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A new cluster complex, $(NH_4)_6[Mo_4Se_4(CN)_{12}]\cdot 6H_2O$, containing a tetranuclear mixed-valence molybdenum core

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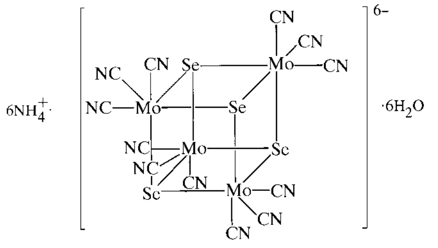
The title compound, hexaammonium tetra-μ_3-selenido-tetrakis(tricyanomolybdenum) hexahydrate, is isostructural with the Mo/S, W/S and W/Se analogues. The structure contains disordered cyclic hydrogen-bonded $[\{(NH_4)(H_2O)\}_3]^{3+}$ cations and $[Mo_4Se_4(CN)_{12}]^{6-}$ cluster anions with $\bar{4}3m$ symmetry. The cation assembly consists of alternating ammonium and water molecules linked by N—H···O hydrogen bonds. The anion has a typical cubane cluster structure. The cations and anions are linked together by hydrogen bonds involving the terminal N atoms of the CN groups.

Comment

Cuboidal clusters with bridging chalcogenide ligands are known for a wide variety of transition metals (Holm, 1992; Coucouvanis, 1991; Saito, 1995, 1997; Shibahara, 1991, 1993; Müller, 1986). Previously, we have prepared and structurally investigated some salts of alkali metal cations and cyanide cluster anions of the general formula $[M_4Q_4(CN)_{12}]^{n-}$, where M = Mo and Q = Te, or M = W and Q = S, Se or Te (Fedin *et al.*, 1999). All these compounds belong to triclinic, monoclinic or orthorhombic crystal systems and the anions are slightly distorted from ideal T_d point symmetry.

Recently, we have found that Mo/W/S/Se anions can give high symmetry cubic crystal structures with six ammonium cations and six water molecules. Three of them, for M = Mo/Q = S and M = W/Q = S or Se, were structurally investigated at room temperature (Fedin *et al.*, 2000). They appeared to be isostructural, the anions having the ideal T_d point symmetry for metal and chalcogen atoms. Unfortunately, our attempts to find the H-atom positions were unsuccessful, due to the disorder of the cations. In the present article, we report the synthesis and low-temperature crystal structure investigation of $(NH_4)_6[Mo_4Se_4(CN)_{12}]\cdot 6H_2O$, (I), which is isostructural with the Mo/S, W/S and W/Se analogues.

The structure of (I) contains an unusual $[\{(NH_4)(H_2O)\}_3]^{3+}$ cation (Fig. 1*a*). This is a ring of alternating ammonium and water molecules linked by N—H···O hydrogen bonds. The ring is not planar but has a chair conformation. The cation assembly is disordered relative to the pseudo-rotation around the centre of the ring in such a way that each position is statistically occupied by one half of NH_4^+ and one half of H_2O. Therefore, the central atom, O1, has a mixed atomic scattering factor, 0.5 N + 0.5O. Due to the low temperature of the experiment, we have found the positions of the H atoms. Two of them, H1 and H3, are fully occupied. They correspond to the water molecule or two of the four H atoms of the NH_4^+ cations. The position of H2 is half-occupied and corresponds to the other two H atoms of the ammonium cations. The N···O hydrogen-bond distance is 2.80 (2) Å, with an angle of 166 (5)° at the H atom.



