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The Structure of a *Meso*-Type Heteropolyion of Tetrahydrogen Disodium Dodecamolybdohexaphosphonate(III) (6^-) Contained in $[NEt_4]_6[H_4Na_2(PH)_6Mo_{12}O_{54}]\cdot 4H_2O$

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(Received November 13, 1998)

The structure of $[NEt_4]_6[H_4Na_2(PH)_6Mo_{12}O_{54}]\cdot 4H_2O$ (**1**) has been determined by the single-crystal X-ray method. The crystals are monoclinic, space group of $C2/c$, with cell parameters $a = 23.790(3)$, $b = 16.319(2)$, $c = 28.788(3)$ Å, $\beta = 114.365(7)°$, and $Z = 4$. The structure model was refined by full-matrix least squares to $R = 0.0624$ and $R_w = 0.0661$ for 6798 independent reflections with $F_o > 3\sigma(F)$ and in $2\theta < 50°$. The existence of a *meso*-type heteropolyion $[H_4Na_2(PH)_6Mo_{12}O_{54}]^{6-}$ (**2**) in the title crystals has been confirmed. It is composed of a pair of enantiomeric moieties of $[H_2Na(PH)_3Mo_6O_{27}]^{3-}$ (**3** and **3^i**, respectively) which are linked by sharing Na^+ ions; here, the superscript i denotes the symmetrical operation code of $(1/2-x, 1/2-y, -z)$. The six MoO_6-octahedra contained in the respective moieties are arranged to form *Plus*- and *Minus*-helices.

Several modifications of heteropolymolybdate complexes are known to form more favorably in aqueous solutions containing certain kinds of water-miscible organic solvents than in plainly aqueous solutions. Typical examples include β-$[PMo_{12}O_{40}]^{3-}$,[1] a family of molybdosulfates, i.e., $[S_2Mo_{18}O_{62}]^{4-}$,[2] $[SMo_{12}O_{40}]^{2-}$,[3] and $[S_2Mo_5O_{23}]^{4-}$,[4] a series of molybdovanadates[5] of $[VMo_{12}O_{40}]^{3-}$ and $[H_{x-1}V(V_xMo_{12-x})O_{40}]^{3-}$ (x = 1, 2, and 3), and a series of molybdopyrophosphates of $[(P_2O_7)Mo_{18}O_{54}]^{4-}$,[6] $[H_6(P_2O_7)Mo_{15}O_{48}]^{4-}$,[7] and $[H_{12}(P_2O_7)Mo_{12}O_{42}]^{4-}$.[8] Although the effects of the solvents are not yet fully understood, such unique heteropolyions have been increasingly synthesized by the aid of organic solvents and their structures analyzed by X-rays, their geometric characteristics showing the structural relationships underlying a large family of heteropolyions.

A recent voltammetric survey of the aqueous solutions composed of Na_2MoO_4, Na_2PHO_3, and HCl in the presence of Me_2CO, MeOH, and/or MeCN found three different molybdophosphonates,[9] $[H_6(PH)_2Mo_{15}O_{54}]^{4-}$, $[H_9(PH)_4Mo_{16}O_{63}]^{5-}$, and $[H_{13}(PH)_2Mo_{12}O_{48}]^{3-}$, which were all yellow and electrochemically active, and isolated as the corresponding $[NEt_4]^+$-salts. During the survey, it was also found that a colorless, electrochemically inactive species of molybdophosphonate was crystallized with the composition of $[NEt_4]_6[H_4Na_2(PH)_6Mo_{12}O_{54}]\cdot 4H_2O$ (**1**). As will be described herein, the X-ray crystallographic analysis of the crystals confirmed the existence of a heteropolyion, $[H_4Na_2(PH)_6Mo_{12}O_{54}]^{6-}$ (**2**), which includes a helical assemblage of MoO_6-octahedra. The first example of the helical assemblage was found by Acerete et al. in $[P_6W_{18}O_{79}]^{20-}$ ion.[10] Such an assemblage, however, has rarely been found in ordinary heteropolyions, since a group of MoO_6- or WO_6-octahedra in ordinary heteropolyions tend either to assemble to form hexagonal rings [as found in the Dawson-,[11] Keggin-,[12] and Anderson-type molecules[13]], pentagonal rings [as found in the Strandberg-type molecules[14]], and tetragonal rings as in the $[P_4W_8O_{40}]^{12-}$ molecule,[15] or assemble to form the infinite zigzag chains as in $Rb_2Mo_3O_{10}\cdot H_2O$[16] and $K_2Mo_3O_{10}$[17] crystals.

