X-Ray Crystallographic Determination of the Structure of the Isopolyanion $[Mo_{36}O_{112}(H_2O)_{16}]^{8-}$ in the Compound $K_8[Mo_{36}O_{112}(H_2O)_{16}]\cdot 36H_2O$

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Summary X-Ray structure determination of $K_8[Mo_{36}O_{112}(H_2O)_{16}]\cdot 36H_2O$ which crystallises from medium-acidified aqueous molybdate solutions (mole ratio added $[H^+]$: added $[MoO_4^{2-}]$, *ca.* 1·8—2·0) shows that the largest isopolyanion known to date reflects the conditions of its formation and contains structural features typical of both the isopolymolybdates which precipitate from slightly acidified molybdate solutions (*i.e.*, compact groups of mainly edge-sharing MoO_6 octahedra) and the polymeric compounds which precipitate from strongly acidic solutions (*i.e.*, groups of corner-sharing MoO_6 octahedra forming three- and four-membered 'rings', and H_2O molecules co-ordinated to Mo atoms); the H_2O molecules in the compound which are simultaneously co-ordinated to two Mo atoms and the MoO_7 polyhedra are hitherto unknown features of the structure.

FROM alkali molybdate(VI) solutions of different (low) acidities several isopolymolybdates have been obtained as solids. In strongly acidified molybdate solutions the aggregate structures of the polyanions break down and the solid compounds crystallizing from such solutions have polymeric structures. If the solutions are slightly less acidic than that necessary for obtaining polymeric compounds, the largest isopolyanion is obtained. There is general agreement that a very large species predominates, but the formulae reported differ considerably, *e.g.*, $H_7Mo_{24}O_{78}^{5-}$,[1] $Mo_{19}O_{59}^{4-}$ and $Mo_{18}O_{56}^{4-}$,[2] and $Mo_{36}O_{112}^{8-}$.[3] The formula $Na_8Mo_{36}O_{112}\cdot 80H_2O$ for the sodium salt was proposed[3] on the basis of approximate molecular weight obtained from ultracentrifuge measurements, the resemblance between the Raman spectra of solution and the corresponding solid, and the determination of lattice parameters.

I report here the *X*-ray crystal structure of probably the largest discrete isopolyanion known to date whose formula, $[Mo_{36}O_{112}(H_2O)_{16}]^{8-}$, is similar to that reported earlier,[3] except for the sixteen H_2O molecules co-ordinated to Mo atoms.

Crystals of $K_8[Mo_{36}O_{112}(H_2O)_{16}]\cdot 36H_2O$ were obtained by mixing equal volumes of 0·2 M K_2MoO_4 solution and 0·4 N HNO_3 at room temperature. The crystals are unstable in dry air and were sealed, together with some mother liquor, in glass capillaries prior to exposure to *X*-rays.

Crystal data: $K_8[Mo_{36}O_{112}(H_2O)_{16}]\cdot 36H_2O$, space group $P2_1/c$, $a = 16{\cdot}436(4)$, $b = 18{\cdot}739(3)$, $c = 27{\cdot}651(5)$ Å, $\beta = 117{\cdot}00(2)°$, $Z = 2$. The unit cell dimensions vary slightly from crystal to crystal probably owing to the difference in the number of molecules of water of crystallization. The structure was solved by direct methods and subsequent ΔF-syntheses. The final R-value is 0·076 for 6156 reflexions [$(\sin\theta)/\lambda \leqslant 0{\cdot}46$, full-matrix least-squares refinement, isotropic vibrational parameters].† A more precise structure determination [$(\sin\theta)/\lambda \leqslant 0{\cdot}64$] is in progress.[4]

The structure of the 36-molybdate ion in $K_8[Mo_{36}O_{112}(H_2O)_{16}]\cdot 36H_2O$ consists of two 18-molybdate sub-units which combine *via* four common oxygen atoms to form a 'ring' around the *b*-axis (see Figure, a and b). The two 18-molybdate sub-units are related by a crystallographic centre of symmetry. Some of the cations and the molecules of water of crystallization are in the middle of this 'ring', the others separate the large anions in the crystal.

As the conditions of acidification for preparing the 36-molybdate are between those for typical isopolymolybdates (low acidification) and the polymeric compounds (strong acidification), structural units of both types of compounds are present in the ion under investigation. Thus the anion contains two compact groups of five mainly edge-sharing MoO_6 octahedra, octahedra around Mo-4, Mo-5, Mo-9, Mo-14, and Mo-15, and the corresponding group of five octahedra related by the centre of symmetry, characteristic of polymolybdate structures. Groups of corner-sharing octahedra forming three- and four-membered rings and H_2O molecules bound to Mo were also found which are characteristic of the polymeric compounds. The 36-molybdate ion contains twelve three-

