$[Se^{IV}S_3{}^{VI}Mo_6O_{33}]^{8-}$—A Novel Cyclic Polar Heteropolyanion

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The novel cyclic polar heteropolyanion $[Se^{IV}S_3{}^{VI}Mo_6O_{33}]^{8-}$ bearing a pyramidal SeO_3 group in its centre and featuring a ring of six MoO_6 coordination octahedra linked by common corners and edges, respectively, to which three SO_4 tetrahedra are attached has been prepared in aqueous solution and characterized by single crystal X-ray structure analysis.

Commonly known types of cyclic heteropolyanions composed of octahedral and tetrahedral building blocks are $[X_2Mo_5O_{21}]^{4-}$ ($X = S^{IV}$, Se^{IV})[1-3] and $[P_2Mo_5O_{23}]^{6-}$.[4] A ring made up by five MoO_6 octahedra linked by four common edges and one common corner is the prominent structural feature of these anions. Polyanions consisting of a ring of six edge-sharing octahedra capped above and below by a tetrahedron are *e.g.* the centrosymmetric α-$[Mo_8O_{26}]^{4-}$, $[As_2Mo_6O_{26}]^{6-}$, and the closely related $[(MeAs)_2Mo_6O_{24}]^{4-}$.[5-7]

A new heteropolyanion type with a six-membered octahedra ring belting a pyramidal $Se^{IV}O_3$ moiety has been prepared in aqueous solution. MoO_3 (6 mmol) and K_2CO_3 (28.9 mmol) were dissolved in 10 ml boiling H_2O. H_2SO_4 (9 mol dm^{-3}, 30 mmol) was added quickly yielding a colourless precipitate which dissolved when a solution of SeO_2 (5 mmol) in H_2O (5 ml) was added. The clear solution (pH 1) was allowed to cool slowly and colourless plate-like crystals of $K_8[SeS_3Mo_6O_{33}]\cdot5.5H_2O$ were formed.

Differential thermal analysis of $K_8[SeS_3Mo_6O_{33}]\cdot5.5H_2O$ on air revealed a diffuse endothermic process in the range between 60 and 100 °C obviously associated with the removal of water of crystallization. Further endothermic gradual decomposition was observed between 260 and 480 °C. Se, K_4MoO_5, $K_2Mo_4O_{13}$ and K_2SO_4 were identified in the residue by their X-ray powder diffraction patterns.

The main feature of the $[Se^{IV}S_3{}^{VI}Mo_6O_{33}]^{8-}$ anion is a ring composed of three pairs of edge-sharing MoO_6 coordination octahedra (Fig. 1).† These octahedra pairs share common corners yielding a cyclic arrangement of six octahedra connected alternately by edges and corners, respectively. The six Mo atoms form an almost perfect plane [max. deviation 4.2

