

**The Geometrical Isomerization on Acidification in
Hexamolybdoheteropoly Oxometalate. The Crystal Structure
of $(\text{NH}_4)_{4.5}[\text{H}_{3.5}\alpha\text{-PtMo}_6\text{O}_{24}] \cdot 1.5\text{H}_2\text{O}$, $(\text{NH}_4)_4[\text{H}_4\beta\text{-PtMo}_6\text{O}_{24}] \cdot 1.5\text{H}_2\text{O}$, and $\text{K}_{3.5}[\text{H}_{4.5}\alpha\text{-PtMo}_6\text{O}_{24}] \cdot 3\text{H}_2\text{O}$**

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Received August 2, 1993

$(\text{NH}_4)_{4.5}[\text{H}_{3.5}\alpha\text{-PtMo}_6\text{O}_{24}] \cdot 1.5 \text{H}_2\text{O}$ (A), $(\text{NH}_4)_4[\text{H}_4\beta\text{-PtMo}_6\text{O}_{24}] \cdot 1.5 \text{H}_2\text{O}$ (B), and $\text{K}_{3.5}[\text{H}_{4.5}\alpha\text{-PtMo}_6\text{O}_{24}] \cdot 3 \text{H}_2\text{O}$ (C) have been synthesized and their molecular structures have been also determined by single-crystal X-ray diffraction technique. The space groups, unit cell parameters, and R factors are as follows: Compound A, monoclinic, $A_{2/a}$, $a=19.074$ (3), $b=21.490$ (3), $c=15.183$ (2) Å; $\beta=109.67$ (1) Å; $z=8$; $R=0.075(|F_o|>4\sigma(|F_o|))$; Compound B, triclinic, $P\bar{1}$, $a=10.776$ (2), $b=15.174$ (4), $c=10.697$ (3) Å; $\alpha=126.29$ (2), $\beta=111.55$ (2), $\gamma=93.18$ (2) Å; $Z=2$; $R=0.046(|F_o|>3\sigma(|F_o|))$; Compound C, triclinic, $P\bar{1}$, $a=12.426$ (2), $b=13.884$ (2), $c=10.089$ (1) Å; $\alpha=102.59$ (2), $\beta=110.73$ (1), $\gamma=53.93$ (1) Å; $Z=2$; $R=0.074(|F_o|>3\sigma(|F_o|))$. Compounds A and C contain the well-known Anderson structure (planar structure) heteropoly oxometalate having approximate $\bar{3}_m(D_{3d})$ symmetry, while compound B contains the bent structure heteropoly oxometalate having approximate $2_{mm}(C_{2v})$ symmetry. The bent structure and the planar one are geometrical isomers. These compounds are not only novel heteropoly molybdates containing platinate(IV) but also the first example of geometrical isomerism in the hexamolybdoheteropoly oxometalates. That isomerization surprisingly occurred because of the change of only 0.5 non-acidic hydrogen atom attached to the polyanion such as $[\text{H}_{3.5}\alpha\text{-PtMo}_6\text{O}_{24}]^{4.5-} \rightarrow [\text{H}_4\beta\text{-PtMo}_6\text{O}_{24}]^{4-} \rightarrow [\text{H}_{4.5}\alpha\text{-PtMo}_6\text{O}_{24}]^{3.5-}$. It seems that the gradual protonation of the polyanion plays an important role in that isomerism. These heteropolyanions form dimers by strong hydrogen bonds between two heteropolyanions in the respective crystal system.

Introduction

The heteropoly oxometalate of early transition elements, that is, Mo and W, will be classified by the coordinate type of hetero atom such as 1) tetrahedral structure, 2) octahedral structure and 3) other structure. The majority of heteropoly oxometalates with tetrahedrally-coordinated heteroatoms has been known as the type of Keggin structure. But those with octahedrally-coordinated heteroatoms have the Anderson type structure. The isomerism attracts considerable interest in the structural study of heteropoly oxometalates.

A number of literature sources on the isomerism of the structures based on the Keggin structure heteropoly oxometalates had been reported¹. However, the isomer of the Anderson structure had not been reported. The Anderson structure heteropoly oxometalates reported for molybdate and tungstate are as follows, $[\text{Te}^{\text{VI}}\text{Mo}_6\text{O}_{24}]^{6-2}$, $[\text{I}^{\text{VII}}\text{Mo}_6\text{O}_{24}]^{5-3}$, $[\text{H}_6\text{Cr}^{\text{III}}\text{Mo}_6\text{O}_{24}]^{3-4}$, $[\text{H}_6\text{Co}^{\text{III}}\text{Mo}_6\text{O}_{24}]^{3-5}$, $[\text{H}_6\text{Al}^{\text{III}}\text{Mo}_6\text{O}_{24}]^{3-6}$, $[\text{H}_6\text{Cu}^{\text{II}}\text{Mo}_6\text{O}_{24}]^{4-7}$, $[\text{H}_6\text{Rh}^{\text{III}}\text{Mo}_6\text{O}_{24}]^{3-8}$, $[\text{Te}^{\text{VI}}\text{W}_6\text{O}_{24}]^{6-9}$, $[\text{Sb}^{\text{V}}\text{W}_6\text{O}_{24}]^{7-10}$, $[\text{Mn}^{\text{IV}}\text{W}_6\text{O}_{24}]^{8-11}$, $[\text{Pt}^{\text{IV}}\text{W}_6\text{O}_{24}]^{8-12}$, $[\text{H}_3\text{Pt}^{\text{IV}}\text{W}_6\text{O}_{24}]^{5-13}$, $[\text{H}_{5.5}\text{Pt}^{\text{IV}}\text{W}_6\text{O}_{24}]^{2.5-14}$. Anderson structure heteropoly oxometalates consist of a slightly flattened central XO_6 (X: heteroatom) octahedron surrounded by an almost hexagonal planar array of distorted six MO_6 (M: Mo or W) octahedra with an approximate symmetry of $\bar{3}_m$. However, $[\text{Sb}^{\text{V}}\text{W}_6\text{O}_{24}]^{7-}$, $[\text{Mn}^{\text{IV}}\text{W}_6\text{O}_{24}]^{8-}$, and $[\text{Pt}^{\text{IV}}\text{W}_6\text{O}_{24}]^{8-}$ polyanions have $\bar{3}_m$ point symmetry.

These heteropoly oxometalates showed two interesting types of behavior in the crystal system. One is the type of protonation in the heteropolyanion; the other is, as expected,

their geometric isomerization. The hexamolybdo heteropoly oxometalates having heteroatoms with higher oxidation states such as $[\text{Te}^{\text{VI}}\text{Mo}_6\text{O}_{24}]^{6-}$ and $[\text{I}^{\text{VII}}\text{Mo}_6\text{O}_{24}]^{5-}$ do not contain hydrogen atoms, but ones with lower oxidation states carry six non-acidic protons attached to the oxygens of the central XO_6 (X: heteroatom) octahedron such as $[\text{X}^{\text{n+}}(\text{OH})_6\text{Mo}_6\text{O}_{18}]^{(6-n)-}$ (X: Co^{III} , Cr^{III} , Cu^{II} , Al^{III} , and Rh^{III}). Therefore, the non-protonated hexatungsto-heteropolyanion $[\text{X}^{\text{n+}}\text{W}_6\text{O}_{24}]^{(12-n)-}$ was obtained with +4, +5, and +6 oxidation state heteroatoms such as, Mn^{IV} ¹¹, Pt^{IV} ¹², Sb^{V} ¹⁰ and Te^{VI} ⁹. The exact crystallographic structural analysis of six non-acidic protons attached to the species $[\text{H}_6\text{X}^{\text{n+}}\text{W}_6\text{O}_{24}]^{(6-n)-}$ had not been reported.

The Anderson structure heteropolyanion has isomeric forms of a planar and a bent structure. Recently we reported the structure of hexamolybdoantimonate(V), $[\text{H}_2\text{Sb}^{\text{V}}\text{Mo}_6\text{O}_{24}]^{5-}$ ¹⁵. It is a bent structure such as the heptamolybdate, $[\text{Mo}_7\text{O}_{24}]^{6-}$ anion reported by Lindqvist¹⁶, Sjobom *et al.*¹⁷ and Evans *et al.*¹⁸ The $[\text{SbMo}_6\text{O}_{24}]^{7-}$ polyanion having a planar structure has not been reported. However, $[\text{SbW}_6\text{O}_{24}]^{7-}$ showed a planar structure¹⁰; the bent structure of this polyanion has not been reported. We call that α -isomer has the planar structure with the $\bar{3}_m(D_{3d})$ point symmetry and β -isomer has the bent structure with the $2_{mm}(C_{2v})$ point symmetry.

