DAEHAN HWAHAK HWOEJEE
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단 신

Hemipentapotassium Hemiundecahydrogen Hexatungstoplatinate(IV) Dihydrate, $K_{2.5}[H_{5.5}PtW_6O_{24}]\cdot 2H_2O$의 결정구조

李 旭† · 佐佐木行美*
부산수산대학 응용화학과
*동경대학 이학부 화학과

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The Crystal Structure of Hemipentapotassium Hemiundecahydrogen Hexatungstoplatinate(IV) Dihydrate, $K_{2.5}[H_{5.5}PtW_6O_{24}]\cdot 2H_2O$

Uk Lee† and **Yukiyoshi Sasaki***
Department of Applied Chemistry, National Fisheries University of Pusan, Pusan 607, Korea
**Department of Chemistry, Faculty of Science, The University of Tokyo, Tokyo 113, Japan*

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The hexatungsto and hexamolybdohetero polyanions containing Pt(IV), such as $[PtW_6O_{24}]^{8-}$, $[H_3PtW_6O_{24}]^{5-}$ and $[H_{4.5}PtMo_6O_{24}]^{3.5-}$ are the typical Anderson-type polyanions.[4] Anderson-type polyanions are divided into two series, A and B. The A series are the nonprotonated polyanion, $[X^{n+}M_6O_{24}]^{(12-n)-}$ (X: heteroatom, M: Mo and W) and the B series are the protonated polyanion, $[H_6X^{n+}M_6O_{24}]^{(6-n)-}$. The hexatungsto- and hexamolybdoplatinate(IV) polyanions ars protonated gradually by decreasing the pH of the mother liquor.[2,3] This paper is a report of structural study for $K_{2.5}[H_{5.5}PtW_6O_{24}].2H_2O$ obtained at pH ca. 3.5. A synthetic method is same as described in the previous reports (potassium salt used).[1,2]

Crystal data: $K_{2.5}[H_{5.5}PtW_6O_{24}].2H_2O$, fw=1821.8, triclinic, $P\bar{1}$, a=11.443(2), b=13.674(1), c=11.427(2) Å, α=101.36(2), β=119.94(2), γ=843.5(2)° V=1519.0(4) Å^3, Z=2, D_c=3.98g/cm^3, μ(Mo Kα)=292.02cm^{-1}, λ=0.7107Å.

Intensities(5529 with $I\geq 3\sigma(I)$) were measured on a Rigaku four circle diffractometer and corrected for X-ray absorption effect. The structure was solved by conventional heavy atom methods and refined to R=0.14 by block-diagonal least-squares with anisotropic thermal parameters for Pt and W atoms, and isotropic thermal parameters for other atoms. Atomic parameters are listed in *Table* 1. The structure of $[H_{5.5}PtW_6O_{24}]^{2.5-}$ polyanion is shown in *Fig.* 1. Interatomic distances in the $[H_{5.5}PtW_6O_{24}]^{2.5-}$ polyanion are listed in *Table* 2. Oxygen in the polyanion are classified into O_c, O_b and O_t according to the coordination form. The stoichiometry of the potassium ions(2.5) and the hydrogen atoms(5.5) were established from the inspection of the electron density map and the elemental analysis data. The peak heights for the K_1, K_2 and K_4 ions were only half of that for K_3, indicating a half occupancy for each of the three K ions. The elemental analysis data on the K ions (calc. 5.4%, found 5.8%) were consistent with a total occupancy factor of 2.5. In order to maintain the charge balance, the number of the hydrogen atoms in the polyanion should be 5.5. The six protonated oxygen atoms

