Structure of Hexatitanooctadecatungstodigermanate

Toshihiro YAMASE,* Tomoji OZEKI, Hiroshi SAKAMOTO, Shigeki NISHIYA,† and Akihiro YAMAMOTO†
Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Yokohama 227
† Research and Development Division, Terumo Corporation, 1500 Inokuchi, Nakai-machi, Ashigarakami-gun, Kanagawa 259-01

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The structure of a dimeric Keggin-typed polyoxotungstate, $[Ge_2Ti_6W_{18}O_{77}]^{14-}$, was investigated by X-ray diffractometry and ^{183}W NMR spectroscopy. $K_9H_5[Ge_2Ti_6W_{18}O_{77}]\cdot 16H_2O$ crystallizes in triclinic $P\bar{1}$ $a=17.582(4)$, $b=22.139(5)$, $c=12.960(2)$ Å, $\alpha=101.26(2)$, $\beta=94.07(2)$, $\gamma=109.20(2)°$, $V=4622(4)$ Å^3. The D_{3d} $[Ge_2Ti_6W_{18}O_{77}]^{14-}$ anion, which gives two ^{183}W NMR resonances at −107.45 and −127.76 ppm, consists of two C_{3v} α-A-$[GeTi_3W_9O_{40}]^{10-}$ moieties fused together at the terminal O atoms of the 6 Ti atoms.

We have pointed out that the substituted Keggin-typed polyoxotungstates containing Ti^{IV} atoms are interesting compounds due to their peculiar photocatalytic and antiviral activities:[1,2] the disubstituted anion, $[PTi_2^{IV}W_{10}O_{40}]^{7-}$,[3,4] catalyzes the photoreduction of CO_2 to CH_4[1] and inhibits any proliferation of human immunodeficiency viruses (HIV) and Herpes simplex viruses.[2] Our previous study concerning the photoreduction of CO_2 to CH_4 showed that the presence of two $Ti^{IV}O_6$ octahedra in the polyoxometalate is essential for a multielectron transfer to CO_2.[1] In addition, these $Ti^{IV}O_6$ sites are the acceptor sites for the attachment of peroxo ligands to polyoxometalate.[5] An X-ray crystal structure analysis of $[PTi_2^{IV}W_{10}O_{40}]^{7-}$ showed the easiness of protonation at the terminal oxygen atoms of the $Ti^{IV}O_6$ sites in the anion.[4] This reflects strong adsorption on the cell in a biological system, which may lead to a significant disturbance of virus adsorption on the cell.[6] In the course of our studies concerning the improvement of biologically active polyoxometalates, the low cytotoxicity of $[GeW_{12}O_{40}]^{4-}$, compared with $[PTi_2^{IV}W_{10}O_{40}]^{7-}$, allowed us to try to prepare Ti^{IV}-substituted Keggin-typed tungstogermanate. We recently found a dimeric structural Ti^{IV}-substituted tungstogermanate of $[GeTi_3W_9O_{40}]^{10-}$. This paper describes the structure of $K_9H_5[Ge_2Ti_6W_{18}O_{77}]\cdot 16H_2O$ determined using single-crystal X-ray structure analysis and ^{183}W NMR spectroscopy.

Experimental

Preparations. α-$Na_{10}[GeW_9O_{34}]\cdot 18H_2O$ was prepared following Ref. 7. To 150 ml of H_2O suspending 45 g of α-$Na_{10}[GeW_9O_{34}]\cdot 18H_2O$, 4 ml of $TiCl_4$ was added dropwise with vigorous agitation. The pH of the solution at this point was less than 1.0. After refluxing for 30 min, the resulting solution was cooled to room temperature and white precipitates were filtered off. To obtain potassium salt, 15 g of KCl was added to the filtrate. The crude product was twice recrystallized; 4.0 g of colorless needle crystals of $K_9H_5[Ge_2Ti_6W_{18}O_{77}]\cdot 16H_2O$ were obtained.

^{183}W NMR Measurements. The ^{183}W NMR spectrum was recorded at 20.7 MHz on a JEOL GX500 spectrometer using a 10 mm diameter NMR tube at 30°C. Twenty microsecond pulses (45°) were applied with a repetition time of 3.78 s; 2000 scans were accumulated. The ^{183}W NMR chemical shifts were referenced to external 2.0 mol dm^{-3} Na_2WO_4 in D_2O.

