May, 1992] *Bull. Chem. Soc. Jpn.*, ***65,*** *1453—1459 (1992)* 1453

^{183}W NMR and X-Ray Crystallographic Studies on the Peroxo Complexes of the Ti-Substituted α-Keggin Typed Tungstophosphates

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(Received February 4, 1992)

Peroxo complexes prepared by the reaction of titanoundecatungstophosphate ($PTiW_{11}O_{40}^{5-}$) and dititanodecatungstophosphate ($PTi_2W_{10}O_{40}^{7-}$) with hydrogen peroxide are characterized by means of the ^{183}W NMR spectroscopy and the single crystal X-ray diffractometry. Electronic spectra and permanganate titration analyses indicated that one peroxo ligand attaches to the $PTiW_{11}O_{40}^{5-}$ anion and two peroxo ligands attach to the $PTi_2W_{10}O_{40}^{7-}$ anion. ^{183}W NMR spectra showed that the C_s symmetry of the $PTiW_{11}O_{40}^{5-}$ anion and the C_2 symmetry of the $PTi_2W_{10}O_{40}^{7-}$ anion are retained in the respective peroxo derivatives. Single crystal X-ray structures of the diisopropyl ammonium salt of $PTiW_{11}O_{40}^{5-}$, the diisopropyl ammonium salt of $PTiW_{11}O_{39}(O_2)^{5-}$ and the isopropyl ammonium salt of $PTi_2W_{10}O_{38}(O_2)_2^{7-}$ indicated that the peroxo anions retain the α-Keggin structures of their parent anions. It was inferred that the peroxo ligands are substituted for the terminal oxygen atom at the TiO_6 octahedra with the side-on format.

Polyoxotungstates or molybdates of the Keggin structure with transition metal atoms such as Ti or V partially substituted for the addenda W or Mo atoms have attracted increasing interest because the transition metal atoms introduced into the Keggin polyoxoanions provide the parent polyoxoanions with novel properties such as i) the enhanced catalytic reactivity,[1—3] ii) the reaction site where the organometallic moieties attach to the polyoxoanions,[4,5] and iii) the stabilization of the new isomer which was not found for the non-substituted species.[6] Among the various substituted Keggin polyoxoanions, our attention has been focused on the Keggin type of Ti/W mixed polyoxoanion of $PTi_2W_{10}O_{40}^{7-}$, which catalyzes the photoreduction of CO_2 to CH_4[2] and inhibits the proliferation of Herpes simplex virus and human immunodeficiency virus type 1.[7] The structure of $PTi_2W_{10}O_{40}^{7-}$ was first proposed using ^{183}W NMR spectroscopy[4] and confirmed by X-ray crystallography.[8] We found that the reaction of $PTiW_{11}O_{40}^{5-}$ (**1**) with hydrogen peroxide gives the peroxo anion of $PTiW_{11}O_{39}(O_2)^{5-}$ (**2**) and that $PTi_2W_{10}O_{40}^{7-}$(**3**) reacts with hydrogen peroxide to give the peroxo anion of $PTi_2W_{10}O_{38}(O_2)_2^{7-}$ (**4**). In this paper, we report the structure analyses of **2** and **4**. These peroxo anions are the first Keggin XM_{12} typed peroxoheteropolyoxotungstates fully characterized by the ^{183}W NMR spectroscopy and the single crystal X-ray crystallography.

Experimental

Preparations. $[(iso\text{-}C_3H_7)_2NH_2]_5[PTiW_{11}O_{40}]\cdot 4H_2O$: Colorless crystals of $[(iso\text{-}C_3H_7)_2NH_2]_5[PTiW_{11}O_{40}]\cdot 4H_2O$ were obtained by adding 15 g of $(iso\text{-}C_3H_7)_2NH\cdot HCl$ to the 250 ml aqueous solution of $Li_5PTiW_{11}O_{40}$.[4] Found: C, 10.76; N, 2.16; H, 2,88%. Calcd for $C_{30}H_{88}N_5O_{44}TiW_{11}P$: C, 10.84; N, 2.11; H, 2.67%.

$[(i\text{-}C_3H_7)_2NH_2]_5[PTiW_{11}O_{39}(O_2)]\cdot 4H_2O$: To the 10 ml aqueous solution dissolving 0.3 g of $[(iso\text{-}C_3H_7)_2NH_2]_5[PTiW_{11}O_{40}]\cdot 4H_2O$, 0.4 ml of 30% hydrogen peroxide was added. The orange crystals of $[(iso\text{-}C_3H_7)_2NH_2]_5[PTiW_{11}O_{39}(O_2)]\cdot 4H_2O$ were obtained after a few days. Found: C, 10.82; N, 2.06; H, 2.73; O_2^{2-}, 0.96%. Calcd for $C_{30}H_{88}N_5O_{45}TiW_{11}P$: C, 10.79; N, 2.10; H, 2.66; O_2^{2-}, 0.96%.

$(i\text{-}C_3H_7NH_3)_6H[PTi_2W_{10}O_{38}(O_2)_2]\cdot H_2O$: To the 20 ml of 0.1 M CH_3COOH/CH_3COOLi buffer ($1M=1\ mol\ dm^{-3}$) at pH 6.1 dissolving 1.6 g of $K_7[PTi_2W_{10}O_{40}]\cdot 6H_2O$,[5] 0.8 ml of 30% hydrogen peroxide was added. After a few minutes when the color of the solution turned to yellow, 1.0 g of $iso\text{-}C_3H_7NH_2\cdot HCl$ was added. The orange crystals of $(iso\text{-}C_3H_7NH_3)_6H[PTi_2W_{10}O_{38}(O_2)_2]\cdot H_2O$ were obtained after several days. Found: C, 6.96; H, 2.09; N, 2.65; O_2^{2-}, 2.15%. Calcd for $C_{18}H_{63}N_6O_{43}Ti_2W_{10}P$: C, 7.16; H, 2.08; N, 2.79; O_2^{2-}, 2.12%.

