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Synthesis and Structure of Ln(W_5O_{18})-Capped Mixed-Ligand Polyoxotungstolanthanoate $[Ln(W_5O_{18})\{Ln(H_2O)_2(SbW_9O_{33})(W_5O_{18})\}]^{15-}$ (Ln = Sm and Er)

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Polyoxotungstolanthanoate, $[Ln_2(H_2O)_2(SbW_9O_{33})(W_5O_{18})_2]^{15-}$ (Ln = Sm and Er), possessing Ln^{3+}, trivacant α-B-Keggin $[SbW_9O_{33}]^{9-}$, and monovacant Lindqvist $[W_5O_{18}]^{6-}$ groups with a ratio of 2 : 1 : 2, was prepared and structurally characterized. In the anion the α-B-$[SbW_9O_{33}]^{9-}$ group coordinates to two $[Ln(W_5O_{18})]^{3-}$ moieties through terminal- and bridging-O atoms at vacant and non-vacant sites, respectively. A ^{183}W-NMR spectrum for Y^{3+}-analog in aqueous solution was consistent with this anion structure.

Polyoxometallolanthanoates (polyoxometalates containing lanthanide elements) can be regarded as lanthanide ($Ln^{3+/4+}$) complexes coordinated by polyoxometalate ligands. Some polyoxometallolanthanoates are photoluminescent, and the behaviors of the intramolecular polyoxometalate ligand → Ln^{3+} [1–3] and $Ln^{3+} \rightarrow Ln'^{\,3+}$ energy transfer[4] have been intensively studied. Interest has also been focused on their synthetic and structural chemistry, since the $Ln^{3+/4+}$ cations in polyoxometallolanthanoates have structurally a function of linking several polyoxometalate groups, in order to construct large high-nuclearity clusters.[5,6]

There have been several polyoxotungstolanthanoates possessing vacant Lindqvist and α-Keggin polyoxotungstate ligands. A well-known Weakley-type mononuclear Ln-decatungstate, $[Ln(W_5O_{18})_2]^{9-/8-}$, [7–11] with a Ln : $\{W_5O_{18}\}$ = 1 : 2 ratio, contains the $Ln^{3+/4+}$ cation sandwiched by the same two monovacant $[W_5O_{18}]^{6-}$ ligands derived from the Lindqvist ($[W_6O_{19}]^{2-}$) anion by the removal of one WO_6 octahedron (or one W=O group). A mixed-ligand mononuclear lanthanate of $[Ln(BW_{11}O_{39})(W_5O_{18})]^{12-}$ [5] with a ratio of Ln : $\{BW_{11}O_{39}\}$: $\{W_5O_{18}\}$ = 1 : 1 : 1 comprises a Ln^{3+} cation sandwiched by both the monovacant α-Keggin $[BW_{11}O_{39}]^{9-}$ and the $[W_5O_{18}]^{6-}$ ligand. A trinuclear $[Ln_3(H_2O)_3(SbW_9O_{33})(W_5O_{18})_3]^{18-}$ (or $[Ln_3(CO_3)(SbW_9O_{33})(W_5O_{18})_3]^{20-}$)[12,13] with a ratio of Ln : $\{SbW_9O_{33}\}$: $\{W_5O_{18}\}$ = 3 : 1 : 3 is constructed by a $[Ln_3(H_2O)_3]^{9+}$ (or $[Ce_3(CO_3)]^{7+}$) core, coordinated by one trivacant α-B-Keggin derivative, $[SbW_9O_{33}]^{9-}$, by removing the edge-shared W_3O_{13} triad from the α-Keggin structure, and three monovacant $[W_5O_{18}]^{6-}$ ligands. In all of these complexes, Ln atoms of the $[Ln(W_5O_{18})]^{3-}$ moieties are coordinated by the $[W_5O_{18}]^{6-}$, $[BW_{11}O_{39}]^{9-}$, and α-B-$[SbW_9O_{33}]^{9-}$ ligands through vacancy-forming terminal-O atoms.

We recently obtained a complex, $[Ln_2(H_2O)_2(SbW_9O_{33})(W_5O_{18})_2]^{15-}$, with a different ligand ratio, Ln : $\{SbW_9O_{33}\}$: $\{W_5O_{18}\}$ = 2 : 1 : 2. In this anion, the Ln^{3+} cation in one $[Ln(W_5O_{18})]^{6-}$ group is bonded to two of the six terminal-O atoms which form the vacancy of the α-B-$[SbW_9O_{33}]^{9-}$ ligand, and that in another $[Ln(W_5O_{18})]^{6-}$ group is to four bridging-O atoms of the same ligand. The latter coordination of Ln^{3+}, capping the vacant α-Keggin ligand, is the first observation in polyoxometalolanthanoates. The present paper describes the preparation and X-ray structural analyses of the $[Ln_2(H_2O)_2(SbW_9O_{33})(W_5O_{18})_2]^{15-}$ (Ln = Sm and Er) anion, and ^{183}W-NMR measurement of the isostructural yttrium analog.