In this paper, we report the syntheses and crystal structures of $(\text{NH}_4)_{4.5}[\text{H}_{3.5}\alpha\text{-PtMo}_6\text{O}_{24}] \cdot 1.5\text{H}_2\text{O}$ (A), $(\text{NH}_4)_4[\text{H}_4\beta\text{-PtMo}_6\text{O}_{24}] \cdot 1.5\text{H}_2\text{O}$ (B), and $\text{K}_{3.5}[\text{H}_{4.5}\alpha\text{-PtMo}_6\text{O}_{24}] \cdot 3\text{H}_2\text{O}$ (C). These structural studies has been reported briefly in letter and communication forms by the authors¹⁹. A series of heteropolymolybdates containing platinum (IV) were reported by

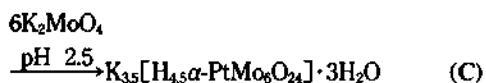
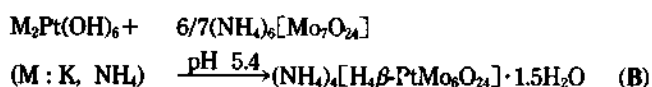
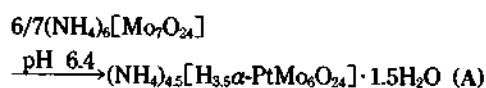
Gibbs(Pt : Mo = 1 : 10, 2 : 8, 2 : 4 and 1 : 60) in 1895²⁰. However, these chemical species have not been reproduced.

Experimental

Preparation of starting material for hetero atom; $M_2Pt(OH)_6(M; K^+ \text{ or } NH_4^+)$. An excess of NaOH solution (3 g/15 ml H_2O) was added to an aqueous solution of K_2PtCl_6 (0.2 g/30 ml H_2O), and the mixture was then heated on a water bath for 4~5 hours (Caution : Use a polyethylene beaker). Dilute acetic acid was then added in slight excess and the hexahydroxoplatinic (IV) acid, $H_2Pt(OH)_6 \cdot hydrate$ was precipitated as a pale buff-yellow compound. The precipitate was filtered through a G4 glass filter and washed well with cold distilled water. $K_2Pt(OH)_6$ solution was obtained by adding 0.3 g of KOH in 20 ml aqueous solution. The ammonium salt was obtained by the same method by adding dilute ammonia water solution instead of KOH solution to the $H_2Pt(OH)_6$ precipitate. $M_2Pt(OH)_6$ (M : NH_4 and K) solution was retreated with acetic acid for the pure $M_2Pt(OH)_6$ solution. The resulting solutions of $K_2Pt(OH)_6$ and $(NH_4)_2Pt(OH)_6$ were used as the starting materials in the following experiments.

Preparation of hexamolybdoplatinate (IV) salts; $(NH_4)_{4.5}[H_{3.5}\alpha-PtMo_6O_{24}] \cdot 1.5H_2O$ (A), $(NH_4)_4[H_4\beta-PtMo_6O_{24}] \cdot 1.5H_2O$ (B), and $K_{3.5}[H_{4.5}\alpha-PtMo_6O_{24}] \cdot 3H_2O$ (C).

Three kinds of crystals, containing α - or β -structure heteropolyanions and different protonation stages, were separated under different pH conditions. A hot mixture solution of the molar ratio Pt : Mo = 1 : 6 was made from the hot $M_2Pt(OH)_6$ (M; K^+ , NH_4^+) and K_2MoO_4 or $(NH_4)_6Mo_7O_{24}$ solution. The pH of the mixture solution was adjusted to ca. 6.0 (at 20°C, with 1 N nitric acid), then the solution was warmed for 30 minutes, and the pH was readjusted to 6.4 (A), 5.4 (B) and 2.5 (C) at 20°C, respectively. The colors of the mixtures were changed from pale yellow by acidification. After the solution was concentrated to about 10 ml on the water bath and cooled at room temperature, the transparent pale yellow hexagonal prism crystal such as $(NH_4)_{4.5}[H_{3.5}\alpha-PtMo_6O_{24}] \cdot 1.5H_2O$ (A), $(NH_4)_4[H_4\beta-PtMo_6O_{24}] \cdot 1.5H_2O$ (B), and $K_{3.5}[H_{4.5}\alpha-PtMo_6O_{24}] \cdot 3H_2O$ (C) were separated from the solution. The reaction scheme is shown as follows.



Sodium salts are unstable in air, but those are obtained easily. The fully protonated solution of hexamolybdoplatinate, $[H_6PtMo_6O_{24}]$ can be obtained by an ion-exchange technique. The IR spectrum patterns of $(NH_4)_4[H_4\beta-PtMo_6O_{24}] \cdot 1.5H_2O$ is almost the same with that of ammonium heptamolybdate, $(NH_4)_6[M_7O_{24}]$.

X-ray Structure Determinations. Single-crystal X-ray diffraction experiments were performed on a Rigaku diffractometer with $Mo-K\alpha(\lambda = 0.7107 \text{ \AA})$ radiation at 293 K. The

Table 1. Summary of Crystal Data, Intensity Collection and Least-Squares Refinement Statistics for $(NH_4)_{4.5}[H_{3.5}\alpha-PtMo_6O_{24}] \cdot 1.5H_2O$ (A), $(NH_4)_4[H_4\beta-PtMo_6O_{24}] \cdot 1.5H_2O$ (B) and $K_{3.5}[H_{4.5}\alpha-PtMo_6O_{24}] \cdot 3H_2O$ (C)

Compound	A	B	C
formula	$H_{24.5}N_{4.5}PtMo_6O_{23.5}$	$H_{23}N_4PtMo_6O_{23.5}$	$H_{10.5}PtMo_6O_{27}K_{3.5}$
fw	1266.23	1248.76	1349.77
space group	monoclinic $A_{2/a}$	triclinic $P\bar{1}$	triclinic $P\bar{1}$
a, Å	19.074(3)	10.776(2)	12.426(2)
b, Å	21.490(3)	15.174(4)	13.884(2)
c, Å	15.183(2)	10.697(3)	10.089(1)
α , deg		126.29(2)	102.59(2)
β , deg	109.67(1)	111.55(2)	110.73(1)
γ , deg		93.18(2)	53.93(1)
V, Å ³	5860(2)	1221.2(4)	1332.2(4)
Z	8	2	2
crystal size, mm	0.15 × 0.20 × 0.16	0.14 × 0.20 × 0.1	0.28 × 0.25 × 0.26
ρ calcd, g/cm ³	2.871	3.396	3.365
$\mu(Mo\ K\alpha)$, cm ⁻¹	75.36	90.23	82.9
F(000)	590	580	623
hkl	26 30 21	15 21 15	17 19 14
(set)	$h\ k \pm l$	$\pm h \pm k l$	$\pm h \pm k l$
no. of unique data	7472	6196	6279
no. of data with ^a	5571(>4 σ)	6044	6126
R	0.075	0.046	0.074
R_w ^b	0.076	0.045	0.075
$(\Delta/\sigma)_{max}$	0.23	0.36	0.63
$\Delta\rho/e\ \text{\AA}^{-3}$	9	7	12
goodness of fit	4.16	7.05	5.38
no. of variable in least squares	344	326	344

$${}^a(F_o) > 3\sigma(F_o), \quad {}^bw^{-1} = \sigma^2(|F_o|) + 0.0004(|F_o|)^2$$

summarized in Table 1. Intensity data collected using ω -2 θ scans over ω scan ranges $(1.2 + 0.6 \tan \theta)^\circ$. The scan speed and 2 θ range is 2° min^{-1} and $3^\circ < 2\theta < 60^\circ$, respectively. The intensities of the standard reflections remained constant throughout the data collection. Cell parameters of crystals were obtained by the least-squares refinement from 25 strong reflections ($38^\circ < 2\theta < 45^\circ$) at 293 K. The structures were solved by Patterson functions and all atoms were located in successive Fourier syntheses. Hydrogen atoms were ignored. All atoms were refined with anisotropic thermal parameters by block-diagonal least-squares. Lorentz and polarization corrections were applied to the intensity data. Absorption correction was made for the crystal (C) (max./min. 0.0281/0.0139). Complex scattering factors for neutral atoms were taken from *International Tables for X-ray Crystallography*²¹, and the calculations were carried out with the HITAC M280-H computer at the Computer Center of the University of Tokyo by the UNICS III programs²².