X-Ray Crystal Structure Analysis. A single crystal with dimensions of 0.15×0.20×0.30 mm was mounted on a RIGAKU AFC5 four-circle diffractometer with graphite-monochromatized Mo $K\alpha$ radiation (λ=0.71069 Å). The lattice parameters were obtained from the least squares of the 2θ values of 20 independent reflections with $10.0° \leq \theta \leq 13.1°$. A total of 22162 reflections was collected with 2θ ranging from 5 to 55°, of which 9206 reflections with $I_{obsd} > 3\sigma(I_{obsd})$ were used for the structure determination. The ω-2θ scan technique was used for data collection; $\Delta\omega=(1.2+0.30\tan\theta)°$, scan speed 8° min^{-1} in ω. The range of the indices was $-22\leq h\leq 22$, $-28\leq k\leq 28$, $0\leq l\leq 16$, $(\sin\theta/\lambda)_{max}=0.65$ Å^{-1}. Lorentz-polarization corrections and absorption corrections based on ψ scan curves of 4 reflections[8] [transmission factors 0.388—1.000] were applied. Three standard reflections (7 $\bar{7}$ 6, $\bar{10}$ 6 2, and $\bar{3}$ $\bar{11}$ 1) monitored every 200 reflections showed intensity variations within ±4.1% in I_{obsd}. The crystal data are listed in Table 1.

The usual direct method gave no reasonable solution. As the IR spectrum showed a typical pattern for the Keggin-type polyoxometalates, we used the program PATSEE[9] to search for a Keggin fragment of $[GeTi_3W_9]$. Together with its result, a difference Fourier synthesis showed 13 strong peaks, which comprise the skeleton of the $Ge_2Ti_6W_{18}$ dimer, along with the original $GeTi_3W_9$ group. After several least-squares cycles, the isotropic thermal parameters indicated that the 6 central metal atoms should be assigned as Ti;

Table 1. Crystal Data for $K_9H_5[Ge_2Ti_6W_{18}O_{77}]\cdot 16H_2O$

Formula weight	5618.9
Space group	$P\bar{1}$
a/Å	17.582(4)
b/Å	22.139(5)
c/Å	12.960(2)
α/°	101.26(2)
β/°	94.07(2)
γ/°	109.20(2)
V/Å^3	4622(4)
Z	2
D_x/g cm^{-3}	4.06
$F(000)$	4960
μ(Mo $K\alpha$)/cm^{-1}	244.2

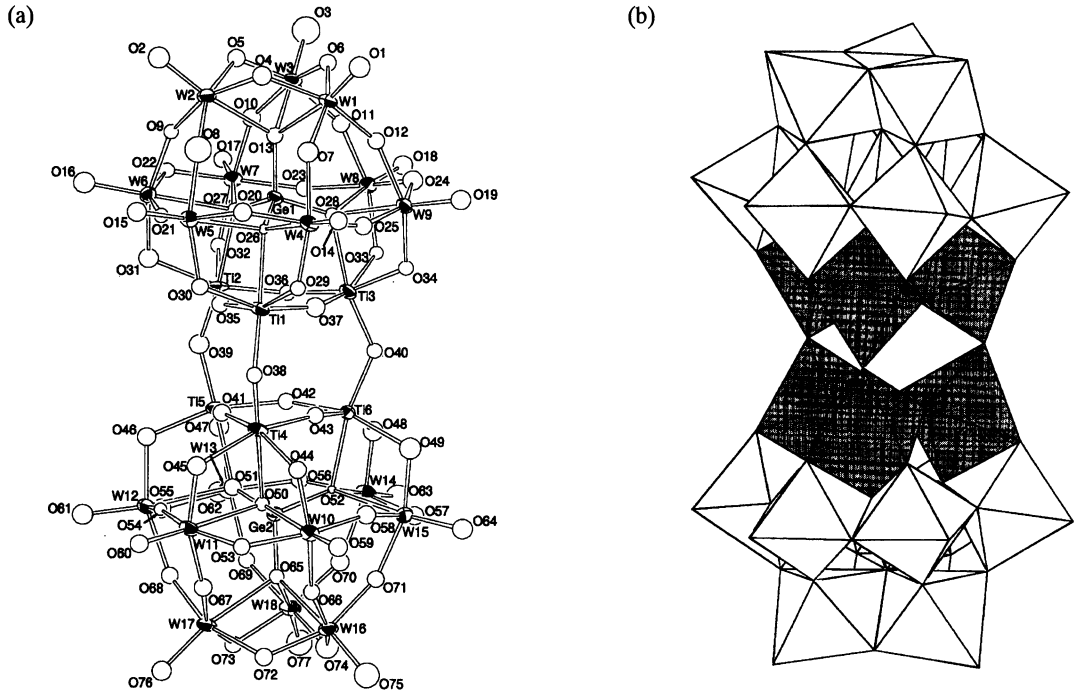

Fig. 2. (a) *ORTEP* drawing of the $[Ge_2Ti_6W_{18}O_{77}]^{14-}$ anion. Thermal ellipsoids are scaled so as to enclose a 50% probability level. (b) Polyhedral representation of the $[Ge_2Ti_6W_{18}O_{77}]^{14-}$ anion. The 6 TiO_6 octahedra are indicated by the hatched region.