Experimental

Syntheses of $K_{12}H_3[Er_2(H_2O)_2(SbW_9O_{33})(W_5O_{18})_2]\cdot 21H_2O$ (1), $K_{13}H_2[Sm_2(H_2O)_2(SbW_9O_{33})(W_5O_{18})_2]\cdot 26.5H_2O$ (2), $K_{15}[Y_2(H_2O)_2(SbW_9O_{33})(W_5O_{18})_2]\cdot 20H_2O$ (3) and Other Ln-analogs. **1** was prepared as follows. Sb_2O_3 (0.13 g, 0.89 mmol Sb) and Er_2O_3 (0.35 g, 1.8 mmol Er) solids were dissolved in an aqueous HCl (12 mol dm^{-3}, 4 mL) with heating (solution 1). WO_3 (4.0 g, 17 mmol) and KOH (2.5 g, 45 mmol) were dissolved in hot water (60 mL at 80 °C) (solution 2). Solution 1 was added to solution 2 with stirring at room temperature. During the addition the pH was kept at ca. 7 by aqueous KOH, and finally adjusted to ca. 7.5. The resulting cloudy solution was filtered and the filtrate was cooled to 5 °C in a beaker. After 1 d, a pink oily phase was isolated from the solution at the bottom of the beaker. After several weeks, the oily substance was transformed to pale pink crystals of **1**, which were collected by filtration and dried in air (yield 80% based on W). The addition of seed crystals to the oily phase significantly promoted the crystallization. The crystals were efflorescent under normal atmospheric conditions. The contents of K, Er, Sb, and W were analyzed on a X-ray fluorescence spectrometer (JEOL JSX-3200). Found: K, 8.6; Er, 5.8; Sb, 1.8; W, 58.4%. Calcd for $H_{49}O_{92}K_{12}SbEr_2W_{19}$: K, 7.90; Er, 5.63; Sb, 2.05; W, 58.81%. IR spectrum: 3434vs, 1627m, 934vs, 849vs, 787vs, 704vs, 583m, 530m, 484m, 439s cm^{-1}.

Isostructural compounds containing Sm (**2**) and other lanthanides (Eu, Dy, and Ho), and Y (**3**) were obtained by the same procedure using 0.9 mmol of the corresponding oxides (M_2O_3, M = Sm, Eu, Dy, Ho and Y) as the starting materials. All of the analogs are efflorescent and exhibit similar IR spectra to that for **1**. Elemental analysis for **2**: Found: K 8.2; Sm, 4.9; Sb, 2.1; W, 57.1%. Calcd for $H_{57}O_{97.5}K_{13}SbSm_2W_{19}$: K, 8.41; Sm, 4.98; Sb, 2.02; W, 57.82%. Elemental analysis for **3**: Found: K 10.3; Y, 3.5; Sb, 1.9; W, 58.0%. Calcd for $H_{44}O_{91}K_{15}SbY_2W_{19}$: K, 9.98; Y, 3.03; Sb, 2.07; W, 59.44%. No Ce- and Nd-analogs could be obtained: the oily phases gave potassium salts of Weakley-type $[Ln(W_5O_{18})_2]^{9-}$ (Ln = Ce and Nd). The approximate yields of the products (based on W) were as follows: Ce, 0%; Nd, 0%; Sm, 20%; Eu, 20%; Dy, 80%; Ho, 80%; Er, 80%.

X-ray Crystallography of 1 and 2.[14] A single crystal of **1** with 0.05 × 0.05 × 0.05 mm was sealed in a capillary and mounted on a Rigaku RAXIS-RAPID imaging-plate X-ray diffractometer with monochromatized Mo$K\alpha$ radiation (λ = 0.71069 Å). The reflection intensities were collected at 173 K using a ω-oscillation method with an oscillation width of 5° and an exposure time 300 s per frame. Of the 39236 total reflections from 44 frames, 19056 were unique (R_{int} = 0.080). A numerical absorption correction (Numabs[15] and Shape[16]) was made with transmission factors ranging from 0.102 to 0.269. The structure was solved by a direct method (SIR92),[17] and refined on F^2 with 7447 observed ($I > 2\sigma(I)$) reflections and 679 variables. H atoms were not included in the refinement. The crystallographic data and results of the refinement are sammarized in Table 1. Selected bond distances are listed in Table 2.

