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Crystal Structure of Cesium Salt of β-Isomer of A-Type Vanadium-Trisubstituted Dodecatungstophosphate Anion, A-β-$Cs_{5.4}H_{0.6}[PV_3W_9O_{40}]\cdot 12H_2O$

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The crystal structure of the title compound as the cesium salt of the vanadium-trisubstituted dodecatungstophosphate anion was determined by a single X-ray analysis. The anion is a geometrical β-isomer and an A-type positional isomer; three V atoms are not in disorder with W atoms, being linked to one another through the corner-sharing oxygen atom. The V–V distances are substantially shortened in comparison with the corresponding W–W ones of the β-tungstosilicate analogs, which is attributable to a difference in ion radii of V^{5+} (0.68 Å) and W^{6+} (0.74 Å). A non-bonded contact between a Cs atom and one of the bridging oxygen atoms in the V–O–V bonds is apparently short compared with the other contacts between the Cs atoms and oxygen atoms of the polyanion. Taking into consideration that this Cs atom is in disorder with a proton, this bridging oxygen atom is considered to be protonated. A bond-valence calculation for the bridging oxygen atoms in the polyanion also suggests protonation of this bridging oxygen atom.

Mixed addenda heteropolyoxometalates have attracted much attention from the viewpoints of catalyst-support materials[1] and magnetic characteristics having interactions between different metals,[2] as well as fundamental structural chemistry[3,4] and their inherent catalytic activities.[5—11] Of primary importance in these fields is an acquisition of the precise structure of the heteropolyanion, including the positional isomerism[12] of the different metal atoms. However, these metal atoms are susceptible to disordered arrangements in the polyanion,[13—15] and, hence, only a few mixed addenda heteropolyanions of the Keggin type have been structurally clarified by a single-crystal X-ray analysis, the sites of the addenda atoms having been determined.[16—22]

In our previous work,[23] we synthesized some novel A-β-$[PV_3W_9O_{40}]^{6-}$ anion salts, and revealed that the β-isomer isomerized to the corresponding α-one both in the solid state and in solution under mild conditions, in which protonation to the polyanion was concerned. In this study, the structure of the cesium salt of the A-β-$[PV_3W_9O_{40}]^{6-}$ anion was determined by a single-crystal X-ray analysis as the first example of a vanadium-trisubstituted dodecatungstophosphate anion. The positional parameters of the cesium cations afford important information concerning protonation to this mixed addenda heteropolyanion.

Experimental

Preparation of the $[PV_3W_9O_{40}]^{6-}$ Anion Salt. $NaVO_3$ (4.23 g, 34.4 mmol) and A-$Na_9[PW_9O_{34}]\cdot 7H_2O$[24] (14.2 g, 5.54 mmol) underwent condensation in a mixed solution of water (90 cm^3), 12 mol cm^{-3} HCl (50 cm^3), and 1,4-dioxane (50 cm^3). The addition of CsCl solids (13.2 g, 78.4 mmol) to the solution afforded red precipitates, which were collected by filtration and dried in vacuo to afford a red powder (12.5 g). The preparation method was reported in detail in a previous paper,[23] in which the red powder was considered to be A-β-$Cs_6[PV_3W_9O_{40}]$. The red powder was recrystallized from water to give dark-red columns of A-β-$Cs_{5.4}H_{0.6}[PV_3W_9O_{40}]\cdot 12H_2O$ (10.5 g, 56% yield). The composition of the cation was determined by the single-crystal X-ray analysis described below. Twelve molar amounts of water were determined by thermogravimetry based on the weight loss of the salt heated up to 300 °C. The complex contained no sodium ion based on atomic absorption spectroscopy. Anal. Found: H, 0.67; Cs, 22; P, 0.91; V, 4.4; W, 48%. Calcd for $H_{24.6}Cs_{5.4}O_{52}PV_3W_9$: H, 0.73; Cs, 21.03; O, 24.38; P, 0.91; V, 4.48; W, 48.48%.