(I)

The anion (Fig. 1*b*) has a typical cubane cluster structure and possesses the highest possible point symmetry, T_d. Mo—

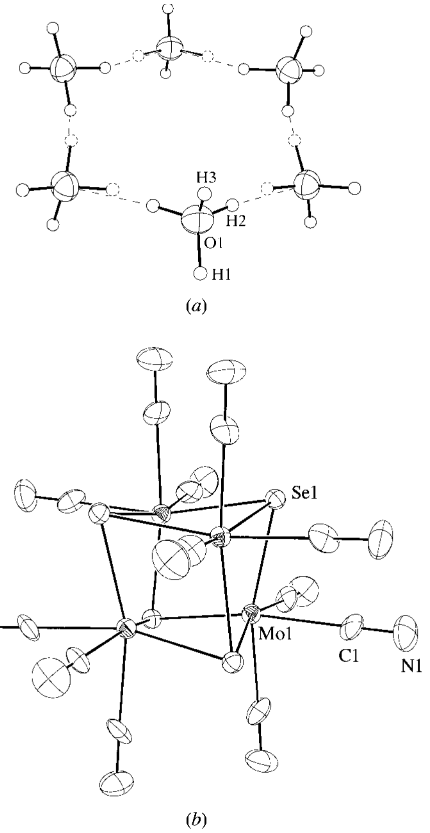


Figure 1
View of the structure of (*a*) the cation and (*b*) the anion of (I). The disordered positions of the H atoms are shown as dashed circles and displacement ellipsoids are shown at the 50% probability level.

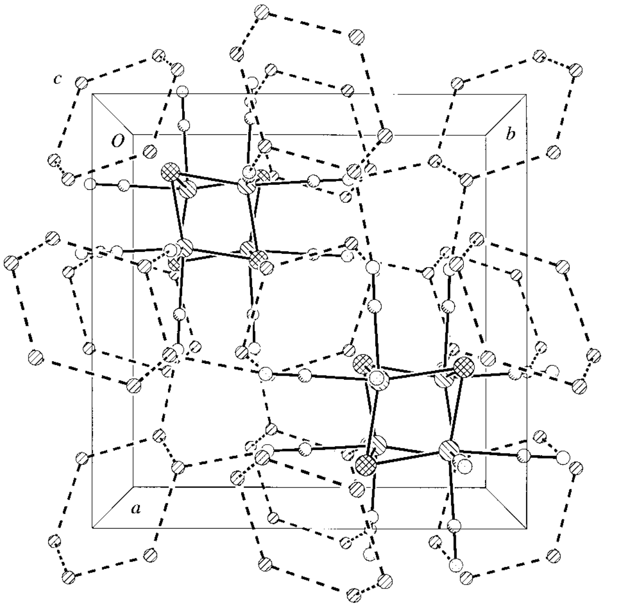


Figure 2
The crystal packing in (I). Hydrogen bonds are shown as dashed lines.

Mo and Mo—Se distances are close to those found for $[W_4Se_4(CN)_{12}]^{6-}$ (Fedin *et al.*, 1999, 2000).

The cations and anions are linked together by hydrogen bonds involving the terminal N atoms of the CN groups (Fig. 2). For each disordered water/ammonium site, there is a hydrogen bond with O/N···N = 2.86 (3) Å and an angle of 174 (17)° at the H1 atom.

Experimental

A mixture of $Mo_3Se_7Br_4$ (1.00 g, 0.862 mmol) and KCN (1.00 g, 15.3 mmol) was heated in a sealed Pyrex tube at 703 K for 48 h. The product was added to water (20 ml) and the mixture was refluxed for 1 h and filtered. The potassium salt isolated by addition of methanol was dissolved in CH_3COONH_4 (1 *M*, 10 ml) and the mixture was allowed to stand at 293 K for 5–7 d. Dark red–brown octahedral crystals were isolated by filtration, washed with methanol and dried in air (yield 0.10 g, 12%). Analysis calculated for $C_{12}H_{36}Mo_4N_{18}O_6Se_4$: C 11.74, H 2.95, N 20.53%; found: C 11.54, H 3.00, N 20.20%; IR (KBr): 2132 (CN) cm^{-1}; UV-visible absorption spectrum of an aqueous solution, λ (ε in M^{-1} cm^{-1}): 340 (9680), 460 (1950, *sh*), 530 (*sh*), 690 (310) nm.