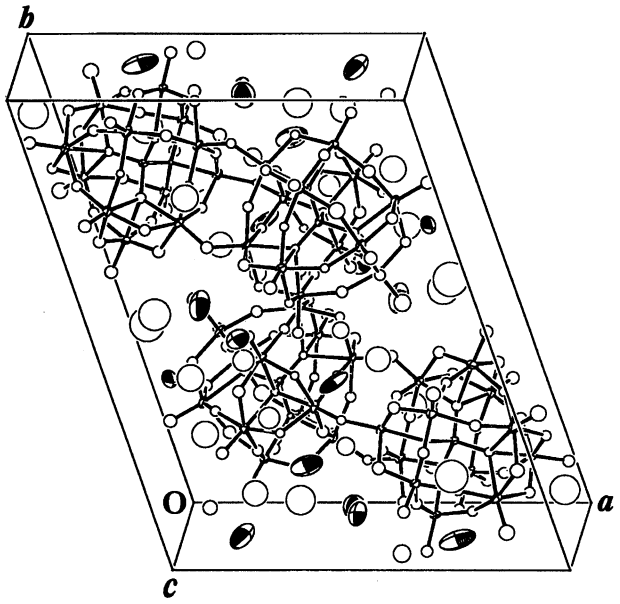

Fig. 1. Packing diagram of the unit cell viewed along the c^* axis. The K atoms are shown in the ellipsoids with their octants shaded.

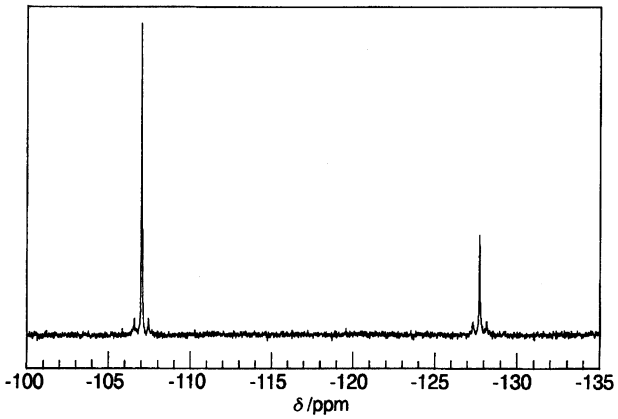

Fig. 3. ^{183}W NMR spectrum of $K_9H_5[Ge_2Ti_6W_{18}O_{77}]\cdot 16H_2O$ in D_2O at 30°C.

the other 18 metal atoms should be W. Succeeding difference Fourier syntheses located the remaining non-H atoms. Anisotropic temperature factors were refined for W, Ti, Ge, and K atoms. A full-matrix least-squares refinement on F converged to $R=0.064$ and $wR=0.054$ for 688 parameters and 9206 independent reflections. The function minimized was $\Sigma w(|F_{obsd}|-|F_{calcd}|)^2$. The weighting scheme employed was $w^{-1}=\sigma^2(F_{obsd})$. $S=\Sigma w^{1/2}F_{obsd}|-|F_{calcd}/(n-m)=2.18$. $(\Delta/\sigma)_{max}=0.41$. The maximum positive and negative peaks in the final difference Fourier map were 3.5 and -3.8 $eÅ^{-3}$, respectively. The complex atomic scattering factors were taken from Ref. 10. All of the calculations were carried out on a Micro VAX II computer using the TEXSAN software package.[11] The final atomic parameters are given in Table 2.[12] Figure 1 shows a packing diagram of the crystal.

Results and Discussion

Figure 2 shows the structure of the $[Ge_2Ti_6W_{18}O_{77}]^{14-}$ anion in an *ORTEP*[13] drawing and in a polyhedral representation. The anion comprises two $[GeTi_3W_9O_{40}]^{10-}$ moieties fused together at the three terminal O atoms of the Ti atoms. Each

Table 2. Fractional Coordinates and Equivalent Isotropic or Isotropic Thermal Parameters (Å^2) for $K_9H_5[Ge_2Ti_6W_{18}O_{77}]\cdot 16H_2O$