Sample Solutions for the ^{183}W NMR Measurements: Li salt of **1** was obtained by passing the aqueous solution of $[(iso\text{-}C_3H_7)_2NH_2]_5[PTiW_{11}O_{40}]\cdot 4H_2O$ through the Li^+ form of the ion exchange resin and evaporating it to dryness. 2.0 g of the Li salt of **1** was dissolved with 1.0 ml of D_2O and used for the ^{183}W NMR measurement. The sample solution for **2** was prepared by dissolving 2.5 g of the Li salt of **1** with 1.0 ml of D_2O and 0.25 ml of 30% hydrogen peroxide. The sample solution for **4** was prepared by dissolving 5 g of hydrated $Li_7PTi_2W_{10}O_{40}$[5] to the mixture of 2.5 ml of D_2O and 0.5 ml of 30% hydrogen peroxide. After the measurements, the sample solutions were precipitated as a Cs salt by adding CsCl. The permanganate titration showed that the precipitates obtained from the sample solutions for **2** and **4** contain one and two equivalents of peroxide ligands, respectively.

Spectroscopy. ^{183}W NMR spectra were recorded on a JEOL GX500 spectrometer using 10 mm diameter NMR tube. ^{183}W NMR chemical shifts were referenced to the external 2 M Na_2WO_4 in D_2O. The electronic spectra were recorded on a Hitachi 330 spectrometer. The spectroscopic data were summarized in Table 1.

X-Ray Structure Analyses. All the calculations were carried out on a micro VAX II computer using the TEXSAN[9] software package. The complex atomic scattering factors were taken from Ref. 10. Crystal data and experimental conditions are listed in Table 2.

$[(i\text{-}C_3H_7)_2NH_2]_5[PTiW_{11}O_{40}]\cdot 4H_2O$: The intensity data were collected on a Rigaku AFC5 diffractometer with the graphite

Table 1. ^{183}W and ^{31}P Chemical Shifts and Electronic Spectra for Compounds **1**—**4**

Compound	δ (^{183}W) in ppm	δ (^{31}P) in ppm	Electronic spectra[a]
1	−70.27 −103.69 −111.59 −116.48 −118.77 −126.68	−13.61	262 (ε=43600)
2	−84.59 −103.92 −110.04 −118.71 −127.64 −134.15	−13.37	262 (ε=42700) 390 (ε=2160)
3	−73.47 −112.03 −123.46 −125.60 −143.13	−11.87	252 (ε=36300)
4	−81.40 −122.34 −127.72 −139.84 −157.21	−12.44	252 (ε=38900) 360 (ε=3990)

a) Absorption maxima in nm and molar absorption coefficients in M^{-1} cm^{-1} in parentheses.

Table 2. Crystal Data and Experimental Conditions

	$[(i\text{-}C_3H_7)_2NH_2]_5$ $[PTiW_{11}O_{40}]\cdot 4H_2O$	$[(i\text{-}C_3H_7)_2NH_2]_5$ $[PTiW_{11}O_{39}(O_2)]\cdot 4H_2O$	$(i\text{-}C_3H_7NH_3)_6H$ $[PTi_2W_{10}O_{38}(O_2)_2]\cdot H_2O$
Formula weight	3324.3	3340.3	3017.0
Space group	$P2_1/n$	$P2_1/n$	Cm
a/Å	24.044(5)	24.107(4)	12.67(1)
b/Å	13.177(1)	13.215(2)	19.32(1)
c/Å	23.809(4)	23.832(4)	11.617(6)
β/°	105.25(2)	105.25(1)	99.51(6)
V/Å^3	7277(4)	7325(4)	2806(4)
Z	4	4	2
μ (Mo $K\alpha$)/cm^{-1}	179.0	177.8	212.5
A	0.156—0.687	0.041—0.207	0.028—0.201
D_x/Mg m^{-3}	3.15	3.15	3.51
Crystal size/mm	0.02×0.12×0.14	0.09×0.20×0.50	0.08×0.22×0.27
Number of reflections for cell parameters	22	22	20
2θ range for cell parameters	22°—25°	22°—25°	22°—26°
Number of measured reflections	22573	10416	8497
Number of observed reflections	7151	6957	6030
Criterion for observed	$I>3\sigma(I)$	$I>3\sigma(I)$	$I>3\sigma(I)$
2θ range	5°—60°	5°—45°	5°—60°
Range of indices	$-34\leq h\leq 34$ $0\leq k\leq 19$ $0\leq l\leq 34$	$0\leq h\leq 27$ $0\leq k\leq 16$ $-27\leq l\leq 27$	$0\leq h\leq 19$ $-27\leq k\leq 27$ $-18\leq l\leq 18$
Scan mode	$2\theta/\omega$	$2\theta/\omega$	$2\theta/\omega$
Scan speed (ω)/° min^{-1}	6	4	8
Number of parameters	434	362	206
R	0.066	0.073	0.057
wR	0.055	0.063	0.064
S	1.69	4.55	1.73
$(\Delta/\sigma)_{max}$	0.14	0.73	0.20
$(\Delta\rho)_{min}$/eÅ^{-3}	−4.2	−3.7	−4.6
$(\Delta\rho)_{max}$/eÅ^{-3}	3.6	4.2	2.9

monochromatized Mo $K\alpha$ radiation (λ=0.71069 Å) generated at 50 kV, 20 mA. Lorentz-polarization and absorption[11] corrections were applied. Heavy atom positions were obtained by the direct method using MITHRIL.[12] The succeeding least-squares and difference syntheses cycles located the remaining non-hydrogen atoms. The refinement was based on F using the full-matrix least-squares with the weighting scheme of $w^{-1}=\sigma^2(F)$. The anion is orientationally disordered and the positions of the Ti atom was not identified. All the 12 metal atoms were refined as W atoms. Anisotropic temperature factors were applied to the 12 metal atoms and the P atom. One of the five diisopropyl ammonium cation is disordered and their positional parameters could not be refined. A common isotropic temperature factor was applied to the seven atoms in the cation. Atomic parameters are listed in Table 3.[13]

