Crystal Structure of $K_4[H_2P_2Mo_5O_{21}]\cdot 2H_2O$

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Synopsis. $K_4[H_2P_2Mo_5O_{21}]\cdot 2H_2O$ crystallizes in monoclinic system, $P2_1/a$ with a=13.648(4), b=15.591(7), c=10.889 (4) Å, β=94.21(2)°, U=2311(1) Å^3, Z=4. It contains a discrete pentamolybdodiphosphite anion, $[H_2P_2Mo_5O_{21}]^{4-}$, which has, approximately, a C_{2v} symmetry. Its framework is the same as those found in the pentamolybdodiphosphate and the pentamolybdodiphosphonate anions. The P-O and Mo-O distances are 1.49—1.55 and 1.69—2.46 Å, respectively.

It has been known since early this century that trivalent phosphorus forms heteropolymolybdates.[1] Kwak et al.[2] reported the synthesis and characterization of a series of anions $[(RP)_2Mo_5O_{21}]^{4-}$, where R=H, CH_3, C_2H_5, C_6H_5, $C_2H_4NH_3^+$, and p-$CH_2C_6H_4NH_3^+$. Stalik and Quicksall[3] carried out X-ray structure analyses of complexes with R=CH_3 and $C_2H_4NH_3^+$. They have identical oxometalate structures as those of the pentamolybdodiphosphate anion[4] and its protonated species[5] containing pentavalent P atoms: $[(HOP)_n(OP)_{2-n}Mo_5O_{21}]^{(6-n)-}$ where n=0, 1, 2. We have investigated the crystal structure of $[(HP)_2Mo_5O_{21}]^{4-}$, which turned out to have the same framework as those of pentamolybdodiphosphate and pentamolybdodiphosphonate anions.

Experimental

Colorless tabular crystals of the title compound were obtained by mixing a K_2MoO_4 solution (3.0 g in 20 ml H_2O) and a H_3PO_3 solution (0.4 g in 10 ml H_2O), followed by the addition of 2.0 ml of acetic acid to adjust the pH to ca. 7. A single crystal (0.05×0.08×0.18 mm^3) was mounted on a RIGAKU AFC-5 diffractometer and intensity data were collected using graphite monochromatized Mo $K\alpha$ radiation (λ=0.71069 Å). The lattice parameters were obtained by least-squares from 40 reflections with 2θ ranging from 30° to 40°. Crystal data are as follows: $K_4[H_2P_2Mo_5O_{21}]\cdot 2H_2O$; Mr=1072.1; monoclinic; space group $P2_1/a$; a=13.648(4), b=15.591(7), c=10.889(4) Å, β=94.21(2)°, U=2311(1) Å^3; Z=4; $F(000)$=2024; D_x=3.08 g cm^{-3}; μ(Mo $K\alpha$)=3.53 mm^{-1}. A total of 7335 reflections ($2\theta \leqq 60°$) were collected by the ω-2θ scan method with the scan rate of 3° min^{-1} in ω. The ranges of the indices were $0 \leqq h \leqq 19$, $0 \leqq k \leqq 21$, $-15 \leqq l \leqq 15$. Three standard reflections were monitored every 100 reflections. Their intensity variations were within ±3%. The intensity data were corrected for the Lorentz-polarization effect. Absorption correction was not applied. 3433 independent reflections with $|F_o| \geqq 3\sigma(|F_o|)$ and $|F_o| \geqq 8.0$ were used for a structure determination and refinement. The Weissenberg photograph of the $h0l$ layer showed some reflections with $h=2n+1$, breaking the extinction rule for the space group $P2_1/a$. However, most of them were not observed. Assuming the space group to be $P2_1$, the Patterson function was analysed to give the positions of ten Mo atoms, followed by Fourier syntheses which were used to locate the P and O atoms of the two independent $[H_2P_2Mo_5O_{21}]^{4-}$ anions. These positional parameters indicated that these two anions are related to each other by a center of symmetry; also, a full-matrix least-squares refinement showed a strong correlation between the parameters related by the center of symmetry. Therefore, the space group was assumed to be $P2_1/a$ and the atomic parameters of these atoms were refined. The difference Fourier map calculated at this stage showed the peaks assigned to the K atoms and O atoms of the water of crystallization. The heights of these peaks and the distances between them indicated that some of them are disordered. The appearance of $h0l$ reflections with $h=2n+1$ is due to the partial order of these groups. These groups tend to keep the 2_1 symmetry rather than the a-glide. The site occupancies of these disordered atoms were fixed to 0.5, and the average structure, based on the centric space group, was refined with

Table 1. Positional Parameters (×10^4) and Thermal Parameters (Å^2) with e. s. d.'s in Parentheses
$B_{eq}=8/3\pi^2\sum_i\sum_j U_{ij}a^*_i a^*_j a_i a_j$