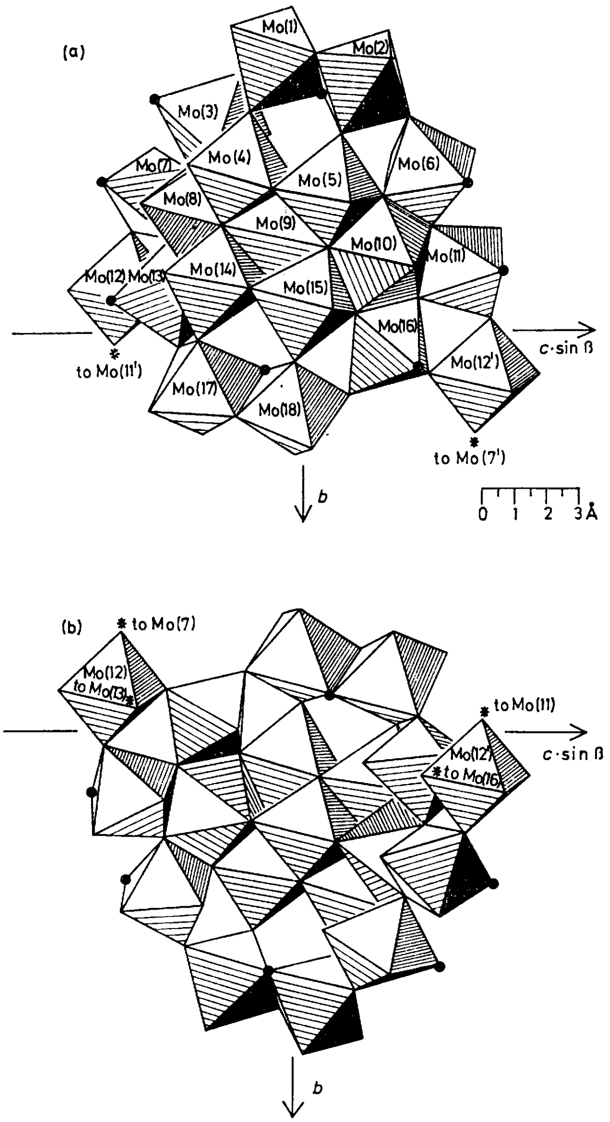

FIGURE. Projection of the $[Mo_{36}O_{112}(H_2O)_{16}]^{8-}$ ion viewed along [100]. The two sub-units of the structure related by a centre of symmetry are shown separately. Surrounding MoO_6 and $[MoO_5(H_2O)]$ octahedra and the MoO_7 polyhedra are indicated by lines. The Mo atoms in the centre of these polyhedra are not shown. H_2O molecules co-ordinated to Mo are indicated by ●. Connecting oxygen atoms of the two sub-units are marked by *. The two combining MoO_6 octahedra (around Mo-12 and Mo-12') are drawn twice (*i.e.*, appear in both a and b).

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† The atomic co-ordinates for this work are available on request from Prof. Dr. G. Bergerhoff, Institut für Anorganische Chemie der Universität, Gerhard-Domagk-Str. 1, D 5300 Bonn 1, West Germany. Any request should be accompanied by the full literature citation for this communication.

membered rings of corner-sharing octahedra (groups of octahedra around Mo-1–Mo-3–Mo-4, Mo-2–Mo-5–Mo-6, Mo-7–Mo-12–Mo-13, Mo-11–Mo-12′–Mo-16, Mo-13–Mo-14–Mo-17, and Mo-15–Mo-16–Mo-18, and the corresponding groups related by the centre of symmetry). Such groups are found in, *e.g.*, the so-called 'decamolybdates' ($KMo_5O_{15}OH\cdot2H_2O$ and $NaMo_5O_{15}OH\cdot2H_2O$) which crystallise either on addition of a little more acid to the solution or by raising the temperature to 40 °C.[5] There are four four-membered rings of corner-sharing octahedra (octahedra around Mo-1–Mo-2–Mo-4–Mo-5 and Mo-14–Mo-15–Mo-17–Mo-18, and the corresponding groups in the other 18-molybdate sub-unit) which resemble those present in the structure of $MoO_3\cdot2H_2O$.[6] H_2O molecules co-ordinated to Mo which were found in all polymeric compounds precipitating from molybdate solutions of high acidities (*i.e.*, 'decamolybdates', α-$MoO_3\cdot H_2O$, and $MoO_3\cdot2H_2O$)[5–7] are part of some outer octahedra {$[MoO_5(H_2O)]$ octahedra around Mo-3, Mo-6, Mo-7, Mo-11, Mo-13, and Mo-16, and the corresponding octahedra related by the centre of symmetry}.

The anion also has two remarkable features hitherto unknown in the chemistry of isopolymolybdates and molybdenum oxide hydrates: the MoO_7 polyhedra and the H_2O molecules which are simultaneously co-ordinated to two Mo atoms. The MoO_7 polyhedra can be viewed as pentagonal bipyramids (polyhedra around Mo-8 and Mo-10, and the polyhedra related by the centre of symmetry). The MoO_7 polyhedra presumably contribute to the instability of the crystals. There are four bridging H_2O molecules in the anion ($[O_5Mo–H_2O–MoO_5]$ groups around Mo-1–Mo-2 and Mo-17–Mo-18, and the corresponding groups related by the centre of symmetry). Our finding bears no resemblance to the structure proposed earlier[3] for the 36-molybdate ion in $Na_8Mo_{36}O_{112}\cdot80H_2O$.

In the anion the Mo–O bond lengths are in the range 1·66—2·42 Å with values of 1·66—1·74 Å for the terminal bonds and the Mo–O(H_2O) bonds lie in the range 2·31—2·41 Å (H_2O co-ordinated to one Mo atom) and 2·38—2·49 Å (H_2O co-ordinated to two Mo atoms). Mo–O bond lengths in the MoO_7 polyhedra are in the range 1·66—2·39 Å (terminal bonds: 1·66 and 1·68 Å) (e.s.d. 0·03 Å).

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