

Geometrical Isomerism of Hexamolybdoplatinate (IV) Polyanion. Crystal Structure of $(\text{NH}_4)_{4.5}\text{H}_{3.5}[\alpha\text{-PtMo}_6\text{O}_{24}]\cdot 1.5\text{H}_2\text{O}$

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Hexamolybdo- and hexatungstoheteropolyanions are typical heteropolyoxometalate and are generally known as the "Anderson structure". Anderson structure heteropolyanion is able to have two isomeric forms such as planar structure (D_{3d} symmetry and α -isomer) and bent structure (C_{2v} symmetry and β -isomer). The first example of α - β geometric isomerism in the Anderson structure heteropolyanion was reported at $[\text{PtMo}_6\text{O}_{24}]^{8-}$ system.¹

Recently, I have found that another species of α -hexamolybdoplatinate polyanion, $\text{H}_{3.5}[\alpha\text{-PtMo}_6\text{O}_{24}]^{8-}$ can be obtained from the result of crystal structure determination of hexamolybdoplatinate salt separated at pH ca. 6.4, and α - β - α isomerization of $[\text{PtMo}_6\text{O}_{24}]^{8-}$ polyanion occurs by the change of only 0.5 hydrogen atom of polyanion.

The single crystals were obtained by mixing $(\text{NH}_4)_2[\text{Pt}(\text{OH})_6]$ and $(\text{NH}_4)_6[\text{Mo}_7\text{O}_{24}]$ aqueous solutions in the molar ratio Pt:Mo = 1:6 and by adjusting the pH to 6.4 with dilute nitric acid. Crystal data: $(\text{NH}_4)_{4.5}\text{H}_{3.5}[\alpha\text{-PtMo}_6\text{O}_{24}]\cdot 1.5\text{H}_2\text{O}$, F.W = 1266.23, monoclinic, space group $A_{2/a}$, $a = 19.074(3)$, $b = 21.490(3)$, $c = 15.183(2)$ Å, $\beta = 109.67(1)^\circ$, $U = 5860(2)\text{Å}^3$, $Z = 8$, $D_c = 2.871\text{g/cm}^3$, $\text{MoK}\alpha$ radiation (graphite monochromator, $\lambda = 0.7107$ Å), $\mu(\text{MoK}\alpha) = 75.36/\text{cm}$.

Intensities (5571 with $I \geq 4\sigma(I)$) 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. The phase of Pt atom was determined by the Harker plane and line of the $A_{2/a}$ space group. Refinement was made to $R = 0.075$ ($R_w = 0.076$) by block diagonal least square with anisotropic-thermal parameter for all atoms. The structure of $\text{H}_{3.5}[\alpha\text{-PtMo}_6\text{O}_{24}]^{8-}$ polyanion is shown in Figure 1 with pertinent average interatomic distances given in the caption. In $(\text{NH}_4)_{4.5}\text{H}_{3.5}[\alpha\text{-PtMo}_6\text{O}_{24}]\cdot 1.5\text{H}_2\text{O}$ crystal, typical Anderson structure ions were found as dimer, $[\text{H}_7(\alpha\text{-PtMo}_6\text{O}_{24})_2]^{9-}$. Dimerization is caused by strong seven hydrogen bonds formed between two anions, as shown in Figure 2. The polyanion of counter part is obtained from the $(-x, 1/2-y, 1/2-z)$ symmetry operation of original polyanion. The protonated oxygen atoms are determined by bond distances of Mo-O (see Figure 1 caption.) and hydrogen-bonding between two polyanions. These protonated three Oc and one Ob atoms are placed on the same side of the polyanion and all of four hydrogen atoms contribute to the formation of hydrogen bonds. Here by, two polyanions are very effectively formed for short and strong seven hydrogen bonds. The hydrogen atom forming Oc3-Oc3 hydrogen-bonding is bound to Oc3 with positional disorder as the same case of $\text{H}_{5.5}[\text{PtW}_6\text{O}_{24}]^{8-}$ polyanion.² Therefore, the number of hydrogen atom is 3.5 per one molecule. The half integral number of the ammonium cations and water molecules are caused by the place on the special position of half multiplicity at $A_{2/a}$ space group.