$[(i\text{-}C_3H_7)_2NH_2]_5[PTiW_{11}O_{39}(O_2)]\cdot 4H_2O$: The intensity data were collected on a Rigaku AFC5 diffractometer with the graphite monochromatized Mo $K\alpha$ radiation (λ=0.71069 Å) generated at 50 kV, 20 mA. They were collected in two shells with 2θ from 5° to 45° and from 45° to 55°. During the colllection of the second shell with $45°<2\theta<55°$, the intensities of the standard reflections dropped to less than half of their initial values. We stopped the data collection and checked the diffractometer setting angles, finding that the cell parameters changed to a=24.025 (9), b=13.181 (5), c=23.837 (9) Å, β=105.30 (3)°, and V=7281 (5) Å^3. The color of the crystal had changed from orange to white. Therefore we used the data from the first shell with $5°<2\theta<45°$ only. The intensities of the standard reflections were 88% of their initial values in I when the collection of the first shell was completed. No correction for the decay effect was applied. Lorentz-polarization and absorption[11] corrections were applied. Heavy atom positions were obtained by the direct method using MITHRIL.[12] Other atoms were located from the difference Fourier map, but two carbon atoms in the diisopropyl

Table 3. Fractional Coordinates and Equivalent or Isotropic Thermal Parameters (Å^2) for $[(i\text{-}C_3H_7)_2NH_2]_5\,[PTiW_{11}O_{40}]\cdot 4H_2O$

Atom	x	y	z	$B_{eq}$$^{a)}$/$B_{iso}$	Atom	x	y	z	B_{iso}
W(1)	0.43507(7)	0.4221(1)	0.74304(6)	2.15	O_d(6)	0.6716(9)	0.076(1)	0.6760(8)	1.5(4)
W(2)	0.54854(8)	0.3506(1)	0.67174(7)	3.14	O_d(7)	0.721(1)	0.145(2)	0.8868(8)	2.3(5)
W(3)	0.58661(6)	0.4026(1)	0.82958(6)	1.77	O_d(8)	0.553(1)	0.249(2)	0.9925(9)	2.7(5)
W(4)	0.35951(8)	0.2072(1)	0.68940(7)	3.27	O_d(9)	0.349(1)	0.275(2)	0.8792(8)	2.2(5)
W(5)	0.47273(7)	0.1391(1)	0.61707(6)	2.40	O_d(10)	0.390(1)	−0.136(2)	0.6778(8)	2.7(5)
W(6)	0.61298(7)	0.1167(1)	0.69696(6)	1.99	O_d(11)	0.611(1)	−0.166(2)	0.8134(8)	1.9(4)
W(7)	0.65175(6)	0.1694(1)	0.85568(6)	1.84	O_d(12)	0.438(1)	−0.061(2)	0.9112(8)	2.2(5)
W(8)	0.54644(7)	0.2349(1)	0.92143(5)	1.89	O_w(1)	0.578(1)	0.072(2)	0.517(1)	6.4(8)
W(9)	0.39383(7)	0.2588(1)	0.83501(6)	2.14	O_w(2)	0.659(1)	0.095(3)	0.451(1)	8.(1)
W(10)	0.42942(7)	−0.0437(1)	0.71588(6)	2.19	O_w(3)	0.797(1)	0.165(2)	0.669(1)	7.4(9)
W(11)	0.56929(6)	−0.0620(1)	0.79756(6)	1.69	O_w(4)	0.667(2)	0.105(3)	0.045(1)	8.(1)
W(12)	0.46248(7)	0.0059(1)	0.86192(6)	1.83	N(1)	0.982(1)	0.251(2)	0.573(1)	2.6(6)
P	0.5060(4)	0.1841(7)	0.7699(4)	1.4	C(1)	0.925(2)	0.242(3)	0.527(1)	3.5(8)
O_a(1)	0.4499(9)	0.240(1)	0.7618(7)	1.5(4)	C(2)	0.877(2)	0.216(3)	0.547(2)	5.(1)
O_a(2)	0.5243(8)	0.194(1)	0.7136(7)	1.2(4)	C(3)	0.917(2)	0.353(3)	0.504(1)	3.2(8)
O_a(3)	0.5540(8)	0.231(1)	0.8224(7)	0.6(3)	C(4)	1.004(2)	0.156(3)	0.612(1)	3.4(8)
O_a(4)	0.4964(8)	0.071(1)	0.7808(7)	0.8(4)	C(5)	1.062(2)	0.183(3)	0.650(1)	3.3(8)
O_b(1)	0.371(1)	0.356(2)	0.6920(8)	2.1(4)	C(6)	1.006(2)	0.070(3)	0.570(2)	4.(1)
O_b(2)	0.5035(8)	0.269(1)	0.6090(7)	1.4(4)	N(2)	0.759(2)	0.050(3)	0.136(1)	6.(1)
O_b(3)	0.6118(8)	0.254(1)	0.6717(7)	1.2(4)	C(7)	0.794(2)	−0.025(4)	0.115(2)	6.(1)
O_b(4)	0.651(1)	0.316(2)	0.8511(8)	2.1(4)	C(8)	0.749(3)	−0.122(4)	0.088(2)	10.(2)
O_b(5)	0.572(1)	0.363(2)	0.9023(9)	2.7(5)	C(9)	0.815(2)	0.034(3)	0.070(2)	5.(1)
O_b(6)	0.4000(9)	0.390(1)	0.8059(7)	1.4(4)	C(10)	0.728(2)	0.022(4)	0.183(2)	7.(1)
O_b(7)	0.3408(9)	0.221(1)	0.7643(8)	1.9(4)	C(11)	0.716(2)	0.114(4)	0.201(2)	7.(1)
O_b(8)	0.5499(8)	0.090(1)	0.6281(7)	1.3(4)	C(12)	0.766(2)	−0.037(4)	0.227(2)	7.(1)
O_b(9)	0.6203(9)	0.187(1)	0.9227(8)	1.5(4)	N(3)	0.267(2)	0.058(3)	0.545(1)	5.0(8)
O_b(10)	0.5019(9)	−0.112(1)	0.7445(8)	1.5(4)	C(13)	0.249(2)	0.115(4)	0.488(2)	6.(1)
O_b(11)	0.5266(8)	−0.073(1)	0.8557(7)	1.3(4)	C(14)	0.300(2)	0.184(4)	0.490(2)	8.(1)
O_b(12)	0.418(1)	−0.063(2)	0.7954(8)	2.2(4)	C(15)	0.249(2)	0.031(4)	0.436(2)	7.(1)
O_c(1)	0.480(1)	0.398(1)	0.6910(8)	1.8(4)	C(16)	0.221(2)	0.002(4)	0.556(2)	6.(1)
O_c(2)	0.585(1)	0.385(2)	0.7543(8)	2.3(5)	C(17)	0.242(2)	−0.045(4)	0.618(2)	8.(2)
O_c(3)	0.5096(8)	0.434(1)	0.8015(7)	1.3(4)	C(18)	0.167(3)	0.055(5)	0.555(2)	12.(2)
O_c(4)	0.4097(9)	0.195(1)	0.6361(8)	1.7(4)	N(4)	0.9502	0.1716	0.8872	11.1(7)
O_c(5)	0.6490(9)	0.166(1)	0.7771(8)	1.6(4)	C(19)	1.0038	0.2004	0.8643	11.1$^{b)}$
O_c(6)	0.472(1)	0.277(2)	0.8865(9)	2.7(5)	C(20)	0.9470	0.1710	0.7977	11.1$^{b)}$
O_c(7)	0.379(1)	0.068(2)	0.7072(8)	2.0(4)	C(21)	1.0729	0.1594	0.8679	11.1$^{b)}$
O_c(8)	0.458(1)	0.018(1)	0.6583(8)	1.9(4)	C(22)	0.9774	0.1412	0.9583	11.1$^{b)}$
O_c(9)	0.5912(8)	0.002(1)	0.7362(7)	1.2(4)	C(23)	1.0326	0.2256	1.0000	11.1$^{b)}$
O_c(10)	0.6147(9)	0.039(1)	0.8436(7)	1.4(4)	C(24)	0.9247	0.0986	0.9913	11.1$^{b)}$
O_c(11)	0.5174(9)	0.100(1)	0.9044(8)	1.8(4)	N(5)	0.219(1)	0.178(2)	0.161(1)	2.0(5)
O_c(12)	0.4117(8)	0.113(1)	0.8461(7)	1.1(4)	C(25)	0.208(2)	0.130(3)	0.100(1)	3.3(8)
O_d(1)	0.414(1)	0.543(2)	0.7292(8)	2.3(5)	C(26)	0.263(2)	0.116(3)	0.086(1)	3.6(9)
O_d(2)	0.569(1)	0.455(2)	0.6325(8)	2.1(4)	C(27)	0.171(2)	0.226(3)	0.066(2)	6.(1)
O_d(3)	0.615(1)	0.517(2)	0.8445(9)	3.1(5)	C(28)	0.251(2)	0.100(3)	0.211(2)	3.7(9)
O_d(4)	0.291(1)	0.203(2)	0.6407(8)	2.3(5)	C(29)	0.216(2)	0.008(3)	0.207(2)	5.(1)
O_d(5)	0.445(1)	0.100(2)	0.5448(8)	2.4(5)	C(30)	0.259(2)	0.158(3)	0.266(2)	5.(1)