A single crystal of **2** with 0.10 × 0.10 × 0.10 mm sealed in a capillary was used for X-ray crystallography. The reflection intensities were measured under the same conditions as for **1**. Of the 38560 total reflections from 44 frames, 19830 were unique (R_{int} = 0.093). A numerical absorption correction[15,16] was carried out with transmission factors ranging from 0.119 to 0.294. The structure was solved by SIR92,[17] and refined on F^2 with 10558 observed ($I > 3\sigma(I)$) reflections and 752 variables. H atoms were not included in the calculation. Crystallographic data and the results of the refinement are summarized in Table 1. Selected bond distances are listed in Table 2.

Of the total anion charge (15−), 12− and 13− were compensated by K^+ cations for **1** and **2**, respectively. The remaining charges, 3− for **1** and 2− for **2**, are assumed to be compensated by protons. The numbers (21 for **1**; 26.5 for **2**) of crystallization water molecules in the chemical formula were based on the crystallographic analysis. A small excess of the observed K content (8.6%) compared with the calculated one (7.9%) for **1** may be due to a disordering of additional K atoms at several O sites of crystallization water molecules, as has also been observed for other polyoxotungstates.[5]

^{183}W-NMR spectroscopy of 3. Although a ^{183}W-NMR spectroscopy of **1** in aqueous solution was attempted, no signal could be observed, probably due to the presence of paramagnetic Er^{3+} cations. The measurement was carried out for the diamagnetic yttrium analog (**3**). The spectrum was obtained on a JEOL-AL300 spectrometer under the following conditions: temperature, 295 K; sample concentration, 5 × 10^{-2} M; spectral width, 2 × 10^3 Hz; acquisition time 1.6 s; pulse delay, 0.4 s; pulse width, 28 μs; 116000 scans. 1 M $Na_2WO_4 \cdot 2H_2O$ was used as a standard.

Results and Discussion

Structures of 1 and 2. Figure 1 represents the structure of $[Ln_2(H_2O)_2(SbW_9O_{33})(W_5O_{18})_2]^{15-}$ (Ln = Sm and Er), which is composed of two Ln^{3+} cations, two $[W_5O_{18}]^{6-}$, and one α-B-$[SbW_9O_{33}]^{9-}$ groups. The two tetradentate $[W_5O_{18}]^{6-}$ ligands chelate the Ln1 and Ln2 atoms via [O28, O29, O30, O32] and [O41, O42, O43, O44] squares respectively, leading to the formation of two $[Ln(W_5O_{18})]^{3-}$ groups, each of which is isostructural with a half moiety of the Weakley-type $[Ln(W_5O_{18})_2]^{9-}$ anion. As shown in Fig. 1, the $[Ln(1)(W_5O_{18})]^{3-}$ group is attached to the α-B-$[SbW_9O_{33}]^{9-}$ ligand via two vacancy-forming terminal O67 and O68 atoms, while the $[Ln(2)(W_5O_{18})]^{3-}$ group caps four bridging O47, O52, O53, and O58 atoms in the same ligand. The anion possesses an approximate C_s symmetry, where the Ln1, Ln2, W1, W2, W5, W6, W11, and Sb1 atoms are positioned on the anion's mirror plane. Each Ln atom achieves a distorted square-anti-

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

	1	**2**
Formula	$H_{49}O_{92}K_{12}SbEr_2W_{19}$	$H_{57}O_{97.5}K_{13}SbSm_2W_{19}$
Formula weight	5939.93	6041.37
Crystal shape/color	prism/pale pink	prism/colorless
Space group	$P\overline{1}$(No. 2)	$P\overline{1}$(No. 2)
Unit cell parameters	a = 15.913(2) Å	a = 16.356(1) Å
	b = 16.216(2) Å	b = 16.995(1) Å
	c = 20.315(2) Å	c = 19.966(2) Å
	α = 76.976(6)°	α = 76.967(4)°
	β = 80.328(4)°	β = 86.031(5)°
	γ = 65.571(7)°	γ = 64.398(4)°
	V = 4633.2(9) Å^3	V = 4873.5(7) Å^3
μ(Mo$K\alpha$)	262.29 cm^{-1}	244.75 cm^{-1}
Z	2	2
D_{calc}	4.257 g cm^{-3}	4.117 g cm^{-3}
F(000)	5212	5330
R_1[a)]	0.076 ($I > 2\sigma(I)$)	0.081 ($I > 3\sigma(I)$)
wR_2[b)]	0.111	0.201
GOF	1.50	1.95

a) $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. b) $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$, $w = [\sigma_c^2(F_o^2) + \{p(\mathrm{Max}(F_o^2,0) + 2F_c^2)/3\}^2]^{-1}$, p = 0.02 for **1**, 0.07 for **2**.

