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Isomerization Behaviors of Hexamolybdoplatinate and Heptamolybdate Polyanions in the Aqueous Solution

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The planar structure (α-isomer)↔bent structure (β-isomer) isomerization of $[PtMo_6O_{24}]^{-8}$ and $[Mo_7O_{24}]^{-6}$ polyanions in solutions of various pH as investigated by reversed-phase high-performance liquid chromatography.

A recent report¹⁾ on the separation of a mixture of heteropolyoxometalates by reversed-phase HPLC was the new opening door for the solution chemistry of polyoxometalates. In this paper, the authors report about isomerization of $[PtMo_6O_{24}]^{-8}$ and $[Mo_7O_{24}]^{-6}$ polyanions in the aqueous solution.

Anderson-structure heteropolyanions, $[X^{+n}Mo_6O_{24}]^{-(12-n)}$ (X:heteroatom) showed two interesting behaviors in the crystal system. One is protonation of the polyanion, and the other is its geometrical isomerization. The hexamolybdopolyanions having heteroatom with higher oxidation states such as $[Te^{VI}Mo_6O_{24}]^{-6}$ 2) and $[I^{VII}Mo_6O_{24}]^{-5}$ 3) do not contain non-acidic hydrogen atom. But, the one with lower oxidation state carries six non-acidic protons attached to oxygen atoms in the central XO_6 octahedron such as $[Co^{III}(OH)_6Mo_6O_{18}]^{-3}$,4) $[Cr^{III}(OH)_6Mo_6O_{18}]^{-3}$,5) $[Cu^{II}(OH)_6Mo_6O_{18}]^{-4}$,6) and $[Al^{III}(OH)_6Mo_6O_{18}]^{-3}$ .7) Anderson-structure heteropolyanion is able to have isomeric forms such as planar (D3d symmetry and α-isomer) and bent (C2v symmetry and β-isomer) structures. The $[Pt^{IV}(OH)_4Mo_6O_{20}]^{-4}$ 8) and $[Sb^{V}(OH)_2Mo_6O_{22}]^{-5}$ 9) polyanions have bent structures, and their oxygen atoms of XO_6 were partly protonated. But, the heptamolybdate, $[Mo_7O_{24}]^{-6}$ polyanion10) showed the properties of bent structure and non-protonated polyanion regardless of high oxidation state of the central Mo atom. Especially, the $[PtMo_6O_{24}]^{-8}$ polyanion

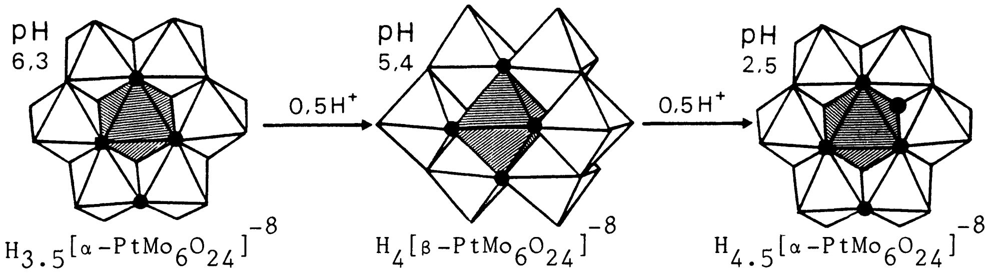


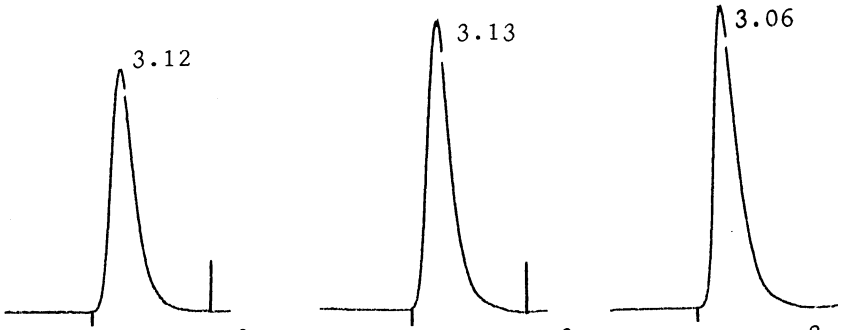
Fig. 1. The α→β→α isomerism by protonation of $[PtMo_6O_{24}]^{-8}$ polyanion shown as polyhedra model. ● : Protonated O atom. ■: Only a half protonated O atom in disorder.

causes α→β→α isomerization according to gradual protonation of the polyanion as shown in Fig. 1.