In this paper we report in detail on the helical assemblage of MoO_6-octahedra in heteropolyion **2** in comparison with the ring structures in the related heteropoly molybdate anions.

Experimental

Preparation of Single Crystals. Under ambient temperature, a 50-ml aliquot of an aqueous solution containing $Na_2MoO_4\cdot 2H_2O$ (3.63 g, 15 mmol) and H_3PO_3 (2.46 g, 30 mmol) was taken into a 100-ml glass beaker and brought to pH 3 by adding 1 M NaOH solution (1 M = 1 mol dm^{-3}), followed by the addition of EtOH (40 ml) with gentle stirring. After standing for 5 min, the solution was mixed with NEt_4Br (5 g, 23.8 mmol), diluted with water to 100 ml, left standing for 30 more minutes, and then cooled to 5 °C in a refrigerator. After one night, the first crystals appeared and grew to sizes of 0.2—0.5 mm in diameter within a few days. The colorless, transparent, rhombohedron-shaped[18] crystals thus grown were picked up with a pincette and dipped quickly[19] into a pool (approximately 100 ml) of neat EtOH twice. One of the crystals having a composition of $[NEt_4]_6[H_4Na_2(HP)_6Mo_{12}O_{54}]\cdot 4H_2O$ (**1**) was coated with a drop of cyanoacrylate glue and used for X-ray crystallography. (Found: C, 18.50; H, 4.40; Mo, 36.67; N, 2.74; Na, 1.40; P, 6.05%. Calcd for **1**: C, 18.53; H, 4.47; Mo, 37.01; N, 2.70; Na, 1.48; P, 5.97%). IR ν_{max} 522, 556, 598, 676, 718, 902, 930, 1002, 1036, 1054, 1090, 1110, 1134, 1184 cm^{-1}. Raman ν_{max} 944, 955 cm^{-1}.

Crystallography. A well-shaped crystal with an approximate diameter of 0.2 mm was glued to the end of a thin glass fiber in such a manner that the fiber could be set along the diagonal line of the crystal and the crystal could be rotated along the fiber. The rotating axis thus chosen was later found to coincide with the b^*-axis of the crystal.

Preliminary Weissenberg camera work showed monoclinic symmetry with systematic absences for $h+k = 2n+1$ and for $h0l$, $l = 2n+1$, indicating possible space groups $C2/c$ and Cc. Finally, $C2/c$ (centrosymmetric) was accepted based on the statistical probability of intensity distributions.[20] All of the reflections were sharp and no super or diffuse reflections were observed in the oscillation and Weissenberg photographs. The intensity data were collected by using a Rigaku-AFC5S four-circle diffractometer. The cell parameters were calculated from 25 reflections in the range of $40° < 2\theta < 50°$ by using the radiation of Mo $K\alpha_1$ ($\lambda = 0.70926$ Å). Although it took approximately one week for data collection, no sign of the decay of the crystal appeared on the magnitude of the standard reflections, which were measured with an interval of 200-data collection. The crystal data and experimental parameters are summarized in Table 1.

The Mo atoms were located by direct methods (SHELXS 86)[21] and refined to R = 0.30. The P, Na, O, N, and C atoms were then located by the successive synthesis of difference Fourier maps. No attempt to locate the H atoms was made. The refinement, the Fourier synthesis, and the calculation of interatomic distances and bond angles were done in the same manner as described previously.[4]

Atomic fractional coordinates and selected interatomic distances and bond angles are listed in Tables 2 and 3, respectively. Lists of anisotropic thermal parameters, interatomic distances, and bond angles have been deposited as Document No. 72023 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Results and Discussion