Atom	x	y	z	B_{eq}[a)]/B_{iso}
W1	0.1271(1)	0.2338(1)	0.1380(2)	1.81[b)]
W2	0.2343(1)	0.3027(1)	−0.0409(2)	1.90
W3	0.2394(1)	0.3948(1)	0.2012(2)	1.98
W4	0.2305(1)	0.1096(1)	0.1094(2)	1.59
W5	0.3374(1)	0.1779(1)	−0.0661(1)	1.63
W6	0.4612(1)	0.3584(1)	0.0033(1)	1.62
W7	0.4671(1)	0.4508(1)	0.2434(2)	1.65
W8	0.3474(1)	0.3734(1)	0.4429(1)	1.61
W9	0.2360(1)	0.2129(1)	0.3794(1)	1.57
W10	0.6430(1)	0.0251(1)	0.3558(2)	1.73
W11	0.7480(1)	0.0910(1)	0.1762(2)	1.76
W12	0.8754(1)	0.2702(1)	0.2436(2)	1.92
W13	0.8819(1)	0.3647(1)	0.4817(2)	2.03
W14	0.7607(1)	0.2906(1)	0.6829(2)	1.97
W15	0.6493(1)	0.1301(1)	0.6253(2)	1.75
W16	0.8316(1)	0.0885(1)	0.5558(2)	2.09
W17	0.9379(1)	0.1545(1)	0.3748(2)	1.85
W18	0.9439(1)	0.2497(1)	0.6144(2)	2.13
Ti1	0.4287(4)	0.1620(4)	0.1518(6)	1.7
Ti2	0.5527(4)	0.3390(4)	0.2186(6)	1.9
Ti3	0.4364(4)	0.2635(4)	0.4085(6)	1.7
Ti4	0.5909(4)	0.1294(4)	0.2449(6)	1.7
Ti5	0.7137(4)	0.3033(4)	0.3070(6)	1.8
Ti6	0.5967(5)	0.2295(4)	0.5026(6)	1.6
Ge1	0.3428(3)	0.2823(3)	0.1826(4)	1.4
Ge2	0.7632(3)	0.1940(2)	0.4304(4)	1.3
K1	0.0934(7)	0.3228(7)	0.406(1)	5.7
K2	0.5018(9)	0.0992(8)	0.857(1)	6.4
K3	0.538(1)	0.3559(8)	0.693(1)	8.1
K4	0.388(1)	0.167(1)	0.618(1)	10.3
K5	0.366(1)	0.4918(8)	0.996(1)	8.0
K6	0.729(1)	0.041(1)	0.834(2)	12.2
K7	0.453(1)	0.050(1)	0.430(2)	10.0
K8	0.176(1)	0.035(1)	0.738(2)	11.0
K9	0.741(1)	0.489(1)	0.365(3)	20.3
O1	0.027(2)	0.192(1)	0.125(2)	2.6(6)
O2	0.205(2)	0.311(2)	−0.167(2)	2.7(6)
O3	0.210(2)	0.466(2)	0.246(3)	4.7(8)
O4	0.134(2)	0.250(1)	−0.005(2)	2.2(6)
O5	0.221(1)	0.379(1)	0.053(2)	1.9(5)
O6	0.142(1)	0.328(1)	0.189(2)	1.7(5)
O7	0.161(2)	0.162(1)	0.083(2)	2.6(6)
O8	0.260(2)	0.223(2)	−0.078(3)	4.2(8)
O9	0.347(1)	0.353(1)	−0.023(2)	1.3(5)
O10	0.350(2)	0.436(1)	0.200(2)	2.1(6)
O11	0.271(2)	0.381(1)	0.332(2)	1.9(5)
O12	0.166(1)	0.235(1)	0.278(2)	1.7(5)
O13	0.260(1)	0.300(1)	0.133(2)	1.6(5)
O14	0.157(2)	0.040(1)	0.098(2)	1.9(5)
O15	0.331(2)	0.151(1)	−0.202(2)	2.2(6)
O16	0.493(2)	0.383(2)	−0.109(2)	2.7(6)
O17	0.506(2)	0.535(1)	0.284(2)	1.8(5)
O18	0.345(2)	0.433(1)	0.548(2)	2.2(6)
O19	0.164(2)	0.168(1)	0.439(2)	2.3(6)
O20	0.248(2)	0.111(1)	−0.034(2)	2.0(6)
O21	0.411(1)	0.262(1)	−0.042(2)	1.2(5)
O22	0.481(1)	0.445(1)	0.099(2)	1.4(5)
O23	0.424(1)	0.423(1)	0.367(2)	1.5(5)
O24	0.263(2)	0.303(1)	0.456(2)	2.3(6)
O25	0.237(1)	0.148(1)	0.257(2)	1.9(5)
O26	0.334(1)	0.202(1)	0.115(2)	0.5(4)

a) $B_{eq}=(8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\boldsymbol{a}_i\cdot\boldsymbol{a}_j$. b) W, Ti, Ge, and K atoms were refined anisotropically.

