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Multicomponent Polyanions. 13. The Crystal Structure of a Hydrated Dodecamolybdophosphoric Acid, $H_3Mo_{12}PO_{40}(H_2O)_{29-31}$

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In $H_3Mo_{12}PO_{40}(H_2O)_{29-31}$ the positions of the atoms in the $Mo_{12}PO_{40}$-groups have been determined from three-dimensional X-ray diffraction data collected with a PAILRED diffractometer using Mo$K\alpha$-radiation. The structure of this group was found to be of Keggin type. The $Mo_{12}PO_{40}$-groups are arranged in a three-dimensional network connected by water molecules through hydrogen bonds. Only six of the water oxygen atoms could be located and the explanation for this is probably that the remaining water molecules are not structural. No proposal for the positions of the protons can be given.

In edge-sharing MoO_6-octahedra the Mo—Mo distances are 3.42 Å, while in corner-sharing octahedra the distances increase to 3.70 Å. Mo—Mo distances fall into three ranges, depending on the coordination number of the coordinated oxygen atom, with the mean values 1.70, 1.92, and 2.43 Å.

The cell dimensions of the tetragonal ($I4_1/amd$) unit cell are $a = 16.473$ Å and $c = 23.336$ Å and it contains four formula units. The structure has been refined by least squares methods using anisotropic vibrational parameters, a final R-value of 0.047, based on 3114 reflexions being obtained.

Recent emf investigations of aqueous equilibria [1,2] involving the three components H^+, MoO_4^{2-}, and HPO_4^{2-} have shown that two series of complexes are formed, one including the pentamolybdodiphosphates $(H^+)_8(MoO_4^{2-})_6(HPO_4^{2-})_2$, $(H^+)_9(MoO_4^{2-})_5(HPO_4^{2-})_2$, and $(H^+)_{10}(MoO_4^{2-})_5(HPO_4^{2-})_2$ and another with the enneamolybdomonophosphates $(H^+)_{14}(MoO_4^{2-})_9(HPO_4^{2-})$, $(H^+)_{15}(MoO_4^{2-})_9(HPO_4^{2-})$, $(H^+)_{16}(MoO_4^{2-})_9(HPO_4^{2-})$, and $(H^+)_{17}(MoO_4^{2-})_9(HPO_4^{2-})$. In the most acidic part of the investigated pH-range, evidence for the formation of 18-molybdodiphosphate $(H^+)_{34}(MoO_4^{2-})_{18}(HPO_4^{2-})_2$ as well as dodecamolybdophosphate $(H^+)_{23}(MoO_4^{2-})_{12}(HPO_4^{2-})$ was found. In connection with these equilibrium investigations a number of crystalline phases corresponding to the mentioned complexes, with sodium as cation, were also prepared and X-ray investigated. By means of these X-ray investigations we were able to give reasonable structural interpretations for the proposed complexes. The pentamolybdodiphosphates were found to be built up of $Mo_5P_2O_{23}$-groups, the enneamolybdophosphates of Mo_9PO_{34}-groups and the 18-molybdodiphosphate of $Mo_{18}P_2O_{62}$-groups. Thus the above mentioned complexes would then be more properly written as $Mo_5P_2O_{23}^{6-}$, $HMo_5P_2O_{23}^{5-}$, $H_2Mo_5P_2O_{23}^{4-}$, $H_3Mo_9PO_{34}^{6-}$, $H_4Mo_9PO_{34}^{5-}$, $H_5Mo_9PO_{34}^{4-}$, $H_6Mo_9PO_{34}^{3-}$, and $Mo_{18}P_2O_{62}^{6-}$. For details of the structural arrangements in these groups the reader is referred to Refs. 3—6.

It has not been possible to prepare a sodium salt of the dodecamolybdomonophosphate. However, the corresponding acid can readily be obtained through crystallization from aqueous solutions, prepared by dissolving the commercial product known as dodecamolybdophosphoric acid (Ventron).