The α - β - α isomerism of $[\text{PtMo}_6\text{O}_{24}]^{8-}$ polyanion is shown

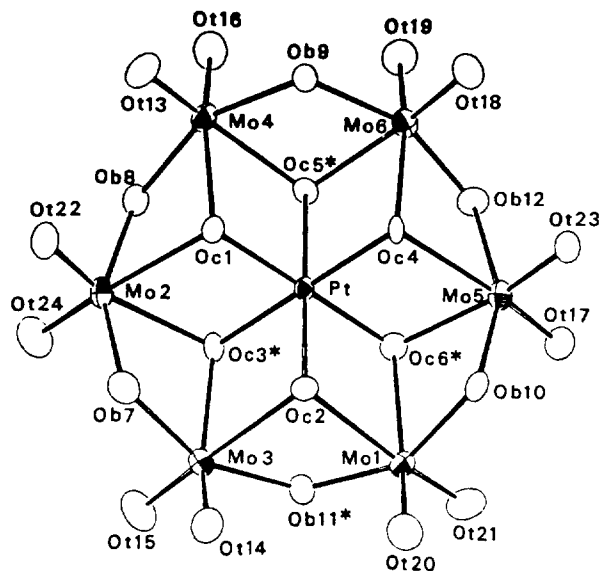


Figure 1. The structure of $\text{H}_{3.5}[\alpha\text{-PtMo}_6\text{O}_{24}]^{8-}$ anion (H atoms not shown, Oc; center O atom, Ob; bridge O atom, Ot; terminal O atom, *; protonated O atom.).

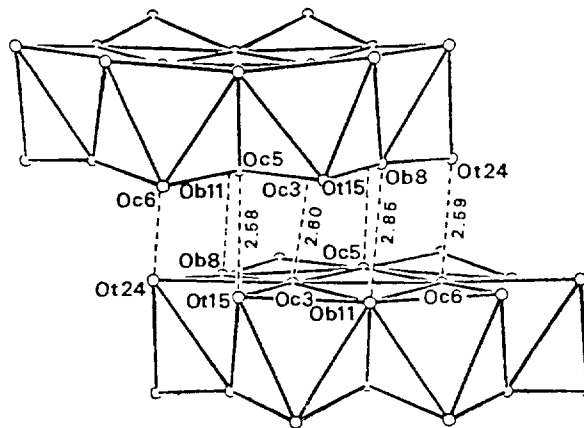


Figure 2. Interanion hydrogen bonds between polyanions. Distances in Angstroms.

graphically in Figure 3. The hexamolybdopolyanions having heteroatom with the higher oxidation state such as $[\text{Te}^{\text{VI}}\text{Mo}_6\text{O}_{24}]^{6-3}$ and $[\text{I}^{\text{VII}}\text{Mo}_6\text{O}_{24}]^{5-4}$ do not contain hydrogen atom. But, the one with lower oxidation state carries six non acidic protons attached to the oxygens of the central XO_6 octahedron such as $[\text{Cr}^{\text{III}}(\text{OH})_6\text{Mo}_6\text{O}_{18}]^{3-5}$ and $[\text{Co}^{\text{III}}(\text{OH})_6\text{Mo}_6\text{O}_{18}]^{3-6}$. As shown in Figure 3, the hydrogen atom of the \blacktriangle marked O atom in $\text{H}_{4.5}[\alpha\text{-PtMo}_6\text{O}_{24}]^{8-}$ polyanion is acidic hy-

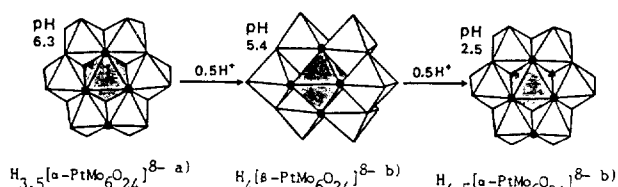


Figure 3. The $\alpha\rightarrow\beta\rightarrow\alpha$ isomerism by protonation of $[\text{PtMo}_6\text{O}_{24}]^{8-}$ anion shown as polyhedra model. a) Present work. b) Reference 1. ●: Protonated O atom. ▲: Protonated O atom by acidic H atom. ■: Only a half protonated O atom in disorder.

drogen atom. It is very difficult to explain clearly that the isomerization occurs in the $[\text{PtMo}_6\text{O}_{24}]^{8-}$ polyanion. However, it seems that the gradual protonation of polyanion plays an important role in that isomerism. The $\alpha\rightarrow\beta\rightarrow\alpha$ isomerism of hexa-

molybdoplatinate(IV) polyanion, $[\text{PtMo}_6\text{O}_{24}]^{8-}$ is the first example of isomerism caused by protonation in the heteropolyoxometalate.