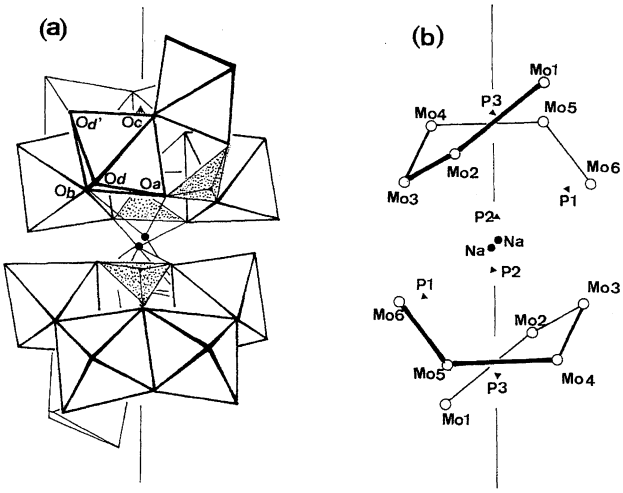

Fig. 1. Polyhederal (a) and schematic representations (b) of the structure of anion **2**, along with the numbering scheme for the Mo and P atoms and the designation of the O atoms, where O_a denotes oxygens which bridge the Mo and P atoms, O_b and O_c those linking MoO_6-octahedra by vertex and edge, respectively, O_d (and $O_{d'}$ or $O_{d''}$) those bonded to one Mo atom.

Geometry of Anion 2. Figure 1(a) illustrates the assemblage of twelve MoO_6-octahedra, six PHO_3-trigonal pyramids, and a pair of Na^+ ions in **2**. The helical arrangements of the MoO_6-octahedra are illustrated in Fig. 1(b), along with the numbering scheme for the Mo and P atoms. It is seen from the Fig. 1 that **2** is composed of a pair of moieties, **3** and **3**^{i}, which are interchangeable with each other through the symmetrical operation i expressed as $(1/2-x,\ 1/2-y,\ -z)$. Since each moiety has no mirror plane in itself, the two moieties are an enantiomeric pair, and thus **2** is a *meso*-type heteropolyion.

In order to describe the geometry of **2** in more detail, an auxiliary axis was drawn to pass through the P(3) and P(3)^i atoms (see Fig. 1). It is seen from the Fig. 1 that the six MoO_6-

Table 1. Crystal Data and Experimental Parameters for **1**

Formula	$C_{48}H_{138}Mo_{12}N_6Na_2O_{58}P_6$
Formula weight	3110.73
Crystal color	Colorless
Crystal system	Monoclinic
Space group	$C2/c$
a, b, c/Å	23.790(3), 16.319(2), 28.788(3)
β/deg	114.365(7)
V/Å^3	10180(2)
Z	4
D_{cal}, D_{mes}/g cm^{-3}	2.03, 2.04
μ(Mo $K\alpha$)/cm^{-1}	1.59
F(000)	6192
Crystal size/mm	$0.2\times0.2\times0.3$
Scan mode	ω (for $k=0$—3), ω–2θ (for $k\geq4$)
2θ Range for data collection/deg	6—50
Scan rate/deg min^{-1}	4
No. data collected	8077
No. data in refinement[$I > 3\sigma(I)$]	6798 (all are independent reflections)
No. refined parameters	294
Final R (R_{w})	0.0624 (0.0661)

$R = \sum||F_o|-|F_c||/\sum|F_o|$, $R_w = [\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}$, $w = 1.0$.