Results and Discussion

α -Isomer (planar structure) salts : $(NH_4)_{4.5}[H_{3.5}\alpha-PtMo_6O_{24}] \cdot 1.5H_2O$ (A) and $K_{3.5}[H_{4.5}\alpha-PtMo_6O_{24}] \cdot 3H_2O$

Table 2. Positional ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($\text{\AA}^2 \times 10^2$ for Pt and Mo, $\times 10$ for N and O) for $(NH_4)_4 [H_{3.5}\alpha\text{-PtMo}_6O_{24}] \cdot 1.5H_2O$ (A) (Estimated Standard Deviations in Parentheses)

atom	x/a	y/b	z/c	Beq, \AA^3
Pt	796(0)	1629(0)	1848(1)	113(1)
Mo 1	-76(1)	474(1)	2494(1)	176(4)
Mo 2	-112(1)	2676(1)	309(1)	161(4)
Mo 3	-1003(1)	1576(1)	1018(1)	163(4)
Mo 4	1689(1)	2645(1)	946(1)	170(4)
Mo 5	1791(1)	480(1)	3214(1)	193(4)
Mo 6	2646(1)	1547(1)	2456(1)	194(4)
O _t 1	750(8)	2000(6)	625(10)	17(3)
O _t 2	-50(7)	1033(6)	1324(9)	14(3)
O _t 3	-43(7)	2229(6)	1717(9)	14(3)
O _t 4	1627(7)	1015(6)	1952(9)	15(5)
O _t 5	1656(7)	2230(6)	2352(9)	16(3)
O _t 6	844(7)	1225(6)	3058(10)	15(3)
O _b 7	-784(8)	1947(6)	32(10)	18(4)
O _b 8	791(8)	3136(6)	1009(10)	18(4)
O _b 9	2306(8)	1912(7)	1209(11)	22(4)
O _b 10	832(8)	99(6)	2485(11)	20(4)
O _b 11	-789(8)	1218(6)	2356(10)	18(4)
O _b 12	2500(8)	1179(7)	3559(11)	22(4)
O _b 13	1606(10)	2771(6)	-173(13)	30(5)
O _b 14	-1568(10)	983(7)	421(12)	26(4)
O _b 15	-1616(8)	2118(7)	1239(11)	22(4)
O _b 16	2293(9)	3211(7)	1560(12)	28(4)
O _b 17	2371(10)	-89(8)	3051(14)	33(5)
O _b 18	3232(10)	1008(9)	2254(13)	33(5)
O _b 19	3198(10)	2144(8)	3081(12)	32(5)
O _b 20	-709(10)	-46(7)	1816(13)	31(5)
O _b 21	-56(10)	373(8)	3624(12)	29(5)
O _b 22	-109(9)	2789(7)	-795(10)	21(4)
O _b 23	1741(9)	369(7)	4302(12)	26(4)
O _b 24	-728(8)	3225(7)	479(11)	23(4)
N 1	4208(15)	2659(15)	2189(20)	49(9)
N 2	-4034(13)	4507(11)	611(17)	35(7)
N 3	-2388(15)	204(16)	1217(21)	57(10)
N 4	886(15)	4225(9)	-44(17)	54(8)
N 5	2500(0)	1936(15)	5000(0)	48(11)
A _q 1	2500(0)	4079(15)	0(0)	35(10)
A _q 2	-2999(21)	1363(16)	1603(21)	66(12)

$${}^a \text{Beq} = \frac{8}{3} \pi^2 \sum_i \sum_j U_{ij} a_i a_j a_k$$

(C). Final atomic parameters and equivalent isotropic thermal parameters are shown in Tables 2 and 3. The structure of $[H_{3.5}\alpha\text{-PtMo}_6O_{24}]^{4.5-}$ (A) and $[H_{4.5}\alpha\text{-PtMo}_6O_{24}]^{3.5-}$ (C) polyanions and unit cell packing are shown in Figure 1 and Figure 2. All the atoms of the polyanion are at general positions. The oxygen atoms in the polyanion are classified as O_t, O_b and O_c according to the condition of coordination. O_t is the terminal O atom joined to a Mo atom, O_b is the bridging atom between two Mo atoms and O_c is the central atom coordinated to the Pt and two Mo atoms. Six O_c atoms make

Table 3. Positional ($\times 10^4$) and Equivalent Isotropic thermal Parameters ($\text{\AA}^2 \times 10^2$ for Pt and Mo, $\times 10$ for N and O) for $K_{3.5}[H_{4.5}\alpha\text{-PtMo}_6O_{24}] \cdot 3H_2O$ (C) (Estimated Standard Deviations in Parentheses)

atom	x/a	y/b	z/c	Beq, \AA^3
Pt	2896(1)	2133(1)	-1288(1)	90(2)
Mo 1	1114(2)	2243(1)	-4782(2)	150(5)
Mo 2	3295(2)	3130(1)	-3761(2)	151(5)
Mo 3	589(2)	1432(1)	-2318(2)	154(5)
Mo 4	4890(2)	3187(1)	-316(2)	155(5)
Mo 5	2308(2)	1445(1)	1112(2)	138(5)
Mo 6	4491(2)	2263(1)	2030(2)	144(5)
K 1	5000(0)	0(0)	5000(0)	44(3)
K 2	-2760(6)	4277(5)	-4181(8)	40(2)
K 3	-2136(7)	879(5)	-2467(8)	39(3)
K 4	-1992(6)	3666(5)	891(9)	45(3)
O _c 1	1720(12)	3284(11)	-2926(13)	14(4)
O _c 2	2458(13)	1079(10)	-2788(14)	14(4)
O _c 3	4449(12)	1892(11)	-1847(14)	13(5)
O _c 4	1353(11)	2390(11)	-758(13)	12(4)
O _c 5	3258(12)	3227(10)	144(13)	13(4)
O _c 6	4049(13)	1010(12)	302(14)	16(5)
O _b 7	2820(14)	2003(11)	-4720(16)	18(5)
O _b 8	-74(12)	2524(11)	-3697(14)	15(5)
O _b 9	3538(15)	4004(11)	-2003(15)	18(5)
O _b 10	2050(13)	355(11)	-629(14)	15(5)
O _b 11	5795(14)	1948(12)	1088(15)	18(5)
O _b 12	2777(14)	2505(11)	2049(15)	16(5)
O _b 13	-36(17)	3376(15)	-5924(17)	28(7)
O _b 14	1268(17)	1031(14)	-5742(17)	27(7)
O _b 15	2225(17)	4268(14)	-4907(17)	25(6)
O _b 16	4898(15)	2400(14)	-4023(18)	24(6)
O _b 17	736(19)	217(15)	-3329(20)	32(8)
O _b 18	-835(15)	2064(15)	-1733(18)	27(7)
O _b 19	-3626(17)	2592(15)	-774(20)	29(7)
O _b 20	4663(18)	4384(14)	754(18)	27(7)
O _b 21	790(15)	1968(13)	1365(17)	23(6)
O _b 22	3511(14)	172(11)	2155(14)	17(5)
O _b 23	5610(16)	1036(13)	3114(15)	24(6)
O _b 24	4402(16)	3410(13)	3087(16)	22(6)
A _q 1	-4843(22)	4506(18)	-3517(21)	37(10)
A _q 2	-1337(24)	4693(19)	-1250(26)	52(10)
A _q 3	-90(18)	4621(15)	2162(19)	32(7)

$${}^a \text{Beq} = \frac{8}{3} \pi^2 \sum_i \sum_j U_{ij} a_i a_j a_k$$

up the central Pt(O_c)₆ octahedron. Six Mo(O_b)₂(O_c)₂(O_t)₂ octahedra are joined to the central Pt(O_c)₆ octahedron by edge sharing. The six molybdenum atoms form almost a regular hexagon around the platinum atom at the center. Interatomic distances and selected angles in the $[H_{3.5}\alpha\text{-PtMo}_6O_{24}]^{4.5-}$ and $[H_{4.5}\alpha\text{-PtMo}_6O_{24}]^{3.5-}$ polyanions are listed in Table 4 and 5. The range of nearest neighbor Mo-Mo distances is 3.222-3.367 \AA (average 3.32 \AA) and the Pt-Mo distances vary from 3.222-3.415 \AA (average 3.32 \AA). Each Mo atom is coordinated by a distorted octahedron of oxygen atoms. The Mo atoms

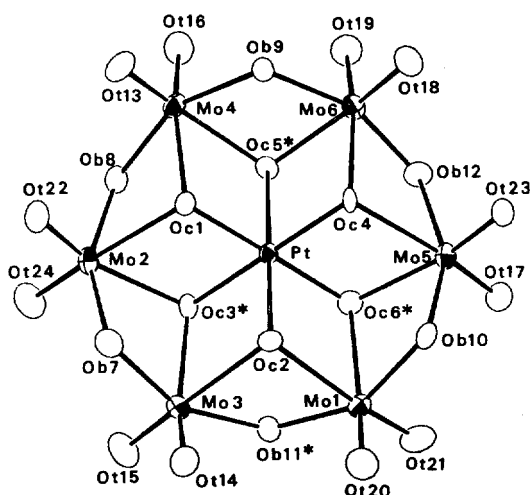


Figure 1. The structure of $[H_{3.5\alpha}\text{-PtMo}_6\text{O}_{24}]^{4.5-}$ polyanion (H atoms not shown, *: protonated O atom) and the crystal packing in the unit cell.