Table 2. Selected Bond Distances (Å)

		1						2			
W1	O1	1.78(3)	W12	O12	1.74(3)	W1	O1	1.69(4)	W12	O12	1.71(3)
	O20	1.90(3)		O46	1.86(3)		O20	1.86(3)		O46	1.85(2)
	O22	1.92(3)		O51	1.82(3)		O22	1.95(3)		O51	1.89(3)
	O23	1.89(3)		O52	1.93(3)		O23	1.85(4)		O52	1.95(3)
	O21	1.93(3)		O47	2.03(3)		O21	1.90(3)		O47	2.01(3)
	O31	2.25(3)		O62	2.36(3)		O31	2.31(3)		O62	2.29(2)
W2	O2	1.72(3)	W13	O13	1.75(3)	W2	O2	1.74(4)	W13	O13	1.75(3)
	O28	1.80(3)		O48	1.84(2)		O28	1.76(3)		O48	1.85(3)
	O24	1.93(3)		O54	1.87(3)		O24	1.95(3)		O54	1.86(3)
	O25	1.95(2)		O53	1.95(3)		O25	1.94(4)		O53	1.92(2)
	O20	2.03(3)		O47	1.98(3)		O20	2.05(3)		O47	1.97(3)
	O31	2.30(3)		O63	2.38(3)		O31	2.29(2)		O63	2.31(2)
W3	O3	1.69(3)	W14	O64	1.74(3)	W3	O3	1.73(4)	W14	O64	1.74(3)
	O29	1.74(3)		O14	1.72(3)		O29	1.78(3)		O14	1.74(3)
	O26	1.94(3)		O55	1.99(3)		O26	1.93(3)		O55	1.97(3)
	O24	1.97(3)		O56	2.00(3)		O24	1.99(3)		O56	1.91(3)
	O21	1.97(3)		O50	2.16(3)		O21	2.00(3)		O50	2.15(3)
	O31	2.31(3)		O61	2.29(2)		O31	2.34(3)		O61	2.28(3)
W4	O4	1.64(3)	W15	O15	1.75(4)	W4	O4	1.66(3)	W15	O15	1.73(3)
	O30	1.80(3)		O65	1.73(3)		O30	1.67(3)		O65	1.70(3)
	O27	1.87(3)		O55	1.90(3)		O27	1.94(3)		O55	1.93(3)
	O25	1.99(3)		O60	1.92(2)		O25	1.97(4)		O60	1.93(3)
	O23	2.07(3)		O49	2.04(3)		O23	2.00(4)		O49	2.07(3)
	O31	2.33(3)		O61	2.27(3)		O31	2.29(3)		O61	2.28(3)
W5	O5	1.74(4)	W16	O16	1.71(3)	W5	O5	1.71(3)	W16	O16	1.71(3)
	O32	1.80(3)		O66	1.75(3)		O32	1.79(3)		O66	1.78(3)
	O26	1.92(3)		O56	1.90(3)		O26	1.94(3)		O56	1.90(3)
	O27	1.97(3)		O57	1.99(3)		O27	1.89(3)		O57	2.01(3)
	O22	1.97(3)		O51	2.10(3)		O22	1.96(3)		O51	2.11(3)
	O31	2.30(3)		O62	2.24(3)		O31	2.35(2)		O62	2.34(3)
W6	O6	1.69(3)	W17	O17	1.69(3)	W6	O6	1.75(3)	W17	O17	1.77(3)
	O33	1.91(3)		O67	1.81(3)		O33	1.88(3)		O67	1.76(3)
	O35	1.92(3)		O57	1.90(3)		O35	1.91(3)		O57	1.88(3)
	O34	1.92(3)		O58	2.03(3)		O34	1.90(2)		O58	2.01(3)
	O36	1.95(3)		O52	2.05(3)		O36	1.88(3)		O52	2.06(3)
	O45	2.29(3)		O62	2.35(3)		O45	2.32(2)		O62	2.26(2)
W7	O7	1.70(3)	W18	O18	1.72(3)	W7	O7	1.71(3)	W18	O18	1.73(3)
	O41	1.83(3)		O69	1.81(3)		O41	1.79(3)		O69	1.74(3)
	O33	2.00(3)		O60	1.89(2)		O33	2.03(3)		O60	1.91(3)
	O37	1.97(3)		O59	2.01(3)		O37	1.93(2)		O59	2.00(3)
	O38	2.03(3)		O54	2.09(3)		O38	1.91(3)		O54	2.08(2)
	O45	2.36(3)		O63	2.31(3)		O45	2.32(3)		O63	2.32(2)
W8	O8	1.70(4)	W19	O19	1.74(3)	W8	O8	1.78(3)	W19	O19	1.71(3)
	O42	1.78(3)		O68	1.79(3)		O42	1.79(3)		O68	1.74(3)
	O37	1.91(3)		O59	1.97(3)		O37	2.00(3)		O59	1.91(3)
	O39	1.90(3)		O58	1.99(3)		O39	1.92(3)		O58	1.96(3)
	O34	2.04(3)		O53	2.09(3)		O34	2.04(3)		O53	2.06(2)
	O45	2.31(3)		O63	2.28(3)		O45	2.30(2)		O63	2.28(2)
W9	O9	1.72(4)				W9	O9	1.70(3)			
	O43	1.74(3)	Sb1	O63	1.94(3)		O43	1.84(3)	Sb1	O63	1.99(2)
	O38	1.89(3)		O61	1.96(3)		O38	1.93(3)		O61	1.97(3)
	O40	1.97(3)		O62	1.94(3)		O40	1.90(3)		O62	1.99(2)
	O35	1.99(3)					O35	1.99(3)			
	O45	2.30(3)	Er1	O28	2.31(3)		O45	2.33(2)	Sm1	O28	2.37(3)
W10	O44	1.72(3)		O67	2.29(3)	W10	O44	1.78(3)		O67	2.40(3)
	O10	1.76(3)		O29	2.33(4)		O10	1.78(4)		O29	2.39(3)
	O39	1.98(3)		O32	2.32(3)		O39	1.92(3)		O32	2.40(2)
	O40	1.98(3)		O30	2.33(3)		O40	1.91(3)		O30	2.46(3)
	O36	2.00(3)		O68	2.35(3)		O36	2.01(3)		O68	2.47(3)
	O45	2.27(3)		O70	2.46(3)		O45	2.30(3)		O70	2.53(2)
W11	O11	1.70(3)		O71	2.55(3)	W11	O11	1.72(3)		O71	2.55(3)
	O50	1.80(3)	Er2	O41	2.32(3)		O50	1.80(3)	Sm2	O41	2.45(3)
	O49	1.81(3)		O58	2.32(3)		O49	1.82(3)		O58	2.47(3)
	O48	1.97(2)		O43	2.35(3)		O48	1.97(3)		O43	2.31(3)
	O46	1.97(3)		O47	2.39(3)		O46	1.98(2)		O47	2.45(3)
	O61	2.37(3)		O44	2.36(2)		O61	2.35(3)		O44	2.34(3)
				O42	2.40(3)					O42	2.39(3)
				O53	2.42(3)					O53	2.54(2)
				O52	2.52(3)					O52	2.51(3)

