A Novel-Type Mixed-Ligand Polyoxotungstolanthanoate, $[Ln(BW_{11}O_{39})(W_5O_{18})]^{12-}$ (Ln = Ce^{3+} and Eu^{3+})

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Two isostructural anions, $[Ln(BW_{11}O_{39})(W_5O_{18})]^{12-}$ (Ln = Ce and Eu), were isolated as K^+ salts from aqueous solutions containing tungstate, Ln^{3+}, and BO_3^{3-}, at pH = 7. An X-ray crystallographic analysis showed that the Ln^{3+} center in the anion is chelated by two kinds of tetradentate polyoxotungstate ligands, $[W_5O_{18}]^{6-}$ and α-$[BW_{11}O_{39}]^{9-}$ with a square antiprismatic LnO_8 configuration, which are monovacant derivatives of $[W_6O_{19}]^{2-}$ and α-$[BW_{12}O_{40}]^{5-}$, respectively. The anion is of approximate C_s symmetry, and the observable asymmetry of K–O bonding between two different K^+ cations and the anion causes the two mirror planes within $[(W_5O_{18})Ln]^{3-}$ and $[(BW_{11}O_{39})Ln]^{6-}$ moieties to be canted to each other by 5.2° for Ln = Ce and 4.1° for Ln = Eu.

Polyoxometallolanthanoates (or lanthanide polyoxometalates), which are complexes between lanthanide cations ($Ln^{3+/4+}$) and polyoxometalate ligands, have attracted attention from diverging points of view, such as structural,[1—16] luminescence,[17—30] biological,[31] and NMR spectroscopic properties.[32—35]

The initial preparation and structure studies on polyoxotungstolanthanoates were performed with the compounds sandwiched by the same two deficient structural polyoxotungstates, $[Ln(W_5O_{18})_2]^{n-}$ (n = 9 for Ln^{3+}; n = 8 for Ln^{4+}), $[Ln(SiW_{11}O_{39})_2]^{n-}$ (n = 13 for Ln^{3+}; n = 12 for Ln^{4+}), and $[Ln(P_2W_{17}O_{61})_2]^{n-}$ (n = 17 for Ln^{3+}; n = 16 for Ln^{4+}).[36] Single-crystal X-ray crystallographic characterization was carried out on $[Ln(W_5O_{18})_2]^{n-}$ (Ln = Ce^{4+},[1] Pr^{3+},[11] Nd^{3+},[11] Sm^{3+},[7,10,11] Eu^{3+},[8] Gd^{3+},[9,11] Tb^{3+},[11] and Dy^{3+}[11]) and $[Ce(P_2W_{17}O_{61})_2]^{16-}$.[2] On the other hand, the structure of $[Ln(XW_{11}O_{39})_2]^{n-}$ has been assumed to be powder-diffractometrically identical[22] with the one of $[U(GeW_{11}O_{39})_2]^{12-}$.[37] The $\{W_5O_{18}\}$, $\{XW_{11}O_{39}\}$, and $\{P_2W_{17}O_{61}\}$ ligands for these anions are monovacant species of the Lindqvist type $[W_6O_{19}]^{2-}$, α-Keggin type $[XW_{12}O_{40}]^{n-}$ (n = 4 for X = Si; n = 3 for X = P), and Wells–Dawson type $[P_2W_{18}O_{62}]^{6-}$, respectively. Two types of the mixed-ligand polyoxotungstolanthanoates have recently been X-ray crystallographically characterized. The first example is $K_{15}H_3[Eu_3(H_2O)_3(SbW_9O_{33})(W_5O_{18})_3]\cdot 25.5H_2O$,[4] the anion of which is a $Eu_3(H_2O)_3^{9+}$ core attached by three monovacant $[W_5O_{18}]^{6-}$ and one trivacant α-Keggin type B-α-$[SbW_9O_{33}]^{9-}$ with the tetrahedral coordination geometry. The other is $(NH_4)_{70}Na_6[Ce_{16}(H_2O)_{36}(AsW_9O_{33})_{12}(WO_2)_4(W_2O_6)\{Ce(W_5O_{18})\}_4]\cdot 175H_2O$,[15] the anion of which has a large cyclic structure, consisting of sixteen Ce^{3+} cations, four $[W_5O_{18}]^{6-}$, and twelve B-α-$[AsW_9O_{33}]^{9-}$ ligands. In the present paper, we describe the crystal structure of the third type of mixed-ligand complex, $[Ln(BW_{11}O_{39})(W_5O_{18})]^{12-}$ (Ln = Ce and Eu), consisting of the Ln^{3+} cation, monovacant $[W_5O_{18}]^{6-}$, and monovacant α-$[BW_{11}O_{39}]^{9-}$ anions with a 1 : 1 : 1 ratio.

Experimental

Preparation of $K_{8.5}H_{3.5}[Ce(BW_{11}O_{39})(W_5O_{18})]\cdot 25H_2O$ (1) and $K_{9.5}H_{2.5}[Eu(BW_{11}O_{39})(W_5O_{18})]\cdot 25H_2O$ (2). H_3BO_3 solids (0.10 g) were dissolved into a hot aqueous solution (70 ml at 90 °C) containing WO_3 (4.0 g) and KOH (2.5 g); hydrochloric acid (12 mol dm^{-3}, 2.5 ml) was then slowly added. An aqueous solution (2 ml) of $CeCl_3\cdot 7H_2O$ (0.60 g) was added dropwise to the hot tungstate solution with stirring to produce a few pale-yellow precipitates. The mixture was neutralized to pH = 7 by KOH, boiled for 1 h, and then cooled to room temperature. After removal of the precipitates by filtration, the slightly acidic (pH = 5—6) filtrate was neutralized again to pH = 7, and kept in the open air for slow evaporation. Dark-brown parallelepiped crystals of **1**, obtained after a few weeks, were collected by filtration (yield, 0.2 g). The contents of K, Ce, and W were analyzed on a X-ray fluorescence spectrometer (JEOL JSX-3200) using $K_{18.5}H_{1.5}[Ce_3(CO_3)(SbW_9O_{33})(W_5O_{18})_3]\cdot 14H_2O$[17] solids as a standard. Observed: K, 8.3; Ce, 2.9; W, 62.0%. Calcd for $H_{53.5}BO_{82}K_{8.5}CeW_{16}$: K, 6.94; Ce, 2.92; W, 61.40%. IR spectrum: 3422vs, 1624m, 1249w, ca. 1000sh, 942vs, ca. 880sh, 839vs, 777vs, 542m, 422m cm^{-1}. Long-term evaporation gave bright-orange crystals of $K_9[Ce(W_5O_{18})_2]\cdot 15H_2O$, as a byproduct, which were discriminated from **1** by their color, and could be manually removed.

