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ISOMERISM OF THE HEXAMOLYBDO-PLATINATE(IV) POLYANION. CRYSTAL STRUCTURES OF $K_{3.5}[\alpha\text{-}H_{4.5}PtMo_6O_{24}]\cdot 3H_2O$ AND $(NH_4)_4[\beta\text{-}H_4PtMo_6O_{24}]\cdot 1.5H_2O$

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The hexamolybdo-platinate(IV) anion, $[PtMo_6O_{24}]^{8-}$ has been found to have two geometrical isomers, one having the Anderson structure and the other having the same framework with the heptamolybdate ion reported by Lindqvist.

It has been widely accepted that 1 : 6 heteropolymolybdate anions, $[X^{+n}Mo_6O_{24}]^{(12-n)-}$ (X : Te^{6+} , I^{7+}) 1) and their protonated species, $[X^{+n}Mo_6O_{24}H_6]^{(6-n)-}$ (X : Cr^{3+} , Co^{3+}) 2) have the well-known Anderson structure, consisting of a central XO_6 octahedron with six MoO_6 octahedra surrounding it in a plane always sharing their edges. But recently in the course of the preparative studies of polymolybdo-platinate(IV) salts, we have found that the hexamolybdo-platinate(IV) anion has two isomeric forms, α and β. We call the planar structure, that is, Anderson structure having $\bar{3}m(D3d)$ point symmetry α-isomer and the other type, the bent structure having the 2mm(C2v) point symmetry β-isomer. These compounds are not only novel 1:6 heteropolymolybdates containing platinum(IV) but also the first example of geometrical isomerism in the 1:6 heteropolyanions.

The α-isomer crystals are precipitated as pale yellow crystals $K_{3.5}[\alpha\text{-}H_{4.5}PtMo_6O_{24}]\cdot 3H_2O$ (A) from 1:6 mixture solution of $K_2[Pt(OH)_6]$ and $K_2[MoO_4]$ at pH ca. 2.5. The β-isomer, $(NH_4)_4[\beta\text{-}H_4PtMo_6O_{24}]\cdot 1.5H_2O$ (B) crystallized at pH ca. 5.4 when the ammonium salts were used.

Crystal data : (A) $K_{3.5}[\alpha\text{-}H_{4.5}PtMo_6O_{24}]\cdot 3H_2O$, F.W.=1349.8, triclinic, a=12.426 (2), b=13.884(2), c=10.089(2) Å, α=102.59(2), β=110.73(1), γ=53.93(1)°, U=1332.2(4) $Å^3$, Z=2, Dc=3.365 g cm^{-3}, F(000)=623, space group $P\bar{1}$, Mo Kα radiation(graphite monochromator), λ=0.7107 Å, μ(Mo Kα)=82.93 cm^{-1}. Intensities[6126 with $I \geqq 3\sigma(I)$]

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were measured on a Rigaku four circle diffractometer at 293 K and corrected for X-ray absorption effect. The structure was solved by conventional heavy atom method and refined to R=0.074(Rw=0.075) by block diagonal least-squares. (B) $(NH_4)_4$-$[\beta\text{-}H_4PtMo_6O_{24}]\cdot 1.5H_2O$, F.W.=1257.76, triclinic, a=10.776(2), b=15.174(4), c=10.697(3) Å, α=126.29(2), β=111.55(2), γ=93.18(2)°, U=1221.2(4) $Å^3$, Z=2, Dc=3.396 g cm^{-3}, F(000)=580, space group $P\bar{1}$, μ(Mo Kα)=90.23 cm^{-1}. Intensities[6044 with I ≧ 3σ(I)] were measured as for α-isomer, refining to R=0.064(Rw=0.046).