X-Ray Crystal Structure Determination. Intensity data were collected on a Rigaku AFC-7R four-circle diffractometer with graphite-monochromated Mo $K\alpha$ ($\lambda = 0.71069$ Å) radiation, at the Faculty of Science, Osaka University. The crystallographic data are summarized in Table 1. The unit-cell parameters were determined from 18 independent reflections with 2θ over the range of 21.9—27.6°. Three standard reflections were monitored after the collection of 150 reflections. No significant decays in their intensities (maximum 8.2%) were observed throughout the data collection. The reflection data were corrected for Lorentz and polarization effects, together with absorption (transmission factors, 0.273—0.999).[25]

The structure was solved by the direct method (SHELXS86)[26] and refined by a full-matrix least-squares technique. The function $\sum w(|F_o| - |F_c|)^2$ with $w = (\sigma^2(F_o) + 0.0009F_o{}^2)^{-1}$ was minimized for the refinement. All of the non-hydrogen atoms, except for O(13) of the polyanion (see Fig. 1) and one oxygen atom (O(30))

Table 1. Crystallographic Data for $Cs_{5.4}H_{0.6}[PV_3W_9O_{40}]\cdot 12H_2O$

Formula	$H_{24.6}Cs_{5.4}O_{52}PV_3W_9$
Formula weight	3412.9
Crystal size/mm	$0.2\times 0.1\times 0.3$
Crystal system	Orthorhombic
Space group	*Pbcm* (No. 57)
a/Å	13.648(4)
b/Å	21.417(2)
c/Å	16.742(2)
V/Å^3	4893(1)
Z	4
D_{calc}/g cm^{-3}	4.632
F(000)	5950.4
μ(Mo $K\alpha$)/mm^{-1}	27.0
T/°C	23
Scan range 2θ/°	3—60
Scan width $\Delta\omega$/°	$1.00+0.35\tan\theta$
Scan speed ω/° min^{-1}	16($3^\circ < 2\theta < 50^\circ$) and 8 ($50^\circ \le 2\theta \le 60^\circ$)
Scan mode	ω–2θ
Number of unique reflections	7844
Number of reflections with $I > 3\sigma(I)$	4123
R_{int}	0.139
R	0.046
R_{w}	0.060
$\Delta\rho_{\text{min}}$/e Å^{-3}	−4.28
$\Delta\rho_{\text{max}}$/e Å^{-3}	3.15
S	1.17

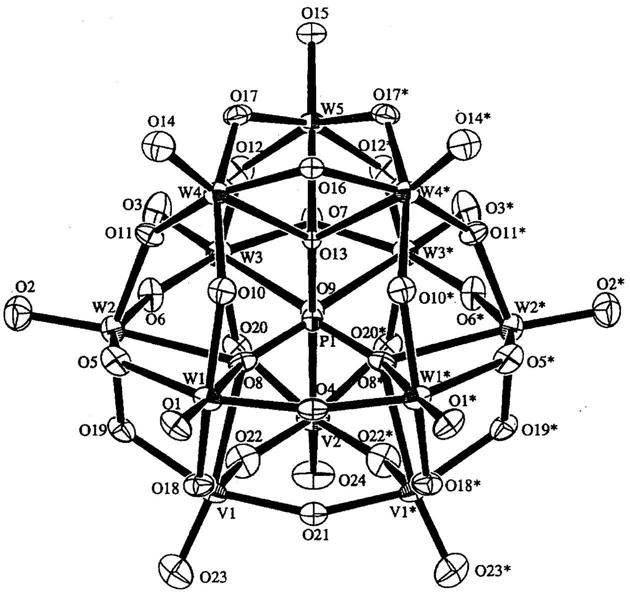

Fig. 1. Structure of the anion of A-β-$Cs_{5.4}H_{0.6}[PV_3W_9O_{40}]\cdot 12H_2O$. Thermal ellipsoids are shown at the 50% probability level. Atoms are related to starred ones by a mirror symmetry.