The europium analog (**2**) was prepared by a similar procedure with $Eu(NO_3)_3\cdot 6H_2O$ (0.65 g) instead of $CeCl_3\cdot 7H_2O$ (yield, 0.3 g). Solids of $K_{15}H_3[Eu_3(H_2O)_3(SbW_9O_{33})(W_5O_{18})_3]\cdot 25.5H_2O$[4] were used as a standard for X-ray fluorescence elemental analysis. Observed: K, 7.2; Eu, 3.3; W, 63.9%. Calcd for $H_{52.5}BO_{82}K_{9.5}EuW_{16}$: K, 7.67; Eu, 3.14; W, 60.77%. IR spectrum: 3434vs, 1624m, 1247w, 996m, 946vs, 884vs, 832vs, 777vs, 716s, 524m, 418m cm^{-1}.

Crystallography.[38] A single crystal of **1** with 0.2×0.2×0.2 mm was sealed in a glass capillary and mounted on a Rigaku AFC5S four-circle diffractometer with a graphite-monochromatized Mo $K\alpha$ radiation (λ = 0.71069 Å). The unit-cell dimensions were determined by least-squares from 20 reflections over the range of 2θ = 20.1—23.8°. Data collection was performed at room temperature over the range 2θ = 5.1—55.1° ($-15 \leq h \leq 15$, $-23 \leq k \leq 0$, $-23 \leq l \leq 23$) with the $\omega/2\theta$-scan mode at a rate of 8 °s^{-1}. The intensities of three standard reflections measured every 150 reflections exhibited no significant decay throughout the data collection. Of the 18052 total reflections, 17485 were independent (R_{int} = 0.066). The Ce and W positions were determined by a direct method, SHELXS86,[39] and other O and K atoms were placed using difference Fourier techniques. Hydrogen atoms were not included in the refinement. Absorption correction DIFABS[40] was applied with resultant transmission factors of 0.65—1.53. K, Ce, and W atoms were refined anisotropically. Full-matrix least-squares refinement were carried out on 6549 observed reflections with $I > 3\sigma(I)$ and 567 variables. The quantity minimized was $\sum w(|F_{obsd}| - |F_{calcd}|)^2$, where the weighting scheme was $w = [\sigma^2(|F_{obsd}|) + (0.003|F_{obsd}|)^2]^{-1}$. The final discrepancy factors were R = 0.073 and R_w = 0.057. The maximum shift/error value and goodness-of-fit parameter were 0.01 and 1.90, respectively. The residual maximum and minimum Fourier peaks were 3.82 and −2.93 e Å^{-3}, respectively.

A single crystal (0.10×0.10×0.10 mm) of **2** sealed in a glass capillary was mounted on a Rigaku RAXIS-RAPID imaging-plate X-ray diffractometer with monochromatized Mo $K\alpha$ radiation (λ = 0.71069 Å). The unit-cell parameters listed in Table 1 were determined from 12511 reflections over a range of 2θ = 4.8—54.9°. Intensity measurements were performed at 173 K using the oscillation method at an oscillation width of 5° and an exposure time of 300 s per photograph. Of the 24784 total reflections from 44 frames, 14748 were unique (R_{int} = 0.052). An empirical absorption correction was made with transmission factors ranging from 0.565 to 1.201. The structure was solved by SIR92[41] and expanded using difference Fourier techniques. K, Ce, and W atoms were refined anisotropically. Full-matrix least-squares refinements were carried out on 8858 observed reflections with $I > 2\sigma(I)$ and 576 variables. The quantity minimized was $\sum w(|F_{obsd}| - |F_{calcd}|)^2$, where $w = [\sigma^2(|F_{obsd}|) + (0.005|F_{obsd}|)^2]^{-1}$. The final discrepancy factors were R = 0.071 and R_w = 0.049. The final maximum shift/error value and goodness-of-fit parameter were 0.007 and 2.38, respectively. The residual maximum and minimum Fourier peaks were 3.26 and −3.58 e Å^{-3}, respectively.

Since the distances between K5 and symmetry related ($1-x$, y, $1-z$) K5′ is too short (3.07(6) Å for **1**, and 2.78(3) Å for **2**) for $K^+ \cdots K^+$ separation, the site occupancy of K5 was fixed at 0.5 for both **1** and **2**. As shown in Table 2, the atomic coordinate of K10 in **2** is similar to that of O76 (of a crystallization water molecule) in **1**. We determined the Fourier peak at the O76 site in **1** as the O atom, because a refinement of the peak as the K atom with full occupancy (1.0) resulted in a too large displacement parameter (B_{iso} = 20.4 Å^2). However, there remains a possibility that the O76 site in **1** is partially replaced by a K atom with a disorder. The slightly larger value of the observed K contents (8.3%) than the calculated one (6.94%) for **1** may be due to the mixing of an additional K atom to the O76 site. Of the total anion charge (−12), −8.5 and −9.5 are compensated by K^+ cations for **1** and **2**, respectively. The remaining −3.5 and −2.5 electrons per anion are assumed to be compensated by protons. The number of crystallization water molecules (=25 for both **1** and **2**) was also determined from the X-ray structural analysis. We thus concluded compounds **1** and **2** to be formulated as $K_{8.5}H_{3.5}[Ce(BW_{11}O_{39})(W_5O_{18})]\cdot 25H_2O$ and $K_{9.5}H_{2.5}[Eu(BW_{11}O_{39})(W_5O_{18})]\cdot 25H_2O$, respectively. No protonation site could be determined. All of the calculations were performed using the TEXSAN software package.[42] Crystallographic data and atomic coordinates with displacement parameters are listed in Tables 1 and 2. Table 3 summarizes the K–O distances (< 3.3 Å).