Table 1. Fractional coordinates

Atom	x	y	z
Pt	−0.0002(3)	0.1502(2)	0.2120(2)
W1	−0.3347(3)	0.1522(2)	0.0654(3)
W2	−0.1719(3)	−0.0562(2)	0.1282(2)
W3	−0.1616(3)	0.3669(2)	0.1648(3)
W4	0.1718(3)	−0.0563(2)	0.3002(2)
W5	0.1615(3)	0.3670(2)	0.3261(3)
W6	0.3349(3)	0.1520(2)	0.4002(3)
K1	0.0004(27)	0.3629(19)	−0.4352(26)
K2	−0.4246(36)	0.2961(26)	−0.2578(36)
K3	0.4643(15)	−0.0006(11)	−0.2677(15)
K4	0.4241(38)	0.2947(27)	0.1652(37)
O_c1	−0.1539(44)	0.2036(31)	0.0528(42)
O_c2	−0.0022(47)	0.0129(33)	0.1184(46)
O_c3	−0.1438(44)	0.1000(31)	0.2244(43)
O_c4	0.1561(47)	0.2031(34)	0.2140(46)
O_c5	0.0071(39)	0.2866(28)	0.3151(38)
O_c6	0.1512(50)	0.1013(35)	0.3818(49)
O_b7	0.0021(40)	−0.0769(28)	0.2931(39)
O_b8	−0.3064(48)	0.0172(34)	−0.0197(48)
O_b9	0.0048(54)	0.3928(39)	0.1678(53)
O_b10	0.2877(43)	0.0246(31)	0.2898(43)
O_b11	−0.2708(46)	0.2788(32)	0.1774(44)
O_b12	0.2696(52)	0.2855(37)	0.4537(51)
O_t13	0.2600(54)	−0.0861(39)	0.4598(54)
O_t14	0.4258(65)	0.1322(47)	0.5612(64)
O_t15	−0.2512(79)	−0.0963(57)	0.2079(79)
O_t16	0.1631(48)	−0.1653(34)	0.1808(47)
O_t17	−0.4377(56)	0.1879(40)	−0.0911(54)
O_t18	−0.1811(61)	−0.1658(44)	0.0075(60)
O_t19	−0.2632(72)	0.3949(51)	0.0041(71)
O_t20	−0.4400(74)	0.1220(54)	0.1235(74)
O_t21	−0.1483(65)	0.4697(47)	0.2921(65)
O_t22	0.2804(84)	0.4051(60)	0.2874(84)
O_t23	0.4540(106)	0.1982(77)	0.3808(107)
O_t24	0.1664(59)	0.4686(42)	0.4490(58)
Aq1	−0.0019(65)	0.1441(47)	0.5084(65)
Aq2	−0.0920(64)	0.4983(46)	0.0457(64)

(O_c1, O_c2, O_cA, O_b7, O_b8 and O_b9) were identified by inspectin the W–O distances and the hydrogen-bonding patterns. Mean distances of W–O_c and W–O_b are 2.18(6) Å and 1.88(6) Å, while mean distances of W–O_cH and W–O_bH are 2.32(5) Å and 1.98(6) Å, respectivity.

Table 2. Interatomic distance (Å) of $(H_{5.5}PtW_6O_{24})^{2.5-}$ polyanion

Pt–W* :	3.32(1)	Pt–O_c* :	1.98(4)
Pt–W1	3.326(4)	Pt–O_t1	2.00(5)
Pt–W2	3.300(4)	Pt–O_c2	1.96(5)
Pt–W3	3.323(4)	Pt–O_c3	1.92(5)
Pt–W4	3.303(4)	Pt–O_c4	1.98(5)
Pt–W5	3.325(4)	Pt–O_c5	1.99(5)
Pt–W6	3.331(4)	Pt–O_c6	2.04(6)
W–W* :	3.31(8)		
W1–W2	3.246(4)	W1–W3	3.379(5)
W2–W4	3.408(4)	W3–W5	3.204(5)
W4–W6	3.246(4)	W5–W6	3.385(5)
W–O_c* :	2.18(6)		
W1–O_c3	2.20(5)	W2–O_c3	2.18(5)
W3–O_c5	2.21(5)	W4–O_c6	2.21(6)
W5–O_c5	2.11(5)	W6–O_c6	2.18(6)
W–O_c* :	2.32(5)	(protonated oxygen atoms)	
W1–O_c1	2.33(5)	W2–O_c2	2.30(5)
W3–O_c1	2.36(5)	W4–O_c2	2.34(5)
W5–O_c4	2.34(5)	W6–O_c4	2.27(5)
W–O_b* :	1.88(6)		
W1–O_b11	1.90(5)	W3–O_b11	1.89(5)
W4–O_b10	1.87(5)	W5–O_b12	1.86(6)
W6–O_b12	1.89(6)	W6–O_b10	1.89(6)
W–O_b* :	1.98(6)	(protonated oxygen atoms)	
W1–O_b8	1.99(6)	W2–O_b7	1.99(5)
W2–O_b8	2.00(6)	W3–O_b9	1.96(6)
W4–O_b7	1.95(5)	W5–O_b9	1.97(5)
W–O_t* :	1.74(10)		
W1–O_t17	1.72(6)	W1–O_t20	1.75(9)
W2–O_t18	1.80(7)	W2–O_t15	1.75(9)
W3–O_t19	1.71(8)	W3–O_t21	1.77(8)
W4–O_t16	1.78(6)	W4–O_t13	1.70(6)
W5–O_t22	1.77(10)	W5–O_t24	1.75(7)
W6–O_t14	1.67(7)	W6–O_t23	1.74(12)