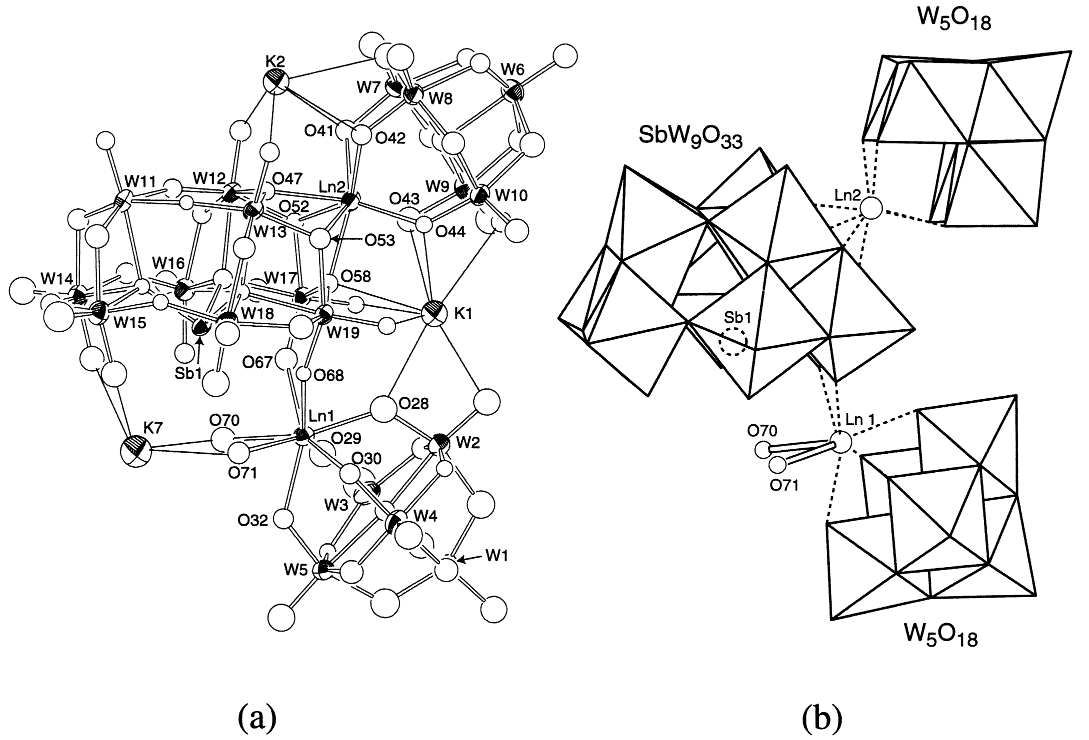

Fig. 1. Structure of $[Ln_2(H_2O)_2(SbW_9O_{33})(W_5O_{18})_2]^{15-}$ with ORTEP (a) and polyhedral (b) representation. K–O bonds shorter than 3.3 Å are drawn by thin solid lines in (a). The anion can be approximated to the C_s symmetry. Ln1, Ln2, W1, W2, W5, W6, W11, Sb1, K1, K2, and K3 are positioned on anion's mirror plane.