of eight water molecules, were refined anisotropically. Although the thermogravimetric analysis determined twelve water molecules for the title complex molecule, eight oxygen atoms of water were clarified from the D-Fourier maps. The positions of the hydrogen atoms were not determined. Since the Cs(4) atom on a mirror plane afforded a very large B_{eq} (about 15 Å^2) compared with those (3.40—6.79 Å^2) of the other Cs atoms, the occupancy factor was refined to be reduced to 0.2. Thus, the counter cations are considered to be $(Cs^+)_{5.4}(H^+)_{0.6}$. Although numerous large peaks (up to 3.15 e Å^{-3}) near to the Cs and W atoms (0.8—1.2 Å) were contained on the D-Fourier map, they were ignored because they make no chemical sense. Calculations were performed with the TEXSAN structure analysis software[27] on an IRIS INDIGO workstation at the Faculty of Science, Osaka University. The atomic-scattering factors were taken from the usual sources.[28] The final positional parameters for non-hydrogen atoms are listed in Table 2. Figures 1 and 3 were drawn with a local version of ORTEP II.[29]

Results and Discussion

Crystal Structure of the Heteropolyanion. A perspective view of the anion of the complex is illustrated in Fig. 1, together with the atom-labeling scheme. The bond distances of the anion are summarized in Table 3. The anion is a geometrical β-isomer[30] (Fig. 2), which results from a 60° rotation about the threefold axis of one trigonal edge-sharing W_3O_{13} unit of the Keggin structure (α-isomer). It belongs to an A-type vanadium-trisubstituted dodecatungstophosphate anion in which three W atoms of three different W_3O_{13} units are replaced by three V atoms.[3]

The central PO_4 moiety adopts almost a regular tetrahedral arrangement having P–O distances of 1.52(2)—1.54(1) Å and O–P–O angles of 108.1(9)—110.2(6)°, compared with the largely distorted tetrahedrons in β-$[PMo_3W_9O_{40}]^{3-}$ (P–O, 1.50—1.70 Å),[19] β-$[SiMoW_{11}O_{40}]^{4-}$ (Si–O, 1.60—1.66 Å; O–Si–O, 109—112°),[13] and β-$[SiW_{12}O_{40}]^{4-}$ (Si–O, 1.37—1.83 Å[31] and 1.64—1.86 Å[32]). The WO_6 and VO_6 octahedra have geometries elongated in the direction of the internal oxygen atoms (O_i)[33] coordinated to the P atom: W–O_i, 2.38(1)—2.43(1) Å; V–O_i, 2.45(1)—2.46(2) Å. The

Table 2. Atomic Coordinates and B_{eq}

Atom	x	y	z	$B_{eq}/Å^2$
W(1)	0.05965(6)	0.03222(3)	0.13790(5)	1.51(1)
W(2)	0.24924(7)	0.08979(3)	0.03766(4)	1.65(1)
W(3)	0.46549(6)	0.15244(3)	0.15019(5)	1.53(1)
W(4)	0.09900(6)	0.20216(3)	0.14820(4)	1.40(1)
W(5)	0.29472(8)	0.26045(4)	0.25	1.38(2)
Cs(1)	0.4821(1)	0.14953(8)	0.59724(10)	3.40(3)
Cs(2)	0.8900(2)	0.1440(1)	0.5013(2)	6.79(6)
Cs(3)	0.2040(2)	0.0355(2)	0.75	5.96(8)
Cs(4)	0.9101(5)	0.1587(3)	0.75	5.2(2)
V(1)	0.2775(2)	−0.0437(1)	0.1424(2)	1.66(6)
V(2)	0.4808(3)	0.0161(2)	0.25	1.63(8)
P(1)	0.2541(5)	0.0979(3)	0.25	1.1(1)
O(1)	−0.055(1)	0.0104(6)	0.1043(9)	2.1(3)
O(2)	0.267(1)	0.1040(7)	−0.0620(9)	2.7(3)
O(3)	0.545(1)	0.1863(7)	0.0847(9)	2.8(3)
O(4)	0.042(1)	0.0231(7)	0.25	1.5(3)
O(5)	0.1166(9)	0.0638(6)	0.0411(8)	1.8(3)
O(6)	0.3709(10)	0.1186(6)	0.0778(8)	1.7(3)
O(7)	0.521(1)	0.1777(9)	0.25	1.6(3)
O(8)	0.2213(9)	0.0618(5)	0.1753(8)	1.4(2)
O(9)	0.365(1)	0.1043(7)	0.25	1.3(3)
O(10)	0.0398(10)	0.1218(5)	0.1539(8)	1.8(2)
O(11)	0.1931(10)	0.1679(5)	0.0769(8)	1.6(2)
O(12)	0.3752(10)	0.2208(6)	0.1724(8)	1.8(2)
O(13)	0.210(1)	0.1633(6)	0.25	0.9(2)
O(14)	0.020(1)	0.2416(6)	0.0870(9)	2.6(3)
O(15)	0.340(1)	0.3337(7)	0.25	1.5(3)
O(16)	0.044(1)	0.2229(7)	0.25	1.0(3)
O(17)	0.195(1)	0.2674(5)	0.1707(8)	1.8(3)
O(18)	0.133(1)	−0.0383(5)	0.1280(8)	1.8(2)
O(19)	0.2869(10)	0.0073(5)	0.0464(8)	1.7(2)
O(20)	0.5209(10)	0.0744(6)	0.1690(8)	1.8(3)
O(21)	0.246(2)	−0.0627(8)	0.25	2.4(4)
O(22)	0.396(1)	−0.0191(6)	0.1747(9)	2.4(3)
O(23)	0.294(1)	−0.1105(6)	0.1028(10)	2.6(3)
O(24)	0.571(1)	−0.0307(8)	0.25	2.4(4)
O(25)	0.345(2)	0.25	0.5	2.9(5)
O(26)	1.069(1)	0.1220(7)	0.632(1)	5.0(5)
O(27)	0.598(2)	0.197(1)	0.75	4.8(7)
O(28)	0.718(1)	0.055(1)	0.112(1)	5.7(6)
O(29)	0.5	0	0	6.4(9)
O(30)	0.839(4)	0.132(2)	0.25	10.5(8)

