Crystal Structure of a Novel Mixed Valence Mo^{V}–Mo^{VI} Heteropolymolybdate Cluster: $[H_3O^+]_6\,[Mo_{57}V_6O_{183}(NO)_6(H_2O)_{18}]^{6-}\cdot 89H_2O$

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Reaction of sodium molybdate ($Na_2MoO_4\cdot 2H_2O$) and ammonium metavanadate (NH_4VO_3) with hydroxylamine hydrochloride results in the formation of the title compound, which consists of three 19-molybdate subunits being connected by six VO_6 octahedra, and six bridging water molecules; both the manner of linking of the VO_6 octahedra to the 19-molybdate subunit and the formation of a polymetallate cluster containing 57 discrete Mo atoms, are hitherto unknown features.

Polyoxoanion models are important for elucidating the biological and catalytic functions of metal-chalcogenide clusters.[1] Many molybdovanadates have been reported with Mo:V ratios between 6:1 and 1:8.[2] Krebs and Paulat-Boschen, and Zhang and Liao have reported respectively the 36-molybdate anions $K_8[Mo_{36}O_{112}(H_2O)_{16}]\cdot 36\text{–}40H_2O$[3] and $[Mo_{36}O_{110}(NO)_4(H_2O)_{14}]\cdot 52H_2O$[4] to be the largest isopolyanion isolated so far. We report here a heteropolyanion which not only contains a new way of linking 19-molybdate subunits with VO_6 octahedra and bridging H_2O molecules, but also contains the largest polymetallate cluster involving molybdenum reported thus far. Indeed, the Mo:V ratio in this compound is as high as 57:6.

Dark-blue crystals of this compound were obtained by the reaction of $Na_2MoO_4\cdot 2H_2O$ (1.492 g) and NH_4VO_3 (0.238 g) with $NH_2OH\cdot HCl$ (2.566 g) in water (40 ml) and 1 mol dm^{-3} HCl (1.9 ml) at reflux temperature for two hours. The crystals are stable in the mother liquor but decompose in open air.

The structure analysis† indicates that this interesting cluster consists of three subunits related to each other by a threefold axis. The cluster centre sits on a special position with $\bar{6}m2$ crystallographic symmetry, and each individual subunit has internal C_{2v} symmetry (see Figs. 1 and 2). In each subunit, there are 17 edge-sharing MoO_6 octahedra, two VO_6 octahedra and two $Mo(NO)O_6$ pentagonal bipyramids. Other similar cases of pentagonal bipyramids have been reported for $K_8[Mo_{36}O_{112}(H_2O)_{16}]\cdot 36\text{–}40H_2O$,[3] which contains MoO_7 fragments, and for $[Mo_{36}O_{110}(NO)_4(H_2O)_{14}]\cdot 52H_2O$,[4] which

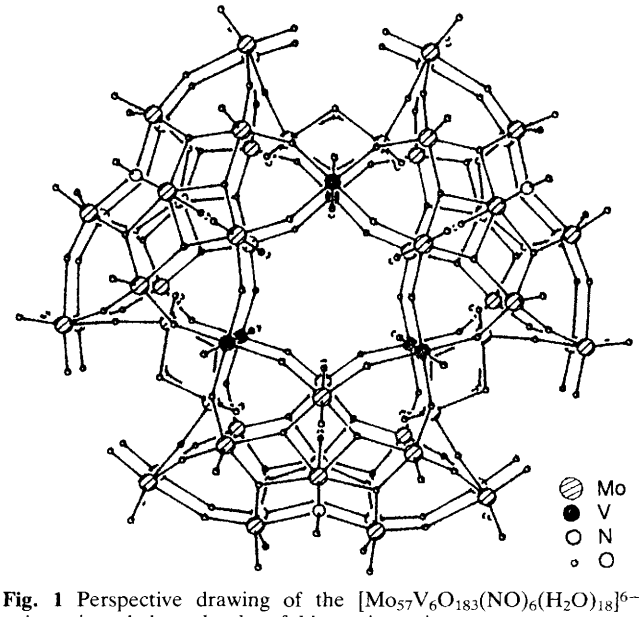

Fig. 1 Perspective drawing of the $[Mo_{57}V_6O_{183}(NO)_6(H_2O)_{18}]^{6-}$ anion, viewed along the threefold rotation axis