a) $B_{eq}=\frac{8}{3}\pi^2\sum_i\sum_j U_{ij}a_i^*a_j^*\boldsymbol{a}_i\cdot\boldsymbol{a}_j$. b) Fixed to be the same as B_{iso} of N(4).

ammonium cations did not give clear peaks in the difference Fourier map and their atomic parameters were not determined. The refinement was based on F using the full-matrix least-squares with the weighting scheme of $w^{-1}=\sigma^2(F)$. The anion is orientationally disordered and the position of the Ti atom was not identified. All the 12 metal atoms were refined as W atoms. Anisotropic temperature factors were applied to the 12 metal atoms and the P atom. Due to the poor qualities of the intensity data, common isotropic temperature factors were applied for O_a, O_b, O_c, O_d, and each diisopropyl ammonium cations. Crystal data are listed in Table 4.[13]

$(i\text{-}C_3H_7NH_3)_6H[PTi_2W_{10}O_{38}(O_2)_2]\cdot H_2O$: The intensity data were collected on a Rigaku AFC5R diffractometer with the graphite monochromatized Mo $K\alpha$ radiation (λ=0.71069 Å) generated at 50 kV, 140 mA. Lorentz-polarization and absorption[11] corrections were applied. Heavy atom positions were determined by the analysis of the Patterson map. The succeeding least-squares and difference Fourier syntheses cycles located the remaining non-hydrogen atoms. The refinement was based on F using the full-matrix least-squares with the weighting scheme of $w^{-1}=\sigma^2(F)+0.000225F^2$. The $[PTi_2W_{10}O_{38}(O_2)_2]^{7-}$ anion, which has the C_2 point symmetry, is located on the crystallographic mirror plane and is orientationally disordered. Thus, the positions of the two Ti

Table 4. Fractional Coordinates and Equivalent or Isotropic Thermal Parameters (Å^2) for $[(i\text{-}C_3H_7)_2NH_2]_5\,[PTiW_{11}O_{39}(O_2)]\cdot4H_2O$

