

## SHORT STRUCTURAL PAPERS

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Dodecamolybdophosphoric Acid *circa* 30-Hydrate

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**Abstract.** Cubic,  $Fd\bar{3}m$ ,  $a = 23.255$  (2) Å,  $H_3PMO_{12}O_{40} \cdot ca\ 30H_2O$ ,  $Z = 8$ . The structure of the anion is similar to that reported for the tungsten analogue, but the environment of the molybdenum atom is more appropriately described as tetragonal pyramidal. Only 6 of the water molecules occupy ordered sites.

**Introduction.** Yellow octahedral crystals were prepared as previously described (Rosenheim & Jaenicke, 1917). They lost water rapidly on exposure and X-ray reflexions became diffuse. For intensity photography a cylindrical crystal of radius 0.078 mm was grown inside a capillary which was then sealed. The axial length was determined from a Weissenberg photograph (from 20 Cu  $K\alpha_2$  reflexions,  $\lambda = 1.5422$  Å) by the least-squares method of Taylor & Sinclair (1945). The density has been reported as  $2.52\ g\ cm^{-3}$  (Hoard, 1933); for a 29-hydrate  $D_c$  is 2.480, for a 30-hydrate 2.499, for a 31-hydrate  $2.518\ g\ cm^{-3}$ . Systematic absences were observed when  $h+k$ ,  $k+l \neq 2n$  for  $hkl$ , and  $k+l \neq 4n$  for  $0kl$ , which together with the  $m\bar{3}m$  diffraction symmetry confirm the space group as  $Fd\bar{3}m$ . Intensity data were measured visually from Weissenberg photographs of the layers  $hk0$  to  $hk11$  (Cu  $K\alpha$  radiation) and were corrected for absorption. A set of 490 independent data was obtained. All atoms of the  $PMO_{12}O_{40}^{3-}$  anion were located from Patterson and difference density syntheses, as was one other large peak on a site of 48-fold multiplicity which represented 6 of the expected water molecules. Coordinates were refined by block-diagonal least squares, assuming anisotropic thermal motion for Mo and isotropic motion for other atoms. Inspec-

tion of the data showed good agreement other than for the largest terms, where the observed  $F$  values were systematically too small. This was assumed to be due either to extinction or to cumulative errors in the film-to-film scaling factors, and the 48 largest data were eliminated. Refinement of the remaining 442 data gave an  $R$  index of 0.099.\* Numerous small peaks of about one-quarter the height of the water oxygen peak appeared where other water molecules would be expected, but inclusion of oxygens at various such sites, with or without appropriate fractional weighting, produced no significant improvement in agreement. It was deduced that the remaining water molecules do not occupy ordered sites in the structure.

Atom coordinates and thermal parameters are listed in Table 1, interatomic distances and angles in Table 2. Projected views of the anion are shown in Fig. 1.

**Discussion.** The essential structure of the 12-heteropoly-anion was established by Keggin's (1934) classic study of 12-tungstophosphoric acid. This crystallizes as a hydrate which is isomorphous with the crystals herein described, and which is reported to contain 29 or 30 molecules of water of crystallization per molecule of acid, the exact number being difficult to determine by chemical analysis because of the ease with which the crystals can be dehydrated. After the loss of 23–24

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31578 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Atom coordinates and temperature factors (origin at centre  $\bar{3}m$ )

The anisotropic temperature factor is of the form  $\exp [-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$ .

	$x$	$y$	$z$	Site multiplicity	Point symmetry	$B_{1so}$ (Å <sup>2</sup> )	$B_{11} = B_{22}$	$B_{33}$	$B_{12}$	$B_{13} = B_{23}$
Mo	0.01681 (4)	0.01681	0.12956 (7)	96	$m$		$0.00086$ (4)	$0.00058$ (4)	$-0.00111$ (5)	$-0.00009$ (3)
P	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{8}$	8	$\bar{4}3m$	0.9 (2)				
O(1)	0.1738 (3)	0.1738	$-0.0024$ (5)	96	$m$	1.4 (2)				
O(2)	0.0617 (4)	0.0617	0.2691 (5)	96	$m$	1.7 (2)				
O(3)	0.2843 (4)	0.2843	0.1180 (6)	96	$m$	2.5 (2)				
O(4)	0.1622 (5)	0.1622	0.1622	96	$m$	1.0 (3)				
O(W)	$\frac{1}{8}$	$\frac{1}{8}$	0.875 (2)	48	$mm$	7.2 (10)				

Table 2. Bond lengths (Å) and angles (°)