Results and Discussion

Structures of 1 and 2. Figure 1 shows the molecular structure of $[Ln(BW_{11}O_{39})(W_5O_{18})]^{12-}$ (Ln = Ce and Eu) with atomic labeling. The central Ln^{3+} cation is attached with tetradentate $[W_5O_{18}]^{6-}$ and $[BW_{11}O_{39}]^{9-}$ ligands via eight O atoms with a distorted square-antiprismatic configuration. The $[W_5O_{18}]^{6-}$ and $[BW_{11}O_{39}]^{9-}$ ligands are monovacant species derived from

Table 1. Crystallographic Data of **1** and **2**

	1	**2**
Formula	$H_{53.5}BO_{82}K_{8.5}CeW_{16}$	$H_{52.5}BO_{82}K_{9.5}EuW_{16}$
Formula weight	4790.74	4840.67
Crystal shape/color	Prism/yellowish brown	Prism/colorless
Space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
Unit cell parameters		
a/Å	11.88(2)	11.7035(7)
b/Å	17.75(2)	17.927(2)
c/Å	18.14(1)	18.028(1)
α/°	87.87(7)	87.401(3)
β/°	86.4(1)	86.723(2)
γ/°	85.78(7)	85.867(3)
V/Å^3	3804(6)	3763.3(4)
μ(Mo $K\alpha$)/cm^{-1}	252.80	258.39
Z	2	2
D_{calc}/g cm^{-3}	4.182	4.272
F(000)	4236	4282

Table 2. Positional and Displacement Parameters (Å^2) of **1** and **2**

	1					**2**			
Atom	x	y	z	B_{eq} or B_{iso}	Atom	x	y	z	B_{eq} or B_{iso}
W(1)	0.3012(2)	0.2062(2)	0.7742(1)	2.75(6)	W(1)	0.3029(1)	0.2050(1)	0.77484(7)	2.62(3)
W(2)	0.0715(2)	0.2186(2)	0.6757(1)	2.88(6)	W(2)	0.0680(1)	0.2158(1)	0.67642(7)	3.20(4)
W(3)	0.2493(2)	0.3513(2)	0.6563(1)	2.93(6)	W(3)	0.2444(2)	0.34841(9)	0.65635(8)	3.16(4)
W(4)	0.4565(2)	0.2248(1)	0.6154(1)	2.22(5)	W(4)	0.4561(1)	0.22637(8)	0.61474(7)	1.90(3)
W(5)	0.2786(2)	0.0920(1)	0.6332(1)	2.15(5)	W(5)	0.2799(1)	0.09296(8)	0.63360(7)	1.98(3)
W(6)	0.1558(2)	0.3328(1)	0.0419(1)	2.16(5)	W(6)	0.1577(1)	0.33218(8)	0.04418(7)	1.96(3)
W(7)	−0.0467(2)	0.4028(1)	0.1631(1)	1.88(5)	W(7)	−0.0516(1)	0.40120(8)	0.16247(7)	1.71(3)
W(8)	−0.0223(2)	0.2193(1)	0.1328(1)	2.35(6)	W(8)	−0.0274(1)	0.21995(8)	0.13294(7)	2.14(3)
W(9)	0.4011(2)	0.2160(2)	0.1074(1)	3.13(6)	W(9)	0.4077(1)	0.21594(9)	0.11231(8)	2.92(4)
W(10)	0.2214(2)	0.1033(2)	0.1936(1)	2.92(6)	W(10)	0.2220(1)	0.10471(9)	0.19656(8)	2.83(4)
W(11)	0.4093(2)	0.1806(2)	0.2916(1)	2.54(6)	W(11)	0.4094(1)	0.18091(9)	0.29700(7)	2.42(4)
W(12)	0.3725(2)	0.4195(1)	0.1418(1)	2.20(5)	W(12)	0.3771(1)	0.41865(8)	0.14649(7)	2.01(3)
W(13)	0.3824(2)	0.3786(1)	0.3240(1)	2.09(5)	W(13)	0.3816(1)	0.37681(8)	0.32874(7)	1.98(3)
W(14)	0.1691(2)	0.4895(1)	0.2581(1)	1.81(5)	W(14)	0.1688(1)	0.48619(8)	0.26013(7)	1.65(3)
W(15)	−0.0207(2)	0.3641(1)	0.3659(1)	1.90(5)	W(15)	−0.0249(1)	0.36059(8)	0.36731(7)	1.70(3)
W(16)	0.0072(2)	0.1779(1)	0.3358(1)	2.21(5)	W(16)	0.0031(1)	0.17837(8)	0.33866(7)	2.03(3)
Ce(1)	0.2188(2)	0.2435(2)	0.4864(2)	1.87(7)	Eu(1)	0.2143(1)	0.2431(1)	0.48654(8)	1.84(4)
K(1)	0.328(1)	0.487(1)	−0.0526(7)	4.4(4)	K(1)	0.3304(7)	0.4815(5)	−0.0507(4)	3.6(2)
K(2)	0.679(1)	0.433(1)	0.2750(9)	5.9(5)	K(2)	0.6816(8)	0.4397(6)	0.2790(5)	4.8(3)
K(3)	0.063(1)	0.381(1)	0.8244(6)	4.2(4)	K(3)	0.0646(7)	0.3859(5)	0.8244(4)	3.4(2)