The aim of the present investigation was to perform a single crystal X-ray investigation of this dodecamolybdomonophosphoric acid, in order to obtain both arrangements and distances within the acid and also to try to elucidate how the protons and the water molecules are arranged in the crystal. In particular, it may be mentioned that a great number of different crystalline dodecamolybdophosphoric acids have been described in the literature. However, no complete single crystal X-ray investigation

seems to have been carried out. A compilation of earlier investigations (mostly based on analysis and X-ray powder data) are collected in the review by Evans.[7]

EXPERIMENTAL

The crystals were prepared by recrystallizing a commercial dodecamolybdophosphoric acid (Ventron). In a typical preparation, 15 g of the commercial acid were dissolved in 20 ml of water on a water bath. The solution was then filtered and placed at room temperature for slow evaporation. After a few days, bright-yellow, octahedronshaped crystals, were obtained. They were very unstable and decomposed in a few seconds in air. During the X-ray exposures they were enclosed together with part of the mother liquor in a sealed capillary of Lindemann glass. The contents of Mo and P were determined by elemental analysis (carried out at the Department of Analytical Chemistry, University of Umeå). (Found weight-%: Mo 49.1, P 1.4. Calc. (30 H_2O): Mo 48.7, P 1.3). The water content of the crystal was determined by thermogravimetric analysis. The result found was 29.9 water molecules per formula unit.

From rotation photographs around [100] and [001] and the corresponding Weissenberg photographs (zero, first and second layer lines) taken with Cu$K\alpha$-radiation it was concluded that the crystals are tetragonal. On account of the instability of the crystals the cell dimensions could not be refined from powder photographs; instead they were calculated from omega measurements on the diffractometer. It seems likely that the crystals lose some water and change their structure in air since indexing of the reflexions of the powder photographs (with the given tetragonal unit cell) is impossible although the photographs are relatively good. Triclinic as well as cubic phases of dodecamolybdophosphoric acid have been reported.[7] Systematic extinctions were found for hkl, $h+k+l=2n+1$; $hk0$, $h=2n+1$ and hhl, $2h+l=4n+1$ and the space group was uniquely determined as $I4_1/amd$ (No. 141). Precession photographs were taken as a check on the space group determination. The origin of the unit cell was chosen at the centre ($2/m$).

The density of the crystals was determined by flotation in a bromoform-xylene solution and found to be 2.42 g/cm³. (Calc. (30 H_2O) 2.48).

Three-dimensional intensity data were collected at 25 °C with a Philips PAILRED linear diffractometer using Mo$K\alpha$-radiation. The crystal, whose approximate dimensions were 0.27 × 0.40 × 0.40 mm, was mounted and rotated along the b-axis. A total of 7220 reflexions from the layers $h0l-h18l$ up to a limit of sin $\theta \approx 0.5$ were scanned. The intensities were corrected for Lorentz and polarization effects and a correction was applied for absorption. Reflexions with a relative statistical error of $\Delta I_0/I_0$ greater than 0.5 were omitted. In each level the reflexions h,l and $h,-l$ were equivalent within experimental errors. For these equivalent reflexions an arithmetic mean value was calculated, giving a final set of 3114 reflexions. The computer programs used were based on the programs given in Ref. 4.

CRYSTAL DATA

$H_3Mo_{12}PO_{40}(H_2O)_{29-31}$	F.W. = 2365.8 (30 H_2O)
Tetragonal, $I4_1/amd$	$Z=4$
$a=16.473$ (5) Å	$d_{calc}=2.48$ g cm^{-3}
$c=23.336$ (7) Å	$d_{exp}=2.42$ g cm^{-3}
$V=6332$ Å^3	$\mu=24.0$ cm^{-1} (Mo$K\alpha$)

STRUCTURE DETERMINATION AND REFINEMENT

From a three-dimensional Patterson synthesis the approximate coordinates for the Mo-atoms were found. The atom Mo1 was located in a general thirty-two-fold position and Mo2 in the special position 16(h). A refinement at this stage gave an R-value of about 0.25. From a Fourier synthesis based on these atoms, the coordinates of the remaining atoms in the $Mo_{12}PO_{40}$-group were determined. The R-value decreased to 0.11 using isotropic temperature factors. A second

Table 1. The fractional atomic coordinates and in parentheses their estimated standard deviations (referring to the last decimal place given). For the oxygen atoms indexed O(ij) or OP(ij) the (ij) means that the atom is bonded to the molybdenum atoms i and j.