Table 2. (Continued)

Atom	x	y	z	B_{iso}
O27	0.426(1)	0.339(1)	0.170(2)	1.1(5)
O28	0.339(1)	0.282(1)	0.313(2)	1.1(5)
O29	0.323(1)	0.093(1)	0.140(2)	1.4(5)
O30	0.413(1)	0.147(1)	−0.003(2)	1.6(5)
O31	0.560(2)	0.360(1)	0.073(2)	2.3(6)
O32	0.563(1)	0.435(1)	0.269(2)	1.4(5)
O33	0.424(1)	0.343(1)	0.501(2)	1.1(5)
O34	0.330(1)	0.212(1)	0.447(2)	1.3(5)
O35	0.508(1)	0.248(1)	0.153(2)	1.7(5)
O36	0.514(1)	0.321(1)	0.345(2)	1.5(5)
O37	0.422(2)	0.194(1)	0.292(2)	2.3(6)
O38	0.497(1)	0.115(1)	0.166(2)	1.5(5)
O39	0.660(2)	0.349(1)	0.252(2)	2.2(6)
O40	0.503(1)	0.249(1)	0.509(2)	1.4(5)
O41	0.651(2)	0.218(1)	0.242(2)	1.8(5)
O42	0.657(1)	0.289(1)	0.427(2)	1.6(5)
O43	0.568(1)	0.166(1)	0.380(2)	1.6(5)
O44	0.565(1)	0.042(1)	0.281(2)	1.9(5)
O45	0.649(2)	0.093(1)	0.127(2)	2.1(6)
O46	0.794(2)	0.305(1)	0.205(2)	2.0(6)
O47	0.801(2)	0.380(1)	0.409(2)	2.2(6)
O48	0.663(2)	0.294(1)	0.635(2)	2.3(6)
O49	0.566(2)	0.159(2)	0.594(2)	2.7(6)
O50	0.703(1)	0.128(1)	0.331(2)	1.2(5)
O51	0.797(1)	0.262(1)	0.385(2)	1.7(5)
O52	0.706(1)	0.207(1)	0.531(2)	0.4(4)
O53	0.693(1)	0.019(1)	0.228(2)	1.7(5)
O54	0.804(1)	0.182(1)	0.189(2)	0.9(5)
O55	0.934(2)	0.351(1)	0.354(2)	2.2(6)
O56	0.813(1)	0.341(1)	0.587(2)	1.6(5)
O57	0.708(2)	0.210(1)	0.723(2)	1.9(6)
O58	0.620(2)	0.068(1)	0.491(2)	2.0(6)
O59	0.589(2)	−0.053(1)	0.351(2)	2.2(6)
O60	0.769(2)	0.056(1)	0.060(2)	2.0(5)
O61	0.933(2)	0.288(1)	0.147(2)	2.4(6)
O62	0.952(2)	0.442(1)	0.537(2)	2.5(6)
O63	0.794(2)	0.347(2)	0.804(2)	3.2(7)
O64	0.604(2)	0.081(1)	0.704(2)	2.3(6)
O65	0.846(1)	0.177(1)	0.484(2)	1.3(5)
O66	0.748(1)	0.045(1)	0.441(2)	1.6(5)
O67	0.842(2)	0.104(1)	0.278(2)	1.9(6)
O68	0.937(1)	0.228(1)	0.322(2)	1.7(5)
O69	0.943(1)	0.315(1)	0.541(2)	1.5(5)
O70	0.857(2)	0.262(1)	0.677(2)	2.0(6)
O71	0.751(1)	0.115(1)	0.622(2)	1.7(5)
O72	0.907(2)	0.087(1)	0.456(2)	1.9(5)
O73	1.003(1)	0.216(1)	0.508(2)	1.7(5)
O74	0.917(2)	0.161(2)	0.643(2)	3.1(7)
O75	0.834(2)	0.026(2)	0.620(2)	3.7(7)
O76	1.016(2)	0.135(1)	0.317(2)	2.2(6)
O77	1.027(2)	0.293(2)	0.712(3)	4.0(8)
O78	0.068(2)	0.029(2)	0.280(2)	3.2(7)
O79	0.581(2)	0.441(2)	0.511(3)	4.4(8)
O80	0.587(2)	0.024(2)	0.923(3)	5.0(9)
O81	0.522(2)	0.232(2)	0.778(3)	5(1)
O82	0.337(2)	0.414(2)	0.768(3)	7(1)
O83	0.343(3)	0.279(2)	0.687(3)	7(1)
O84	0.690(3)	0.429(3)	0.855(4)	10(1)
O85	0.172(3)	0.357(3)	0.633(4)	12(2)
O86	0.229(3)	0.103(3)	0.579(4)	11(2)
O87	0.315(3)	0.058(3)	0.368(5)	14(2)
O88	0.112(4)	0.459(3)	0.403(5)	16(2)
O89	0.644(3)	0.208(3)	0.007(4)	11(2)
O90	0.160(3)	0.237(3)	0.640(4)	11(2)
O91	0.956(3)	0.040(3)	0.089(5)	14(2)
O92	0.780(4)	0.187(4)	0.915(5)	17(2)
O93	0.048(4)	0.390(4)	0.067(6)	19(3)