K(4)	0.740(1)	0.114(1)	0.2499(9)	5.8(5)	K(4)	0.7354(8)	0.1150(5)	0.2478(5)	4.6(3)
K(5)[a]	0.501(2)	0.076(2)	0.465(1)	4.3(7)	K(5)[a]	0.488(1)	0.0726(9)	0.4693(7)	2.8(4)
K(6)	0.772(1)	0.3139(9)	0.6375(8)	4.8(4)	K(6)	0.7687(8)	0.3211(5)	0.6377(5)	4.1(2)
K(7)	0.179(1)	0.4757(8)	0.4738(7)	3.8(3)	K(7)	0.1786(8)	0.4737(5)	0.4763(4)	3.6(2)
K(8)	0.536(2)	0.046(2)	0.750(1)	14(1)	K(8)	0.541(2)	0.0469(9)	0.7481(9)	13.0(6)
K(9)	0.805(2)	0.144(2)	0.831(1)	14(1)	K(9)	0.806(1)	0.1444(8)	0.8338(8)	11.1(5)
					K(10)	0.717(1)	0.3538(7)	0.8975(7)	8.8(4)
O(1)	0.325(3)	0.195(2)	0.870(2)	2.9(7)	O(1)	0.328(2)	0.194(1)	0.868(1)	3.5(5)
O(2)	−0.064(3)	0.209(2)	0.710(2)	3.5(8)	O(2)	−0.075(2)	0.208(2)	0.707(1)	4.9(6)
O(3)	0.242(3)	0.438(3)	0.680(2)	5(1)	O(3)	0.236(3)	0.435(2)	0.678(2)	9(1)
O(4)	0.605(3)	0.229(2)	0.606(2)	3.6(8)	O(4)	0.597(2)	0.231(1)	0.607(1)	3.5(5)
O(5)	0.283(3)	0.005(3)	0.634(2)	6(1)	O(5)	0.299(2)	−0.003(1)	0.633(1)	3.6(5)
O(6)	0.179(3)	0.358(2)	−0.055(2)	3.1(8)	O(6)	0.174(2)	0.355(1)	−0.048(1)	3.0(5)
O(7)	−0.160(2)	0.468(2)	0.146(2)	1.9(6)	O(7)	−0.163(2)	0.467(1)	0.147(1)	2.4(4)
O(8)	−0.121(3)	0.159(3)	0.106(2)	5(1)	O(8)	−0.120(2)	0.167(1)	0.096(1)	3.2(5)
O(9)	0.508(3)	0.205(2)	0.034(2)	4.0(9)	O(9)	0.505(2)	0.198(1)	0.040(1)	2.3(4)
O(10)	0.204(3)	0.021(2)	0.184(2)	4.0(9)	O(10)	0.209(2)	0.013(1)	0.183(1)	4.1(6)
O(11)	0.529(3)	0.131(3)	0.328(2)	5(1)	O(11)	0.527(2)	0.138(1)	0.332(1)	3.1(5)
O(12)	0.458(3)	0.472(2)	0.078(2)	3.3(8)	O(12)	0.453(2)	0.470(1)	0.081(1)	3.1(5)
O(13)	0.493(3)	0.412(2)	0.370(2)	3.9(8)	O(13)	0.491(2)	0.407(1)	0.378(1)	2.5(5)
O(14)	0.133(3)	0.580(2)	0.274(2)	4.1(9)	O(14)	0.130(2)	0.577(1)	0.272(1)	2.8(5)
O(15)	−0.134(2)	0.415(2)	0.413(2)	2.6(7)	O(15)	−0.141(2)	0.409(1)	0.4093(9)	1.3(4)
O(16)	−0.094(2)	0.109(2)	0.356(1)	1.3(6)	O(16)	−0.095(2)	0.112(1)	0.359(1)	3.6(5)
O(17)	0.141(2)	0.202(2)	0.773(2)	1.7(6)	O(17)	0.138(2)	0.205(1)	0.776(1)	2.6(5)
O(18)	0.283(4)	0.307(3)	0.760(2)	7(1)	O(18)	0.280(2)	0.311(1)	0.760(1)	2.8(5)
O(19)	0.447(2)	0.212(2)	0.728(2)	2.2(7)	O(19)	0.450(2)	0.213(1)	0.728(1)	1.7(4)
O(20)	0.306(2)	0.106(2)	0.740(2)	1.9(6)	O(20)	0.304(2)	0.106(1)	0.741(1)	2.5(5)
O(21)	0.105(3)	0.323(2)	0.683(2)	3.8(8)	O(21)	0.090(2)	0.318(1)	0.683(1)	3.1(5)
O(22)	0.414(3)	0.331(2)	0.639(2)	2.6(7)	O(22)	0.407(2)	0.330(1)	0.637(1)	3.1(5)
O(23)	0.425(3)	0.124(2)	0.619(2)	3.1(8)	O(23)	0.433(2)	0.120(1)	0.623(1)	1.5(4)
O(24)	0.117(3)	0.109(2)	0.670(2)	3.2(8)	O(24)	0.128(2)	0.114(1)	0.668(1)	3.6(5)
O(25)	0.061(2)	0.234(2)	0.577(2)	1.8(6)	O(25)	0.066(2)	0.232(1)	0.579(1)	2.7(5)
O(26)	0.222(2)	0.354(2)	0.557(2)	1.7(6)	O(26)	0.217(2)	0.346(1)	0.561(1)	2.1(4)
O(27)	0.412(3)	0.234(2)	0.520(2)	2.9(7)	O(27)	0.414(2)	0.236(1)	0.523(1)	2.3(4)
O(28)	0.255(2)	0.118(2)	0.541(2)	2.1(7)	O(28)	0.257(2)	0.118(1)	0.541(1)	2.0(4)
O(29)	0.265(2)	0.220(2)	0.649(1)	0.9(5)	O(29)	0.267(2)	0.221(1)	0.650(1)	2.6(5)