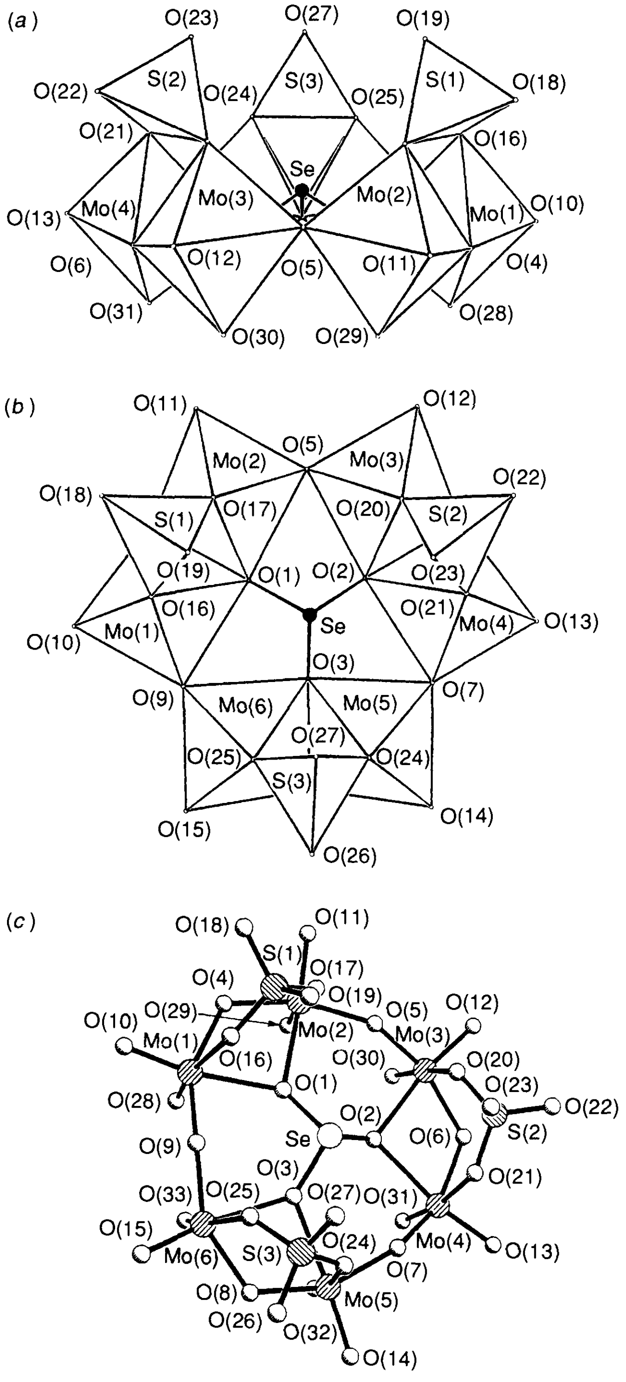

Fig. 1 (*a*) and (*b*): Different views of the $[SeS_3Mo_6O_{33}]^{8-}$ anion show the connection of octahedra and tetrahedra. (*c*) A perspective view of a ball and stick model of $[SeS_3Mo_6O_{33}]^{8-}$ with the atomic labelling scheme. Se–O(1) 170.0(3), Se–O(2) 170.2(4), Se–O(3) 169.5(3) pm, O–Se–O angles 98.10(15)–98.73(17)°; range of Mo–O bonds: short 169.0(4)–171.4(4), medium 189.0(3)–193.6(4), long 225.5(4)–232.3(4) pm. Mo–Mo short: 337.0(1)–338.5(1), long: 359.1(1)–363.3(1) pm. S–O: S(1) 143.0(5)–149.7(4), S(2) 145.0(5)–149.2(4), S(3) 141.5(7)–149.9(5) pm.

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† *Crystal data* for $K_8[SeS_3Mo_6O_{33}]\cdot5.5H_2O$: triclinic, $a = 1028.5(2)$, $b = 1144.5(2)$, $c = 1677.6(2)$ pm, $\alpha = 95.46(1)$, $\beta = 96.12(1)$, $\gamma = 103.60(1)°$, $V = 1893.7 \times 10^6$ pm^3, space group $P\bar{1}$ (no. 2). $Z = 2$, $M_r = 1690.7$, $D_c = 2.97$ g cm^{-3}, $\mu = 39.0$ cm^{-1} (Mo-Kα). 7270 Reflections were collected on a Siemens R3m/V four-circle diffractometer (graphite-monochromated Mo-Kα radiation) in the ω–2θ scan mode to $2\theta_{max} = 50°$; $T = 295$ K; a numerical absorption correction and an empirical extinction correction were applied. 6719 Unique reflections ($R_{int} = 0.0099$) of which 5692 were considered observed with $|F| > 3\sigma_{|F|}$. The phase problem was solved by direct methods (SHELXTL-Plus program package). Hydrogen atoms have not been located. All non-hydrogen atoms were refined anisotropically (542 parameters). $R = 0.0366$, $R_w = 0.0288$, $R_g = 0.0268$, $w = \sigma_{|F|}^{-2}$; maximum features in final difference Fourier synthesis $+1.33/-1.29$ e $\times 10^{-6}$ pm^{-3}.

All atoms except K(2) occupy the general site of space group $P\bar{1}$. Least-squares refinement showed three K^+ [K(8), K(9), K(10)] and three water molecules [O(w1), O(w2), O(w3)] to be statistically distributed on their sites with site occupation factor 0.5.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the University of Bonn. See Notice to Authors, Issue No. 1.