Table 3. Bond Distances (Å) of the Anion

Atom	Atom	Distance	Atom	Atom	Distance
W(1)	O(1)	1.73(1)	W(4)	O(14)	1.71(2)
W(1)	O(4)	1.901(3)	W(4)	O(16)	1.913(7)
W(1)	O(5)	1.92(1)	W(4)	O(17)	1.95(1)
W(1)	O(8)	2.38(1)	W(5)	O(12)	1.90(1)
W(1)	O(10)	1.96(1)	W(5)	O(13)	2.38(1)
W(1)	O(18)	1.82(1)	W(5)	O(15)	1.69(2)
W(2)	O(2)	1.71(1)	W(5)	O(17)	1.91(1)
W(2)	O(5)	1.90(1)	V(1)	O(8)	2.45(1)
W(2)	O(6)	1.90(1)	V(1)	O(18)	1.99(1)
W(2)	O(8)	2.41(1)	V(1)	O(19)	1.95(1)
W(2)	O(11)	1.95(1)	V(1)	O(21)	1.896(7)
W(2)	O(19)	1.85(1)	V(1)	O(22)	1.79(2)
W(3)	O(3)	1.71(2)	V(1)	O(23)	1.59(1)
W(3)	O(6)	1.91(1)	V(2)	O(9)	2.46(2)
W(3)	O(7)	1.915(9)	V(2)	O(20)	1.92(1)
W(3)	O(9)	2.40(1)	V(2)	O(22)	1.87(2)
W(3)	O(12)	1.95(1)	V(2)	O(24)	1.59(2)
W(3)	O(20)	1.86(1)	P(1)	O(8)	1.54(1)
W(4)	O(10)	1.90(1)	P(1)	O(9)	1.52(2)
W(4)	O(11)	1.90(1)	P(1)	O(13)	1.53(2)
W(4)	O(13)	2.43(1)			

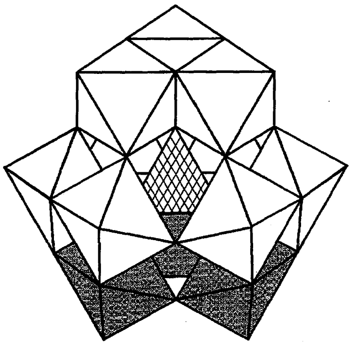

Fig. 2. Polyhedral model of the A-β-$[PV_3W_9O_{40}]^{6-}$ anion. Hatched, plain, and shaded parts indicate the central PO_4 tetrahedron, WO_6 octahedra, and VO_6 octahedra, respectively.