Table 2. (Continued)

	1				2				
Atom	x	y	z	B_{eq} or B_{iso}	Atom	x	y	z	B_{eq} or B_{iso}
O(30)	0.272(2)	0.255(2)	0.055(2)	1.7(6)	O(30)	0.270(2)	0.259(1)	0.061(1)	1.8(4)
O(31)	0.048(2)	0.257(2)	0.040(1)	1.2(5)	O(31)	0.044(2)	0.259(1)	0.039(1)	2.6(5)
O(32)	0.028(2)	0.404(2)	0.065(2)	2.4(7)	O(32)	0.030(2)	0.402(1)	0.064(1)	2.0(4)
O(33)	0.254(3)	0.404(2)	0.073(2)	3.6(8)	O(33)	0.249(2)	0.397(1)	0.084(1)	1.5(4)
O(34)	0.063(2)	0.474(2)	0.190(2)	1.5(6)	O(34)	0.064(2)	0.465(1)	0.1925(9)	1.2(4)
O(35)	−0.071(2)	0.380(2)	0.263(1)	1.0(5)	O(35)	−0.074(2)	0.374(1)	0.259(1)	1.8(4)
O(36)	−0.117(2)	0.320(2)	0.137(2)	2.3(7)	O(36)	−0.121(2)	0.317(1)	0.133(1)	1.4(4)
O(37)	−0.047(3)	0.203(2)	0.234(2)	3.3(8)	O(37)	−0.055(2)	0.206(1)	0.233(1)	2.1(4)
O(38)	0.102(2)	0.143(2)	0.136(2)	2.3(7)	O(38)	0.103(2)	0.153(1)	0.140(1)	2.5(4)
O(39)	0.433(3)	0.311(3)	0.117(2)	4(1)	O(39)	0.433(2)	0.319(1)	0.124(1)	3.2(5)
O(40)	0.488(2)	0.185(2)	0.186(2)	2.5(7)	O(40)	0.491(2)	0.186(1)	0.191(1)	3.0(5)
O(41)	0.321(2)	0.123(2)	0.114(1)	1.3(6)	O(41)	0.322(2)	0.124(1)	0.116(1)	2.3(4)
O(42)	0.345(3)	0.095(2)	0.260(2)	3.2(8)	O(42)	0.344(2)	0.093(1)	0.264(1)	3.8(6)
O(43)	0.120(2)	0.116(2)	0.277(2)	2.2(7)	O(43)	0.123(2)	0.121(1)	0.280(1)	2.4(4)
O(44)	0.451(3)	0.274(2)	0.288(2)	2.8(7)	O(44)	0.451(2)	0.282(1)	0.296(1)	2.1(4)
O(45)	0.312(3)	0.192(2)	0.367(2)	2.8(7)	O(45)	0.313(2)	0.189(1)	0.376(1)	2.0(4)
O(46)	0.274(2)	0.508(2)	0.177(2)	1.8(6)	O(46)	0.276(2)	0.502(1)	0.181(1)	1.8(4)
O(47)	0.448(2)	0.417(2)	0.226(2)	2.4(7)	O(47)	0.460(2)	0.420(1)	0.230(0)	1.5(4)
O(48)	0.293(2)	0.476(2)	0.322(1)	1.1(5)	O(48)	0.292(2)	0.473(1)	0.323(1)	2.9(5)
O(49)	0.292(3)	0.338(2)	0.393(2)	3.7(8)	O(49)	0.289(2)	0.335(1)	0.396(1)	2.4(4)
O(50)	0.081(2)	0.445(2)	0.335(2)	2.0(6)	O(50)	0.073(2)	0.440(1)	0.335(1)	1.8(4)
O(51)	0.061(2)	0.336(2)	0.443(1)	1.4(6)	O(51)	0.053(2)	0.332(1)	0.443(1)	1.8(4)
O(52)	−0.087(2)	0.270(2)	0.368(1)	1.5(6)	O(52)	−0.096(2)	0.268(1)	0.365(1)	1.5(4)
O(53)	0.086(2)	0.171(2)	0.417(2)	1.8(6)	O(53)	0.081(2)	0.176(1)	0.417(1)	1.5(4)
O(54)	0.108(2)	0.309(2)	0.164(1)	1.0(5)	O(54)	0.091(2)	0.310(1)	0.165(1)	1.5(4)
O(55)	0.274(2)	0.229(2)	0.208(2)	2.1(6)	O(55)	0.280(2)	0.225(1)	0.216(1)	3.0(5)
O(56)	0.253(2)	0.363(2)	0.232(1)	0.7(5)	O(56)	0.260(2)	0.368(1)	0.237(1)	1.8(4)
O(57)	0.118(2)	0.279(2)	0.301(1)	1.1(5)	O(57)	0.105(2)	0.281(1)	0.3025(9)	1.2(4)
O(58)	0.404(3)	0.428(3)	−0.185(2)	5(1)	O(58)	0.044(2)	0.591(1)	0.431(1)	4.1(6)
O(59)	0.129(3)	0.564(3)	0.048(2)	5(1)	O(59)	0.123(2)	0.560(1)	0.052(1)	3.8(6)
O(60)	0.468(4)	0.332(4)	−0.063(3)	10(1)	O(60)	0.574(3)	0.404(2)	0.704(2)	6.7(8)
O(61)	0.326(6)	0.652(5)	−0.085(4)	16(1)	O(61)	0.845(2)	0.223(1)	0.520(1)	4.4(6)
O(62)	0.706(3)	0.278(3)	0.287(2)	6(1)	O(62)	0.402(3)	0.425(2)	−0.187(2)	6.7(8)
O(63)	−0.017(5)	0.248(4)	0.897(3)	13(1)	O(63)	0.731(3)	0.194(2)	0.973(2)	6.9(8)
O(64)	0.912(4)	−0.009(3)	0.208(3)	9(1)	O(64)	0.564(3)	0.113(2)	0.880(2)	9(1)
O(65)	0.616(6)	0.027(5)	0.155(4)	15(1)	O(65)	0.477(3)	0.328(2)	0.935(2)	6.9(8)
O(66)	0.738(3)	0.097(2)	0.485(2)	4.0(9)	O(66)	0.732(2)	0.103(1)	0.487(1)	3.7(5)
O(67)	0.660(5)	0.398(4)	0.518(3)	12(1)	O(67)	0.697(3)	0.280(2)	0.272(2)	8.0(9)
O(68)	0.572(5)	0.553(5)	0.480(4)	15(1)	O(68)	0.737(3)	0.103(2)	0.675(2)	10(1)
O(69)	0.574(3)	0.399(3)	0.703(2)	6(1)	O(69)	0.966(3)	0.259(2)	0.882(2)	7.2(8)
O(70)	0.647(4)	0.265(3)	0.780(3)	8(1)	O(70)	0.654(3)	0.267(2)	0.785(2)	7.5(9)
O(71)	0.849(3)	0.225(2)	0.516(2)	4.1(9)	O(71)	0.902(3)	−0.002(2)	0.206(2)	9(1)
O(72)	0.555(4)	0.119(3)	0.873(3)	9(1)	O(72)	0.621(3)	0.026(2)	0.154(2)	9(1)
O(73)	0.729(4)	0.094(4)	0.694(3)	9(1)	O(73)	0.331(3)	0.608(2)	0.484(2)	7.8(9)
O(74)	0.728(4)	0.198(4)	0.989(3)	10(1)	O(74)	0.322(3)	0.643(2)	−0.057(2)	9(1)
O(75)	0.631(3)	0.260(2)	0.435(2)	3.8(8)	O(75)	0.191(2)	0.128(1)	0.980(1)	2.9(5)
O(76)	0.719(3)	0.353(2)	0.903(2)	3.3(8)	O(76)	0.824(3)	0.029(2)	0.035(2)	9(1)
O(77)	−0.012(4)	0.061(3)	0.541(3)	10(1)	O(77)	0.376(3)	−0.003(2)	0.018(2)	9(1)
O(78)	0.186(3)	0.127(2)	0.975(2)	3.4(8)	O(78)	0.627(1)	0.2603(9)	0.4316(8)	0.3(3)
O(79)	0.233(2)	0.031(2)	0.409(2)	1.9(6)	O(79)	−0.016(3)	0.063(2)	0.533(2)	9(1)
O(80)	0.938(4)	0.036(3)	0.676(3)	9(1)	O(80)	0.945(3)	0.027(2)	0.681(2)	9(1)
O(81)	0.036(2)	0.591(2)	0.426(2)	2.3(7)	O(81)	0.235(1)	0.0326(9)	0.4145(8)	0.2(3)
O(82)	0.138(7)	−0.030(7)	0.965(6)	27.3(8)	O(82)	0.409(4)	0.448(3)	0.519(2)	12(1)
B(1)	0.19(1)	0.285(8)	0.239(7)	10(1)	B(1)	0.183(7)	0.296(5)	0.223(4)	10(1)

a) Site occupancy of K(5) was fixed at 0.5.