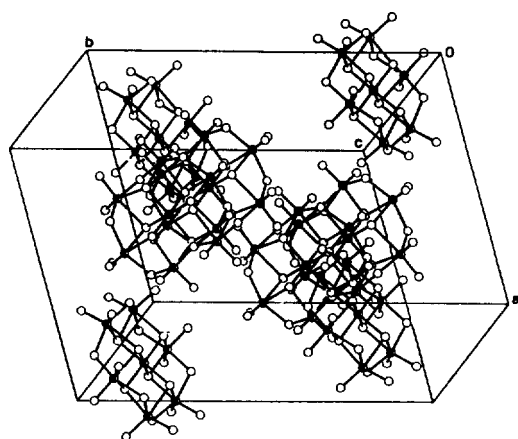


Table 4. Interatomic Distances(Å) and Selected Angles(°) in the $[H_{3.5\alpha}\text{-PtMo}_6\text{O}_{24}]^{4.5-}$ Polyanion

a) distances; O*: protonated oxygen atom, **: average distance		
Pt-Mo : 3.31(4)**	Pt-Oc : 2.01(2)**	Mo-Mo : 3.31(5)**
Pt-Mo1 3.315(2)	Pt-Oc1 2.00(2)	Mo1-Mo3 3.330(4)
Pt-Mo2 3.286(2)	Pt-Oc2 2.00(1)	Mo1-Mo5 3.355(3)
Pt-Mo3 3.235(2)	Pt-Oc*3 2.01(1)	Mo2-Mo3 3.296(3)
Pt-Mo4 3.334(2)	Pt-Oc4 2.03(1)	Mo2-Mo4 3.241(3)
Pt-Mo5 3.369(2)	Pt-Oc*5 2.03(1)	Mo4-Mo6 3.367(3)
Pt-Mo6 3.338(2)	Pt-Oc*6 2.01(2)	Mo5-Mo6 3.241(3)
Mo-Oc* : 2.33(3)**		
Mo1-Oc*6 2.33(1)	Mo2-Oc*3 2.31(1)	Mo3-Oc*3 2.27(1)
Mo4-Oc*5 2.33(1)	Mo5-Oc*6 2.37(1)	Mo6-Oc*5 2.36(1)
Mo-Oc : 2.15(4)**		
Mo1-Oc2 2.16(1)	Mo2-Oc1 2.12(1)	Mo3-Oc2 2.08(1)
Mo4-Oc1 2.19(1)	Mo5-Oc4 2.17(1)	Mo6-Oc4 2.16(1)
Mo-Ob* : 2.07(2)**		
Mo1-Ob*11 2.06(1)	Mo3-Ob*11 2.08(2)	
Mo-Ob : 1.95(4)**		
Mo1-Ob10 1.91(2)	Mo2-Ob8 1.96(1)	Mo2-Ob7 1.98(1)
Mo3-Ob7 1.86(2)	Mo4-Ob8 2.04(2)	Mo4-Ob9 1.93(2)

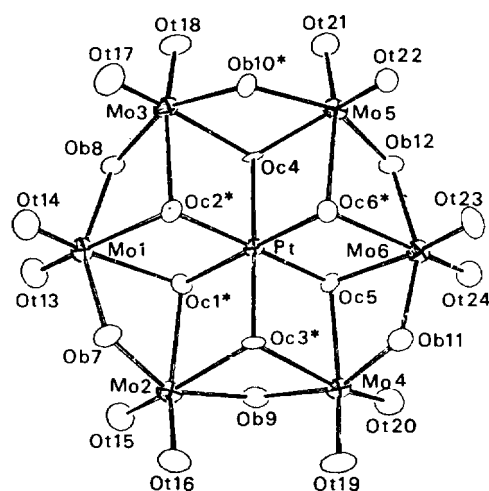
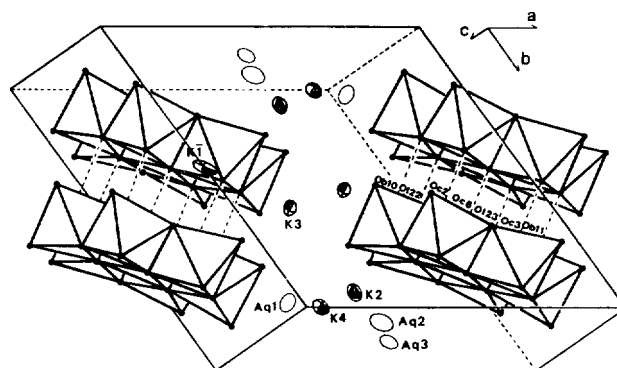


Figure 2. The structure of $[H_{4.5\alpha}\text{-PtMo}_6\text{O}_{24}]^{3.5-}$ polyanion (H atoms not shown, *: protonated O atom) and the crystal packing in the unit cell shown as polyhedra model with hydrogen bonds of interanion.



Mo5-Ob10 1.97(1)	Mo5-Ob12 1.97(2)	Mo6-Ob9 1.95(2)
Mo6-Ob12 1.96(2)		
Mo-Ot : 1.71(2)**		
Mo1-Ot21 1.72(2)	Mo1-Ot20 1.67(2)	Mo2-Ot22 1.70(2)
Mo2-Ot24 1.74(2)	Mo3-Ot14 1.72(2)	Mo3-Ot15 1.76(2)
Mo4-Ot13 1.67(2)	Mo4-Ot16 1.72(2)	Mo5-Ot17 1.72(2)
Mo5-Ot23 1.70(2)	Mo6-Ot18 1.71(2)	Mo6-Ot19 1.73(2)
b) selected angles		
Mo1-Pt-Mo4 171.3(1)	Mo2-Pt-Mo5 173.0(1)	
Mo3-Pt-Mo6 171.8(1)	Mo1-Pt-Mo3 61.1(>0)	
Mo1-Pt-Mo5 60.3(>0)	Mo2-Pt-Mo3 60.7(>0)	
Mo2-Pt-Mo4 58.6(>0)	Mo4-Pt-Mo6 60.0(>0)	
Mo5-Pt-Mo6 57.8(>0)	Oc1-Pt-Oc6 177.9(6)	
Oc2-Pt-Oc5 178.8(5)	Oc3-Pt-Oc4 178.7(5)	

are all displaced from the centers of their octahedra toward the outer oxygens (O) of the anion so that all Mo-Mo distances are increased. These distortions are depicted clearly by the interatomic distances and selected angles in the molecule as listed in Tables 4 and 5. The observed distortions from ideal octahedra are in accord with generally accepted structural principles and have been observed in all iso- and hete-

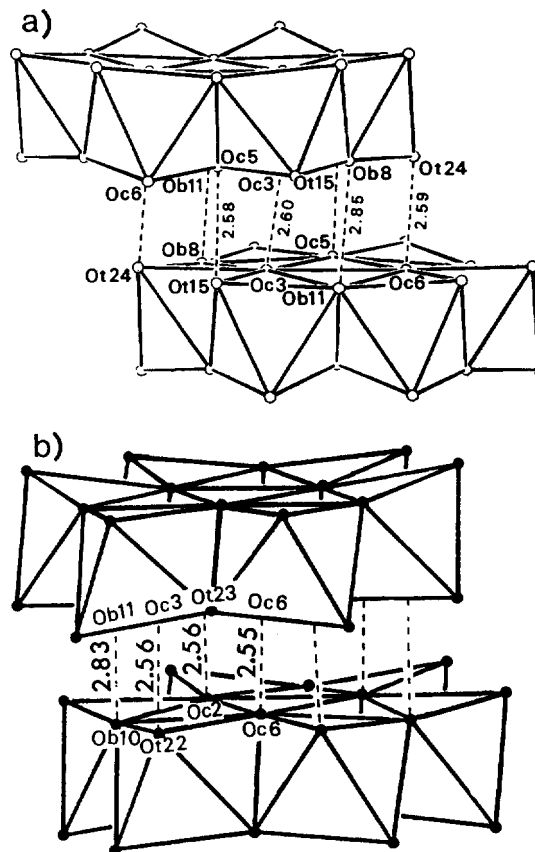
Table 5. Interatomic Distances(Å) and Selected Angles(°) in the $[H_{4.5}\alpha\text{-PtMo}_6\text{O}_{24}]^{3.5-}$ Polyanion