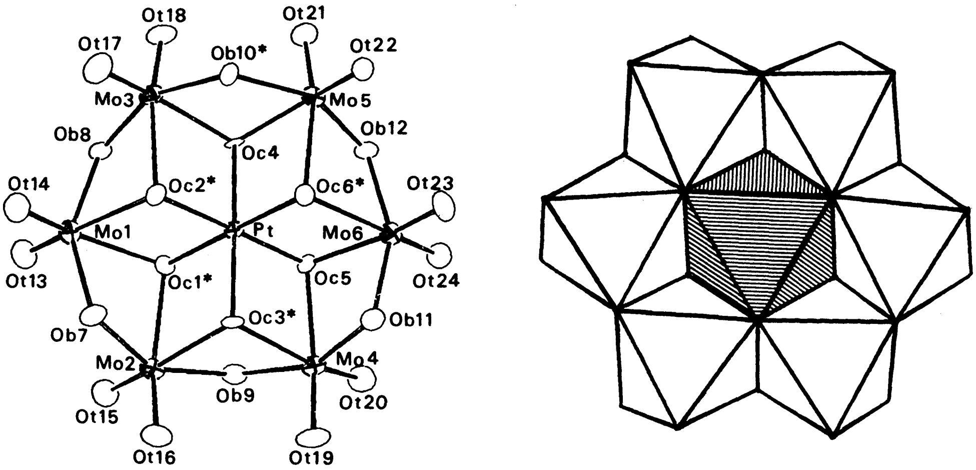

Fig. 1. The structure of $[\alpha\text{-}H_{4.5}PtMo_6O_{24}]^{3.5-}$ anion(H atoms not shown) and its polyhedra model. * : Protonated O atom.
Average distance(range). : Pt-Mo 3.32(7) (3.222-3.417), Mo-Mo 3.32(5) (3.222-3.365), Pt-Oc 2.01(3) (1.99-2.04), Mo-Oc^* 2.30(2) (2.28-2.34), Mo-Oc 2.14(4) (2.10-2.20), Mo-Ob^* 2.09(3) (2.06-2.12), Mo-Ob 1.93(4) (1.84-1.99), and Mo-Ot 1.72(3) (1.68-1.77) Å.

In $K_{3.5}[\alpha\text{-}H_{4.5}PtMo_6O_{24}]\cdot 3H_2O$ crystals, typical Anderson structure ions were found as dimers, $[H_9(PtMo_6O_{24})_2]^{7-}$. Dimerization was caused by seven hydrogen-bonds formed between two anions. But the crystallograpic unit is a polyanion of a conventional formula, $[H_{4.5}PtMo_6O_{24}]^{3.5-}$. The $[\alpha\text{-}H_{4.5}PtMo_6O_{24}]^{3.5-}$ polyanion structure and its polyhedra model are shown in Fig. 1 with pertinent bond distances given in the caption. This polyanion has approximate $\bar{3}m$ symmetry. The Ot is terminal O atom bound to a Mo atom, Ob is the bridging atom between two Mo atoms and Oc is the central atom coordinated to the Pt and two Mo atoms. The hydrogen atoms were not observed in the electron density difference map. However, we can guess the hydrogen atoms are bound to the Oc1, Oc2, Oc3, and Ob10 atoms from longer Mo-Oc^* and Mo-Ob^* bond distances(See Fig. 1 caption.) and the hydrogen-bonding between two polyanions. The bond distances of protonated Mo-Oc* and Mo-Ob* are about 0.16 Å longer than unprotonated ones. A polyanion in a unit cell is bound to another one in a neighbouring cell (1-x, -y, -z) by seven hydrogen-bonds, two Oc2H-Ot23 2.56(2) Å, two Oc3H-Ot22 2.56(2) Å, two Ob10H-Ob11 2.83(2) Å and Oc6-H-Oc6 2.55(2) Å. The hydrogen atom forming Oc6-Oc6 hydrogen-bond is bound to Oc6 as positional disorder. The half integral number of the potassium cation is caused by one K^+ on the special position of $P\bar{1}$ space group (1/2, 0, 1/2). As a result, the number of H^+ and K^+ in a molecule is 4.5 and 3.5, respectively.

