	1.953 (7)
Mo1—O113	2.247 (7)	Mo3—O123	2.235 (7)
Mo2—O2*B*	1.691 (8)	Mo3—O113$^{\rm i}$	2.248 (7)
Mo2—O2*A*	1.721 (8)		
O112—Zn—O123$^{\rm i}$	97.4 (3)	O112—Zn—O113	82.6 (3)
O112—Zn—O123	82.6 (3)	O123$^{\rm i}$—Zn—O113	83.0 (3)
O112—Zn—O113$^{\rm i}$	97.4 (3)	O123—Zn—O113	97.0 (3)

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

A complete asymmetric unit of data was collected although it was not continuous within the index ranges stated above. As no H atoms could be located, the positions of the N atoms of the NH_4^+ ions and the O atoms of the water molecules were determined using the following procedure. For the five potential sites there are ten possible atom combinations. Refinements for all possible combinations were carried out and the selection of the positions of the N and O atoms was made on the basis of crystallographic as well as crystal chemical considerations. The former include R_1 and wR_2, goodness of fit and, most importantly, the least spread in the $(U_{11} + U_{22} + U_{33})/3$ values. In view of the extensive hydrogen-bonded network involving the NH_4^+ ions, water molecules and $(H_6ZnMo_6O_{24})^{4-}$ ions, the environments of the N and O atoms were expected to be similar and hence to have similar displacement factors for the atoms involved. The crystal chemical criterion was based on the condition that in structures involving N and O atoms of NH_4^+ ions and water molecules, the N···N distances are always greater than 3.7 Å (Evans, Gatehouse & Leverett, 1975). While some variation in the R_1 and wR_2 values was noted, more variation in the goodness of fit and $(U_{11} + U_{22} + U_{33})/3$ values was observed, which allowed a definitive choice to be made subject to the above criterion. At this stage in the refinement, all water O-atom sites were assumed to be fully occupied, giving six water molecules of crystallization. However, the compound is reported to contain only five water molecules, based on chemical analysis and a thermogravimetric study (Nomiya *et al.*, 1987; La Ginestra & Delli Quadri, 1966). Attempts to model five rather than six water molecules of crystallization provided no improvement in the refinement, and the compound was therefore assumed to contain six water molecules of crystallization.

Data reduction: *TEXSAN* (Molecular Structure Corporation, 1985, 1992). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976).

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Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: TA1107). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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$Os_3Sn_{15}O_{14}$, ein ternäres Oxid mit osmiumgefüllten Sn_6-Oktaedern

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(Eingegangen am 25. März 1996; angenommen am 15. Juli 1996)

Abstract

Triosmium pentadecatin tetradecaoxide, $Os_3Sn_{15}O_{14}$, is isostructural with $Ru_3Sn_{15}O_{14}$. It is a metal-rich stannate and contains osmium-centred tin octahedra. These $OsSn_6$ octahedra form triple chains in which the Sn atoms which link the octahedra have the oxidation state +1.

Kommentar

Vor kurzem berichteten wir über das erste sauerstoffarme ternäre Oxid im System Ru–Sn–O: $Ru_3Sn_{15}O_{14}$ (Reichelt *et al.*, 1995). Vergleichende Untersuchungen im System Os–Sn–O haben ergeben, daß eine Phase mit analoger Zusammensetzung auch in diesem System existiert. Zentrales Motiv dieses metallreichen Oxides sind über Ecken verknüpfte $OsSn_6$-Oktaeder, die entlang der kristallographischen *b*-Achse verlaufende Dreifachstränge ausbilden (Fig. 1). Die formale Zusammensetzung eines Stranges ist $(Os_3Sn_{14})_n$.

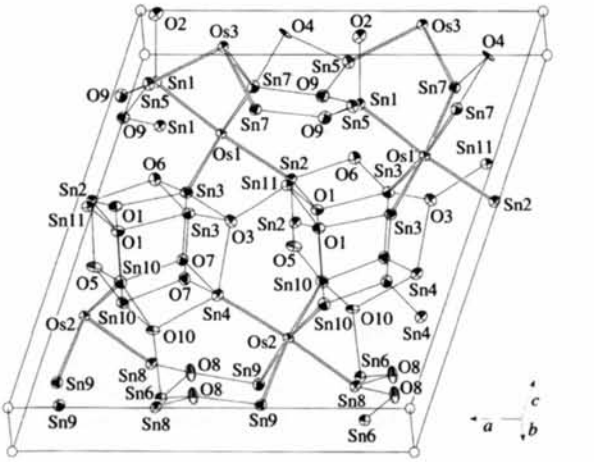

Fig. 1. *ORTEP*II-Darstellung (Johnson, 1976) des Inhaltes einer Elementarzelle.

Verbunden sind diese Stränge untereinander durch die Sauerstoffatome (Fig. 2). Die Bindungslängen in den Oktaedern betragen zwischen Os und Sn 2,531 (1) bis 2,632 (1) Å. Die Sn—Sn-Abstände betragen zwischen 3,333 (1) und 3,791 (1) Å. Aufgefüllt wird die Struktur durch ein weiteres Sn-Atom, das zum Verlust des Symmetriezentrums führt. Die durch ein Pseudoinversionszentrum erzeugte Position bleibt nach röntgenographischem Befund unbesetzt. Eine Verfeinerung in der Raumgruppe *C*2/*m* mit einer Halbbesetzung dieser Position führt zu signifikant schlechteren *R*-Werten: $R1 = 0{,}083$ $wR2 = 0{,}212$. Die Abweichung

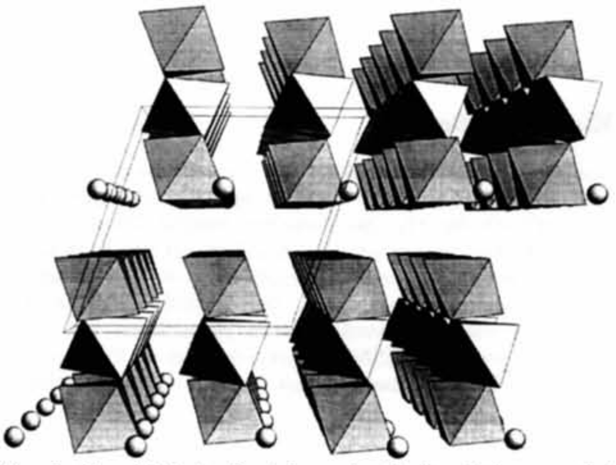

Fig. 2. Perspektivische Darstellung der Os_3Sn_{14}-Stränge parallel [010]; einzelne Atome: Sn11.

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