Mo-O(1)	1.910 (9)	Mo...O(4)	2.455 (11)
Mo-O(2)	1.911 (10)	P—O(4)	1.499 (11)
Mo-O(3)	1.703 (12)	O(3)...O(W)	2.99 (3)
O(1)-Mo-O(1)	85.2 (4)	O(2)-Mo-O(3)	100.9 (5)
O(1)-Mo-O(2)	155.2 (4)	O(2)-Mo-O(4)	72.9 (4)
O(1)-Mo-O(3)	88.1 (4)	O(2)-Mo-O(4)	73.2 (4)
O(1)-Mo-O(3)	103.8 (5)	O(3)-Mo-O(4)	171.1 (5)
O(1)-Mo-O(4)	82.6 (4)	O(3)...O(W)...O(3)	173.5 (10)
O(1)-Mo-O(4)	83.0 (4)	O(W)...O(3)-Mo	163.6 (8)
O(2)-Mo-O(2)	88.0 (4)		

molecules of water a different crystalline phase results, and it was this phase which was studied by Keggin. From the structural analysis he deduced that it was a pentahydrate, but this particular deduction was scarcely conclusive. Bradley & Illingworth (1936) analysed the structure of the higher hydrate, demonstrated that it contains the same tungstophosphate anion, concluded that it was a 29-hydrate, and proposed an arrangement for the assembly of water molecules. On the basis of present knowledge of such structures (*e.g.* Jeffrey & McMullan, 1967) this arrangement appears rather improbable, and again even the deduction of the number of water molecules is unconvincing.

The crystals of 12-molybdophosphoric acid herein described are isomorphous with the 29–30 hydrate of 12-tungstophosphoric acid, although they were described as containing 31.5 molecules of water per molecule (Rosenheim & Jaenicke, 1917). They differ in that the first stage of dehydration does not lead to a different crystalline phase but instead decomposition becomes evident, as reported by Illingworth & Keggin (1935) and confirmed in this study. The interest which prompted the present investigation was in the assembly of water molecules, and the molybdenum compound was preferred in order to minimize the dominance of the heavy atoms.

The coordinates of the atoms of the anion deduced differ from those of Bradley & Illingworth (1936) only in detail, and the structure is essentially as described, *i.e.* large independent anions arranged on a diamond lattice, with cavities of diameter approximately 11.5 Å between, these being occupied by the water molecules. Each of the ordered water molecules O(W) is shown in this study to make approaches of 2.99 Å to a peripheral atom O(3) of two distinct anions, and there is no other linkage between anions. These contacts may represent very weak hydrogen bonds, but they can only be weak as the angle O(3)...O(W)...O(3') is 173.5°. The remaining water molecules show little evidence of an ordered structure, and it must be assumed that there are numerous possible arrangements within the available volume which are energetically comparable. It may be noted again that the crystals when freshly prepared dehydrate very readily, and that there is confusion as to the actual number of molecules of water of crystallization. 12-Molybdophosphoric acid itself decomposes on dehydration, but 12-tungstophosphoric

acid loses 23 or 24 molecules of water to form a different crystalline phase, which then decomposes on further dehydration (Keggin, 1934). While it was disappointing that the feature of the structure which inspired the investigation could not be observed, the above hydration phenomena are readily explicable on the basis that only six of the water molecules have an essential structural function, and that the remainder occupy a large void in the structure in a non-ordered manner.

The classical description of the anion has been in terms of WO<sub>6</sub> octahedra, three of which share faces to

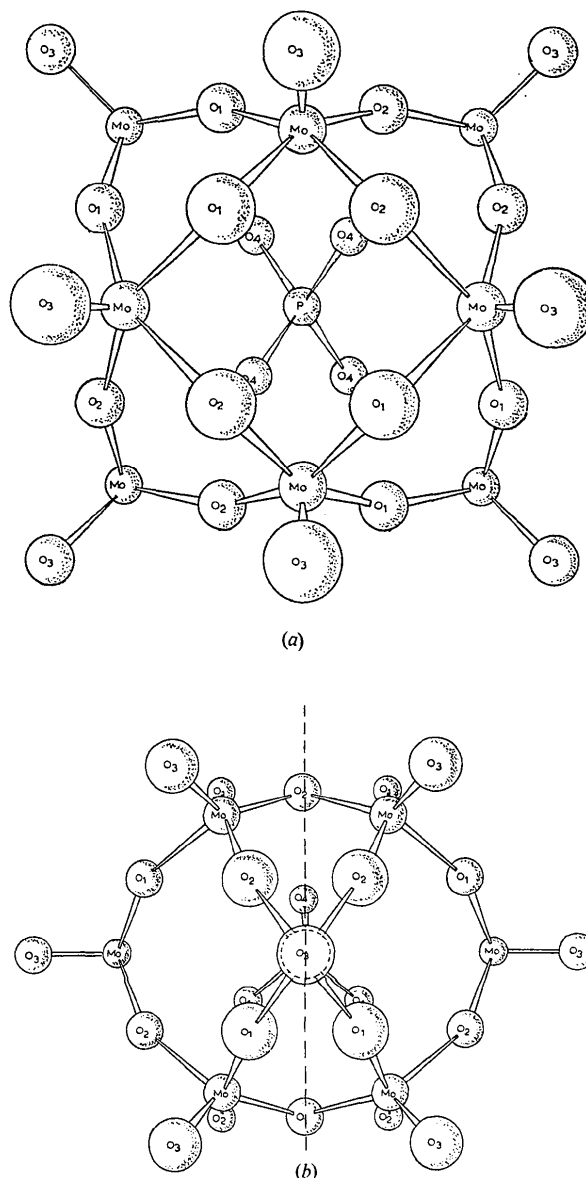


Fig. 1. Perspective views of the anion viewed (a) approximately down [010], (b) down the Mo-O(3) bond, the dashed line being the (110) mirror plane. For clarity only the top half of the Mo-O cage is shown in each case, together with the enclosed PO<sub>4</sub><sup>3-</sup> ion.