Table 3. Interatomic Distances (Å) among the Ge, Ti, and W Atoms in the $[Ge_2Ti_6W_{18}O_{77}]^{14-}$ Anion

Edge-shared W_{cap}-W_{cap}		
W1	W2	3.371(3)
W2	W3	3.369(3)
W3	W1	3.358(3)
W16	W17	3.362(3)
W17	W18	3.369(3)
W18	W16	3.362(3)
Edge-shared W_{belt}-W_{belt}		
W4	W5	3.329(3)
W6	W7	3.347(3)
W8	W9	3.345(3)
W10	W11	3.334(3)
W12	W13	3.344(3)
W14	W15	3.346(3)
Edge-shared W_{belt}-Ti		
W4	Ti1	3.258(7)
W5	Ti1	3.284(8)
W6	Ti2	3.293(8)
W7	Ti2	3.270(7)
W8	Ti3	3.277(7)
W9	Ti3	3.296(7)
W10	Ti4	3.277(8)
W11	Ti4	3.278(7)
W12	Ti5	3.281(7)
W13	Ti5	3.304(8)
W14	Ti6	3.293(8)
W15	Ti6	3.273(8)
Corner-shared W_{cap}-W_{belt}		
W1	W9	3.736(3)
W1	W4	3.740(3)
W2	W5	3.750(3)
W2	W6	3.732(3)
W3	W7	3.745(3)
W3	W8	3.739(3)
W16	W15	3.736(3)
W16	W10	3.739(3)
W17	W11	3.746(3)
W17	W12	3.734(3)
W18	W13	3.729(3)
W18	W14	3.741(3)
Corner-shared W_{belt}-W_{belt}		
W4	W9	3.763(3)
W5	W6	3.756(3)
W7	W8	3.766(3)
W10	W15	3.771(3)
W11	W12	3.748(3)
W13	W14	3.768(3)
Corner-shared Ti-Ti		
Ti1	Ti2	3.69(1)
Ti2	Ti3	3.62(1)
Ti3	Ti1	3.60(1)
Ti4	Ti5	3.63(1)
Ti5	Ti6	3.67(1)
Ti6	Ti4	3.60(1)
Bridging Ti-Ti		
Ti1	Ti4	3.36(1)
Ti2	Ti5	3.366(9)
Ti3	Ti6	3.36(1)
Ge-Ti		
Ge1	Ti1	3.442(8)
Ge1	Ti2	3.449(9)
Ge1	Ti3	3.420(9)
Ge2	Ti4	3.431(9)
Ge2	Ti5	3.444(9)
Ge2	Ti6	3.418(8)
Ge-W_{cap}		
Ge1	W1	3.554(5)
Ge1	W2	3.540(5)
Ge1	W3	3.518(5)
Ge2	W16	3.548(5)
Ge2	W17	3.543(5)
Ge2	W18	3.535(5)
Ge-W_{belt}		
Ge1	W4	3.573(6)
Ge1	W5	3.556(5)
Ge1	W6	3.533(5)
Ge1	W7	3.543(6)
Ge1	W8	3.557(5)
Ge1	W9	3.564(5)
Ge2	W10	3.534(6)
Ge2	W11	3.558(5)
Ge2	W12	3.561(5)
Ge2	W13	3.566(6)
Ge2	W14	3.555(5)
Ge2	W15	3.556(5)

$[GeTi_3W_9O_{40}]^{10-}$ moiety has an α-A-XM_{12} configuration with C_{3v} symmetry in which the three TiO_6 octahedra are linked to one another by corner-sharing. The dimer, a $[Ge_2Ti_6W_{18}O_{77}]^{14-}$ anion, has D_{3d} symmetry. Based on this symmetry, the 18 W atoms could be classified into two categories: 6 cap W atoms at the two ends of the anion (W1 through W3 and W16 through W18) and 12 belt W atoms between the cap W atoms and the Ti atoms (W4 through W15). The dimer of the Keggin-type $XM_{12}O_{40}^{n-}$ anion is only known for $(Bu_4N)_6H_2[Si_2W_{18}Nb_6O_{77}]$,[14] the dimer of β-A-$SiNb_3W_9O_{40}^{7-}$, whose structure was deduced from both a ^{183}W NMR measurement and FAB mass spectroscopy. The compound, $K_9H_5[Ge_2Ti_6W_{18}O_{77}]\cdot 16H_2O$, has a new type of dimeric α-A-$XM_{12}O_{40}^{n-}$ Keggin structure determined by an X-ray crystal structure analysis.[15]