prismatic eight-fold coordination by the O atoms. Mean Sm–O distance (2.427 Å) is longer than Er–O one (2.363 Å) due to a larger size[18] Sm^{3+} (1.079 Å) compared to Er^{3+} (1.004 Å). The small bond valence sum (BVS)[19] values for O70 and O71 (0.30 and 0.23 for **1**; 0.30 and 0.29 for **2**, respectively) suggest that both O atoms are aqua-ligands of Ln1. Three K^+ cations (K1, K2, and K7) positioned on the anion's mirror plane (Fig. 1a) are attached to the polyoxotungstate ligands by K–O bond lengths of < 3.3 Å, which seem to effectively stabilize the anion framework. Stabilizations (and distortions) of polyoxotungstolanthanoate anions by the attachment of K^+ cations have also been pointed out for $[Ce_3(CO_3)(SbW_9O_{33})(W_5O_{18})_3]^{20-}$ [13] and $[Ln(BW_{11}O_{39})(W_5O_{18})]^{12-}$ (Ln = Ce^{3+}, Eu^{3+}).[5]

Chelation of the polyoxometalate ligand to the Ln^{3+} cation through bridging-O atoms is also observed in $[\{Ln_3O(OH)_3(H_2O)_3\}_2Al_2(Nb_6O_{19})_5]^{26-}$ (Ln = Eu, Er, Lu) anion,[20–22] where two terminal- and five bridging-O atoms in a $[Nb_6O_{19}]^{8-}$ group chelate four different Ln^{3+} cations. The chelation of α-Keggin polyoxotungstates (and its vacant derivatives) with Ln^{3+} cations has occurred through their terminal-O atoms in the solid state and aqueous media. For example, in $[As_{12}Ce_{16}(H_2O)_{36}W_{148}O_{524}]^{76-}$ anion,[6] trivacant α-B-$[AsW_9O_{33}]^{9-}$ ligands (isostructural with the α-B-$[SbW_9O_{33}]^{9-}$ groups) coordinated a Ce^{3+} cation through terminal-O atoms of the ligands. Also, in $K_2H_3[Eu(H_2O)_8]_3[(GeTi_3W_9O_{37})O_3]\cdot 13H_2O$,[23] three terminal-O atoms of a double-Keggin type $[(GeTi_3W_9O_{37})O_3]^{14-}$ anion coordinated three Eu^{3+} cations. A study of the solvent extraction suggested that terminal-O atoms in the α-Keggin $[SiW_{12}O_{40}]^{4-}$ anion were the binding sites to Eu^{3+} cations in aqueous solutions.[24] It should, however, be noted that there have been a few α-Keggin derivatives where two sets of four bridging-O (corresponding to O47, O52, O53, and O58 in Fig. 1a) at opposite positions can be capped by VO^{2+}, VO^{3+}, MoO_2^{2+}, and AsO^{3+} groups with highly charged V^{4+}, V^{5+}, Mo^{6+}, and As^{5+} centers, as exemplified by $[PMo_{12}O_{40}(V^{IV}O)_2]^{5-}$, $[XV_{12}O_{40}(V^{V}O)_2]^{9-}$ (X = P, As),[25,26] $[SiMo^{V}_4Mo^{VI}_8O_{40}(Mo^{VI}O_2)_2]^{4-}$,[27] and $[H_{12}As^{V}V_{12}O_{40}(As^{V}O)_2]^{3-}$,[28] respectively. Table 3 lists the W···W distances within the α-B-$[SbW_9O_{33}]^{9-}$ ligand. In Table 3, the [W12···W13, W13···W19, W19···W17, and W17···W12] distances are longer than [W11···W12, W12···W16, W16···W14, W14···W11] and [W11···W13, W13···W18, W18···W15, W15···W11] for both **1** and **2**, and also longer than the corresponding distances in a free α-B-$[SbW_9O_{33}]^{9-}$ anion in $Na_9[SbW_9O_{33}]\cdot 9.5H_2O$.[29] Such a distortion of the α-B-$[SbW_9O_{33}]^{9-}$ ligand to C_s symmetry for **1** and **2** may be due to the coordination to Ln1 and Ln2 atoms. Similar lengthening of the metal–metal separations in bicapped α-Keggin has also been pointed out for $[H_4As^{III}As^{V}Mo_{12}O_{40}]^{-}$.[30] The BVS (1.4(1) for **1**; 1.4(1) for **2**) for Ln2–O47, O52, O53, and O58 are larger than those (1.6(1) for **1**; 1.9(1) for **2**) for Ln2–O41, O42, O43, and O44, indicating that the binding of Ln2 with α-B-$[SbW_9O_{33}]^{9-}$ is weaker than $[W_5O_{18}]^{6-}$.