Characteristic IR absorption data for $K_8[SeS_3Mo_6O_{33}]\cdot5.5H_2O$: ν/cm^{-1} (Nujol) 3429s, 1626m, 1188s, 1135vs, 1060s, 988m, 930vs, 904vs, 780vs, 740vs, 667vs, 648vs sh, 624vs, 511m, 450m, 378m, 341m and 287s.

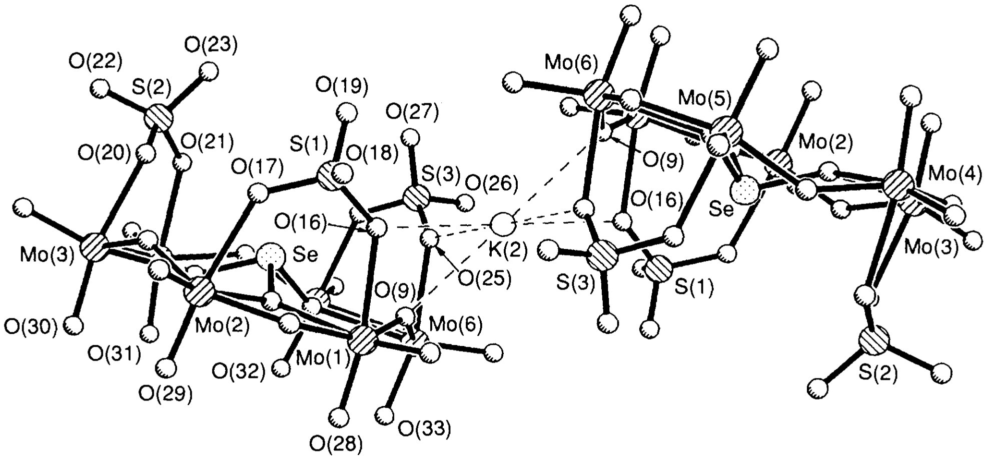

Fig. 2 K(2) situated on a crystallographic centre of symmetry links two $[SeS_3Mo_6O_{33}]^{8-}$ anions [K(2)–O(9) 280.6(4), K(2)–O(25) 289.0(4), K(2)–O(16) 292.0(4) pm]. Two water molecules [2 × O(w5) not shown; K(2)–O(w5) 281.5(6) pm] complete the coordination sphere to yield coordination number (CN) 8.

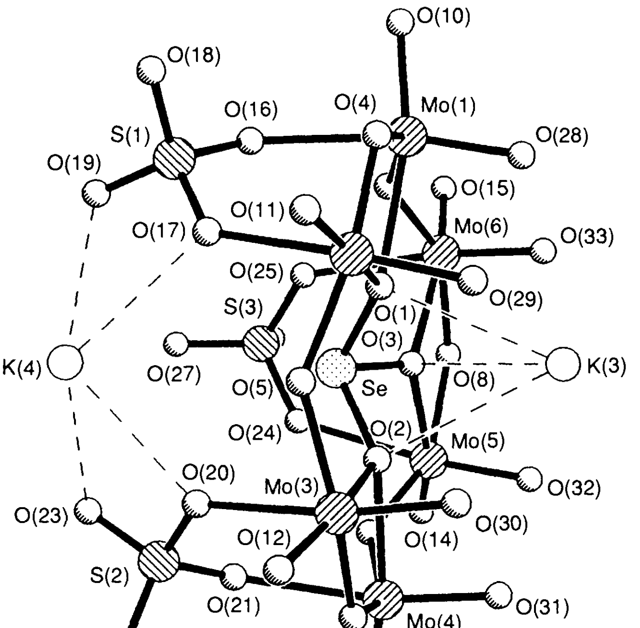

Fig. 3 O(1), O(2) and O(3) coordinate K(3) in a coronand-like arrangement [K(3)–O(1) 292.3(4), K(3)–O(2) 305.6(4), K(3)–O(3) 296.6(4) pm]. Further oxygen atoms (not shown) establish CN 9 for K(3) with K–O bond lengths ranging from 272.7–333.0 pm.