	X	Y	Z
Mo1	0.38764(3)	0.35375(3)	0.01693(2)
Mo2	0.28386(4)	0.25	0.12068(3)
P	0.5	0.25	0.125
O(1)	0.3340(3)	0.0998(3)	0.2832(2)
O(2)	0.1833(3)	0.25	0.1327(3)
O(11″)	0.5	0.1220(4)	0.2691(2)
O(11′)	0.4024(3)	0.25	0.2529(2)
O1(12)	0.3234(2)	0.1709(2)	0.1739(2)
O2(12)	0.4197(2)	0.0419(2)	0.1889(2)
OP(11′2)	0.4236(3)	0.25	0.0868(2)
Aq1	0.5	0.75	0.1240(7)
Aq2	0.2489(6)	0.4989(6)	0.375

(Space group No. 141, origin at centre.)

Table 2. Final anisotropic thermal parameters ($\times 10^4$) and their estimated standard deviations ($\times 10^4$) in parentheses. The parameters are calculated according to the formula $\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})]$.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo1	21(0)	20(0)	12(0)	−2(0)	−4(0)	5(0)
Mo2	13(0)	31(0)	11(0)	0	1(0)	0
P	15(1)	15(1)	8(1)	0	0	0
O(1)	28(2)	26(2)	15(1)	1(1)	10(1)	8(1)
O(2)	11(2)	49(3)	14(1)	0	1(1)	0
O(11″)	26(2)	22(2)	10(1)	0	0	4(1)
O(11′)	25(2)	20(2)	9(1)	0	1(1)	0
O1(12)	18(1)	22(1)	12(1)	−1(1)	1(1)	1(1)
O2(12)	24(2)	17(1)	13(1)	−4(1)	2(1)	2(1)
OP(11′2)	14(2)	17(2)	8(1)	0	−1(1)	0
Aq1	177(19)	44(7)	33(4)	0	0	0
Aq2	102(6)	102(6)	61(5)	−33(7)	41(4)	−41(4)

Fourier synthesis gave the positions of two water oxygen atoms. Considerable time was spent in locating the remaining water oxygen atoms, but without positive result. Oxygen atoms placed in positions corresponding to the highest peaks in the difference Fourier map or the remaining maxima in the Fourier synthesis, could not be refined (their temperature factors did not converge) and furthermore many of the peaks were too close to the oxygen atoms in the $Mo_{12}PO_{40}$-group. In the description and discussion of the structure the water content will be treated further. The positional parameters and anisotropic temperature factors for the atoms were refined by full-matrix least squares methods, a final R-value of 0.047 being obtained. $R=\sum||F_o|-|F_c||/\sum|F_o|$. The atomic scattering factors used for Mo^{3+} were those given by Cromer and Waber,[8] for P those given by Hanson, Herman, Lea and Skillman [9] and for O^- the values in International Tables. Account was taken of the real part of the dispersion correction. A weighting scheme according to Cruickshank was applied: $\omega=1/(a+|F_o|+c|F_o|^2+d|F_o|^3)$ where the values of the constants were $a=200$, $c=0.00002$ and $d=0.000001$.

The final difference Fourier synthesis showed no anomalies, the highest peaks being equivalent to an electron density of about 1.5 $e^-/Å^3$. In Tables 1 and 2 final atomic coordinates, vibrational parameters and corresponding standard deviations are given. The structure factor table is available from the author on request.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The structure is built up of $Mo_{12}PO_{40}$-groups connected by water molecules. In this way

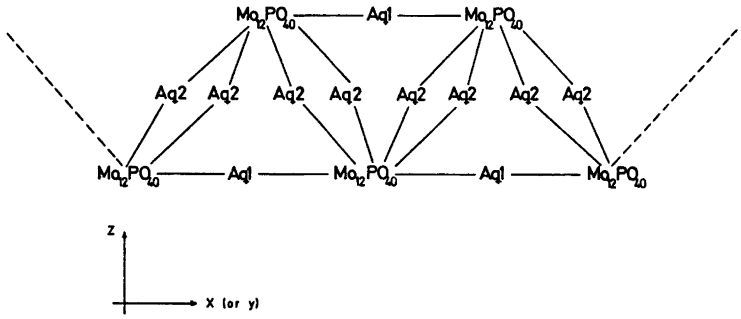

Fig. 1. The coupling O – Aq – O between the $Mo_{12}PO_{40}$-groups within the zigzag chains (schematically drawn).

zigzag chains are formed parallel to the x- and y-axes with the two-dimensional zigzag arrangement parallel to the xz- and yz-planes, respectively. The chains in the x-direction are linked to those in the y-direction thus forming a three-dimensional network. The two water-oxygen atoms located seem to provide the connecting links within the chains by forming O – Aq – O-bridges (Fig. 1). The shortest O – O distances between oxygens in adjacent groups within the chains are only 3.0 Å which means that the groups are quite close to each other.