Table 2. Atomic Coodinates and Equivalent Isotropic Thermal Parameters

Atoms[a)]	x	y	z	B /Å^2	Atoms[a)]	x	y	z	B /Å^2
Mo1	0.272 33(5)	−0.039 86(6)	0.071 05(4)	2.317(2)[b)]	Oa6	0.294 6(3)	0.297 5(5)	0.175 6(3)	2.5(1)
Mo2	0.174 55(4)	0.109 02(6)	0.002 87(3)	1.888(2)[b)]	Oa′6	0.332 7(3)	0.200 6(4)	0.123 1(3)	2.4(1)
Mo3	0.099 01(4)	0.244 74(6)	0.059 13(4)	2.106(2)[b)]	Od6	0.419 7(3)	0.249 9(5)	0.222 2(3)	2.7(1)
Mo4	0.108 10(4)	0.190 44(6)	0.174 78(4)	2.394(2)[b)]	Od′6	0.381 1(3)	0.094 3(5)	0.202 1(3)	2.5(1)
Mo5	0.257 83(4)	0.147 00(6)	0.253 47(4)	2.485(3)[b)]	Ow1	0.228 7(7)	0.387 4(9)	0.291 0(6)	8.6(4)
Mo6	0.353 95(4)	0.193 62(6)	0.198 75(3)	1.935(2)[b)]	Ow2	0.192 6(5)	0.437 3(7)	0.040 9(4)	5.4(2)
P1	0.328 3(1)	0.149 5(2)	0.077 0(1)	1.97(4)	N1	0.034 0(4)	0.499 3(6)	0.136 7(4)	3.1(2)
P2	0.227 9(1)	0.312 2(2)	0.166 3(1)	2.10(5)	N2	0.449 7(4)	0.379 5(6)	0.367 6(4)	2.8(2)
P3	0.203 6(1)	0.087 9(2)	0.131 4(1)	1.71(4)	N3	0.152 4(6)	0.151 7(8)	0.388 2(5)	4.5(2)
Na	0.244 0(2)	0.301 4(3)	0.060 2(2)	2.96(8)	C11	0.049 1(6)	0.583 1(8)	0.164 6(5)	3.4(2)
Oa1	0.338 6(3)	0.058 1(4)	0.088 3(3)	2.1(1)	C12	−0.001 3(6)	0.617 6(9)	0.177 4(5)	4.0(3)
Oa12	0.219 2(3)	0.071 0(4)	0.085 6(3)	2.0(1)	C13	−0.021 2(7)	0.512(1)	0.084 7(6)	4.7(3)
Oc12	0.229 6(3)	0.010 8(4)	0.009 0(3)	2.2(1)	C14	−0.038 7(8)	0.433(1)	0.051 6(7)	5.7(4)
Od1	0.219 2(4)	−0.101 8(5)	0.078 2(3)	3.5(2)	C15	0.016 1(8)	0.435(1)	0.167 1(6)	5.3(3)
Od′1	0.319 4(4)	−0.105 7(6)	0.058 9(3)	3.9(2)	C16	0.060 7(9)	0.430(1)	0.223 1(8)	6.8(4)
Od″1	0.320 0(4)	−0.040 2(5)	0.151 8(3)	3.2(2)	C17	0.091 2(6)	0.469 9(9)	0.130 3(5)	4.1(3)
Oa2	0.269 0(3)	0.170 4(4)	0.031 7(3)	2.1(1)	C18	0.114 1(8)	0.524(1)	0.101 0(7)	6.0(4)
Ob23	0.153 8(3)	0.205 3(4)	0.028 5(3)	2.2(1)	C21	0.470 4(7)	0.303 9(9)	0.402 7(6)	4.5(3)
Od2	0.166 2(3)	0.138 0(5)	−0.056 3(3)	2.7(1)	C22	0.419 7(9)	0.266(1)	0.414 4(7)	6.7(4)
Od′2	0.110 5(4)	0.052 8(5)	−0.009 1(3)	3.0(1)	C23	0.506 5(6)	0.419 7(8)	0.364 5(5)	3.8(3)
Oa3	0.186 7(3)	0.303 6(5)	0.110 1(3)	2.8(1)	C24	0.536 3(7)	0.366(1)	0.336 8(6)	5.1(3)
Oa34	0.145 0(3)	0.138 6(4)	0.116 3(3)	2.1(1)	C25	0.402 8(6)	0.353 0(8)	0.315 0(5)	3.7(2)
Oc34	0.082 3(3)	0.264 0(5)	0.119 0(3)	2.7(1)	C26	0.382 5(7)	0.420(1)	0.274 8(6)	5.1(3)
Od3	0.076 3(4)	0.335 5(5)	0.027 2(3)	3.3(2)	C27	0.418 6(6)	0.443 5(8)	0.388 4(5)	3.3(2)
Od′3	0.038 6(4)	0.181 4(5)	0.027 7(3)	3.2(2)	C28	0.457 2(6)	0.473 1(9)	0.441 6(5)	3.9(3)
Oa45	0.206 5(3)	0.261 4(5)	0.200 7(3)	2.7(1)	C31	0.147(1)	0.178(2)	0.439(1)	12.4(9)
Oc45	0.173 6(3)	0.118 9(5)	0.217 7(3)	2.5(1)	C32	0.093(1)	0.150(2)	0.445 8(9)	9.0(6)
Od4	0.048 8(4)	0.121 4(5)	0.155 6(3)	3.7(2)	C33	0.163(1)	0.059(1)	0.389 3(8)	7.7(5)
Od′4	0.095 9(4)	0.248 2(6)	0.218 7(3)	3.8(2)	C34	0.185 7(9)	0.028(1)	0.350 7(8)	7.1(5)
Oa56	0.258 1(3)	0.125 5(4)	0.175 3(3)	2.1(1)	C35	0.205(1)	0.204(1)	0.391 6(8)	7.4(5)
Oc56	0.333 5(3)	0.196 1(4)	0.255 1(3)	2.4(1)	C36	0.270(1)	0.180(1)	0.433 1(9)	8.8(6)
Od5	0.257 7(4)	0.199 0(6)	0.304 9(3)	4.0(2)	C37	0.099(1)	0.173(2)	0.339(1)	11.9(8)
Od′5	0.285 3(4)	0.051 4(5)	0.275 1(3)	3.8(2)	C38	0.077(1)	0.264(2)	0.338(1)	10.3(7)