We expected that the retention time and the chromatographic shape of each structure would be different. And then, we investigated on the α→β isomeric behaviors of $[PtMo_6O_{24}]^{-8}$ and $[Mo_7O_{24}]^{-6}$ polyanions in solutions with various pHs by using reversed-phase HPLC.

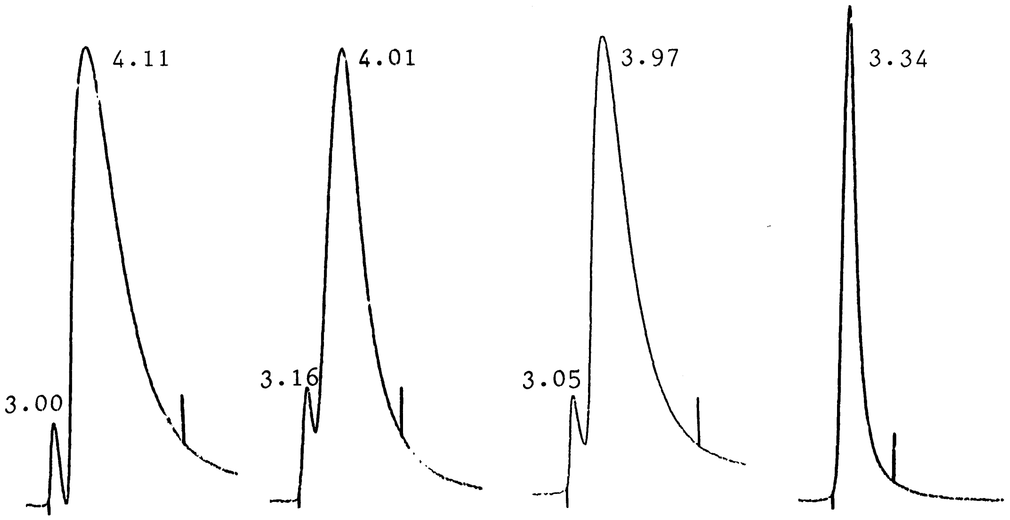
A Waters Associate liquid chromatographic system was used, which is consisted of M440 absorbance detector, M-45 solvent delivery system, and M-U6K universal injector. A 3.9 mm x 30 cm Waters μ-Bondapak C_{18} reversed-phase-column was also used. Chromatograms were recorded on Shimadzu graphic print PR-1. The detection wavelength was selected as 254 and 280 nm. The chart speed was 1.0 cm/min and the flow rate of eluent was 0.9 ml/min . Chromatographic separation was carried out at room temperature. The hexamolybdo heteropolyoxometalates used in this work were synthesized in this laboratory, except for ammonium heptamolybdate which was obtained commercially(Wako). Injection samples were used as a twice-diluted saturated solution. Buffer solution (pH range 3.7 - 5.6) made by 0.2 M CH_3COOH - 0.2 M CH_3COONa solutions were used as each eluent. The eluents with pHs beyond the buffer range were obtained by adding NaOH or HCl to the buffer solution. The pHs of each sample solution were adjusted before injection to the same pH values of the eluent.

Figure 2 showed the chromatogram of the polyanion having a typical planar structure. The elution peaks were close to single Gaussian shape. Figure 3 showed the chromatograms of the $[Mo_7O_{24}]^{-6}$ polyanion having bent structure at various pHs. The retention data of polyanions are shown in Table 1. The chromatogram of $[PtMo_6O_{24}]^{-8}$ polyanion was obtained at an interval of about 0.25 pH unit. The retention time of typical planar structure polyanions showed 2.92 - 3.15 min at vari-



Sample ion	$[Al(OH)_6Mo_6O_{18}]^{-3}$	$[Cr(OH)_6Mo_6O_{18}]^{-3}$	$[PtMo_6O_{24}]^{-8}$
Eluent pH	4.79	4.52	5.00
λ (nm)	280	254	280

Fig.2. Chromatograms of planar structure polyanions. Top number is retention time (min). Chart speed is 3.0 cm/min .