Atom	x	y	z	B_{eq}
Mo(1)	853(1)	1322(1)	1124(1)	1.4
Mo(2)	2064(1)	1303(1)	3983(1)	1.4
Mo(3)	2160(1)	3346(1)	5070(1)	1.4
Mo(4)	1463(1)	4718(1)	2355(1)	1.4
Mo(5)	280(1)	3351(1)	319(1)	1.4
P(6)	158(3)	2799(3)	3368(4)	1.2
P(7)	2554(3)	2868(3)	1898(4)	1.2
Ot(1a)	66(11)	493(9)	1429(12)	2.4
Ot(1b)	1271(11)	1048(9)	−245(12)	2.5
Ot(2a)	1317(10)	533(9)	4526(12)	2.3
Ot(2b)	3245(11)	931(9)	4255(14)	2.6
Ot(3a)	1808(10)	3735(9)	6462(12)	2.1
Ot(3b)	3438(10)	3428(9)	5207(13)	2.3
Ot(4a)	424(11)	5259(10)	2723(13)	2.6
Ot(4b)	2287(10)	5522(9)	2228(14)	2.6
Ot(5a)	−885(10)	3766(10)	197(14)	2.6
Ot(5b)	631(11)	3269(10)	−1148(13)	2.6
Op(36)	531(8)	3143(8)	4595(12)	1.7
Op(456)	388(10)	3449(8)	2350(11)	1.6
Op(126)	536(8)	1900(8)	3113(10)	1.3
Op(47)	2732(8)	3825(8)	1899(11)	1.2
Op(157)	1690(8)	2599(8)	1021(12)	1.5
Op(237)	2405(9)	2577(8)	3216(11)	1.6
Ob(12)	1965(9)	1050(8)	2244(11)	1.3
Ob(23)	2025(10)	2111(8)	5325(11)	1.8
Ob(24)	1839(9)	4274(9)	3970(10)	1.7
Ob(45)	1053(10)	4361(8)	728(12)	1.9
Ob(15)	−82(9)	2175(8)	654(11)	1.4
K(1)	3411(3)	−83(3)	1601(4)	2.4
K(2)	4147(4)	4559(3)	3524(5)	2.9
K(3)$^{a)}$	0	5000	5000	4.1
K(4)$^{a)}$	3687(9)	6981(7)	2419(9)	3.8
K(5)$^{a)}$	641(9)	7034(7)	3346(9)	3.4
K(6)$^{a)}$	2594(17)	7248(10)	1662(19)	10.0
O(aq1)	3239(14)	4050(15)	9381(21)	6.5
O(aq2)$^{a)}$	4852(36)	3941(29)	7076(31)	7.2
O(aq3)$^{a)}$	3224(26)	2511(21)	8321(33)	4.0

a) Multiplicities of these atoms are 0.5.

the block-diagonal least-squares method on F with anisotropic temperature factors for all atoms by using UNICSIII program system.[6] The final refinement converged at $R(=\sum||F_o|-|F_c||/\sum|F_o|)=0.072$, $wR(=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2})=0.092$ and $S(=[\sum w(|F_o|-|F_c|)^2/(m-n)]^{1/2})=1.55$. The weighting scheme employed was $w^{-1}=\sigma^2(|F_o|)+(0.03|F_o|)^2$. All of the calculations were carried out on HITAC M680-H computers at the Computer Centre of the University of Tokyo. The complex atomic scattering factors were taken from the International Tables for X-Ray Crystallography.[7] The H atoms, which are supposed to be attached to the P atoms, were not found by this X-ray analysis. The final atomic parameters are given in Table 1.[††] The notation of the O atoms in the anion is as follows: Ot for the terminal O atoms, Op for the O atoms shared by one P atom and one or two Mo atoms, and Ob for those shared by two Mo atoms, with appended numerals in the following parentheses representing the numbers of the Mo and/or P atoms to which they are bound.

Results and Discussion

Figure 1 shows an ORTEP[8] view of the $[H_2P_2Mo_5O_{21}]^{4-}$ anion with the Mo-O and P-O bond distances in it. The anion consists of five MoO_6 octahedra which form a ring. These octahedra are joined together by sharing edges, except at one contact (Mo(3)-Mo(4)), where they share only one corner. Two P atoms are attached to this ring, one above and the other below, each having three O atoms in common with the ring and forming a PO_3 trigonal pyramid. This anion nearly possesses a twofold rotation axis running through the Mo(1) and Ob(34) atoms.

The Mo-Mo, Mo-P, and P-P distances are listed in Table 2. The Mo-Mo distances for the edge shared octahedra are 3.360—3.397 Å (av. 3.39(2) Å while that for the corner shared octahedra is 3.716 Å. The deviations of the P-Mo distances are explained by the shifts of the Mo atoms from the least-squares plane calculated for the five Mo atoms which crosses the P(6)-P(7) vector with the angle of 86.8°. Mo(1) lies almost on the plane, Mo(3) and Mo(5) are displaced toward the same direction with P(6), and Mo(2) and Mo(4) to the opposite side, thus forming a skew conformation of the Mo_5 ring.