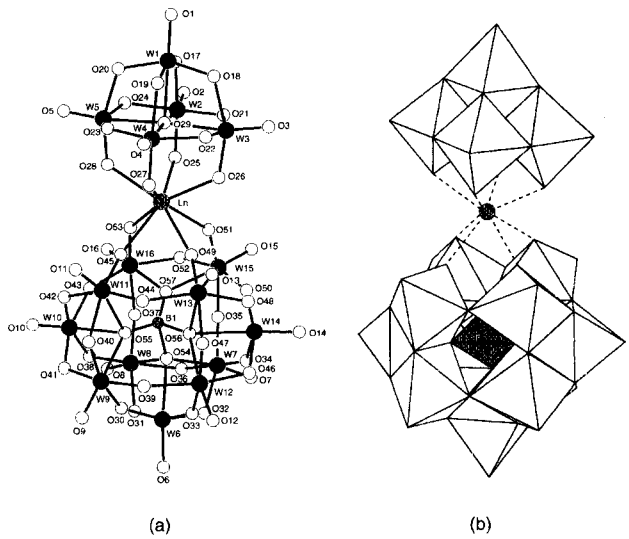
Table 3. K–O Bond Distances (< 3.3 Å) in **1** and **2**

		1						**2**			
K1	O12^{i}	2.70(4)	K6	O4	2.68(4)	K1	O62	2.76(3)	K6	O4	2.76(3)
	O58	2.73(4)		O71	2.82(4)		O12^{i}	2.76(2)		O73^{iii}	2.77(3)
	O7^{ii}	2.76(3)		O14^{iii}	2.86(4)		O7^{ii}	2.77(2)		O14^{iii}	2.85(2)
	O33	2.79(4)		O69	2.92(4)		O12	2.84(2)		O60	2.87(3)
	O12	2.91(3)		O67	2.92(6)		O74	2.88(4)		O61	2.89(2)
	O61	2.97(8)		O2^{iv}	2.94(4)		O33	2.94(2)		O2^{iv}	2.91(3)
	O6	2.99(4)		O70	3.04(5)		O6	3.02(3)		O58^{iii}	2.97(3)
	O60	3.11(6)		O81^{iii}	3.08(4)		O65^{viii}	3.16(3)		O70	3.06(3)
	O59	3.16(4)	K7	O26	2.63(3)		O59	3.24(2)	K7	O58	2.66(3)
	O3^{iii}	2.71(5)		081	2.71(3)	K2	O3^{iii}	2.68(4)		O26	2.72(2)
K2	O62	2.75(5)		O15^{vi}	2.88(4)		O47	2.85(2)		O82	2.85(5)
	O13	2.75(4)		O50	2.91(3)		O13	2.85(2)		O48	2.99(2)
	O47	2.97(3)		O48	2.99(3)		O67	2.86(4)		O15^{vi}	3.00(2)
	O7^{iv}	3.00(3)		O51	3.02(4)		O7^{iv}	2.95(2)		O50	3.00(2)
	O35^{iv}	3.04(3)		O67^{iii}	3.07(7)		O62^{i}	3.01(3)		O49	3.10(2)
	O58^{i}	3.05(4)		O49	3.09(4)		O35^{iv}	3.02(2)		O73	3.11(4)
K3	O6^{v}	2.66(3)		O68^{iii}	3.13(6)		O15^{iv}	3.22(2)		O51	3.12(2)
	O21	2.80(4)	K8	O72	2.64(6)	K3	O6^{v}	2.71(2)		O58^{vi}	3.27(3)
	O63	2.87(7)		O73	2.64(6)		O69^{ix}	2.76(3)	K8	O64	2.74(4)
	O34^{vi}	2.90(3)		O65^{vii}	2.77(8)		O21	2.87(2)		O42^{vii}	2.78(3)
	O18	3.03(4)		O42^{vii}	2.78(4)		O14^{vi}	2.96(2)		O68	2.80(4)
	O14^{vi}	3.05(4)		O20	2.88(3)		O18	2.97(2)		O72^{vii}	2.86(4)
	O7^{vi}	3.07(4)		O23	3.03(4)		O34^{vi}	2.98(2)		O23	2.88(2)
	O59^{vi}	3.27(4)		O19	3.08(4)		O7^{vi}	3.04(2)		O20	2.90(3)
K4	O11	2.80(4)	K9	O2^{iv}	2.86(4)		O59^{vi}	3.18(2)		O19	3.10(2)
	O16^{iv}	2.83(3)		O73	2.89(6)	K4	O11	2.82(2)	K9	O63	2.77(3)
	O65	2.89(8)		O70	2.91(5)		O72	2.83(4)		O2^{iv}	2.85(3)
	O5^{vii}	2.95(5)		O10^{vii}	2.97(5)		O71	2.86(3)		O70	2.86(4)
	O64	2.97(5)		O72	3.08(5)		O16^{iv}	2.89(3)		O10^{vii}	2.86(3)
	O62	3.00(5)		O74	3.13(6)		O5^{vii}	2.90(3)		O64	2.99(4)
	O37^{iv}	3.07(4)		O63^{iv}	3.21(7)		O67	3.01(3)		O69	3.07(4)
	O8^{iv}	3.11(4)					O37^{iv}	3.04(2)		O68	3.15(4)
K5	O11	2.66(4)					O40	3.25(2)	K10	O59^{iii}	2.73(3)
	O66	2.92(5)					O8^{iv}	3.26(2)		O70	2.78(3)
	O23	3.01(4)				K5	O11	2.72(3)		O74^{iii}	2.89(4)
	O27	3.10(4)					O23	2.95(2)		O46^{iii}	2.89(2)
	O28	3.19(4)					O66	2.99(3)		O65	2.91(3)
							O28	3.00(2)		O63	3.12(3)
							O27	3.18(2)		O69	3.27(3)
							O5^{vii}	3.23(3)			
							O45	3.29(2)			

Symmetry codes: (i) $-x+1, -y+1, -z$; (ii) $-x, -y+1, -z$; (iii) $-x+1, -y+1, -z$; (iv) $x+1, y, z$; (v) $x, y, z+1$; (vi) $-x, -y+1, -z+1$; (vii) $-x+1, -y, -z+1$; (viii) $x, y, z-1$; (ix) $x-1, y, z$.