The $Mo_{12}PO_{40}$-group. This group consists of a central PO_4-tetrahedron surrounded by twelve MoO_6-octahedra. The twelve octahedra may be subdivided into four Mo_3O_{13}-groups. In these groups each MoO_6-octahedron is linked to its neighbour on either side by a shared edge making one corner common to the three octahedra. The four groups are then linked to each other by sharing corners and to the PO_4-tetrahedron by the three-coordinated oxygen atoms. This structure is often named the Keggin-molecule. A stereoscopic view of the $Mo_{12}PO_{40}$-

Table 3. Distances (Å) and angles (degrees) within the $Mo_{12}PO_{40}$-group. The designation of the atoms is explained in Table 1. The estimated standard deviations given in parentheses refer to the last decimal place given.

Mo, P			
Mo1 – Mo1′	3.418(1)	Mo1 – Mo2′	3.706(1)
Mo1 – Mo1″	3.702(1)	Mo1 – P	3.565(1)
Mo1 – Mo2	3.421(1)	Mo2 – P	3.562(1)
MoO_6-octahedra			
Mo1 – O(1)	1.676(4)	O(1) – Mo1 – O(11″)	100.9(2)
Mo1 – O(11″)	1.922(2)	O(1) – Mo1 – O(11′)	102.9(2)
Mo1 – O(11′)	1.910(2)	O(1) – Mo1 – O1(12)	103.1(2)
Mo1 – O1(12)	1.910(4)	O(1) – Mo1 – O2(12)	101.1(2)
Mo1 – O2(12)	1.924(4)	OP(11′2) – Mo1 – O(11″)	72.6(2)
Mo1 – OP(11′2)	2.436(3)	OP(11′2) – Mo1 – O(11′)	83.7(2)
O(1) – O(11″)	2.779(5)	OP(11′2) – Mo1 – O1(12)	83.5(1)
O(1) – O(11′)	2.809(5)	OP(11′2) – Mo1 – O2(12)	72.5(2)
O(1) – O1(12)	2.812(6)	O(11″) – Mo1 – O(11′)	88.7(2)
O(1) – O2(12)	2.784(6)	O(11″) – Mo1 – O2(12)	86.9(2)
OP(11′2) – O(11″)	2.613(7)	O1(12) – Mo1 – O(11′)	86.0(2)
OP(11′2) – O(11′)	2.925(6)	O1(12) – Mo1 – O2(12)	88.5(2)
OP(11′2) – O1(12)	2.919(4)		
OP(11′2) – O2(12)	2.610(6)		
O(11″) – O(11′)	2.678(6)		
O(11″) – O2(12)	2.645(6)		
O1(12) – O(11′)	2.605(6)		
O1(12) – O2(12)	2.674(5)		
Mo2 – O(2)	1.680(6)	O(2) – Mo2 – O1(12)	103.2(2)
Mo2 – O1(12)	1.914(4)	O(2) – Mo2 – O2(12)	100.9(2)
Mo2 – O2(12)	1.923(4)	OP(11′2) – Mo2 – O1(12)	83.6(1)
Mo2 – OP(11′2)	2.433(5)	OP(11′2) – Mo2 – O2(12)	72.6(1)
O(2) – O1(12)	2.820(6)	O1(12) – Mo2 – O1(12)′	85.8(2)
O(2) – O2(12)	2.782(6)	O1(12) – Mo2 – O2(12)	88.7(2)
OP(11′2) – O1(12)	2.923(6)	O2(12) – Mo2 – O2(12)′	86.9(2)
OP(11′2) – O2(12)	2.610(6)		
O1(12) – O1(12)′	2.606(8)		
O1(12) – O2(12)	2.682(5)		
O2(12) – O2(12)′	2.645(8)		
PO_4-tetrahedron			
P – OP(11′2)	1.542(5)	OP(11′2) – P – OP(11′2)′	109.5(2)
OP(11′2) – OP(11′2)′	2.518(8)	OP(11′2) – P – OP(11′2)″	109.4(4)
OP(11′2) – OP(11′2)″	2.52(1)		