The O-P-O angles in the PO_3 pyramids are listed in Table 3. These angles agree well with those found in the simple salts containing HPO_3^{2-} anions.[9] The P-O distances for the Op atoms doubly shared by one P and one Mo atoms (Op(36) and Op(47)) are 1.49 and 1.51 Å, while they are 1.52—1.55 Å (av. 1.53(2) Å) for those triply shared by one P and two Mo atoms. However, the O-P-O angles are not affected by the differences of the coordination around the O atoms. In the penta-

Table 2. Interatomic Distances (Å) between Mo and P Atoms with e.s.d.'s in Parentheses

Mo(1)-Mo(2)	3.416(2)	P(6)-Mo(1)	3.538(5)
Mo(2)-Mo(3)	3.397(2)	P(6)-Mo(2)	3.520(5)
Mo(3)-Mo(4)	3.716(2)	P(6)-Mo(3)	3.300(5)
Mo(4)-Mo(5)	3.397(2)	P(6)-Mo(4)	3.692(5)
Mo(5)-Mo(1)	3.360(2)	P(6)-Mo(5)	3.446(5)
Mo(1)-Mo(3)	5.521(2)	P(7)-Mo(1)	3.410(5)
Mo(2)-Mo(4)	5.652(2)	P(7)-Mo(2)	3.432(5)
Mo(3)-Mo(5)	5.604(2)	P(7)-Mo(3)	3.612(5)
Mo(4)-Mo(1)	5.511(2)	P(7)-Mo(4)	3.300(5)
Mo(5)-Mo(2)	5.533(2)	P(7)-Mo(5)	3.518(5)
		P(6)-P(7)	3.930(6)

Table 3. O-P-O Angles(°) in the PO_3 Moieties with e.s.d.'s in Parentheses

Op(36)-P(6)-Op(456)	109.3(7)
Op(456)-P(6)-Op(126)	112.4(7)
Op(126)-P(6)-Op(36)	113.3(7)
Op(47)-P(7)-Op(157)	113.0(7)
Op(157)-P(7)-Op(237)	110.8(7)
Op(237)-P(7)-Op(47)	108.9(7)

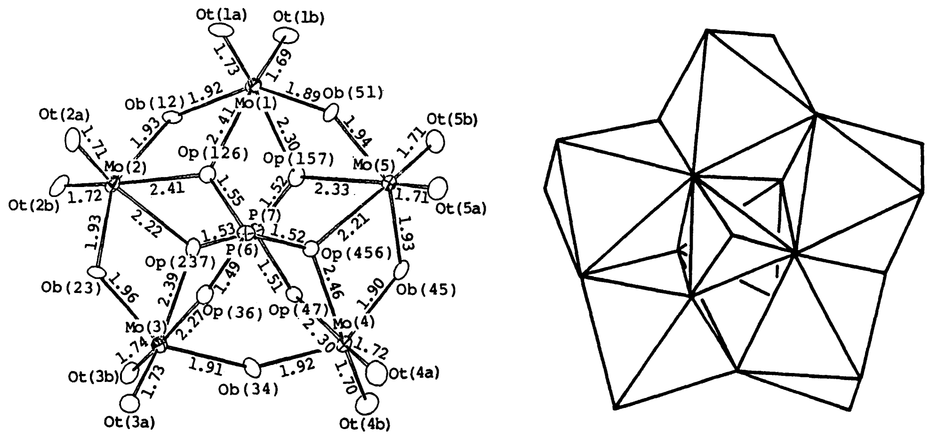

Fig. 1. The structure of the $[H_2P_2Mo_5O_{21}]^{4-}$ anion by the ORTEP[8] drawing and the polyhedra representation. The P-O and Mo-O distances are given in Å. Their e.s.d.'s are 0.02 Å for Mo(4)-Ot(4a) and 0.01 Å elsewhere. Thermal ellipsoids are scaled to enclose 30% probability level.

[††] Lists of the structure factors and the anisotropic thermal parameters are deposited at the office of the Chemical Society of Japan as Document No. 8842.

molybdodiphosphonate anions, the P–O distances for doubly shared Op atoms are 1.52(1) Å, for triply shared Op atoms 1.54(1) Å, and the O–P–O angles are 111(1)°. This shows that the organic groups covalently bonded to the P atoms have only a little influence on the coordination of the PO_3 trigonal pyramids.

The MoO_6 octahedra are highly distorted in forming this polyanion. Each Mo atom is surrounded by six O atoms which are divided into three groups: two Ot's in the *cis* position relative to each other, two Op's each of which is in the *trans* position to an Ot atom. and two Ob's in the *trans* position to each other. The average Mo–O distances are 1.72(1), 2.38(8), and 1.92(2) Å, for Mo–Ot, Mo–Ob, and Mo–Ob, respectively. These values agree well with those of the pentamolybdodiphosphate and pentamolybdodiphosphonate anions.

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