† Crystal data for $[H_3O^+]_6[Mo_{57}V_6O_{183}(NO)_6(H_2O)_{18}]^{6-}\cdot 89H_2O$; M_r = 10690, space group $P6_3/mmc$, a = 23.859(4), c = 27.378(6) Å, V = 13497(7) Å^3, D_c = 2.63 g cm^{-3}, Z = 2, $F(000)$ = 9980 electrons, μ(Mo-Kα) = 2.81 mm^{-1}. Data were collectd on a Siemens R3 diffractometer and the SHELXTL PLUS program was used to solve and refine the structure. The positions of the Mo and V atoms were obtained by direct methods and subsequent ΔF-syntheses gave the coordinates of O and N atoms. With anisotropic thermal parameters for all non-hydrogen atoms, the refinement yielded a final R value of 0.0459 for 2005 reflections [$F > 4.0\sigma(F)$]. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the University of Bonn, Germany. See Notice to Authors, Issue No. 1.

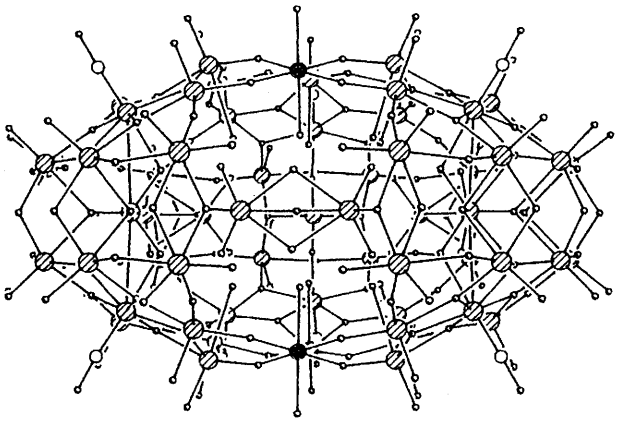

Fig. 2 The $[Mo_{57}V_6O_{183}(NO)_6(H_2O)_{18}]^{6-}$ anion, viewed along the 2/*m* axis and perpendicular to the threefold axis of symmetry

also contains $Mo(NO)O_6$ units. In the central cavity there are 12 water molecules, which are situated around a sixfold axis and are coordinated to six molybdate and six vanadate groups respectively. Moreover, these 12 water molecules are linked to each other by hydrogen bonding to form two six-membered rings.

In the polyoxoanion, there are six bridging H_2O molecules. Other similar cases of bridging H_2O molecules have been reported.[3]

The compound is not neutral, as confirmed by conductivity experiments. Analysis of the valence of the metal atoms, according to valence bond theory,[5,6] leads to the assertion that the compound is a cluster anion with six negative charges. The oxidation state of V is 4^+ and that of most of the Mo atoms is 6^+, except for the pentagonal bipyramidal Mo atoms which are in the 5^+ oxidation state.

Two 17-Mo units are linked to each other by two MoO_6 octahedra to form the previously reported cluster $[Mo_{36}O_{110}(NO)_4(H_2O)_{14}]\cdot 52H_2O$,[4] and a similar 17-Mo unit exists in the 19-Mo subunit of the title polyoxoanion. We therefore assume that such a 17-Mo unit is a relatively stable entity, and could be linked together by other appropriate elements. This is demonstrated by our recent experiment on the synthesis and structure analysis of $Na_6[Mo_{57}Fe_6O_{177}(OH^-)_6(NO)_6(H_2O)_{18}]\cdot 95H_2O$.[7]

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