Yields of $[Ln_2(H_2O)_2(SbW_9O_{33})(W_5O_{18})_2]^{15-}$ seems to increase with a decrease in the ionic radius of Ln^{3+}: Ln^{3+} (ionic size for 8-fold coordination[18], yield) = Ce^{3+} (1.143 Å, 0%), Nd^{3+} (1.109 Å, 0%), Sm^{3+} (1.079 Å, 20%), Eu^{3+} (1.066 Å, 20%), Dy^{3+} (1.027 Å, 80%), Ho^{3+} (1.015 Å, 80%), Er^{3+} (1.004 Å, 80%). Zero yield for the Ce-complex is in contrast

Table 3. Selected W···W distances (Å) within α-B-$[SbW_9O_{33}]^{9-}$ groups in **1**, **2**, and $Na_9[SbW_9O_{33}]\cdot19.5H_2O$

1	W12···W13	3.803(3)	W13···W19	3.444(3)	W19···W17	3.744(3)	W17···W12	3.437(3)
	W11···W12	3.763(3)	W12···W16	3.389(3)	W16···W14	3.697(3)	W14···W11	3.387(3)
	W11···W13	3.750(3)	W13···W18	3.391(3)	W18···W15	3.688(3)	W15···W11	3.393(3)
2	W12···W13	3.776(2)	W13···W19	3.436(2)	W19···W17	3.742(2)	W17···W12	3.425(2)
	W11···W12	3.752(2)	W12···W16	3.386(2)	W16···W14	3.681(3)	W14···W11	3.374(2)
	W11···W13	3.755(2)	W13···W18	3.388(2)	W18···W15	3.676(3)	W15···W11	3.386(2)
$Na_9[SbW_9O_{33}]\cdot19.5H_2O$[29]	3.7424(8)–3.7551(9) mean 3.749(6)		3.3928(6)–3.4255(9) mean 3.412(14)		3.6920(8)–3.7012(9) mean 3.696(5)		3.3928(6)–3.4255(9) mean 3.412(14)	

to a high yield (ca. 75%) for $[Ce_3(CO_3)(SbW_9O_{33})(W_5O_{18})_3]^{20-}$,[13] where only the trivacancy of α-B-$[SbW_9O_{33}]^{9-}$ ligand is occupied by three $[Ce(W_5O_{18})]^{6-}$ moieties. The above results of the yield suggest that the coordination of the O47, O52, O53, and O58 atoms to Ln2 occurs favorably for a small size of Ln^{3+}. An attempt to prepare Lu-analog containing small Lu^{3+} cations (0.977 Å) has been unsuccessful: the same synthesis procedure using Lu_2O_3 gave a different-structural $[Lu_3(H_2O)_4(SbW_9O_{33})_2(W_5O_{18})_2]^{21-}$ anion in high yield (ca 75%).[31] This anion also contains two $[Lu(SbW_9O_{33})(W_5O_{18})]^{12-}$ groups, each of which comprises a α-B-$[SbW_9O_{33}]^{9-}$ ligand capped by a $[Lu(W_5O_{18})]^{3-}$ moiety.

The structures of $[Ln_2(H_2O)_2(SbW_9O_{33})(W_5O_{18})_2]^{15-}$ and $[Ln_3(CO_3)(SbW_9O_{33})(W_5O_{18})_3]^{20-}$ are compared in Figs. 2a and 2b, respectively. A set of four O atoms as capping sites for Ln^{3+} in the α-B-$[SbW_9O_{33}]^{9-}$ ligand may provide a possibility to prepare a series of $[Ln_n(SbW_9O_{33})(W_5O_{18})_n]^{-(9+3n)}$ (n = 1–6) anions. Figure 2c represents an example of a hypothetical largest (n = 6) anion, where all six sites in the α-B-$[SbW_9O_{33}]^{9-}$ group are fully capped by six $[Ln(W_5O_{18})]^{3-}$ groups. We are pursuing the synthesis of the $[Ln_n(SbW_9O_{33})(W_5O_{18})_n]^{-(9+3n)}$ anions at a variety of Ln:{SbW_9O_{33}}:{W_5O_{18}} ratios.