Atom	x	y	z	$B_{eq}$$^{a)}$/$B_{iso}$	Atom	x	y	z	B_{iso}
W(1)	0.43453(7)	0.4213(1)	0.74359(8)	2.24	$O_d(5)$	0.445(1)	0.110(2)	0.545(1)	$3.4^{e)}$
W(2)	0.54772(8)	0.3502(1)	0.67185(8)	2.80	$O_d(6)$	0.670(1)	0.067(2)	0.673(1)	$3.4^{e)}$
W(3)	0.58619(7)	0.4022(1)	0.82967(8)	2.22	$O_d(7)$	0.722(1)	0.144(2)	0.888(1)	$3.4^{e)}$
W(4)	0.35935(8)	0.2065(2)	0.68960(9)	3.28	$O_d(8)$	0.551(1)	0.245(2)	0.984(1)	$3.4^{e)}$
W(5)	0.47188(8)	0.1384(2)	0.61720(9)	3.43	$O_d(9)$	0.354(1)	0.271(2)	0.886(1)	$3.4^{e)}$
W(6)	0.61217(8)	0.1171(2)	0.69702(8)	2.68	$O_d(10)$	0.389(1)	−0.133(2)	0.677(1)	$3.4^{e)}$
W(7)	0.65122(7)	0.1697(1)	0.85517(8)	2.08	$O_d(11)$	0.607(1)	−0.166(2)	0.807(1)	$3.4^{e)}$
W(8)	0.54623(7)	0.2348(1)	0.92145(7)	2.12	$O_d(12)$	0.443(1)	−0.059(2)	0.911(1)	$3.4^{e)}$
W(9)	0.39373(7)	0.2580(2)	0.83523(8)	2.55	$O_w(1)$	0.574(1)	0.072(3)	0.514(1)	6.(1)
W(10)	0.42909(8)	−0.0425(1)	0.71605(8)	2.67	$O_w(2)$	0.658(1)	0.097(3)	0.453(1)	7.(1)
W(11)	0.56873(7)	−0.0611(1)	0.79747(8)	1.98	$O_w(3)$	0.803(2)	0.171(3)	0.673(2)	8.(1)
W(12)	0.46247(7)	0.0059(1)	0.86203(8)	2.28	$O_w(4)$	0.669(2)	0.116(3)	0.045(2)	8.(1)
P	0.5053(5)	0.1836(9)	0.7683(5)	1.9	N(1)	0.980(1)	0.250(3)	0.572(1)	3.6(4)
$O_a(1)$	0.445(1)	0.241(2)	0.762(1)	1.2(2)	C(1)	0.925(2)	0.243(4)	0.524(2)	$3.6^{f)}$
$O_b(2)$	0.525(1)	0.195(2)	0.714(1)	$1.2^{b)}$	C(2)	0.876(2)	0.214(3)	0.550(2)	$3.6^{f)}$
$O_a(3)$	0.552(1)	0.228(2)	0.823(1)	$1.2^{b)}$	C(3)	0.918(2)	0.360(3)	0.503(2)	$3.6^{f)}$
$O_a(4)$	0.496(1)	0.074(2)	0.783(1)	$1.2^{b)}$	C(4)	0.999(2)	0.155(4)	0.608(2)	$3.6^{f)}$
$O_b(1)$	0.373(1)	0.355(2)	0.689(1)	1.9(1)	C(5)	1.057(2)	0.180(3)	0.652(2)	$3.6^{f)}$
$O_b(2)$	0.501(1)	0.275(2)	0.607(1)	$1.9^{c)}$	C(6)	1.005(2)	0.073(3)	0.564(2)	$3.6^{f)}$
$O_b(3)$	0.611(1)	0.253(2)	0.674(1)	$1.9^{c)}$	N(2)	0.759(2)	0.044(4)	0.135(2)	6.2(5)
$O_b(4)$	0.651(1)	0.305(2)	0.850(1)	$1.9^{c)}$	C(7)	0.790(2)	−0.028(4)	0.113(2)	$6.2^{g)}$
$O_b(5)$	0.570(1)	0.368(2)	0.900(1)	$1.9^{c)}$	C(8)	0.752(2)	−0.134(4)	0.081(2)	$6.2^{g)}$
$O_b(6)$	0.403(1)	0.393(2)	0.806(1)	$1.9^{c)}$	C(9)	0.813(2)	0.036(4)	0.062(2)	$6.2^{g)}$
$O_b(7)$	0.342(1)	0.217(2)	0.759(1)	$1.9^{c)}$	C(10)	0.733(2)	0.016(5)	0.183(2)	$6.2^{g)}$
$O_b(8)$	0.555(1)	0.093(2)	0.624(1)	$1.9^{c)}$	C(11)	0.720(2)	0.096(4)	0.211(2)	$6.2^{g)}$
$O_b(9)$	0.623(1)	0.182(2)	0.918(1)	$1.9^{c)}$	C(12)	0.767(2)	−0.044(4)	0.229(2)	$6.2^{g)}$
$O_b(10)$	0.503(1)	−0.111(2)	0.743(1)	$1.9^{c)}$	N(3)	0.259(2)	0.060(4)	0.540(2)	7.9(7)
$O_b(11)$	0.528(1)	−0.077(2)	0.855(1)	$1.9^{c)}$	C(13)	0.255(3)	0.109(5)	0.488(3)	$7.9^{h)}$
$O_b(12)$	0.418(1)	−0.058(2)	0.786(1)	$1.9^{c)}$	C(14)	0.294(2)	0.206(5)	0.494(3)	$7.9^{h)}$
$O_c(1)$	0.477(1)	0.405(2)	0.690(1)	2.4(2)	C(15)	0.253(3)	0.014(5)	0.443(3)	$7.9^{h)}$
$O_c(2)$	0.588(1)	0.389(2)	0.757(1)	$2.4^{d)}$	C(16)	0.226(3)	−0.005(5)	0.554(3)	$7.9^{h)}$
$O_c(3)$	0.503(1)	0.431(2)	0.804(1)	$2.4^{d)}$	C(17)	0.235(3)	−0.042(5)	0.622(3)	$7.9^{h)}$
$O_c(4)$	0.407(1)	0.203(2)	0.636(1)	$2.4^{d)}$	C(18)	0.173(3)	0.073(5)	0.554(3)	$7.9^{h)}$
$O_c(5)$	0.649(1)	0.165(2)	0.784(1)	$2.4^{d)}$	N(4)	0.965(2)	0.164(4)	0.898(2)	8.3(7)
$O_c(6)$	0.469(1)	0.274(2)	0.888(1)	$2.4^{d)}$	C(19)	0.994(3)	0.198(5)	0.841(3)	$8.3^{i)}$
$O_c(7)$	0.379(1)	0.070(2)	0.709(1)	$2.4^{d)}$	C(20)	0.949(3)	0.174(5)	0.785(3)	$8.3^{i)}$
$O_c(8)$	0.455(1)	0.014(2)	0.656(1)	$2.4^{d)}$	C(21)	1.066(3)	0.175(5)	0.868(3)	$8.3^{i)}$
$O_c(9)$	0.590(1)	−0.009(2)	0.736(1)	$2.4^{d)}$	C(22)	0.903(3)	0.209(5)	0.879(3)	$8.3^{i)}$
$O_c(10)$	0.616(1)	0.038(2)	0.847(1)	$2.4^{d)}$	C(23)	0.916(3)	0.337(5)	0.888(3)	$8.3^{i)}$
$O_c(11)$	0.520(1)	0.103(2)	0.910(1)	$2.4^{d)}$	N(5)	0.223(2)	0.167(3)	0.168(2)	4.5(5)
$O_c(12)$	0.411(1)	0.124(2)	0.842(1)	$2.4^{d)}$	C(25)	0.211(2)	0.140(4)	0.107(2)	$4.5^{j)}$
$O_d(1)$	0.416(1)	0.540(2)	0.733(1)	3.4(2)	C(26)	0.264(2)	0.107(4)	0.083(2)	$4.5^{j)}$
$O_d(2)$	0.565(1)	0.454(2)	0.638(1)	$3.4^{e)}$	C(27)	0.177(2)	0.220(4)	0.059(2)	$4.5^{j)}$
$O_d(3)$	0.614(1)	0.516(2)	0.844(1)	$3.4^{e)}$	C(28)	0.234(2)	0.050(4)	0.208(2)	$4.5^{j)}$
$O_d(4)$	0.293(1)	0.201(2)	0.637(1)	$3.4^{e)}$	C(29)	0.255(2)	0.147(4)	0.261(2)	$4.5^{j)}$