a) distances; O* : protonated oxygen atom, ** : average distance			
Pt-Mo : 3.32(7)**	Pt-Oc : 2.01(2)**	Mo-Mo : 3.32(5)**	
Pt-Mo1 3.415(2)	Pt-Oc*1 2.04(1)	Mo1-Mo2 3.351(4)	
Pt-Mo2 3.398(3)	Pt-Oc*2 2.03(1)	Mo1-Mo3 3.330(4)	
Pt-Mo3 3.304(3)	Pt-Oc*3 2.02(2)	Mo2-Mo4 3.346(3)	
Pt-Mo4 3.324(3)	Pt-Oc4 1.99(2)	Mo3-Mo5 3.365(3)	
Pt-Mo5 3.222(3)	Pt-Oc5 1.99(1)	Mo4-Mo6 3.222(4)	
Pt-Mo6 3.258(3)	Pt-Oc*6 1.99(1)	Mo5-Mo6 3.288(4)	
Mo-Oc* : 2.30(2)**			
Mo1-Oc*1 2.29(1)	Mo1-Oc*2 2.32(1)	Mo2-Oc*1 2.28(2)	
Mo2-Oc*3 2.32(1)	Mo3-Oc*2 2.29(2)	Mo4-Oc*3 2.29(2)	
Mo5-Oc*6 2.29(2)	Mo6-Oc*6 2.34(2)		
Mo-Oc : 2.14(4)**			
Mo3-Oc4 2.15(1)	Mo4-Oc5 2.20(2)	Mo5-Oc4 2.10(1)	
Mo6-Oc4 2.10(1)	Mo6-Oc5 2.11(1)		
Mo-Ob* : 2.09(3)**			
Mo3-Ob*10 2.06(1)	Mo5-Ob*10 2.12(1)		
Mo-Ob : 1.93(4)**			
Mo1-Ob7 1.93(2)	Mo1-Ob8 1.96(2)	Mo2-Ob7 1.93(2)	
Mo2-Ob9 1.95(1)	Mo3-Ob8 1.89(2)	Mo5-Ob12 1.84(2)	
Mo4-Ob9 1.91(1)	Mo4-Ob11 1.99(2)	Mo6-Ob11 1.95(2)	
Mo6-Ob12 1.96(2)			
Mo-Of : 1.72(3)**			
Mo1-Of13 1.70(2)	Mo1-Of14 1.69(2)	Mo2-Of15 1.70(2)	
Mo2-Of16 1.73(2)	Mo3-Of17 1.72(2)	Mo3-Of18 1.73(2)	
Mo4-Of20 1.70(2)	Mo4-Of19 1.73(2)	Mo5-Of22 1.77(2)	
Mo5-Of21 1.68(2)	Mo6-Of23 1.75(2)	Mo6-Of24 1.68(2)	
b) selected angles			
Mo1-Pt-Mo6 175.2(1)	Mo2-Pt-Mo5 174.5(1)		
Mo3-Pt-Mo4 172.8(1)	Mo1-Pt-Mo2 58.9(1)		
Mo1-Pt-Mo3 59.4(1)	Mo2-Pt-Mo4 59.7(1)		
Mo3-Pt-Mo5 62.1(1)	Mo4-Pt-Mo6 58.6(1)		
Mo5-Pt-Mo6 61.0(1)	Oc1-Pt-Oc6 178.8(9)		
Oc2-Pt-Oc5 177.6(6)	Oc3-Pt-Oc4 179.1(7)		

ropolyoxomolybdates.

A remarkable point in this heteropolyanion involves the protonation of the anion and the variability of distances according to the protonation. The position of the hydrogen atoms, as expected, could not be observed even in the electron density difference maps. Generally, six protons in the $[H_6X^{3+}Mo_6O_{24}]^{3-}$ (X : Cr, Co, Al and Rh) heteropolyanion are considered to be attached to each six oxygen atoms of the central XO_6 . The arguments about the position of the hydrogen atoms had been discussed in the crystal structure study on $Na_3[H_6CrMo_6O_{24}] \cdot 8H_2O$.⁴

In this study, we could obtain clearer evidence for the position of the hydrogen atoms in the heteropolyanions. The attached positions of the hydrogen atoms are determined from the unusually long Mo-O bond distances and short O-O distances between two polyanions, suggesting hydrogen bonds (see Figure 3). It was concluded that hydrogen atoms of the $[H_{3.5}\alpha\text{-PtMo}_6\text{O}_{24}]^{4.5-}$ polyanion are bound to the O,3, O,5, O,6 and O,11 atoms by longer Mo2-O,3, Mo3-O,3, Mo4-O,5, Mo6-O,5, Mo1-O,6, Mo5-O,6, Mo1-O,11, and Mo3-O,11

**Figure 3.** The scheme of hydrogen-bonding of (a) $[H_7\alpha\text{-PtMo}_6\text{O}_{24}]^{2-}$ and (b) $[H_9\alpha\text{-PtMo}_6\text{O}_{24}]^{2-}$. Distances is angstrom.

bond distances (see Table 4). The elongation of average bond length for Mo-O_c and Mo-O_b caused by protonation are about 0.18 Å and 0.12 Å, respectively, suggesting that the Mo-O bond orders are reduced. Those of the $[H_{4.5}\alpha\text{-PtMo}_6\text{O}_{24}]^{3.5-}$ polyanion also involve the protonation of O_c1, O_c2, O_c3, O_c6, and O_b10 atoms as deduced from the longer Mo1-O_c1, Mo1-O_c2, Mo2-O_c1, Mo2-O_c3, Mo3-O_c2, Mo4-O_c3, Mo5-O_c6, Mo6-O_c6, Mo3-O_b10, and Mo5-O_b10 bond distances (see Table 5). The polyanions in this study are the first example of protonation of O_b atoms among the hexamolybdoheteropolyanions studied thus far. However, the Pt-O_c distances are almost the same (average 2.01 Å), and PtO₆ forms a relatively regular octahedron. The Pt-O bond distance in the $[PtW_6O_{24}]^{6-}$, shown to have ideal Anderson structure (point symmetry $\bar{3}_m$), is 2.01 (2) Å.¹² It seems that the bond distance of Pt-O_c is not influenced considerably by protonation of the O_c atom as are those of Pt-O_c. The Pt-O bond distance in the $Li_2Pt(OH)_6$ and $Na_2Pt(OH)_6$ is 2.11 Å and 2.05 Å, respectively.²³

In the (A) and (C) crystals, these heteropolyanions were found to be dimers, such as $[H_7(\alpha\text{-PtMo}_6\text{O}_{24})_2]^{9-}$ and $[H_9(\alpha\text{-PtMo}_6\text{O}_{24})_2]^{7-}$, respectively. Dimerization is caused by seven strong hydrogen bonds in both cases, two O₆H-O₂₄ (2.59 (2) Å), two O₅H-O₁₅ (2.58 (2) Å), two O₁₁H-O₈ (2.85 (2) Å) and one O₃H-O₃ (2.60 (3) Å) in the $[H_7(\alpha\text{-PtMo}_6\text{O}_{24})_2]^{9-}$ polyanion and two O₂H-O₂₃ (2.56 (2) Å), two O₃H-O₂₂ (2.56 (2) Å), two O₁₀H-O₁₁ (2.83 (2) Å) and one O₆H-O₆ (2.55 (2) Å) in the $[H_9(\alpha\text{-PtMo}_6\text{O}_{24})_2]^{7-}$ polyanion formed between adjacent anions as shown in Figure 3. The coordinates

Table 6. Probable Hydrogen Bond Distances in the $(\text{NH}_4)_{4.5}[\text{H}_{3.5}\alpha\text{-PtMo}_6\text{O}_{24}] \cdot 1.5\text{H}_2\text{O}$ (A), and $\text{K}_{3.5}[\text{H}_{4.5}\alpha\text{-PtMo}_6\text{O}_{24}] \cdot 3\text{H}_2\text{O}$ (C)

$(\text{NH}_4)_{4.5}[\text{H}_{3.5}\alpha\text{-PtMo}_6\text{O}_{24}] \cdot 1.5\text{H}_2\text{O}$ (A) crystal					
a) by ammonium ion (<3.2 Å)					
N1-Or13 ⁱⁱ	2.94(3)	N2-Ob12 ⁱⁱⁱ	3.14(3)	N3-Or20	3.07(3)
Or19	2.92(4)	Or21 ⁱⁱⁱ	3.00(3)	Or14	2.83(4)
Or22 ^{iv}	3.16(4)	Or23 ⁱⁱⁱ	2.86(4)	Or17 ⁱⁱⁱ	2.98(4)
Or22 ⁱⁱⁱ	3.05(4)			Aq2	2.89(5)
N4-Or21 ^v	3.19(4)	N5-Ob12	2.73(3)		
Aq1	3.07(4)	Or15 ^{vi}	2.90(3)		
Aq1 ^v	3.07(4)	Or15 ^{vi}	2.90(3)		
Ob8	2.87(3)				
b) by water molecules (<3.1 Å)					
Aq1-N4	3.07(3)	Aq2-N3	2.89(5)		
N4 ^v	3.07(3)	Or16 ^v	2.81(3)		
$\text{K}_{3.5}[\text{H}_{4.5}\alpha\text{-PtMo}_6\text{O}_{24}] \cdot 3\text{H}_2\text{O}$ (C) crystal					
a) by water molecules (>3.0 Å)					
Aq1-Or16 ^v	3.04(4)	Aq2-Or4	2.98(2)		
Or20 ⁱⁱⁱ	2.88(3)	Or5 ⁱⁱⁱ	2.80(2)		
		Aq3 ⁱⁱⁱ	2.89(5)		
Aq3-Or1 ⁱⁱⁱ	2.55(2)	Aq3-Ob12	3.07(2)		
Or13 ⁱⁱⁱ	2.82(4)	Aq2 ⁱⁱⁱ	2.89(5)		

symmetry code for (A):

i) $1/2-x, y, -z$ ii) $1/2+x, 1/2-y, 1/2+z$ iii) $-1/2+x, 1/2-y, -1/2+z$ iv) $-1/2+x, -y, z$ v) $-x, 1/2-y, 1/2-z$

symmetry code for (C):

i) $-1+x, y, z$ ii) $-x, 1-y, -z$ iii) $x, y, 1+z$ iv) $1-x, -y, -z$

of the counterpart polyanions are generated from the $(-x, 1/2-y, 1/2-z)$ (A) and $(1-x, -y, -z)$ (C) symmetry operations of the original coordinates.