Eluent pH	3.49	3.99	4.45	5.49

Fig. 3. The chromatograms of $[Mo_7O_{24}]^{-6}$ polyanion at various eluent pHs. Top number is retention time (min). Chart speed is 1.0 cm/min. λ = 254 nm.

ety of pH range. The appearances of chromatograms of $[PtMo_6O_{24}]^{-8}$ polyanion were the same as those of $[Al(OH)_6Mo_6O_{18}]^{-3}$ and $[Cr(OH)_6Mo_6O_{18}]^{-3}$, and the retention time (2.92 - 3.14 min) was obtained at a pH 4.25 - 6.51 range. Therefore, it seems that the $[PtMo_6O_{24}]^{-8}$ polyanion always has a planar structure in aqueous solution. On the other hand, the peaks of $[Mo_7O_{24}]^{-6}$ polyanions were separated into smaller (t_R : 3.00 - 3.16) and larger (t_R : 3.44 - 4.11) peaks at below pH 5.05. But, only one peak (t_R : 3.15 - 3.34) was observed at above pH 5.49 as shown in Fig. 3. The retention times of the smaller peaks were similar to that of the corresponding planar structure sample. Judging from the retention time, it seems that the smaller

Table 1. The retention data of polyanions at various pH range

Sample ion	Eluent pH	t_R/min	Sample ion	Eluent pH	t_R/min	
$[Al(OH)_6Mo_6O_{18}]^{-3}$	3.55	3.10	$[Cr(OH)_6Mo_6O_{18}]^{-3}$	3.52	3.14	
	4.79	3.12		4.52	3.13	
	5.75	3.10		5.75	3.15	
$[PtMo_6O_{24}]^{-8}$	4.25	2.92	$[Mo_7O_{24}]^{-6}$	3.49	3.00	4.11
	4.51	2.95		3.99	3.16	4.01
	4.74	3.00		4.45	3.05	3.97
	5.00	3.06		5.05	3.13	3.44
	5.25	3.09		5.49	3.34	
	5.50	3.10		5.93	3.24	
	5.78	3.09		6.19	3.19	
	6.00	3.14		7.06	3.15	
	6.25	3.10				
	6.51	3.09				

peak is responsible for the planar structure polyanion and the larger peak is for the bent structure polyanion. As a result, we confirmed that the bent structure $\rightleftarrows$ planar structure equilibrium of $[Mo_7O_{24}]^{-6}$ polyanion in aqueous solution existed at pH lower than ca. 5.05 and the planar structure exists only at pH 5.49 or higher. But, the ammonium heptamolybdate salt obtained at ca. pH 10 was shown to have a typtypical bent structure by IR spectrum.

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References

1) A. D. Kirk, W. Riske, D. K. Lyon, B. Rapko, and R. G. Finke, Inorg. Chem., 28, 792 (1989).
2) H. T. Evans, Jr., Acta Crystallogr., Sect. B, 30, 2095 (1974).
3) H. Kondo, A. Kobayashi, and Y. Sasaki, Acta Crystallogr., Sect. B, 36, 661 (1980).
4) O. Nagano, Ph. D. Thesis, The University of Tokyo, Tokyo (1980).
5) A. Perloff, Inorg. Chem., 9, 2228 (1970).
6) F. Ito, MS Thesis, The University of Tokyo, Tokyo (1988).
7) H. Y. Lee, MS Thesis, National Fisheries University of Pusan, Pusan, Korea (1989).
8) U. Lee and Y. sasaki, Chem. Lett., 1984 1297; U. Lee, Bull. Korean Chem. Soc., 9, 256 (1988).
9) A. Ogawa, H. Yamato, U. Lee, H. Ichida, A. Kobayashi, and Y. Sasaki, Acta Crystallogr., Sect. C, 44, 1879 (1988).
10) I. Lindqvist, Arkiv. Kemi., 2, 323 (1959).

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