a) $B_{eq}=\frac{8}{3}\pi^2\sum_i\sum_j U_{ij}a_i^*a_j^*\boldsymbol{a}_i\cdot\boldsymbol{a}_j$. b) Fixed to be the same as B_{iso} of $O_a(1)$. c) Fixed to be the same as B_{iso} of $O_b(1)$. d) Fixed to be the same as B_{iso} of $O_c(1)$. e) Fixed to be the same as B_{iso} of $O_d(1)$. f) Fixed to be the same as B_{iso} of N(1). g) Fixed to be the same as B_{iso} of N(2). h) Fixed to be the same as B_{iso} of N(3). i) Fixed to be the same as B_{iso} of N(4). j) Fixed to be the same as B_{iso} of N(5).

atoms were not identified and all the 12 metal atoms were refined as W atoms. Anisotropic temperature factors were applied to the 12 metal atoms and the P atom. Atomic parameters are listed in Table 5.[13)]

Results and Discussion

^{31}P and ^{183}W NMR Spectroscopy. Figure 1 shows the ^{183}W NMR spectra of the compounds **1**—**4**. Their chemical shifts are listed in Table 1 together with the other spectroscopic data. Each compound shows single ^{31}P resonance, indicating that the anion **1** reacts with hydrogen peroxide to give a single species of peroxo complex and so does the anion **3**. ^{183}W spectrum of **2** consists of six lines with the intensity ratio of 2:2:1:2:2:2, indicating that the C_s symmetry of the parent anion **1** is retained in the peroxo anion of **2**. ^{183}W NMR spectrum of **4** shows five lines with equal intensities, which indicates that the C_2 symmetry of the parent anion **3** is also retained in the peroxo anion of **4**. ^{31}P chemical shifts are not very sensitive to the

Table 5. Fractional Coordinates and Equivalent or Isotropic Thermal Parameters (Å^2) for $(i\text{-}C_3H_7NH_3)_6H[PTi_2W_{10}O_{38}(O_2)_2]\cdot H_2O$

Atom	x	y	z	$B_{eq}$$^{a)}$/$B_{iso}$	Atom	x	y	z	B_{iso}
W(1)	0.1475(2)	0	0.2199(2)	1.70	O_c(7)	0.596(1)	0.0688(8)	0.608(2)	1.4(3)
W(2)	0.2078	0.09539(7)	0.4993	1.60	O_d(1)	0.019(2)	0	0.167(3)	2.7(5)
W(3)	0.3480(1)	0.08944(7)	0.1194(1)	1.56	O_d(2)	0.098(2)	0.126(1)	0.550(2)	2.7(4)
W(4)	0.4078(2)	0.18526(4)	0.3968(2)	1.75	O_d(3)	0.339(2)	0.144(1)	0.006(2)	2.8(4)
W(5)	0.4613(1)	0.09602(6)	0.6563(1)	1.42	O_d(4)	0.432(2)	0.2744(8)	0.377(2)	2.6(4)
W(6)	0.6224(1)	0.08865(7)	0.2860(1)	1.67	O_d(5)	0.509(1)	0.126(1)	0.797(2)	2.1(3)
W(7)	0.6764(2)	0	0.5465(2)	1.34	O_d(6)	0.712(2)	0.146(1)	0.237(2)	2.6(4)
P	0.412(1)	0	0.389(1)	1.2	O_d(7)	0.797(2)	0	0.650(2)	1.9(4)
O_a(1)	0.348(2)	0	0.270(2)	1.3(4)	O_w	0.917(1)	0.0737(6)	0.369(1)	1.1(2)
O_a(2)	0.387(1)	0.0635(7)	0.455(1)	0.9(2)	N(1)	1.110(2)	0.208(1)	0.218(3)	3.1(6)
O_a(3)	0.531(2)	0	0.378(2)	1.3(3)	C(1)	1.033(2)	0.231(1)	0.114(2)	1.5(3)
O_b(1)	0.203(1)	0.0703(8)	0.127(2)	1.7(3)	C(2)	1.101(3)	0.246(2)	0.019(4)	4.0(8)
O_b(2)	0.272(1)	0.1793(8)	0.447(2)	1.6(3)	C(3)	0.948(4)	0.179(2)	0.091(4)	3.8(8)
O_b(3)	0.314(1)	0.1088(8)	0.641(2)	1.5(3)	N(2)	0.702(2)	0.206(1)	0.569(2)	1.9(4)
O_b(4)	0.357(2)	0	0.040(2)	1.9(4)	C(4)	0.756(3)	0.189(2)	0.688(3)	3.4(6)
O_b(5)	0.468(1)	0.1752(8)	0.563(2)	1.8(3)	C(5)	0.878(4)	0.181(2)	0.695(5)	4.5(9)
O_b(6)	0.710(1)	0.0693(8)	0.438(2)	1.3(2)	C(6)	0.732(3)	0.245(2)	0.775(4)	3.9(8)
O_b(7)	0.671(2)	0	0.235(2)	1.5(4)	N(3)	0.583(3)	0	0.964(4)	2.3(7)
O_c(1)	0.162(1)	0.0668(9)	0.345(2)	1.8(3)	C(7)	0.684(2)	0	0.917(3)	1.3(5)
O_c(2)	0.206(2)	0	0.542(2)	2.0(4)	C(8)	0.749(3)	0.065(2)	0.964(4)	3.7(7)
O_c(3)	0.352(1)	0.1526(8)	0.249(2)	1.3(3)	N(4)	1.239(4)	0	0.807(5)	3.3(9)
O_c(4)	0.444(2)	0	0.688(2)	1.3(4)	C(9)	1.122(3)	0	0.781(4)	3.2(8)
O_c(5)	0.503(1)	0.0823(9)	0.164(2)	2.0(3)	C(10)	1.090(3)	0.070(2)	0.837(4)	3.8(8)
O_c(6)	0.546(1)	0.1508(8)	0.369(2)	1.9(3)					

a) $B_{eq}=\frac{8}{3}\pi^2\sum_i\sum_j U_{ij}a_i^*a_j^*\boldsymbol{a}_i\cdot\boldsymbol{a}_j$.