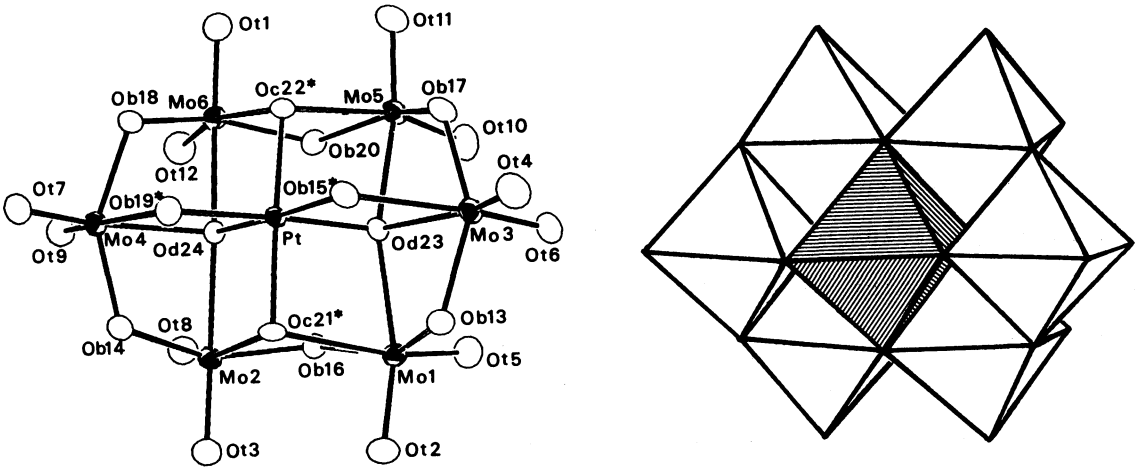

Fig. 2. The structure of $[\beta\text{-}H_4PtMo_6O_{24}]^{4-}$ anion (H atoms not shown) and its polyhedral model. * : Protonated O atom.

Average distance(range). : Pt-Mo 3.34(2) (3.315-3.349), Mo-Mo 3.28(7) (3.210-3.391), Pt-Oc,Od,Ob 2.01(1) (2.001-2.016), Mo-Od 2.25(4) (2.190 -2.310), Mo-Oc* 2.37(3) (2.336-2.423), Mo-Ob 1.94(2) (1.912-1.968), Mo-Ob* 2.34(1) (2.332-2.341), Mo-Ot 1.71(1) (1.691-1.736), Mo1-Mo5 4.424(2), and Mo2-Mo6 4.443(2) Å

As is shown in Fig. 2, the $[\beta\text{-}H_4PtMo_6O_{24}]^{4-}$ polyanion structure and its polyhedra model, unlike the α-isomer, is not planar. The polyhedra model of this anion has not only edge sharing but also corner sharing between octahedra of $Mo2O_6$-$Mo6O_6$ and $Mo1O_6$-$Mo5O_6$. Od is a four coordinated oxygen atom surrounded by a Pt and three Mo atoms, that is, it is the center of corner sharing, and Ob* is the bridging atom between the Pt and Mo atoms. The skeleton of the anion is the same as that of $[Mo_7O_{24}]^{6-}$ 3) having approximate 2mm symmetry the "central" molybdenum atom lying on both of the mirror planes is replaced by platinum(IV). From comparison of Mo-O bond distances, as made in the case of α-isomer, it was deduced that Oc21, Oc22, Ob15, and Ob19 atoms are protonated. A unit cell contains two polyanions forming a pair with a center of symmetry by four hydrogen-bonds, two Ob19-Ob18 2.83(2) Å and two Oc22H-Ot7 2.64(2) Å. The bond distances of protonated Mo-Ob and Mo-Oc are longer than those of Mo-Ob and Mo-Od which are not protonated, respectively. Even if consider that Ob^* is protonated, the bond distances of $\mathrm{Mo\text{-}Ob}^*$ are abnormally long. As a result, $\mathrm{Mo3O_6}$ and $\mathrm{Mo4O_6}$ octahedra are more distorted than another $\mathrm{MoO_6}$ octahedra. $\mathrm{PtO_6}$ octahedron of β-isomer is more distorted than that of α-isomer, but Pt-O bond distances of both isomer are the same. It seems that the formation of β-isomer needs to the considerable distortion of $\mathrm{Mo3O_3}$, $\mathrm{Mo4O_6}$, and $\mathrm{PtO_6}$ octahedra.

It is well-known that in the structure of polymetallate anions, $\mathrm{WO_6}$ octahedra are have been always found less deformed than $\mathrm{MoO_6}$, this "rigid" character of $\mathrm{WO_6}$ may explain why only Anderson structures have been found in the tungsten homologues, $\mathrm{Na_5[H_3PtW_6O_{24}]\cdot 20H_2O}$ 4) and $\mathrm{Na_2K_6[PtW_6O_{24}]\cdot 12H_2O}$. 5)

Now we are planning to measured $^{195}\mathrm{Pt}$ NMR of hexamolybdo-platinate(IV) solutions in order to confirm the presence of α- and β-isomer species.

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