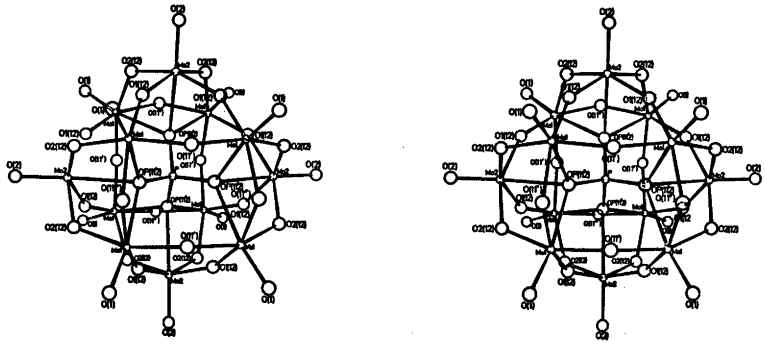

Fig. 2. Stereoscopic view of the $Mo_{12}PO_{40}$-group.

group is given in Fig. 2 and in Fig. 3 the coupling of the MoO_6-octahedra and the PO_4-tetrahedron is shown with idealized polyhedra.

Distances within the group are given in Table 3. It can be seen that for edge-sharing MoO_6-octahedra the Mo – Mo distances are 3.42 Å, while for corner-sharing octahedra the distances increase to 3.70 Å. These distances are in good agreement with those found in other structures.

The MoO_6-octahedra. As can be seen from the distances and angles in Table 3 the MoO_6-octahedra are somewhat distorted. The trend of increasing distances with increasing coordination numbers found in many other structures is also found in this investigation. The Mo – O distances can be divided into three groups according to the number of atoms that the oxygen atom is coordinated to:

(i) Coordinated to only one Mo-atom, the distances are 1.68 Å;
(ii) coordinated to two Mo-atoms, the distances vary between 1.91 and 1.92 Å;

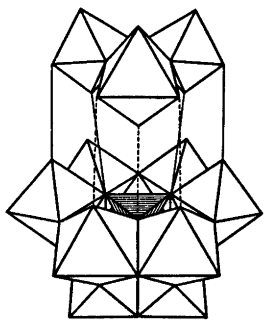

Fig. 3. The coupling of the twelve MoO_6-octahedra and the PO_4-tetrahedron in the $Mo_{12}PO_{40}$-group shown with idealized polyhedra.

(iii) coordinated to P and to three Mo-atoms, the distances are 2.43 and 2.44 Å.

These distances are in good agreement with those found in other heteropolyanions containing molybdenum and phosphorus. Perhaps it should be pointed out that in this $Mo_{12}PO_{40}$-group the two unique octahedra ($Mo(1)O_6$ and $Mo(2)O_6$) are very similar. The distances in the group (ii) are almost the same and independent of whether the oxygen atom is situated between edge-sharing or corner-sharing octahedra. The two distances to unshared oxygen atoms indicate that these oxygens are not protonized.

The PO_4-tetrahedron. This group is almost regular and the distances P – O = 1.54 Å and O – O = 2.52 Å are in good agreement with those found in other structures. The angles O – P – O are 109.5° and 109.4°, *i.e.* quite close to the tetrahedral angle.

The water molecules and the protons. Although much time was spent in attempting to locate the water oxygen atoms, only six atoms per formula unit, corresponding to two positions, could be found. These oxygen atoms, Aq1 and Aq2, seem to connect the $Mo_{12}PO_{40}$-groups in O – Aq – O bridges (Fig. 1). The oxygens connected in this way are the unshared oxygen atoms O(1) and O(2). The distances Aq1 – O(2) and Aq2 – O(1) are 3.02 and 3.03 Å, respectively, and these values indicate hydrogen bonds. With regard to the instability of the crystals and the positions of the anions in the unit cell (leaving unoccupied channels) it may be assumed that the remaining water molecules are not structural.

The protons must either be hydrated or

bonded to Mo-oxygen atoms. The Mo–O distances indicate that these oxygen atoms are not protonized. If this is the case then the protons must be hydrated. Examination of the environment of the water oxygen atoms located provided no information which could be used to resolve the question of whether these water molecules are, or are not, protonized.

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