terminal M–O_t[33] (M = W and V) bonds opposite to the internal M–O_i ones are appreciably short in the octahedron: W–O_t, 1.69(2)—1.73(1) Å; V–O_t, 1.59(1)—1.59(2) Å. The O_b atoms[33] of each MO_6 octahedron share those of the adjacent octahedra so as to construct the longitudinal and latitudinal framework of the anion like a ball: W–O_{bc},[33] 1.90(1)—1.96(1) Å; W–O_{be},[33] 1.82(1)—1.95(1) Å; V–O_{bc}, 1.79(2)—1.896(7) Å; V–O_{be}, 1.92(1)—1.99(1) Å. The V–O_{bc} distances are appreciably short compared with the other M–O ones described above. This is attributable to the facts that the ion radius[34] of V^{5+} (coordination number 6), 0.68 Å, is shorter than that of W^{6+} (coordination number 6), 0.74 Å, and that three V atoms of the present heteropolyanion form the corner-sharing V_3O_{13} unit of A-type through the three O_{bc} atoms (O(21), O(22), and O(22*)). The sum of the four O_b–M–O_b angles of each MO_6 octahedron is considerably smaller than 360° for a perfect octahedron (350.2—351.2°). The M–O_b bonds make angles ranging from 98.1(7) to 105.2(7)° with the M–O_t ones and from 70.3(5) to 86.8(5)° with the M–O_i ones. These values show that the W and V atoms deviate from the planes formed by four O_b atoms to the outside of the anion in order to construct the framework.

The non-bonded metal–metal distances between neighboring MO_6 octahedra are summarized in Table 4. Since the spatial locations of the W_{cap} atoms (W(4), W(4*), and W(5)) are closer to those of the W_{belt} atoms (W(1), W(1*), W(2), W(2*), W(3), and W(3*)) in the β-isomer compared with in the α-isomer, the corner-shared W_{belt}–W_{cap} distances (av. 3.68 Å) are obviously shorter than the corner-shared W_{belt}–W_{belt} ones (av. 3.75 Å). Accordingly, the edge-sharing W_3O_{13} unit comprising the W_{cap} atoms is distorted and the edge-shared W_{cap}–W_{cap} distances (av. 3.41 Å) are apparently longer than the edge-shared W_{belt}–W_{belt} ones (av.

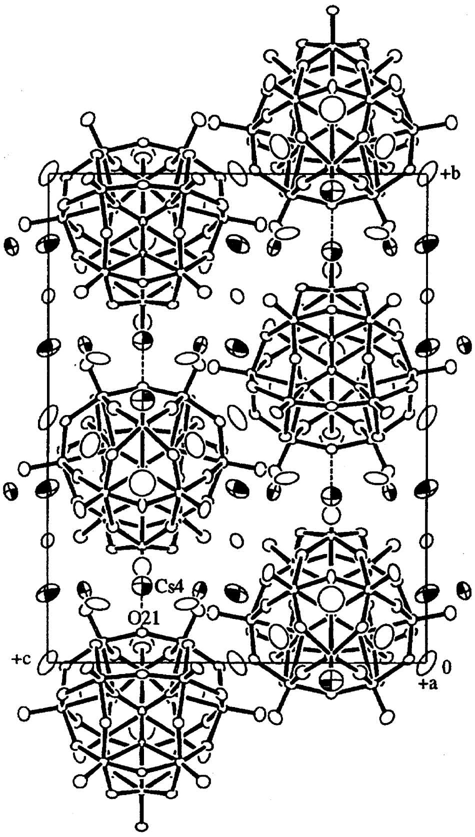

Fig. 3. Crystal structure of A-β-$Cs_{5.4}H_{0.6}[PV_3W_9O_{40}]$ $\cdot 12H_2O$. Shaded and plain ellipsoids indicate cesium and water-oxygen atoms, respectively. Dashed lines represent the shortest non-bonded contact between Cs(4) and O(21) (2.96(2) Å).