Table 6. Average Values of the Interatomic Distances (Å)

	$[(i\text{-}C_3H_7)_2NH_2]_5$ $[PTiW_{11}O_{40}]\cdot 4H_2O$	$[(i\text{-}C_3H_7)_2NH_2]_5$ $[PTiW_{11}O_{39}(O_2)]\cdot 4H_2O$	$(i\text{-}C_3H_7NH_3)_6H$ $[PTi_2W_{10}O_{38}(O_2)_2]\cdot H_2O$
Edge shared W–W	3.42(1)	3.42(1)	3.44(1)
Corner shared W–W	3.70(1)	3.70(1)	3.69(1)
P–W	3.56(1)	3.56(3)	3.57(2)
W–O_a	2.44(3)	2.42(3)	2.46(3)
W–O_b	1.92(4)	1.93(7)	1.93(3)
W–O_c	1.91(5)	1.92(10)	1.91(3)
W–O_d	1.70(4)	1.67(7)	1.73(4)
P–O_a	1.54(3)	1.56(5)	1.51(3)

introduction of the peroxo ligands, while some of the ^{183}W chemical shifts change with at least 10 ppm. Due to the low S/N ratio of the spectra, the assignment of each peak was not available except for the W atoms on the mirror planes of the anions **1** and **2**. The chemical shift of this W atom is changed only by 1.55 pm upfield upon peroxidation.

Electronic Spectra. Figure 2 shows the electronic spectra of the anions **1**—**4**. All the compounds show strong absorption bands around 250—260 nm, which are assigned to the O→W ligand-to-metal charge transfer band. Peroxo species give the new absorption bands at 390 nm (ε=2160) for **2** and 360 nm (ε=3990) for **4**. The $H_2W_{12}O_{39}(O_2)^{6-}$ anion, which was obtained by the reaction of hydrogen peroxide with the α-Keggin structured $H_2W_{12}O_{40}^{6-}$ anion, exhibits no band at the near ultraviolet region.[14] On the other hand, the treatment of the aqueous $TiCl_4$ solution with H_2O_2 gives a peroxo species showing the absorption band around 410 nm.[15] Therefore, it is reasonable to assume that the absorption bands at the near ultraviolet regions are assigned to the O_2→Ti ligand-to-metal charge transfer band.

Crystal Structures. Anions **1**—**4** have the α-Keggin $XM_{12}O_{40}^{n-}$ structure in which four M_3O_{13} groups consisting of three edge-shared MO_6 octahedra are linked together with corner-sharing and with a central XO_4 tetrahedron. As shown in Fig. 3, the Keggin structure has four types of O atoms: The central O_a atoms, the edge-shared O_b atoms, the corner-shared O_c atoms, and the terminal O_d atoms. The idealized α-Keggin anion has a T_d symmetry. The monosubstituted anion **1** has the C_s symmetry and the disubsituted anion **3** has the C_2 symmetry. All the three anions in the crystals examined here are statistically disordered. Therefore, the

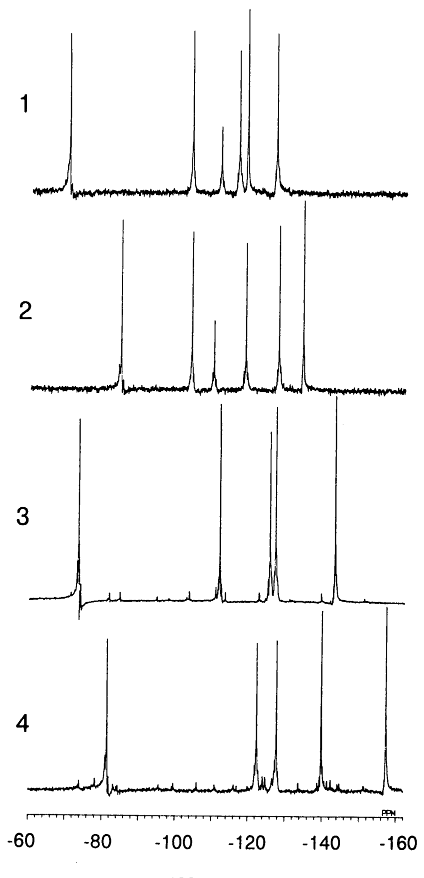

Fig. 1. ^{183}W NMR spectra of compounds **1**—**4**.

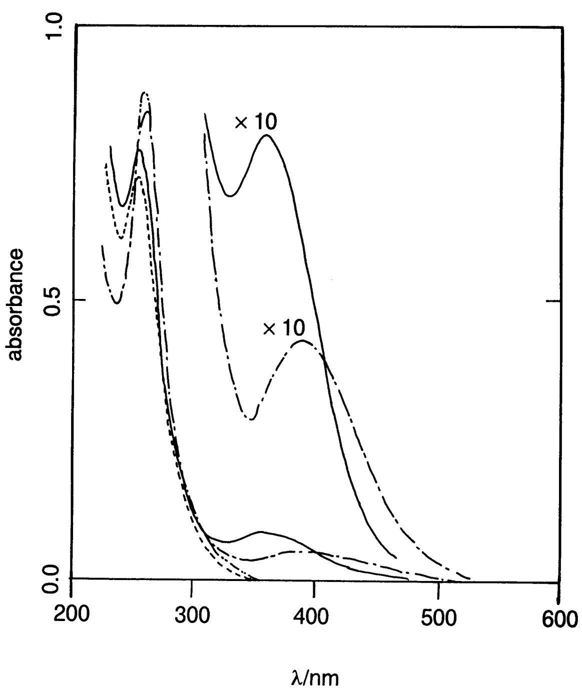

Fig. 2. Electronic spectra of 0.02 mM aqueous solutions of $[(i\text{-}C_3H_7)_2NH_2]_5[PTiW_{11}O_{40}]\cdot 4H_2O$ (—··—··—··—), $[(i\text{-}C_3H_7)_2NH_2]_5[PTiW_{11}O_{39}(O_2)]\cdot 4H_2O$ (—·—·—·—), $[(C_2H_5)_2NH_2]_4NaH_2[PTi_2W_{10}O_{40}]\cdot 11H_2O$ (--------), and $(i\text{-}C_3H_7NH_3)_6H[PTi_2W_{10}O_{38}(O_2)_2]\cdot H_2O$ (———).