a) The O atoms in $[H_4Na_2(PH)_6Mo_{12}O_{54}]^{6-}$ (**2**) polyhedra and the C atoms in $[NEt_4]^+$ are designated, respectively, by the numbers of the Mo atom(s) and the N atom(s) to which they are linked. Ow denotes the water oxygen. The numbering scheme for the N atoms is given in Fig. 2.
b) $B = \{\sum_i \sum_j \beta_{ij} \boldsymbol{a}_i \cdot \boldsymbol{a}_j\}$.

Table 3. Selected Interatomic Distances (Å) and Bond Angles (deg) for **3**

Mo1–Oa1	2.154(7)	Mo6–Oa56	2.371(7)	P1–Oa1	1.524(7)
Mo1–Oa12	2.342(7)	Mo6–Oa6	2.129(7)	P1–Oa2	1.514(6)
Mo1–Oc12	1.847(7)	Mo6–Oa′6	2.027(8)	P1–Oa′6	1.532(8)
Mo1–Od1	1.70(1)	Mo6–Oc56	1.877(9)		
Mo1–Od′1	1.69(1)	Mo6–Od6	1.696(7)	Na–Oa2	2.449(9)
Mo1–Od″1	2.124(8)	Mo6–Od′6	1.732(8)	Na–Oa2^i	2.573(9)
O–Mo–O (*cis*)		O–Mo–O (*trans*)		O–P–O	
Oa1–Mo1–Oa12	77.5(3)	Oa1–Mo1–Od1	157.7(4)	Oa1–P1–Oa2	114.6(4)
Oa1–Mo1–Oc12	87.1(3)	Oa12–Mo1–Od′1	168.9(4)	Oa1–P1–Oa′6	113.6(4)
Oa1–Mo1–Od′1	92.0(4)	Oc12–Mo1–Od″1	153.2(3)	Oa2–P1–Oa′6	109.3(4)
Oa1–Mo1–Od″1	74.9(3)	Oa6–Mo6–Od′6	161.1(3)		
Oa6–Mo6–Oa′6	77.3(3)	Oa′6–Mo6–Oc56	152.8(3)	Mo···Mo···Mo	
Oa6–Mo6–Oa56	81.3(3)	Oa56–Mo6–Od6	171.2(4)	Mo3···Mo4···Mo5	109.55(4)
Oa6–Mo6–Oc56	83.0(3)			Mo4···Mo5···Mo6	111.58(4)
Oa6–Mo6–Od6	94.4(3)	*μ-oxo* Bridge between **3** and **3**^{i}			
		Oa2–Na–Oa2^i	75.8(3)		
		Na–Oa2–Na^i	104.2(3)		

The superscript i denotes the symmetry operation code of $(1/2-x,\ 1/2-y,\ -z)$.