^{183}W-NMR spectroscopy of 3. Figure 3 shows the ^{183}W-NMR spectrum of **3** at 298 K, which displays eight main resonance bands labeled by A–H. ^{183}W-NMR bands for the $[W_5O_{18}]^{6-}$ group in Weakley-type $[Y(W_5O_{18})_2]^{9-}$ [32] have been observed at −11 and −28 ppm with a 4:1 intensity ratio, and those for the α-B-$[XW_9O_{33}]^{9-}$ (X = As and Sb) groups in $[(AsW_9O_{33})_2(WO)_3(H_2O)]^{6-}$,[33] $[(Hg_2)_2WO(H_2O)(AsW_9O_{33})_2]^{10-}$,[34] $[\{(C_6H_5Sn)_2O\}_2H(AsW_9O_{33})_2]^{9-}$, and $[(C_6H_5Sn)_3Na_3(SbW_9O_{33})_2]^{6-}$ [35] have in the −70–−190 ppm region. Thus, we tentatively assign bands A–C in the +4–−18 ppm region (in approximate ratio of 8:1:1) and D–H in the −70–−150 ppm region (in approximate ratio of 1:2:4 (= 2 + 2):2) to the two $[W_5O_{18}]^{6-}$ and one α-B-$[SbW_9O_{33}]^{9-}$ ligands in C_s-symmetry, respectively, assuming that the broad band, A, with a shoulder (inserted figure in Fig. 3) consists of five unresolved resonances due to W2/W3,4/W5/W7,8/W9,10 (Fig. 1).

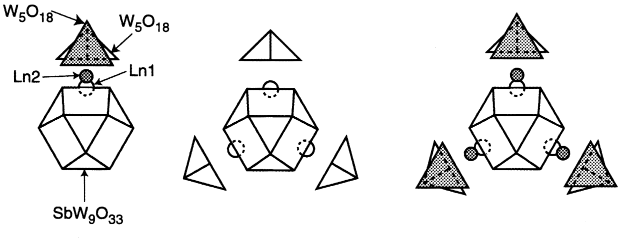

Fig. 2. Schematic representation of $[Ln_2(H_2O)_2(SbW_9O_{33})(W_5O_{18})_2]^{15-}$ (a), $[Ln_3(CO_3)(SbW_9O_{33})(W_5O_{18})_3]^{20-}$ (b) and hypothetical $[Ln_6(SbW_9O_{33})(W_5O_{18})_6]^{27-}$ (c). A set of a shaded triangle and circle denotes the $[Ln(W_5O_{18})]^{3-}$ moiety capping the non-vacant position of the α-B-$[SbW_9O_{33}]^{9-}$ ligand.

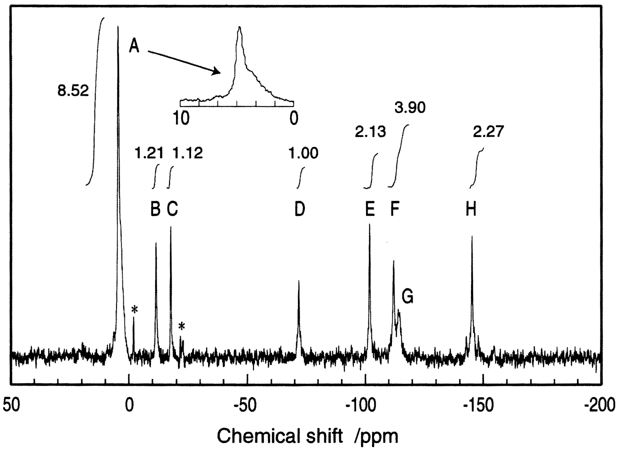

Fig. 3. ^{183}W-NMR spectrum of **3** at 298 K. Weak impurity bands are marked with asterisks. The integration curves and intensities for bands A–H are also indicated. An expanded band A is inserted.

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31 Crystal data of $K_{21}[Lu_3(H_2O)_4(SbW_9O_{33})_2(W_5O_{18})_2]\cdot{\approx}30H_2O$: monoclinic, C2/*c* (No.15); a = 42.598(7), b = 12.9206(2), c = 25.380(5) Å, β = 114.492(5)°, V = 12711(4) Å^3, Z = 4. The $[Lu_3(H_2O)_4(SbW_9O_{33})_2(W_5O_{18})_2]^{21-}$ anion consists of same two $[Lu(SbW_9O_{33})(W_5O_{18})]^{12-}$ groups linked by a $[Lu(H_2O)_4]^{3+}$ cation. Each of the $[Lu(SbW_9O_{33})(W_5O_{18})]^{12-}$ group comprises a α-B-$[SbW_9O_{33}]^{9-}$ ligand capped by a $[Lu(W_5O_{18})]^{3-}$ moiety. The $[Lu(H_2O)_4]^{3+}$ cation is bonded to vacancy-forming four terminal-O atoms (two for each) of the two α-B-$[SbW_9O_{33}]^{9-}$ ligands. Structural details will be published elsewhere.

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