The metal-metal distances in the anion are listed in Table 3. The edge-shared Ti–W distances are 3.282(12) Å, while the edge-shared W–W distances are 3.365(5) and 3.341(7) Å among the cap W atoms and among the belt W atoms, respectively. As was discussed regarding the structure of the $[PTi_2^{IV}W_{10}O_{40}]^{7-}$ anion,[4] the short Ti–W distances are due to the small electrostatic repulsion between the Ti^{IV}–W^{VI} atoms, compared with that between two W^{VI} atoms. The corner-shared W–W distances are 3.762(8) and 3.739(6) Å for the W_{cap}–W_{belt} and W_{belt}–W_{belt} pairs, respectively. The corner-shared Ti–Ti distance is 3.64 (3) Å, which is also shorter than that for the corner-shared W–W pairs. The metal-oxygen bond distances are listed in Table 4. The terminal W–O distances are 1.75(4) Å at the cap W atoms and 1.69(3) Å at the belt ones. The edge-shared W–

Table 4. Metal–Oxygen Bond Distances (Å) in the $[Ge_2Ti_6W_{18}O_{77}]^{14-}$ Anion

Atom	Atom	Distance	Atom	Atom	Distance
W1	O1	1.67(3)	W11	O60	1.67(3)
W1	O12	1.88(3)	W11	O45	1.82(2)
W1	O7	1.90(3)	W11	O53	1.86(3)
W1	O4	1.95(3)	W11	O54	1.90(3)
W1	O6	1.98(3)	W11	O67	1.95(3)
W1	O13	2.33(3)	W11	O50	2.31(2)
W2	O2	1.74(3)	W12	O61	1.70(3)
W2	O9	1.91(2)	W12	O54	1.90(2)
W2	O4	1.92(3)	W12	O46	1.91(2)
W2	O8	1.94(3)	W12	O55	1.98(3)
W2	O5	1.97(3)	W12	O68	1.99(2)
W2	O13	2.29(3)	W12	O51	2.38(2)
W3	O3	1.82(3)	W13	O62	1.72(3)
W3	O6	1.83(3)	W13	O47	1.80(3)
W3	O11	1.85(3)	W13	O56	1.93(2)
W3	O10	1.85(3)	W13	O55	1.97(3)
W3	O5	1.87(3)	W13	O69	1.98(2)
W3	O13	2.26(3)	W13	O51	2.31(3)
W4	O14	1.61(3)	W14	O63	1.73(3)
W4	O29	1.82(2)	W14	O48	1.81(3)
W4	O20	1.90(3)	W14	O56	1.91(3)
W4	O25	1.91(3)	W14	O57	1.92(3)
W4	O7	2.00(3)	W14	O70	2.00(2)
W4	O26	2.24(2)	W14	O52	2.32(2)
W5	O15	1.73(3)	W15	O64	1.69(3)
W5	O21	1.84(3)	W15	O49	1.83(3)
W5	O30	1.88(2)	W15	O57	1.88(3)
W5	O20	1.92(3)	W15	O58	1.92(3)
W5	O8	1.95(3)	W15	O71	1.92(2)
W5	O26	2.31(2)	W15	O52	2.29(2)
W6	O16	1.72(3)	W16	O75	1.76(3)
W6	O31	1.88(3)	W16	O66	1.87(3)
W6	O21	1.97(3)	W16	O74	1.89(3)
W6	O9	1.97(2)	W16	O71	1.91(2)
W6	O22	1.98(3)	W16	O72	1.91(2)
W6	O27	2.37(2)	W16	O65	2.28(3)
W7	O17	1.71(3)	W17	O76	1.75(2)
W7	O32	1.86(2)	W17	O68	1.89(3)
W7	O22	1.89(2)	W17	O67	1.89(3)
W7	O23	1.94(2)	W17	O72	1.95(3)
W7	O10	2.00(3)	W17	O73	1.98(3)
W7	O27	2.31(3)	W17	O65	2.34(2)
W8	O18	1.71(3)	W18	O77	1.74(3)
W8	O24	1.82(3)	W18	O70	1.85(2)
W8	O33	1.86(2)	W18	O69	1.89(3)
W8	O23	1.90(3)	W18	O73	1.96(2)
W8	O11	1.98(3)	W18	O74	1.98(3)
W8	O28	2.33(2)	W18	O65	2.26(3)
W9	O19	1.67(3)	Ti1	O37	1.84(3)
W9	O34	1.83(2)	Ti1	O38	1.85(2)
W9	O24	1.93(3)	Ti1	O29	1.94(3)
W9	O25	1.93(3)	Ti1	O35	1.95(3)
W9	O12	1.98(2)	Ti1	O30	1.96(3)
W9	O28	2.30(2)	Ti1	O26	2.19(2)
W10	O59	1.66(3)	Ti2	O39	1.83(3)
W10	O44	1.80(2)	Ti2	O36	1.88(3)
W10	O53	1.93(2)	Ti2	O35	1.90(3)
W10	O66	1.96(2)	Ti2	O32	2.04(3)
W10	O58	1.96(3)	Ti2	O31	2.04(3)
W10	O50	2.27(3)	Ti2	O27	2.27(2)
Ti3	O40	1.84(2)	Ti5	O47	2.03(3)
Ti3	O37	1.87(3)	Ti5	O51	2.23(3)
Ti3	O36	1.89(3)	Ti6	O43	1.82(3)
Ti3	O34	1.99(3)	Ti6	O40	1.83(2)
Ti3	O33	2.02(3)	Ti6	O42	1.89(3)
Ti3	O28	2.23(2)	Ti6	O48	2.00(3)
Ti4	O38	1.78(2)	Ti6	O49	2.10(3)
Ti4	O41	1.90(3)	Ti6	O52	2.17(2)
Ti4	O43	1.91(3)	Ge1	O27	1.63(2)
Ti4	O44	2.00(3)	Ge1	O28	1.70(2)
Ti4	O45	2.08(3)	Ge1	O13	1.74(2)
Ti4	O50	2.20(2)	Ge1	O26	1.77(2)
Ti5	O39	1.80(3)	Ge2	O51	1.67(3)
Ti5	O41	1.84(3)	Ge2	O50	1.73(3)
Ti5	O42	1.92(3)	Ge2	O52	1.74(2)
Ti5	O46	2.01(3)	Ge2	O65	1.74(2)