octahedra in moiety **3** (the upper half in Fig. 1b) are arranged to form a *Plus*-helix twisting around the auxiliary axis and the other six MoO_6-octahedra in $\mathbf{3}^i$ (the lower half in Fig. 1b) form a *Minus*-helix. Both **3** and $\mathbf{3}^i$ consist of three pairs of edge-sharing MoO_6-octahedra, i.e., Mo(1)O_6–Mo(2)O_6, Mo(3)O_6–Mo(4)O_6, and Mo(5)O_6–Mo(6)O_6. Of these, the first and the second pairs are linked by sharing a vertex, and the second and the third pairs are linked by sharing an edge. The helix thus formed is further reinforced by the co-ordination of three PHO_3-trigonal pyramids, which span the helix by sharing oxygen atoms; the P(1)HO_3-pyramid spanning the first and the third pairs of edge-sharing MoO_6-octahedra, the P(2)HO_3 spanning the second and the third pairs, and the P(3)HO_3 three of the pairs.

The enantiomeric **3** and $\mathbf{3}^i$ are linked together by sharing two Na^+ ions to give the entire structure of heteropolyion **2**, in which each Na^+ ion is co-ordinated by seven oxygen atoms with distances ranging from 2.35 to 2.70 Å: One of the seven oxygens, $O_w(2)$, is donated from a water molecule; the next four oxygens, $O_a(2)$, O_b (23), $O_a(3)$, and, $O_{a'}(6)$ are from moiety **3**; the last two oxygens, $O_a(2)^i$ and $O_d(2)^i$ are from moiety $\mathbf{3}^i$. In other words, the Na^+ belonging to moiety **3** and the $(Na^+)^i$ belonging to moiety $\mathbf{3}^i$ are linked by two μ-oxo bridges formed through $O_a(2)$ and $O_a(2)^i$ oxygen atoms. In consequence, the pair of Na^+ and $(Na^+)^i$ in heteropolyion **2** come close to each other at a distance of 3.96 Å.

The MoO_6-octahedra in **3** are all distorted. The dimensions of the representative octahedra are listed in Table 3. As for the Mo(1)O_6-octahedron, for example, the Mo–O distance varies in the range of 1.69—2.34 Å, and the O–Mo–O angles corresponding to the *trans*- and *cis*-configurations vary in the respective ranges of 153—169° and 72—92°. Unlike the other five octahedra, Mo(1)O_6 has three terminal oxygen atoms designated as O_d, $O_{d'}$, and $O_{d''}$, and the distances

Table 4. Comparison of Interatomic Distances Occuring in Anion **2** and the Related Anions of **4**—**7**

Atoms	Average interatomic distance (minimum, maximum) / Å				
	$[H_4Na_2(PH)_6Mo_{12}O_{54}]^{6-}$ (**2**) (present work)	Strandberg-type anion $[(MeP)_2Mo_5O_{21}]^{4-}$ (**4**) (Ref. 22)	Strandberg-type anion $[P_2Mo_5O_{23}]^{6-}$ (**5**) (Ref. 14)	Dawson-type anion $[P_2Mo_{18}O_{62}]^{6-}$ (**6**) (Ref. 23)	Kggin-type anion $[PMo_{12}O_{40}]^{3-}$ (**7**) (Ref. 24)
Mo···P (l_1)	3.481 (3.340, 3.716)	3.477 (3.302, 3.628)	3.471 (3.335, 3.644)	3.499 (3.459, 3.535)	3.564 (3.562, 3.565)
Mo···Mo (l_2)$^{a)}$	3.627	3.693	3.647	3.745 (3.658, 3.841)	3.704 (3.702, 3.706)
Mo···Mo (l_3)$^{a)}$	3.378 (3.356, 3.415)	3.380 (3.375, 3.394)	3.360 (3.356, 3.364)	3.367 (3.345, 3.888)	3.420 (3.418, 3.421)
P–O_a (l_4)	1.523 (1.513, 1.536)	1.532 (1.508, 1.560)	1.536 (1.495, 1.570)	1.538 (1.528, 1.557)	1.542
Mo–O_a (l_5)$^{b)}$	2.320 (2.252, 2.354)	2.326 (2.207, 2.423)	2.295 (2.181, 2.398)	2.334 (2.311, 2.356)	
Mo–O_a (l_6)$^{b)}$	2.216 (2.154, 2.281)	2.250 (2.242, 2.257)	2.220		
Mo–O_b (l_7)	1.922 (1.887, 1.957)	1.917 (1.912, 1.921)	1.920	1.926 (1.758, 2.140)	1.911 (1.910, 1.914)
Mo–O_c (l_8)	1.921 (1.847, 2.031)	1.927 (1.912, 1.940)	1.92 (1.91, 1.932)	1.924 (1.829, 2.048)	1.923 (1.922, 1.924)
Mo–O_d (l_9)	1.73 (1.69, 2.124)	1.711 (1.683, 1.733)	1.72 (1.72, 1.73)	1.686 (1.674, 1.690)	1.677 (1.676, 1.680)