* : average value.

These values agree with those in the other protonated Anderson-type polyanions.[2,3,5] *Fig.* 2. shows the hydrogen bonding pattern in the structure. Two polyanions related by a center of symmetry form a pair through seven hydrogen bonds, namely, two O_cA–O_t18, two O_c1–O_t16, two O_b8–O_b10 and one O_c2–O_c2 hydrogen bonds. The last hydrogen bond is formed between two

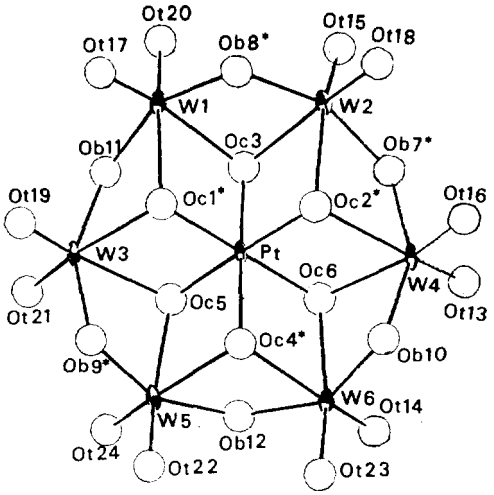

Fig. 1. The structure of $(H_{5.5}PtW_6O_{24})^{2.5-}$ polyanion H(atoms not shown, * : Protonated O atoms).

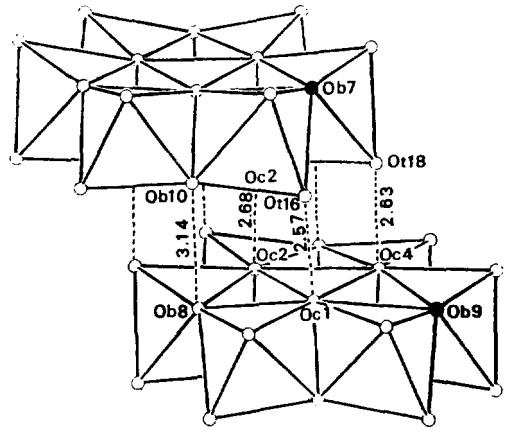

Fig. 2. Interanion hydrogen bonds between polyanions. (distances is Å unit).

O_c2 atoms related by a center of symmetry. A half occupancy of a hydrogen atom is caused by the O_c2-O_c2 hydrogen bond. It is probably that the hydrogen atom distributing to O_c2-O_c2 hydrogen bond is located at a center of symmetry (multiplicity: 1/2) of the $P\bar{1}$ space group, or attached to the O_c2 oxygen atom in positional disorder. But as considering bond distance of O_c2-O_c2 (2.68 Å), we assume that bonding in positional disorder is more reasonable than locating at a center of symmetry. Hydrogen atoms of O_b7 and O_b9 are not involved in the hydrogen bond.

The polyanion in this study is the most protonated form and the first example having the protonated O_b atoms among the hexatungstohetero polyanions studied thus far. This polyanion is not the B series Anderson-type polyanion, since all hydrogen atoms are bound to the O_c atoms in the B series Anderson-type polyanion.

$\alpha(\bar{3}m)\rightarrow\beta(2mm)$ isomerism in the hexamolybdoplatinate(IV) polyanion is occured by protonation of polyanion.[3] However, we could not seperate the isomer in the hexatungstoplatinate (IV) polyanion at pH range of ca. 3.5~7.5.

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