As a result, the formation of hydrogen bonds between the two polyanions strongly supports the assumption that the hydrogen atoms of the polyanion are bound to the respective O_c and O_b atoms. These all-protonated oxygen atoms are on the same side of the polyanion, and all hydrogen atoms contribute to the formation of hydrogen bonds, except the protonated O_{c1} atom in the $[\text{H}_3(\alpha\text{-PtMo}_6\text{O}_{24})_2]^{7-}$ (C) polyanion. Thus, the adjacent two polyanions form short and strong hydrogen bonds very effectively. The formation of dimers from the two polyanions by seven hydrogen bonds in the Anderson type polyanion has been found only in these polyanions and the $[\text{H}_{5.5}\text{PtW}_6\text{O}_{24}]^{3.5-14}$ polyanion. Structurally, the formation of hydrogen bonds is impossible between two $[\text{H}_6\text{X}^{3+}\text{Mo}_6\text{O}_{24}]^{3-}$ (X: Co^{III} , Cr^{III} , Al^{III} , Rh^{III} etc.) polyanions, because of each of three protonated O_c atoms are located on both sides of the polyanion.

The half integral numbers of the hydrogen atoms are caused by the hydrogen atom related to the hydrogen bond of $\text{O}_{c3}\text{-O}_{c3}$ in the $[\text{H}_7(\alpha\text{-PtMo}_6\text{O}_{24})_2]^{9-}$ polyanion and $\text{O}_{c6}\text{-O}_{c6}$ in the $[\text{H}_6(\alpha\text{-PtMo}_6\text{O}_{24})_2]^{7-}$ polyanion. The hydrogen atoms forming the $\text{O}_{c3}\text{-O}_{c3}$ (A) hydrogen bond and the $\text{O}_{c6}\text{-O}_{c6}$ (C) hydrogen bond are bound to O_{c3} and O_{c6} in the positional disorder or are located at the center of two O_{c3} and two O_{c6} . The center of the two O_{c3} and two O_{c6} coordinates are (0.00, 0.25, 0.25) and (0.50, 0.00, 0.00), respectively. These coordinates are special position of the $A_{2/a}$ and $\bar{P}1$ space

Table 7. Potassium Coordinate Spheres in $\text{K}_{3.5}[\text{H}_{4.5}\alpha\text{-PtMo}_6\text{O}_{24}] \cdot 3\text{H}_2\text{O}$ (<3.3 Å)

K1-Ob7 ⁱⁱⁱ	2.59(1)	K2-Ob8	2.71(1)	K3-Or16 ⁱⁱⁱ	2.99(1)
Or17 ⁱⁱⁱ	2.78(1)	Or24 ^v	2.87(2)	Or18	2.75(3)
Or16 ⁱⁱⁱ	3.20(2)	Aq1	2.73(3)	Or19	2.72(2)
Or16 ^{iv}	3.20(2)	Aq2	2.99(3)	Or22 ^{iv}	2.93(2)
Or22	2.78(1)	K4-Ob9 ^v	2.87(1)	K4-Or13 ⁱⁱⁱ	3.21(2)
Or22 ⁱⁱⁱ	2.78(1)	Or18	3.24(2)	Or20 ^v	2.97(1)
Or23	3.21(2)	Or19	3.02(2)	Aq3	3.12(3)
Or23 ⁱⁱⁱ	3.12(2)	Or21	2.77(1)		

symmetry code: i) $-x, -y, -z$ ii) $1-x, -y, 1-z$ iii) $1-x, -y, -z$ iv) $x, y, 1+z$ v) $-x, 1-y, -z$ vi) $-1+x, y, z$

group having a multiplicity of 4/8 and 1/2, respectively. In any case, the number of hydrogen atoms per molecules is 1/2. We cannot determine whether the disorder involves special positions for the coordination of the hydrogen atoms. However, considering the bond distances of $\text{O}_{c3}\text{-O}_{c3}$ (2.60 Å) and $\text{O}_{c6}\text{-O}_{c6}$ (2.55 Å), we assume that bonding in positional disorder is more reasonable than locating at the center of symmetry. The number of hydrogen atoms is 3.5 (A) and 4.5 (C) per molecule, respectively.

Since it is impossible to distinguish the ammonium ions and the water molecules (Aq) directly from electron density maps, they were identified from the distances of N-N^{24} , N-Aq and Aq-O and the coordination number of ammonium ions and water molecules in the $(\text{NH}_4)_9[\text{H}_7\alpha\text{-PtMo}_6\text{O}_{24}]_2$ crystal (see Table 6).

The half integral number of the ammonium cation is caused by the fact that one ammonium ion (N5) is at the special position, $(1/4, y, 1/2)$: multiplicity 4/8) of the $A_{2/a}$ space group. Thus, the numbers of H^+ and $(\text{NH}_4)^+$ ions are exactly explained. Aq1 is also placed at the special position $(1/4, y, 0)$: multiplicity 4/8). According to thermogravimetric analysis (TG), the mass decrease due to the dehydration is in good agreement with the theoretical value (found 2.1%; calcd. 2.13 %). Another half integral number for the potassium cation is caused by the K1 atom at the special position of the $\bar{P}1$ space group $(1/2, 0, 1/2)$: multiplicity 1/2) in the crystal (C). From this result, the number of K^+ ions is 3.5 per molecule.

The probable hydrogen bonds and $\text{K}^+\text{-O}$ distances for (C) are listed in Table 6 and 7.

β -Isomer (bent structure) salts: $(\text{NH}_4)_4[\text{H}_4\beta\text{-PtMo}_6\text{O}_{24}] \cdot 1.5\text{H}_2\text{O}$ (B). The final parameters resulting from the anisotropic least-squares refinement are listed in Table 8. The structure of the $[\text{H}_4\beta\text{-PtMo}_6\text{O}_{24}]^{4-}$ polyanion and the crystal packing are shown in Figure 4. Interatomic distances and selected angles are summarized in Table 9. Oxygen atoms of the polyanion are similarly classified in the same manner as that the α -isomer. O_c is a four-coordinated oxygen atom surrounded by one Pt and three Mo atoms, that is, the center of corner sharing. As shown in Figure 4, the β -isomer is not planar. It consists of six MoO_6 and a PtO_6 octahedra condensed by edge and corner sharing into a structure that has an approximate point symmetry of $2_{mm}(C_{2v})$. The framework of the polyanion is fundamentally the same as that of $[\text{Mo}_7\text{O}_{24}]^{6-}$ and $[\text{H}_2\text{SbMo}_6\text{O}_{24}]^{5-}$. The molybdenum atoms, such as, Mo1, Mo2, Mo5 and Mo6, are situated at