a) Average of Mo···Mo distances between the neighbouring MoO_6 octahedra which are, respectively, linked by sharing vertex (O_b oxygen atom) and edge (O_c oxygen atoms). b) Average of the interatomic distances between P and the neighbouring O atoms which are, respectively, shared triply by one P atom and two Mo atoms and shared doubly by one P atom and one Mo atom.

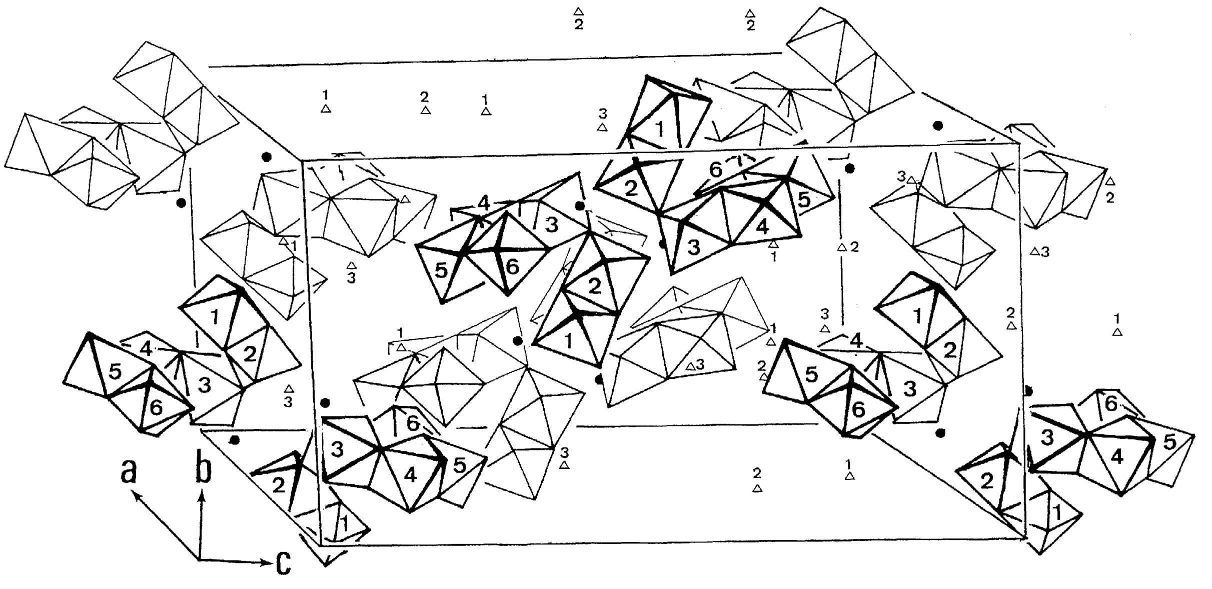

Fig. 2. The arrangement of anion **2** and the NEt_4^+ counter ions in the unit cell. For simplisity, the C atoms of the NEt_4^+ ions and the P atoms of the PHO_3^{2-} ions are omitted. Here, the symbols of ● and △ indicate the locations of Na and N atoms, respectively.

between the kernel Mo atoms and the respective ligand oxygen atoms were found to be 1.70, 1.69, and 2.124 Å. The first two distances fall within a range of 1.65—1.70 Å, which is known for the ordinary $Mo{=}O_{terminal}$ bond, but the last is elongated up to 2.124 Å. The unusually elongated distance of the $Mo–O_{d''}$ would be better attributed to the formation of an $Mo–OH_2$ bond, although the hydrogen atoms are not located crystallographically yet.