$[W_6O_{19}]^{2-}$ and α-$[BW_{12}O_{40}]^{5-}$ anions, respectively. While the $[W_5O_{18}]^{6-}$ ligand has been used for the preparation of polyoxotungstolanthanoates, such as $[Ln(W_5O_{18})_2]^{n-}$ ($n = 9$ for Ln^{3+}, $n = 8$ for Ln^{4+}),[1,7–11] $[Eu_3(H_2O)_3(SbW_9O_{33})(W_5O_{18})_3]^{18-}$,[4] $[Ce_3(CO_3)(SbW_9O_{33})(W_5O_{18})_3]^{20-}$,[17] and $[Ce_{16}(H_2O)_{36}(AsW_9O_{33})(WO_2)_4(W_2O_6)(Ce\{W_5O_{18}\})_4]^{76-}$,[15] **1** and **2** are the first examples for crystallographically characterized polyoxotungstatolanthanoate possessing the α-$[XW_{11}O_{39}]^{n-}$ ligand, although $[Ln(XW_{11}O_{39})_2]^{n-}$ (X = B, Si, P) anions have been prepared.[22,26,36] It is noteworthy that the W11···W13 distance (3.572(5) Å for **1**; 3.573(2) Å for **2**) for the corner-sharing WO_6 octahedra adjacent to the vacant site is shorter than the W···W separations (mean 3.702 Å in **1** and **2**) for other corner-sharing WO_6 octahedra. Such a distortion seems to be induced by the WO_6-vacancy, since similar short distances of the W···W separation adjacent to the vacancy site have been observed for monovacant α-$\{XW_{11}O_{39}\}$-containing complexes: $[U(GeW_{11}O_{39})_2]^{12-}$,[37] $[(BW_{11}O_{39})_3(W_6O_{15})]^{21-}$,[43] and the free $[HPW_{11}O_{39}]^{6-}$ anion.[44]

The overall symmetry of the anion can be approximated as C_s, where the anion's mirror plane passes through the Ln,



(a) (b)

Fig. 1. Molecular structure and atomic labeling of $[Ln(BW_{11}O_{39})(W_5O_{18})]^{12-}$ (Ln = Ce^{3+} and Eu^{3+}) represented by ball-and-stick (a) and polyhedral (b) models.

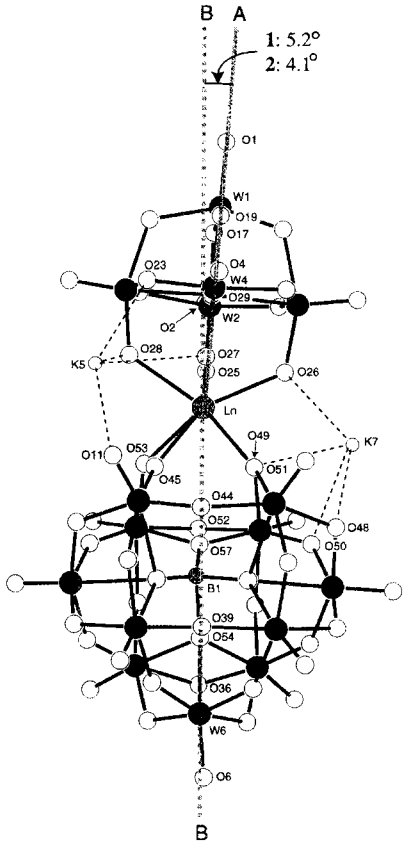


Fig. 2. The $[Ln(BW_{11}O_{39})(W_5O_{18})]^{12-}$ anion viewed parallel to a mirror plane of the approximate C_s symmetry. The thick solid (A) and dashed (B) lines indicate the mirror planes defined by $[(W_5O_{18})Ln]^{3-}$ and $[(BW_{11}O_{39})Ln]^{6-}$ groups, respectively (see text). The inserted values are dihedral angles between A and B planes for **1** and **2**. K–O bonds (< 3.3 Å) for K5 and K7 cations are denoted by the thin dashed lines.

W1, W2, W4, and B1 atoms. However, as shown in Fig. 2, the two mirror planes including the Ln atom are not parallel; the dihedral angle of the two least-square planes defined by [W1, W2, W4, O1, O2, O4, O17, O19, O25, O27, O29, Ln] (in the $[\{W_5O_{18}\}Ln]^{3-}$ group) and [W6, O6, O36, O39, O44, O52, O54, O57, B1, Ln] (in the $[\{BW_{11}O_{39}\}Ln]^{6-}$ group) is 5.2° for **1**, and 4.1° for **2**. Figure 2 also represents the K5 and K7 cations which link the $[W_5O_{18}]^{6-}$ and $[BW_{11}O_{39}]^{9-}$ ligands via K–O bonds (denoted by dashed line). The bond valence sums (BVS),[45] which denote the bond strengths empirically in valence units, for these bonds calculated from their K–O distances (Table 3) were as follows: K5–O (0.43) and K7–O (0.60) for **1**; K5–O (0.46) and K7–O (0.48) for **2**. The asymmetry of the bond strengths between two K–O bonds increases if we consider the half occupancy for K5 (see Experimental Section). Such an increased asymmetry of the K–O bonds demonstrates the above canted mirror planes for the anion. This is supported by the fact that the larger BVS value for the K7–O bonds (**1**, 0.60; **2**, 0.48) is reflected in a larger dihedral angle (**1**, 5.2°; **2**, 4.1°).