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Photoreactions of Quinonoid Compounds with Alkynes and Cyclic Olefins

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The photochemical reactions of p-quinones to olefins have been reported as a widely-applicable reaction.¹⁻⁵ Photodimerization of p-benzoquinone (p-BQ) and some of its methyl derivatives give either cyclobutanes or spiro-oxetanes depending on the nature of the quinone. The photoaddition of diphenyl acetylene (DPA) to p-BQ forms a quinone methide (2,3), probably through an unstable intermediate, spiro-oxetane(1).¹⁻⁴

We recently reported that tetrachloro-p-benzoquinone (chloranil) readily forms a novel photorearrangement product by the reaction with some cyclic olefins, such as cyclohexene, 1,3-cyclohexadiene and cycloheptatriene.⁶ By contrast, irradiation of a solution of p-BQ and 1,3-cyclohexadiene in benzene yielded a Diels-Alder reaction product, which was found to be 1:1 adduct reacted at C=C double bond of p-BQ. In connection with our continuous studies toward the photoreactions of p-quinone derivatives with alkynes, we now report that irradiation of quinonoid compounds and DPA in dichloromethane gives the same type of photoadduct (4,5,8 and 9) as a major product. Irradiation was carried out in a cylindrical water-cooled Pyrex glass reaction vessels with 350 nm UV light (The Southern New England Ultraviolet Company). The photoproducts were isolated by column chromatography (silica gel) using n-hexane-diethyl ether-dichloromethane (4:1:1, v/v) as an eluting solvent. The structure for the photoproducts was identified by the mass spectra (electron impact method), ¹H-NMR, IR, UV, and fluorescence spectra. The 1:1 adduct from p-BQ and cyclopentadiene reacts with DPA giving 5. The mass spectrum (EI, 70 eV) shows a peak at m/e 286 (M-C₅H₆). The peaks at m/e 105 (100%) and 77 prove the existence of benzoyl group. The IR spectrum shows two C=O stretching bands at 1675 and 1668

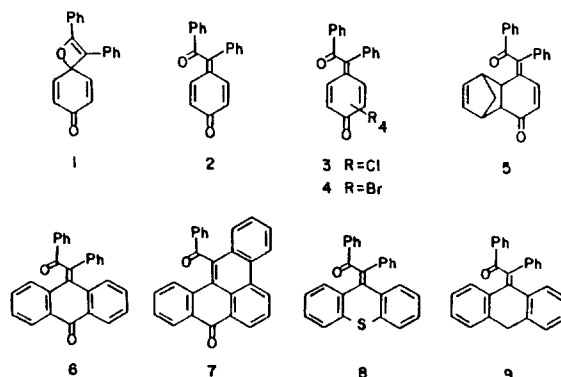


Figure 1. Photoproducts of the quinonoid compounds and 1,4-diphenylacetylene.

cm^{-1} . The two kinds of vinyl protons appear at 6.45 ppm (d. of d.) and 6.22 ppm (d. of d.) in ¹H-NMR spectrum (CDCl₃). On the other hand, the photochemical reaction of anthraquinone and DPA with 350 nm UV light afforded a photocyclization product(7), not 6. The structure of 7 was characterized by the following spectral data. The UV spectrum in methanol shows the different absorption bands in comparison with that of anthraquinone. The absorption bands of anthraquinone are observed at 324, 270, and 252 nm in methanol. The longest absorption band of 7 was shifted to 380 nm. This red shift results from the formation of phenanthrene moiety. The IR spectrum shows the presence of different carbonyl groups at 1660 and 1650 cm^{-1} . Mass spectrum (EI method) shows a parent ion peak at m/e 384, not at m/e 386. The base peak at m/e 105 is indicative of benzoyl group. Thioxanthone and