As aforementioned, one of the important, geometric characters of this anion **2** (or moiety **3**) is that it contains a set of six MoO_6-octahedra assembled into a pair of *P*- and *M*-helices. In order to deduce the geometric nature inherent to the helices, Table 4 compares the geometry of anion **2** with those of the well-established anions of $[(MeP)_2Mo_5O_{21}]^{4-}$ (**4**), $[P_2Mo_5O_{23}]^{6-}$ (**5**), $[P_2Mo_{18}O_{62}]^{6-}$ (**6**), and $[PMo_{12}O_{40}]^{3-}$ (**7**), with respect to the variation range and the average of the interatomic distances of Mo···P (denoted as l_1), Mo···Mo (l_2 and l_3), P–O (l_4), and Mo–O(l_5–l_9). The first row in the Table 4 shows the dependence of l_1 on the types of the heteropolymolybdate skeletons being changed from the helix (in anion **2**) to the pentagonal (**4**, **5**) and hexagonal rings (**6**, **7**). It is seen in the Table 4 that except for anion **7**, the average of l_1 varies in a narrow range of 3.471 Å (anion **5**)—3.499 Å (anion **6**), depending little on the change of the type of molybdate skeletons. In anion **7**, the average of l_1 becomes longer by approximately 0.08 Å. Quite similarly, both averages of l_3 and l_7 vary little in all anions except for anion **7**. It seems that the elongation of l_1 and l_3 and the shortening of l_7 in anion **7** is more likely to be attributable to the effect given by the high molecular symmetry of the Keggin-type anion and not specifically attributed to the hexagonal ring structure, because such an effect is not found in the Dawson-type anion (**6**).

In contrast to the constancy of the $P–O_a$ (l_4) and $Mo–O_c$ (l_8) distances through all the anions cited in Table 4, the Mo···Mo (l_2) and the $Mo–O_d$ (l_9) distances vary depending on the types of the heteropoly anions. The dependencies are divided into two groups; one is for anions **2**, **4**, and **5**, and the l_2 and l_9 fall into the respective narrow ranges of 3.627—3.693 Å and 1.711—1.73 Å, and the other is for anions **6** and **7**, and the l_2 and l_9 into the respective ranges of 3.704—3.745 Å and 1.677—1.686 Å. In this respect, the geometric nature of this anion **2** is much closer to those of Strandberg-type anions rather than Keggin- and Dawson-type anions. Generally, however, no significant or essential differences can be pointed out among the geometry of the molybdate skeletons inspected here, but it is noteworthy to say that the helical arrangements of the molybdate skeletons rarely occur in comparison with the ring or the infinite chain arrangements.

Crystal Structure of 1. Figure 2 shows the orientation in the unit cell of anion **2**, along with the location of the $[NEt_4]^+$ counter ions. Viewing the whole cell in Fig. 2 along the *c*-axis, it appears that two rather diffusive layers are formed. One of the layers contains anions of **2**, which are linked by the $[N(3)Et_4]^+$ counter ion contained in the same layer. The layer of anion **2** is further linked by the other interstitial layer containing the $[N(1)Et_4]^+$ and $[N(2)Et_4]^+$ ions.

The unit cell contains two, crystallogrpahically independent water molecules. One of the two, $H_2O_w(2)$, hydrates strongly to the Na^+ ion with a distance of 2.48 Å. The other H_2O_w (1) hydrates to anion **2**, and the distances between the H_2O_w (1) oxygen and the neighbouring $Mo{=}O_{terminal}$ oxygens of $O_{d''}$ $(1)^{ii}$, $O_d(5)$, and $O_{d'}$ $(5)^{ii}$ are 2.65, 3.14, and 3.22 Å, respectively [here, the symmetric operation code *ii* denotes $(1/2-x, 1/2+y, 1/2-z)$]. Thus, the association of the water molecules to anion **2** is rather weak, and it is anticipated that the decay[19] of crystal **1** on being left in open air would be attributable to the gradual losses of H_2O_w (1) molecules.

We are grateful for the financial support (Grant No. 08354016) from the Ministry of Education, Sciences and Culture.

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