Figures 3(a) and (b) represent the coordination geometry for the square-antiprismatic CeO_8 and EuO_8 sites for **1** and **2**, respectively. The mean Ln–O distance for the $[W_5O_{18}]^{6-}$ ligand (2.41 Å for **1**; 2.40 Å for **2**) is slightly shorter than that (2.53 Å for **1**; 2.47 Å for **2**) for the $[BW_{11}O_{39}]^{9-}$ ligand, suggesting that the Ln–O distance depends on the structure of the polyoxotungstate ligands. Similar Ln–O distances have been observed for polyoxotungstouranates; the mean U–O distance (2.31 Å) in $[U(W_5O_{18})_2]^{8-}$[46] is shorter than that (2.40 Å) in $[U(GeW_{11}O_{39})_2]^{12-}$.[37] Two least-square planes of [O25,26,27,28] and [O45,49,51,53] for the LnO_8 square antiprism are not parallel, with 7.0° and 4.3° dihedral angles between the two planes for **1** and **2**, respectively (Fig. 3 bottom), as a result of the canted mirror planes for the ligands (Fig. 2). Moreover, the O45···O49 separations (2.64(5) Å for **1** and 2.65(3) Å for **2**) are much shorter than the other O···O distances (mean 2.94 Å for **1**, and 2.89 Å for **2**) of the [O25,26,27,28] and [O45,49,51,52] squares. Thus, in **1** and **2**, the ligand field of the LnO_8 square antiprismatic configuration is reduced from D_{4d}.

Comparison with Other Mixed-Ligand Polyoxotungstolanthanoates. Figure 4 shows the molecular structures of three mixed-ligand polyoxotungstolanthanoates: $[Ln(BW_{11}O_{39})(W_5O_{18})]^{12-}$ (this study), $[Eu_3(H_2O)_3(SbW_9O_{33})(W_5O_{18})_3]^{18-}$,[4] and the $[(AsW_9O_{33})(W_2O_6)_2\{Ce(W_5O_{18})\}]^{12-}$ moiety of a large $[Ce_{16}(H_2O)_{36}(AsW_9O_{33})_{12}(WO_2)_4(W_2O_6)\{Ce(W_5O_{18})\}_4]^{76-}$[15] anion. The latter two contain the trivacant Keggin structural B-α-$[XW_9O_{33}]^{9-}$ ligands. It is interesting to note that both the $\{W_5O_{18}\}$ and α-$\{XW_9O_{33}\}$ groups are common to the three anions (shown by the shaded octahedra in Fig. 4), to show a similar chelation, leading to a square antiprismatic coordination. Therefore, the mixed-ligand anion $[Ln(BW_{12}O_{40})(W_5O_{18})]^{12-}$ provides a simple block unit to design a systematic construction of highly condensed polyoxotungstolanthanoates.

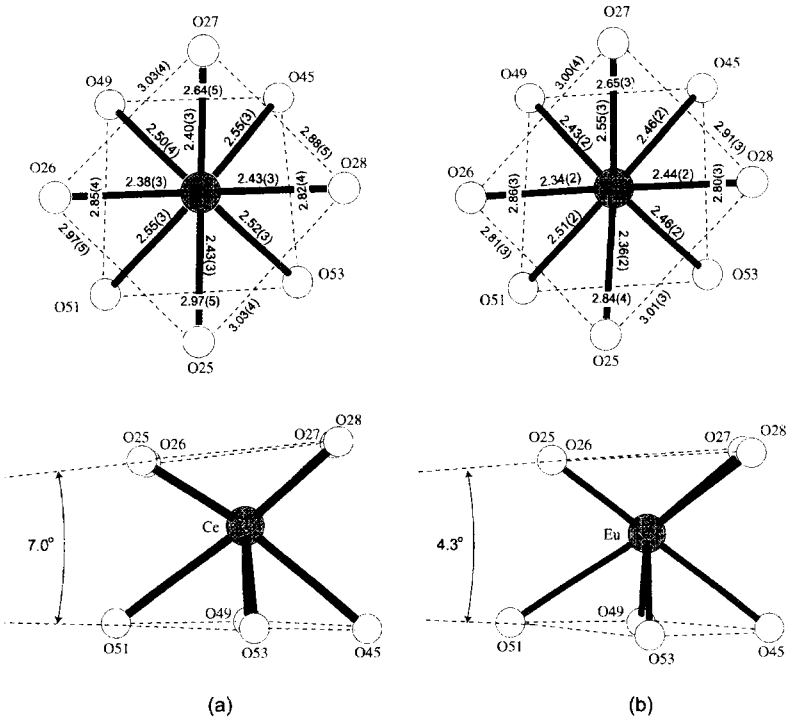


Fig. 3. Coordination environments of the square antiprismatic CeO_8 (a) and EuO_8 (b) sites.

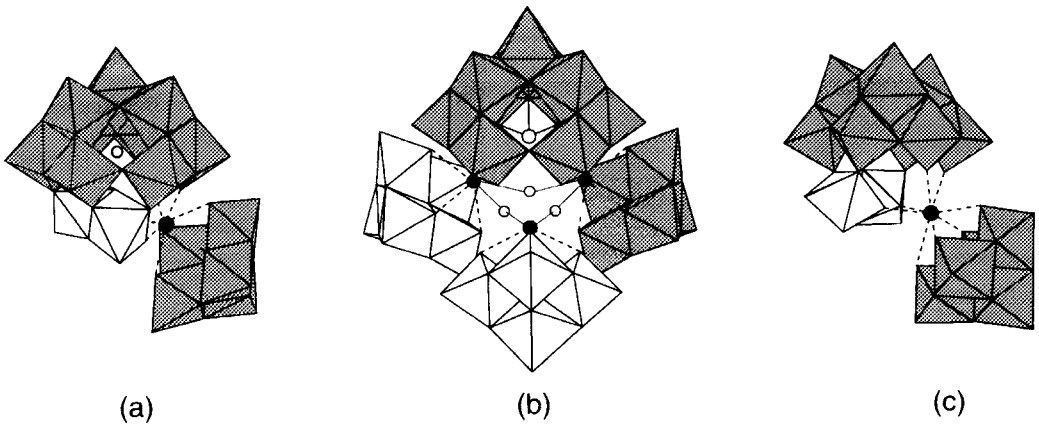


Fig. 4. Structures of $[Ln(BW_{11}O_{39})(W_5O_{18})]^{12-}$ (a), $[Eu_3(H_2O)_3(SbW_9O_{33})(W_5O_{18})_3]^{18-}$ (b),[4] and $[(AsW_9O_{33})(W_2O_6)_2\{Ce(W_5O_{18})\}]^{12-}$ moiety (c) of $[Ce_{16}(H_2O)_{36}(AsW_9O_{33})_{12}(WO_2)_4(W_2O_6)\{Ce(W_5O_{18})\}_4]^{76-}$.[15] Both $\{W_5O_{18}\}$ and α-$\{XW_9O_{33}\}$ groups shown by the shaded octahedra are common to the three anions.

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