form assemblies  $W_3O_{13}$ , four of which assemblies share edges to form the unit  $W_{12}O_{40}$ , which has at its centre four oxygens disposed tetrahedrally and defining a cavity wherein the phosphorus is located. Whereas our description of the 12-molybdophosphate anion does differ only in detail, we note that the environment of each Mo atom is more appropriately described as a tetragonal pyramid, with an oxygen of the central  $PO_4^{3-}$  ion making a reasonably close approach on the open side of the pyramid, as is shown in Fig. 1. Thus the base of the pyramid is formed by two atoms each of type O(1) and O(2), with Mo–O bond lengths of 1.91 Å in each case. The Mo atom does not lie in this basal plane, but is displaced axially by 0.41 Å towards O(3). The Mo–O(3) bond length is 1.70 Å. By contrast the other axial approach, Mo–O(4), is 2.46 Å, and the atom O(4) is distinctly displaced from the Mo–O(3) axis. This geometry is very similar to that reported about the molybdenum atom in the structure of  $MoOPO_4$  (Kierkegaard & Westerland, 1964). This can formally be described in terms of  $MoO_6$  octahedra and  $PO_4$  tetrahedra, but again the authors noted that whereas the octahedra are considerably distorted, one neighbour oxygen is at a much greater distance than the remaining five, and exclusion of this one leaves a reasonably regular tetragonal pyramid about the molybdenum.

On this basis the anion may be described in terms of tetragonal pyramidal  $MoO_5$  units, each sharing two basal edges to form an assembly  $Mo_{12}O_{36}$ . The atoms Mo, O(1), O(2) form an almost spherical shell, with bonds Mo–O(3) projecting radially. The radius (to the

Mo atom) is 3.56 Å, so that the shell is of appropriate size to house a guest orthophosphate ion. The  $PO_4^{3-}$  ion is perfectly tetrahedral by space group requirement, and the P–O bond length is slightly short but within error of the values normally observed, 1.51–1.55 Å (*International Tables for X-ray Crystallography*, 1962). The orientation of the orthophosphate ion within the cage is such as to minimize repulsive interactions between atom O(4) and the oxygen atoms of the shell [the shortest contact O(4)···O(2) is 2.63 (2) Å]. The 12-molybdophosphate ion is thus described as a clathrate, and it may well be that this is the essential basis of the formation of the heteropolyacids.

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## Tri- $\mu$ -chloro-hexakis(dimethylphenylphosphine)diruthenium(II) Hexafluorophosphate

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**Abstract.**  $[Ru_2Cl_3(PMe_2Ph)_6]PF_6$ ,  $Ru_2Cl_3P_7F_6C_{48}H_{66}$ ,  $M = 1282$ . Monoclinic,  $P2_1/c$ ,  $a = 14.43$  (1),  $b = 16.41$  (1),  $c = 23.86$  (2) Å,  $\beta = 97.5$  (1)°,  $V = 5601$  Å<sup>3</sup>,  $D_m = 1.55$  (1),  $D_c = 1.53$  g cm<sup>-3</sup>,  $Z = 4$ ,  $\mu = 9.25$  cm<sup>-1</sup>.  $R = 0.069$  for 4983 observed data; two Ru, seven P and three Cl atoms anisotropic. The Ru atoms are approximately octahedrally coordinated: Ru···Ru = 3.39, Ru–Cl range from 2.46 to 2.52, Ru–P from 2.28 to 2.30 Å; average Ru–Cl–Ru = 86°.

**Introduction.** During an investigation of the reactivity of cationic hydrazine complexes of Ru (Hough & Singleton, 1972), it was found that addition of the

appropriate stoichiometric amount of  $PMe_2Ph$  to  $[CODRuH(NH_2NMe_2)_3]PF_6$  under nitrogen yielded either  $[CODRuH(PMe_2Ph)_3]PF_6$  or  $[RuH(PMe_2Ph)_5]PF_6$ . Reaction of  $[CODRuH(NH_2NMe_2)_3]PF_6$  with three moles of  $PMe_2Ph$  per Ru in acetone–ethanol solvent in the presence of air gave the unusual triply bridged hydroxo salt  $[Ru_2(OH)_3(PMe_2Ph)_6]PF_6$ . When the above reaction was done in a chloroform–ethanol mixture a different compound formed. It was isolated as a  $PF_6$  salt and chemical and spectroscopic studies suggested that it was  $[Ru_2Cl_3(PMe_2Ph)_6]PF_6$  (Ashworth & Singleton, 1975; Chatt & Hayter, 1961; Chatt, Shaw &