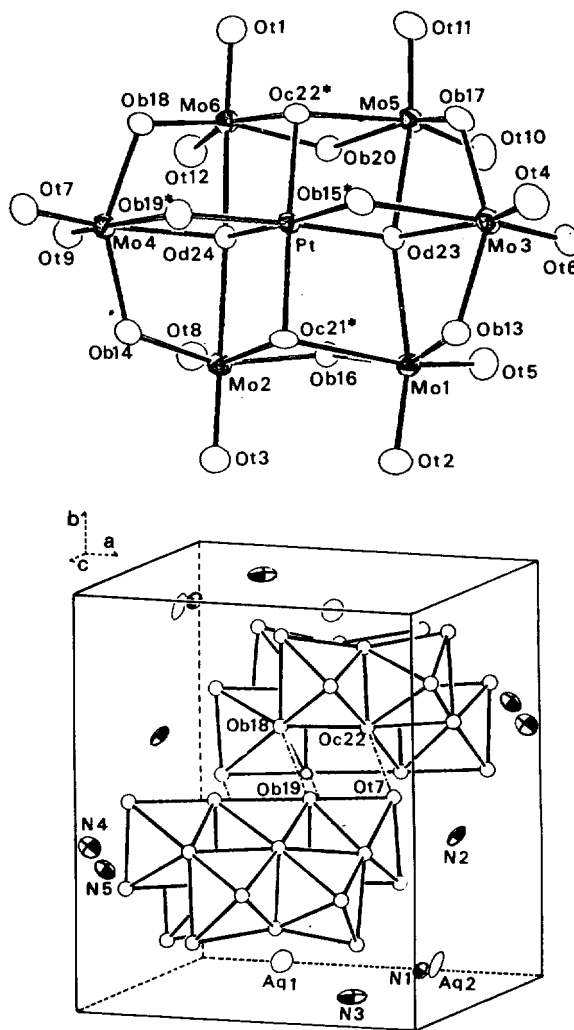
Table 8. Positional ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($\text{\AA}^2 \times 10^2$ for Pt and Mo, $\times 10$ for N and O) for $(NH_4)_4[H_4\beta\text{-PtMo}_6\text{O}_{24}] \cdot 1.5H_2O$ (B) (Estimated Standard Deviations in Parentheses)

atom	<i>n/a</i>	<i>y/b</i>	<i>z/c</i>	<i>Beq.</i> \AA^2
Mo 1	1448(1)	2476(1)	-2659(1)	153(4)
Mo 2	-1328(1)	2469(1)	-1876(1)	153(4)
Mo 3	3759(1)	1420(1)	-1712(1)	159(4)
Mo 4	-1792(1)	1277(1)	-292(1)	163(4)
Mo 5	4191(1)	3167(1)	2306(1)	166(4)
Mo 6	1420(1)	3044(1)	3003(1)	168(4)
O ₁	2480(10)	3109(8)	4704(12)	22(4)
O ₂	221(9)	2031(7)	-4686(11)	19(4)
O ₃	-2398(9)	2139(7)	-3840(11)	20(4)
O ₄	4178(9)	195(7)	-2928(11)	22(4)
O ₅	2797(9)	3666(7)	-1709(12)	21(4)
O ₆	4967(8)	2554(8)	-1119(12)	20(4)
O ₇	-2942(9)	-2(7)	-1110(12)	20(4)
O ₈	-1519(9)	3700(7)	-299(11)	20(4)
O ₉	-2303(9)	2363(7)	991(11)	20(4)
O ₁₀	5196(9)	4285(8)	2679(12)	22(4)
O ₁₁	5173(9)	3213(8)	4012(12)	23(4)
O ₁₂	747(10)	4134(8)	3920(12)	24(4)
O _{b13}	2158(8)	1203(6)	-3646(10)	15(3)
O _{b14}	-2516(8)	1211(7)	-2289(10)	16(4)
O _{b15}	1888(8)	126(6)	-2301(10)	14(3)
O _{b16}	501(8)	3263(6)	-1322(10)	14(3)
O _{b17}	4516(8)	1819(7)	557(10)	15(3)
O _{b18}	-132(8)	1653(7)	1745(10)	15(4)
O _{b19}	-755(8)	37(6)	-1842(11)	15(4)
O _{b20}	2825(8)	3826(6)	2943(10)	13(3)
O _{c21}	-338(7)	1046(6)	-3237(9)	12(3)
O _{c22}	2241(7)	1671(6)	1212(9)	12(3)
O _{d23}	2509(7)	2394(6)	-519(9)	11(3)
O _{d24}	60(7)	2337(6)	168(9)	10(3)
A _{q1}	-1006(15)	3533(12)	-4810(19)	40(8)
A _{q2}	-4685(16)	3755(16)	-2527(21)	27(12)
N 1	-2474(12)	4609(9)	2160(15)	26(5)
N 2	-3472(14)	1342(11)	2325(17)	29(7)
N 3	-2147(16)	4664(10)	-2344(17)	37(6)
N 4	4581(36)	1039(27)	-4914(35)	32(14)
N 5	4119(33)	1522(26)	-4952(41)	30(15)

$${}^a Beq = \frac{8}{3} \pi^2 \sum_i \sum_j U_{ij} a_i a_j a_k$$

the corners of the almost regular rectangle (average angle of corners is 90.0°), with the Pt atom lying nearly above the center of the rectangle plane and the Mo3-Pt-Mo4 angle is 174.2° . With corner sharing, the distances for Mo2-Mo6 and Mo1-Mo5 are $4.443(2) \text{ \AA}$ and $4.424(2) \text{ \AA}$, respectively. The polyanion has no center of symmetry.

The Mo-O bond length spans a considerable range in the structure ($1.70\text{-}2.42 \text{ \AA}$). From the comparison of the Mo-O bond distances and the hydrogen bond, as was done in the case of the α -isomer, it was deduced that the O₂₁, O₂₂, O_{b15} and O_{b19} oxygen atoms are protonated. These protona-

**Figure 4.** The structure of $[H_4\beta\text{-PtMo}_6\text{O}_{24}]^{4-}$ polyanion (H atoms not shown, *: protonated O atom) and the crystal packing in the unit cell shown as polyhedra model with hydrogen bonds of interanion.

ted oxygen atoms are located on the same side of the polyanion. A unit cell contains two polyanions forming a pair with a center of symmetry ($-x, -y, -z$) by four hydrogen bonds (see Figure 4), such as two O_{b19}H-O_{b18} ($2.83(2) \text{ \AA}$) and two O₂₂H-O₇ ($2.64(2) \text{ \AA}$). The protonated O₂₁ and O_{b15} oxygen atoms did not contribute to hydrogen bond formation. Protonated Mo-O_c bond distances of the β -isomer and those of the α -isomer gave reasonable values. The bond distances of triple-coordinated Mo-O_c (average distance 2.37 \AA) are longer than those of quadruple-coordinated Mo-O_d (average distance 2.25 \AA), because the O_c atoms are protonated. In fact, the bond distance of the protonated Mo-O_c minus 0.16 \AA (lengthened average distance of Mo-O_c by protonation) is shorter than that of Mo-O_d. Even if it is considered that the O_{b15} and O_{b19} oxygen atoms are protonated, the bond distances of Mo3-O_{b15} (2.34 \AA) and Mo4-O_{b19} (2.33 \AA) are abnormally long. This is similar to that of the Mo-O_cH distance (2.37 \AA). Originally, the positions of the O_{b15} and O_{b19} oxygen atoms are classified as O_c atoms in the planar structure. The O_{b15} and O_{b19} atoms are less shared with Mo3

Table 9. Interatomic Distances and Angles in the $[\text{H}_4\beta\text{-PtMo}_6\text{O}_{24}]^{4-}$ Polyanion