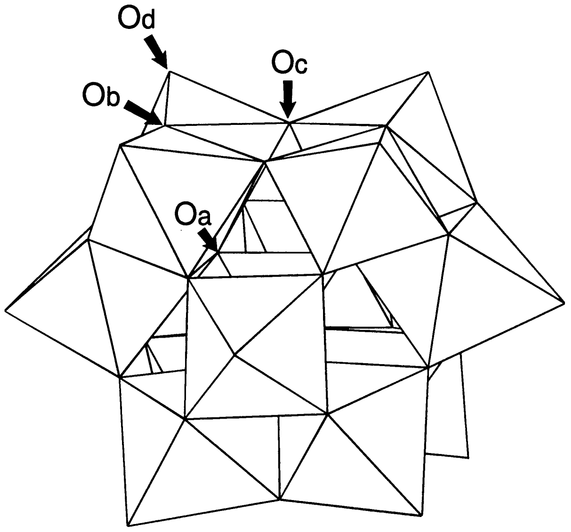

Fig. 3. The α-Keggin structure shown in the polyhedral representation. Oxygen atoms are at the corners of the octahedra and the tetrahedron and the metal atoms are at the center of the polyhedra.

locations of the Ti atoms or the peroxo ligands in the anions were not determined. However, it was clearly shown that the α-Keggin structures of the parent anions **1** and **3** are retained in their peroxo derivatives of **2** and **4**. As shown in the Table 5, the metal-metal and metal-oxygen bond distances show typical values common to the other α-Keggin type of heteropolyoxoanions. The final difference Fourier map indicated the existence of the side-on O_2 groups attached to some of the metal atoms. Figure 4 shows the typical difference Fourier map around the metal atom.

The orange color of $[(i\text{-}C_3H_7)_2NH_2]_5[PTiW_{11}O_{39}(O_2)]\cdot 4H_2O$ disappeared during the X ray measurement and its cell dimensions changed approaching to that of $[(i\text{-}C_3H_7)_2NH_2]_5[PTiW_{11}O_{40}]\cdot 4H_2O$. These facts suggest that the interconversion of $[(i\text{-}C_3H_7)_2NH_2]_5[PTiW_{11}O_{39}(O_2)]\cdot 4H_2O$ into $[(i\text{-}C_3H_7)_2NH_2]_5[PTiW_{11}O_{40}]\cdot 4H_2O$ in the solid state occurred, since the crystal structures of these two compounds are very similar.

Structures of the Peroxo Anions 2 and 4. As the anion **2** has one peroxo group, its peroxo ligand should lie on the molecular mirror plane and should be bonded either to the Ti atom or to the W atom on the mirror plane. The change in the ^{183}W chemical shift at the W atom on the mirror plane induced by the peroxidation was only 1.55 ppm. It is very small compared with the change at the other W atoms. We conclude that the peroxo ligand

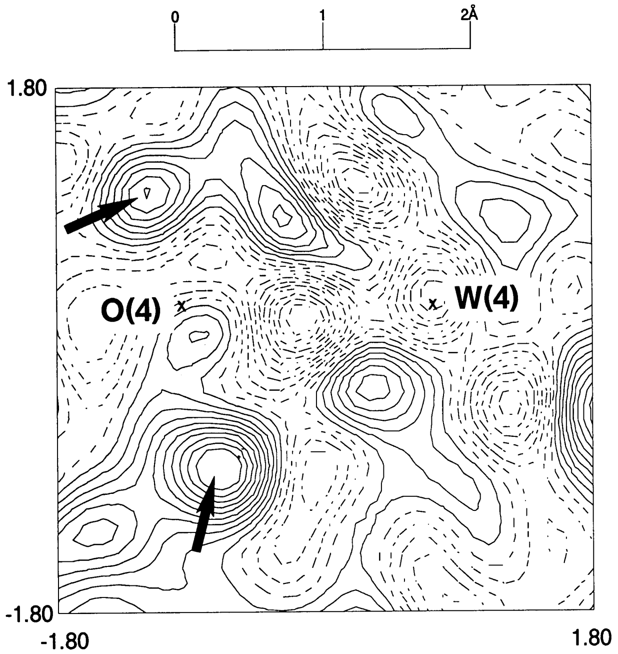

Fig. 4. The difference Fourier map around W(4) in the crystal of (iso-$C_3H_7NH_3)_6H[PTi_2W_{10}O_{38}(O_2)_2]\cdot H_2O$. Peaks due to the peroxo oxygen atoms are indicated by the arrows.

is bonded to the Ti atom, since the chemical shift of the W atom on the mirror plane, which is located as far as 7.1 Å from the Ti atom, would be affected very little by the peroxidation at the Ti atom. The appearance of the new absorption band at 390 nm also supports the peroxidation at the Ti atom.

Similarly, as the anion **4** has two peroxo groups, the two peroxo ligands should be bonded either to the two Ti atoms or to the two W atoms related to each other by the molecular twofold axis. Anion **4** shows near ultraviolet absorption band at 360 nm with the molar extinction coefficient of ε=3990 M^{-1} cm^{-1}. It should be noted that this value is about twice stronger than that for the monoperoxo anion of **2** at 390 nm (ε=2160 M^{-1} cm^{-1}). Therefore we conclude that the two peroxo ligands in the anion **4** attach to the two Ti atoms.

Conclusion. Two titanotungstophosphates and their peroxo compounds are investigated using the NMR and UV-vis spectroscopies and the X-ray crystallography. The peroxo groups are found to attach to the Ti atoms of the anions without breaking the Keggin structures of the anions. The ^{183}W NMR spectra are found to be very sensitive to the peroxidation of the polyoxoanions. The ^{183}W NMR technique can be a good probe to the peroxidation of the hetero- and isopolyoxotungstates in general. The possibility of the peroxo ligand loss in the crystalline state is also indicated.

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