3.33 Å). The corner-sharing V_3O_{13} unit becomes compact, as mentioned above, which results in the shorter corner-shared V–V distances (av. 3.58 Å) compared with the corner-shared W_{belt}–W_{cap} ones (av. 3.68 Å) and the corner-shared W_{belt}–W_{belt} ones (av. 3.75 Å). Consequently, the edge-shared W_{belt}–V distances (av. 3.38 Å) are somewhat longer than the edge-shared W_{belt}–W_{belt} ones (av. 3.33 Å).

The metal atoms of the β-isomer of the Keggin-type heteropolyanion are classified into three species: the three (M_{cap}) in the rotated, trigonal edge-sharing M_3O_{13} unit, the three (M_{bottom}) on the opposite side of the M_{cap} unit, and the six (M_{belt}) in octahedra adjacent to both M_{cap} and M_{bottom} atoms. The distances between these metal atoms of some β-isomers are summarized in Table 5. The present β-$[PV_3W_9O_{40}]^{6-}$ anion has striking characteristics compared with the β-tungstosilicate anions;[13,31,32] the corner-shared M_{bottom}–M_{bottom} (V–V) distance is substantially shortened, while the edge-shared M_{cap}–M_{cap} one is apparently lengthened, and the other metal–metal distances are almost unchanged. These findings are also attributable to the difference in the ion radius of V^{5+} and W^{6+}; the corner-sharing V_3O_{13} unit of A-type is apparently contracted, whereas the trigonal edge-sharing W_3O_{13} unit located on the opposite side is somewhat spread out, as described above.

Table 4. Non-Bonded Metal–Metal Distances (Å)

Atom	Atom	Distance	Average
Edge-shared W_{belt}–W_{belt}			3.33
W(1)	W(2)	3.321(1)	
W(3)	W(3*)	3.342(2)	
Edge-shared W_{belt}–V			3.38
W(3)	V(2)	3.371(4)	
W(2)	V(1)	3.377(3)	
W(1)	V(1)	3.390(3)	
Edge-shared W_{cap}–W_{cap}			3.41
W(4)	W(5)	3.406(1)	
W(4)	W(4*)	3.409(1)	
Corner-shared V–V			3.58
V(1)	V(2)	3.548(5)	
V(1)	V(1*)	3.604(7)	
Corner-shared W_{belt}–W_{cap}			3.68
W(2)	W(4)	3.663(1)	
W(1)	W(4)	3.6829(9)	
W(3)	W(5)	3.685(1)	
Corner-shared W_{belt}–W_{belt}			3.75
W(2)	W(3)	3.750(1)	
W(1)	W(1*)	3.754(2)	

Protonation Site of the Heteropolyanion. Cesium cations are surrounded by six to nine oxygen atoms of the polyanion and of water molecules with the Cs–O contacts of 2.96(2)—3.50(1) Å, although all water molecules have not been found in the structure determination. Non-bonded contact (2.96(2) Å) between Cs(4) and O(21) bridging V(1) to V(1*) is the shortest among them, as illustrated in the packing diagram of the complex (Fig. 3). The other non-bonded contacts between Cs atoms and oxygen atoms of the polyanion are 3.07(2)—3.50(1) Å. As described in the experimental section, the occupancy factor of the Cs(4) atom on the mirror in the symmetry operation was reduced to 0.2, indicating the disordered arrangement of Cs(4) and a proton in the fractions of 0.4 and 0.6, respectively. The

Table 5. Averaged Non-Bonded Metal–Metal Distances (Å) of the β-Isomers of the Keggin-Type Heteropolyanions