a) distances; O** : protonated oxygen atom, ** : average distance					
Pt-Mo : 3.32(2)**	Pt-O : 2.01(1)**	Mo-Mo : 3.31(5)**			
Pt-Mo1 3.315(2)	Pt-O _b *15 2.011(9)	Mo1-Mo2 3.391(2)			
Pt-Mo2 3.328(1)	Pt-O _b *19 2.001(10)	Mo1-Mo3 3.210(2)			
Pt-Mo3 3.373(1)	Pt-O _c *21 2.004(10)	Mo2-Mo4 3.247(2)			
Pt-Mo4 3.348(1)	Pt-O _c *22 2.003(9)	Mo4-Mo6 3.227(1)			
Pt-Mo5 3.349(1)	Pt-O _d 23 2.016(9)	Mo5-Mo6 3.353(2)			
Pt-Mo6 3.342(1)	Pt-O _d 24 2.014(8)	Mo3-Mo5 3.259(1)			
Mo-Mo(corner sharing) : 4.43(1)**					
Mo2-Mo6 4.443(2)	Mo1-Mo5 4.424(2)				
Mo1-O _d : 2.25(4)**					
Mo1-O _d 23 2.235(11)	Mo2-O _d 24 2.282(10)	Mo3-O _d 23 2.209(8)			
Mo4-O _d 24 2.190(9)	Mo5-O _d 23 2.310(8)	Mo6-O _c 24 2.081(1)			
Mo-O _c * : 2.37(4)**					
Mo1-O _c *21 2.423(11)	Mo2-O _c *21 2.365(8)	Mo5-O _c *22 2.336(9)			
Mo6-O _c *22 2.349(8)					
Mo-O _b * : 2.337**					
Mo3-O _b *15 2.341(10)	Mo4-O _b *19 2.332(9)				
Mo-O _b : 1.94(2)**					
Mo1-O _b 13 1.943(9)	Mo1-O _b 16 1.923(10)	Mo2-O _b 14 1.948(12)			
Mo2-O _b 16 1.929(10)	Mo3-O _b 17 1.917(11)	Mo3-O _b 13 1.968(9)			
Mo4-O _b 18 1.956(9)	Mo4-O _b 14 1.922(12)	Mo5-O _b 17 1.959(9)			
Mo5-O _b 20 1.930(9)	Mo6-O _b 18 1.912(9)	Mo6-O _b 20 1.915(11)			
Mo-O _t : 1.71(2)**					
Mo1-O _t 5 1.691(10)	Mo1-O _t 2 1.723(10)	Mo2-O _t 3 1.704(11)			
Mo2-O _t 8 1.716(9)	Mo3-O _t 6 1.706(12)	Mo3-O _t 4 1.736(9)			
Mo4-O _t 9 1.697(10)	Mo4-O _t 7 1.730(11)	Mo5-O _t 10 1.699(14)			
Mo5-O _t 11 1.696(13)	Mo6-O _t 1 1.695(13)	Mo6-O _t 12 1.720(11)			
b) selected angles					
Mo1-Pt-Mo2 61.4(>0)	Mo1-Pt-Mo3 57.4(>0)				
Mo2-Pt-Mo4 58.2(>0)	Mo3-Pt-Mo5 58.0(>0)				
Mo4-Pt-Mo6 57.7(>0)	Mo5-Pt-Mo6 60.2(>0)				
Mo1-Pt-Mo4 119.6(>0)	Mo2-Pt-Mo3 118.6(>0)				
Mo3-Pt-Mo6 118.2(>0)	Mo1-Pt-Mo6 114.6(>0)				
Mo2-Pt-Mo5 112.0(>0)	Mo4-Pt-Mo5 117.7(>0)				
Mo3-Pt-Mo4 174.2(>0)	Mo2-Mo1-Mo5 89.2(>0)				
Mo1-Mo2-Mo6 90.3(>0)	Mo1-Mo5-Mo6 91.1(>0)				
Mo2-Mo6-Mo5 89.4(>0)	O _b 15-Pt-O _d 24 176.2(3)				
O _c 21-Pt-O _c 22 169.4(4)	O _b 19-Pt-O _d 23 176.5(4)				

and Mo4. Therefore, Mo3O₆ and Mo4O₆ octahedra are more distorted than the other MoO₆ octahedra (see Table 9). The Pt-O bond distances (average 2.01 Å) of the α - and β -isomers are almost the same, but the PtO₆ octahedron of the β -isomer is considerably more distorted than that of the α -isomer. The function contributing most to the distortion is the O₂₁-Pt-O₂₂ bond angle (169.4°). The need for the Mo3, Mo4 and Pt atoms to adopt this distorted coordination may help to explain why this polyanion has the unusual bent configuration rather than the more symmetrical α -isomer configuration.

All structural characters of the $[\text{H}_4\beta\text{-PtMo}_6\text{O}_{24}]^{4-}$ polyanion are the same as those of the $[\text{H}_2\text{SbMo}_6\text{O}_{24}]^{5-}$ polyanion. The protonated oxygenatoms in the $[\text{H}_2\text{SbMo}_6\text{O}_{24}]^{5-}$ correspond

Table 10. Probable Hydrogen Bond Distances in the $(\text{NH}_4)_4[\text{H}_4\beta\text{-PtMo}_6\text{O}_{24}] \cdot 1.5\text{H}_2\text{O}$ Crystal

a) by ammonium ions (<3.0 Å).					
N1-O _t 8 2.78(2)	N2-O _t 4 ⁱ 2.90(3)	N3-Aq1 2.95(3)			
O _t 9 2.90(2)	O _t 15 ⁱⁱ 2.87(2)	Aq2 2.88(3)			
O _t 5 ⁱⁱⁱ 2.95(2)	O _t 17 ⁱⁱⁱ 2.75(2)	O _b 20 ⁱⁱⁱ 2.79(2)			
O _t 10 ⁱⁱⁱ 2.84(2)	Aq1 ^{iv} 2.91(2)				
N4-O _t 3 ^{viii} 3.01(4)	N5-Aq2 ^{viii} 2.52(3)				
b) by water molecules (<3.0 Å).					
Aq1-O _t 2 2.74(2)	Aq2-N3 2.88(3)				
N3 2.95(3)	N5 ⁱⁱ 2.52(3)				
N2 ^{vii} 2.91(2)					

Symmetry code: i) $-x, -y, -z$ ii) $-1+x, y, z$ iii) $-x, 1-y, -z$ iv) $-1+x, y, -1+z$ v) $x, y, 1+z$ vi) $-x, 1-y, 1-z$ vii) $x, y, -1+z$ viii) $1+x, y, z$

to O_b15 and O_b19 of the $[\text{H}_4\beta\text{-PtMo}_6\text{O}_{24}]^{4-}$ polyanion. The ionic charge (Pt⁴⁺ and Sb⁵⁺) and ionic radius (Pt⁴⁺ : 0.70 Å and Sb⁵⁺ : 0.64 Å) of the heteroatoms are different, but the average Pt-O (2.01 Å) and Sb-O (1.98 Å) distances are very similar. Mo-Oc distances (average 2.37 Å) of $[\text{H}_4\beta\text{-PtMo}_6\text{O}_{24}]^{4-}$ are longer than those (average 2.26 Å) of $[\text{H}_2\text{SbMo}_6\text{O}_{24}]^{5-}$ because the Oc atoms of $[\text{H}_4\beta\text{-PtMo}_6\text{O}_{24}]^{4-}$ are protonated.

The sites of Aq1, Aq2, N1, N2 and N3, are determined similarly to those of the $(\text{NH}_4)_{4.5}[\text{H}_{3.5}\alpha\text{-PtMo}_6\text{O}_{24}] \cdot 1.5\text{H}_2\text{O}$ (A) crystal structure. Four ammonium ions per molecule are determined from the results of elemental analysis and the number of protons (4H) per molecule. Two residual electron density peaks (distance is about 1 Å) whose heights are about half of the nitrogen atom electron density were attributed to one nitrogen atom. It seems that these two peaks are caused by the positional disorder of one ammonium ion. N4 and N5 refer to these two peaks. The numbers of hydrogen atoms and ammonium ions are thus explained. The probable hydrogen bonds by ammonium ion and water molecules are listed Table 10.

Supplementary Material Available. The final Fo-Fc table (total 189 pp.) and anisotropic thermal parameters (3 pp.), complete angles for (A), (B), and (C) (total 7 pp.) are available as supplementary materials from author.

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A Theory of Interface between Polymer and Polymer Mixture

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Received August 3, 1993

We present a theoretical study of the non-symmetrical A/BC polymeric system. The polymer blends consist of two phases, a pure polymeric phase A on one side and a mixture of polymers B as a compatibilizer and C on the other. The adsorption of homopolymer B to the interface improves the interfacial adhesion between two phases. By employing the functional integral techniques, we derive the mean-field equations and solve them numerically to obtain the interfacial properties including the concentration profiles in the limit of infinite molecular weight for the polymers. The calculations of the interfacial properties are performed for typical values of the Flory χ parameters and the volume fraction of polymer B in the asymptotic mixture phase. The interfacial adsorption of polymer B and the degrees of the specific interaction between the polymers play an important role in modification of the interfacial properties.

Introduction

For most polymers it is thermodynamically unfavorable to form the homogeneous mixtures with each other. This is so because the combinatorial entropy of mixing of two polymers is dramatically smaller than that for the low molecular weight components. The enthalpy of mixing, on the other hand, is often a small positive quantity or, at best, zero. In such cases immiscibility results when polymers are mixed. For that reason, it is worthwhile and interesting that the understanding and adjusting of the interfacial properties between the phases in the immiscible polymeric systems.

There has been a great deal of interest in experimental¹⁻⁵ and theoretical⁶⁻²⁰ studies of the interfacial properties of inhomogeneous multicomponent polymeric systems. Helfand and co-workers⁸⁻¹⁰ developed a mean-field theory for predic-

ting the interfacial properties between two immiscible polymers, and Noolandi and co-workers¹³⁻¹⁵ also presented fully self-consistent calculations of the polymer density profiles and resulting interfacial tension at polymer/polymer interfaces in the presence of a solvent and the effects of copolymers at these interfaces. However, relatively little work has been done to extend the immiscible polymer-polymer systems to include the effects of third homopolymers as compatibilizers, which polymeric systems usually show the intrinsic non-symmetrical interfaces. Recently Helfand¹⁶ extended the theory of the A/B interface to the specific one of A/BC for the interfacial tension via equations of motion.^{8-10,21}

In this work the A/BC interface between two phases is considered, which is the same model as recent Helfand's work,¹⁶ a pure polymeric phase A on one side and a mixture of polymer B as a compatibilizer and polymer C on the other