Four oxygen atoms of the anion bind K(4) in a chelate-like manner with short K–O contacts [K(4)–O(17) 273.5(4), K(4)–O(19) 281.4(5), K(4)–O(20) 276.2(4), K(4)–O(23) 287.4(5) pm]. K(4) has CN 9 with K–O distances between 273.5 and 325.5 pm.

pm at Mo(4)]. There are three categories of Mo–O bonds. Each Mo is involved in two short, two long and two Mo–O bonds of medium length (Fig. 1). The overall bonding orders (5.96–6.08) calculated according to the method of Brown[8] reach closely the expected value of 6.0.

The central void of the ring is occupied by Se^{IV} belonging to a $Se^{IV}O_3$ pyramid linked to the three octahedra pairs by common corners [O(1), O(2), O(3)]. Two edge-sharing octahedra at one time are capped by a SO_4 tetrahedron sharing one common corner with each of the two octahedra [O(16) and O(17), O(20) and O(21), O(24) and O(25)].

The polar character of the $Se^{IV}O_3$ pyramid is retained in the entire anion similar to $[MeAsMo_6O_{21}(H_2O)_6]^{2-}$ that consists of an analogous ring of six $MoO_5(H_2O)$ octahedra binding the tetrahedral $MeAsO_3$ moiety by common corners.[9] However, the polar moments of the $[SeS_3Mo_6O_{33}]^{8-}$ anions cancel out, since $K_8[SeS_3Mo_6O_{33}]\cdot5.5H_2O$ possesses the space group $P\bar{1}$.

A different six-membered octahedra ring was found in various molybdophosphates[10] containing the $[Mo_6{}^{V}O_{15}(HPO_4)(H_2PO_4)_3]^{5-}$ group which is primarily featured by a ring of six edge-sharing $Mo^{V}O_6$ octahedra. This ring resembles a close packing of O^{2-} ions accommodating molybdenum cations in octahedral voids and hence may be regarded as a lacunary derivative of the Anderson–Evans type heteropolyanions like $[TeMo_6O_{24}]^{6-}$.[11] Tetrahedral groups (1 × $HPO_4{}^{2-}$ and 3 × $H_2PO_4{}^{-}$) are attached to one side of the octahedra ring *via* common corners yielding $[Mo_6O_{15}(HPO_4)(H_2PO_4)_3]^{5-}$ units which are dimerized by octahedrally coordinated metal cations to clusters of $\{M^{n+}[Mo_6O_{15}(HPO_4)(H_2PO_4)_3]_2\}^{(10-n)-}$ composition.

Since these contain Mo^{V} there are bonding Mo–Mo contacts in the range between 258.8(1) and 259.9(1) pm.[12] Whereas the shortest non-bonding Mo^{V}–Mo^{V} distances are similar [358.0(2)–359.1(2) pm] to the longer Mo^{VI}–Mo^{VI} contacts [359.1(1)–363.3(1) pm] in the $[SeS_3Mo_6O_{33}]^{8-}$ anion (Fig. 1).

Each oxygen atom of the $[SeS_3Mo_6O_{33}]^{8-}$ anion coordinates K^+ except O(5) and O(7) which show rather long K–O contacts only. K(2) links two centrosymmetrically related anions (Fig. 2) by six K–O bonds. It is noteworthy that even O(1), O(2) and O(3) coordinate K^+ establishing a coronand-like environment for K(3) (Fig. 3). Two SO_4 tetrahedra bind K(4) in a chelate-like manner *via* O(17), O(19), O(20) and O(23) (Fig. 3).

The anions $[Se^{IV}Se_3{}^{VI}Mo_6O_{33}]^{8-}$ and $[Se^{IV}Se_2{}^{VI}Mo_6O_{29}(OH)_2]^{8-}$ have been prepared as well and X-ray structure analysis has proven them to possess a structure analogous to $[SeS_3Mo_6O_{33}]^{8-}$.[3] Hence we obviously deal with a new versatile family of polar cyclic heteropolyanions with the general formula $[XY_nMo_6O_{21+4n}(OH)_{6-2n}]^{8-}$ ($n = 0, 1, 2, 3$; $X = Se^{IV}$, $Y = Se^{VI}$, S^{VI}). Since those with $n < 3$ possess chemically active Mo–OH groups they promise to be valuable precursors for the synthesis of new larger anionic heteropolyoxo clusters.

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