Heteropolyanion	Edge-shared M_{cap}–M_{cap}	Corner-shared M_{cap}–M_{belt}	Edge-shared M_{belt}–M_{belt}	Corner-shared M_{belt}–M_{belt}	Edge-shared M_{belt}–M_{bottom}	Corner-shared M_{bottom}–M_{bottom}	Ref.
$\beta-[SiW_{12}O_{40}]^{4-}$	3.34	3.65	3.32	3.74	3.36	3.71	31
$\beta-[SiW_{12}O_{40}]^{4-}$	3.35	3.65	3.31	3.74	3.37	3.68	32
$\beta-[SiMoW_{11}O_{40}]^{4-}$ [a]	3.35	3.65	3.32	3.73	3.36	3.70	13
$\beta-[PV_3W_9O_{40}]^{6-}$	3.41	3.68	3.33	3.75	3.38	3.58	This work

a) The Mo atom is statistically disordered over the three equivalent sites of M_{bottom} atoms.

short Cs(4)–O(21) distance is, therefore, considered to be due to the contribution of binding of the proton to the O(21) atom. In accordance, the V(1)–O(21) distance (1.896(7) Å) is appreciably longer than the V(1)–O(22) one (1.79(2) Å), which supports protonation of the O(21) atom. The lengthened distance between a metal atom and a protonated oxygen atom was also observed for α-$K_{3.5}[H_{4.5}PtMo_6O_{24}]$.[35]

In our previous work,[23] protonation at the bridging oxygen atom in A-β-$(NBu^n{}_4)_4H_2[PV_3W_9O_{40}]$ was also indicated by its ^{31}P, ^{51}V, and ^{183}W NMR spectral behavior. The most probable protonation site was thought to be the bridging oxygen atom in the V–O–V bond, since this atom was suggested to be the most basic one among the oxygen atoms in the polyanion, as previously described for the A-β-$[HSiV_3W_9O_{40}]^{6-}$ anion.[3] Thus, the present finding concerning protonation at the O(21) atom in the V–O–V bond accords with the previously estimated protonation site.

The bond-valence sums (BVS)[36] of the oxygen atoms of the present heteropolyanion are summarized in Table 6. The BVS value of the O(21) atom, 1.56, is apparently smaller compared with those of the other bridging oxygen atoms (O_{bc}, O_{be}, and O_i), 1.87—2.09, which are in good agreement with their formal charges of 2. Since the O(21) atom is expected to be protonated as described above, a reduction in the BVS values for this oxygen atom may be compensated by O–H bond formation, as previously reported for some heteropolyanions.[18,37] Valences of the terminal M–O_t bonds are in the range of 1.66—1.85, which are comparable to those of the terminal W–O_t bonds calculated for $[H_2PTi_2W_{10}O_{40}]^{5-}$.[18] The BVS values of the P, V, and W atoms of the present heteropolyanion were calculated to be 5.03, 5.04—5.07, and 6.02—6.27, respectively, which were also consistent with these formal charges of 5, 5, and 6.

Table 6. Bond-Valence Sums of the Oxygen Atoms

Oxygen atom	BVS
Corner-sharing oxygen atom (O_{bc})	
O(21)	1.56
O(22)	1.87
O(10)	1.94
O(11)	1.96
O(12)	1.96
O(6)	2.07
O(4)	2.09
Edge-sharing oxygen atom (O_{be})	
O(19)	1.87
O(20)	1.90
O(18)	1.90
O(17)	1.93
O(7)	2.01
O(16)	2.02
O(5)	2.04
Internal oxygen atom (O_i)	
O(8)	1.96
O(9)	2.01
O(13)	2.05
Terminal oxygen atom (O_t)	
O(1)	1.66
O(2)	1.75
O(3)	1.75
O(14)	1.75
O(23)	1.79
O(24)	1.79
O(15)	1.85

The tetrabutylammonium salt of the present polyanion, A-β-$(NBu^n{}_4)_4H_2[PV_3W_9O_{40}]$, was found to be isomerized to the corresponding α-isomer both in the solid state and in solution under mild conditions, the protonation to the polyanion of the β-isomer facilitating the β-to-α isomerization.[23] The protonation was considered to occur at the bridging oxygen atom in the V–O–V bond and at the bridging oxygen atom between the W_{cap} and W_{belt} atoms. On the other hand, the present cesium salt, A-β-$Cs_{5.4}H_{0.6}[PV_3W_9O_{40}]$, does not isomerize under the same conditions. It is, therefore, suggested that protonation to the bridging oxygen atom in the V–O–V bond is not responsible for the β-to-α isomerization.

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