Crystal data

$(NH_4)_6[Mo_4Se_4(CN)_{12}]\cdot 6H_2O$
$M_r = 1228.19$
Cubic, $Pn\bar{3}m$
$a = 12.180$ (1) Å
$V = 1806.9$ (3) Å^3
$Z = 2$
$D_x = 2.257$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4887 reflections
$\theta = 2.9$–$28.6°$
$\mu = 5.440$ mm^{-1}
$T = 160$ (2) K
Octahedron, black
0.20 × 0.18 × 0.15 mm

Data collection

Siemens SMART CCD diffractometer
ω rotation with narrow frame scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1997)
$T_{min} = 0.784$, $T_{max} = 0.928$
10 436 measured reflections
468 independent reflections
384 reflections with $I > 2\sigma(I)$
$R_{int} = 0.039$
$\theta_{max} = 28.65°$
$h = -7 \rightarrow 16$
$k = -16 \rightarrow 15$
$l = -15 \rightarrow 15$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.068$
$wR(F^2) = 0.184$
$S = 1.480$
468 reflections
33 parameters
Only coordinates of H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0111P)^2 + 84.4748P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.007$
$\Delta\rho_{max} = 0.973$ e Å^{-3}
$\Delta\rho_{min} = -1.13$ e Å^{-3}
Extinction correction: *SHELXTL* (Sheldrick, 1998)
Extinction coefficient: 4 (14) × 10^{-5}

Table 1
Selected geometric parameters (Å, °).

Mo1—Mo1^{i}	2.886 (4)	Mo1—C1	2.17 (2)
Mo1—Se1	2.502 (3)	C1—N1	1.13 (2)
Se1—Mo1—Mo1^{i}	54.78 (6)	C1—Mo1—Mo1^{iii}	95.1 (5)
Se1—Mo1—Mo1^{ii}	102.98 (7)	C1—Mo1—C1^{iv}	82.6 (8)
Se1—Mo1—Se1^{iii}	106.52 (8)	Mo1—Se1—Mo1^{iii}	70.4 (1)
C1—Mo1—Mo1^{i}	138.5 (3)	N1—C1—Mo1	179 (2)

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

The largest difference peak is near the anion, 0.6 Å from Se1. The deepest hole is near the disordered cation, 1.36 Å from H3.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and local programs.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GS1060). Services for accessing these data are described at the back of the journal.

References

Bruker (1998). *SMART* and *SAINT* for Windows NT. Bruker AXS Inc., Madison, Wisconsin, USA.
Coucouvanis, D. (1991). *Acc. Chem. Res.* **24**, 1–8.
Fedin, V. P., Kalinina, I. V., Samsonenko, D. G., Mironov, Yu. V., Sokolov, M. N., Tkachev, S. V., Virovets, A. V., Podberezskaya, N. V., Elsegood, M. R. J., Clegg, W. & Sykes, A. G. (1999). *Inorg. Chem.* **38**, 1956–1965.
Fedin, V. P., Samsonenko, D. G., Virovets, A. V., Kalinina, I. V. & Naumov, D. Yu. (2000). *Russ. Chem. Bull.* **49**. In the press.
Holm, R. H. (1992). *Adv. Inorg. Chem.* **38**, 1–71.
Müller, A. (1986). *Polyhedron*, **5**, 323–340.
Saito, T. (1995). *Early Transition Metal Clusters with π-Donor Ligands*, edited by M. H. Chisholm, pp. 63–128. New York: VCH.
Saito, T. (1997). *Adv. Inorg. Chem.* **44**, 45–91.
Sheldrick, G. M. (1997). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (1998). *SHELXTL* for Windows NT. Bruker AXS Inc., Madison, Wisconsin, USA.
Shibahara, T. (1991). *Adv. Inorg. Chem.* **37**, 143–173.
Shibahara, T. (1993). *Coord. Chem. Rev.* **123**, 73–147.