O(··Ti) distances are 1.84(3) Å, which is significantly shorter than the edge-shared W–O(··W) distances of 1.94(5) and 1.92(5) Å at the cap-cap and belt-belt pairs. This is explained by the fact that the O atoms between the Ti and W atoms are attracted toward a more positive W^{VI} center from a less-positive Ti^{IV} center. As a result of its trans influence, the corner-shared W_{belt}–O(··W_{cap}) distance becomes as long as 1.97(3) Å. The W–O distance of its trans position becomes as short as 1.89(3) Å. The Ti–O distances at the O atoms bridging the two $[GeTi_3W_9O_{40}]^{10-}$ moieties are 1.80—1.84 Å, which is regarded as being single bonds. These O atoms are the terminal O atoms at the three Ti^{IV} atoms in the hypothetical monomer of $[GeTi_3W_9O_{40}]^{10-}$. In the $[PTi_2^{IV}W_{10}O_{40}]^{7-}$ anion, the terminal Ti^{IV}–O bond distances were 1.75—1.77 Å, and are expected to be protonated. Since the terminal O atoms at the Ti^{IV} atoms of $[GeTi_3W_9O_{40}]^{10-}$ would be similarly protonated, its dimerization reaction may be possible as follows:

$$[GeTi_3W_9O_{40}]^{10-} + 3H^+ \rightleftarrows [GeTi(OH)_3W_9O_{37}]^{7-}$$

and

$$2[GeTi(OH)_3W_9O_{37}]^{7-} \rightleftarrows [Ge_2Ti_6W_{18}O_{77}]^{14-} + 3H_2O.$$

This indicates that the substitution of Mo or W atoms of the Keggin (or other) heteropolyoxometalates for the less-positive heteroatoms gives rise to a more negative charge on the polyoxometalate surface, with a resultant easiness for undergoing protonation, dimerization, peroxidation and other reactions at the heteroatom site. The dimerization reaction induced by a partial replacement of Mo or W atoms with lower valent heteroatoms suggests the possibility of constructing new heteropolyoxometalates with a higher degree of oligomerization.

Figure 3 shows the ^{183}W NMR spectrum of $K_9H_5[Ge_2Ti_6W_{18}O_{77}]\cdot 16H_2O$ in D_2O. It shows 2 resonances at −107.45 and −127.76 ppm with an integrated intensity ratio of 1.94 : 1. The $^2J_{w-o-w}$ coupling con-

stants are 17.4 Hz at both lines. From the integrated intensity ratio, the peaks at −107.45 and −127.76 ppm may be assigned to the 12 belt W atoms (W4 through W15) and the 6 cap W atoms (W1 through W3 and W16 through W18), respectively. The $^{2}J_{w-o-w}$ coupling constant of 17.4 Hz is the typical value for the edge-shared WO_6 pairs,[16] and is reasonable for the structure determined from the X-ray crystal structure analysis.

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