Bull. Chem. Soc. Jpn., 72, 1775—1779 (1999) 1775

X-Ray Structural Characterization of $[Eu(H_2O)_8]_2[V_{10}O_{28}]\cdot 8H_2O$

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(Received December 11, 1998)

Europium decavanadate, $[Eu(H_2O)_8]_2[V_{10}O_{28}]\cdot 8H_2O$, crystallizes in triclinic, $P\bar{1}$, $a = 9.413(1)$, $b = 9.885(1)$, $c = 23.556(4)$ Å, $\alpha = 81.31(2)$, $\beta = 82.08(2)$, $\gamma = 89.51(2)^\circ$, $V = 2145.8(5)$ Å^3, $Z = 2$. There are two crystallographically independent $[Eu(H_2O)_8]^{3+}$ cations and two centrosymmetric $[V_{10}O_{28}]^{6-}$ anions in a unit cell. Each $[Eu(H_2O)_8]^{3+}$ cation achieves eight-fold coordination by aqua-ligands with an approximately square-antiprismatic configuration. The Eu–O distances for the $[Eu(H_2O)_8]^{3+}$ cations were found to be 2.38(1)—2.54(1) Å (mean 2.44 ± 0.02 Å). The crystal structure consists of two crystallographically inequivalent $[Eu(H_2O)_8]_2[V_{10}O_{28}]$ layers and interstitial water molecules, the former being piled up alternately along the c-direction, and the latter linking the two adjacent layers with hydrogen-bonds.

The crystal structures and photoluminescence properties of polyoxometalloeuropates have been intensively studied.[1—9] These compounds contain Eu^{3+} cations which are coordinated by polyoxometalate anions as ligands. For example, in the polyoxomolybdoeuropate, $(NH_4)_{12}H_2[Eu_4(H_2O)_{16}(MoO_4)(Mo_7O_{24})_4]\cdot 14H_2O$,[2] a central $[Eu_4(H_2O)_{16}(MoO_4)]^{10+}$ core is linked with a D_{4d} configuration by four paramolybdate anions, $[Mo_7O_{24}]^{6-}$, to yield $EuO_5(H_2O)_4$ sites. The polyoxotungstoeuropate, $K_{15}H_3[Eu_3(H_2O)_3(SbW_9O_{33})(W_5O_{18})_3]\cdot 25.5H_2O$,[1] has a central trinuclear $Eu_3(H_2O)_3$ core attached tetrahedrally by one B-α type $[SbW_9O_{33}]^{9-}$ and three $[W_5O_{18}]^{6-}$ anions to provide $EuO_6(H_2O)_2$ sites. We report here on the crystal structure of $[Eu(H_2O)_8]_2[V_{10}O_{28}]\cdot 8H_2O$ (**1**),[10] in which the Eu^{3+} cation is not coordinated by the $[V_{10}O_{28}]^{6-}$ anion, but by eight aqua-ligands to form $Eu(H_2O)_8$ sites. The lattice parameters of lanthanide (Ln) decavanadates, $Ln_2V_{10}O_{28}\cdot nH_2O$, were measured and could be tentatively classified into four categories: (i) Ln = La-Ce, $n = 20$, monoclinic $P2_1/n$, $Z = 2$; (ii) Ln = La-Sm, $n = 28$, monoclinic, $P2_1/a$, $Z = 1$; (iii) Ln = Eu-Lu, $n = 25$, triclinic, $P\bar{1}$, $Z = 1$; (iv) Ln = Er-Lu, $n = 24$, triclinic, $P\bar{1}$, $Z = 2$.[11] The crystal structures of $[\{La(H_2O)_7\}_2V_{10}O_{28}]\cdot 6H_2O$,[12] $[Nd(H_2O)_9]_2[V_{10}O_{28}]\cdot 10H_2O$,[13] $[Er(H_2O)_8]_2[V_{10}O_{28}]\cdot 9H_2O$,[14] and $[Yb(H_2O)_8]_2[V_{10}O_{28}]\cdot 8H_2O$,[15] belonging to categories (i), (ii), (iii), and (iv), respectively, have been determined. Since Eu in the lanthanide series is positioned between Nd and Er, the crystal of the Eu-complex may be predicted to be isostructural with either $[Nd(H_2O)_9]_2[V_{10}O_{28}]\cdot 10H_2O$ or $[Er(H_2O)_8]_2[V_{10}O_{28}]\cdot 9H_2O$. Unexpectedly, however, **1** is isostructural with $[Yb(H_2O)_8]_2[V_{10}O_{28}]\cdot 8H_2O$. This paper describes the crystal structure of **1** and its difference in the mode of unit-cell packing from $[Er(H_2O)_8]_2[V_{10}O_{28}]\cdot 9H_2O$.

Experimental

Preparation. An aqueous solution (20 ml) of sodium metavanadate (0.27 g) was acidified with nitric acid to pH 4.1. Europium(III) chloride hexahydrate (0.15 g) dissolved in water (5 ml) was added to the vanadate solution (Eu : V = 1 : 5). The resulting orange-colored solution was kept at room temperature in an open vessel for slow evaporation. Orange crystals of $[Eu(H_2O)_8]_2[V_{10}O_{28}]\cdot 8H_2O$ (**1**) were obtained.

Crystallography.[16] A single crystal with the dimensions of 0.2×0.2×0.1 mm was mounted on a Rigaku AFC-5S four-circle X-ray diffractometer. The unit-cell parameters were refined for 25 reflections with a 2θ range of 20.7—24.6° using graphite-monochromatized Mo $K\alpha$ radiation. The crystal data are as follows: $P\bar{1}$, $a = 9.413(1)$, $b = 9.885(1)$, $c = 23.556(4)$ Å, $\alpha = 81.31(2)$, $\beta = 82.08(2)$, $\gamma = 89.51(2)^\circ$, $V = 2145.8(5)$ Å^3, F.W. = 1693.68, $Z = 2$, $D_{\mathrm{calc}} = 2.621$ g cm^{-3}, $F(000) = 1640$, $\mu(\mathrm{Mo}\,K\alpha) = 50.74$ cm^{-1}. 10454 total reflections in the range of $5^\circ < 2\theta < 55^\circ$ ($0 \leqq h \leqq 12$, $-12 \leqq k \leqq 12$, $-30 \leqq l \leqq 30$) were measured using the ω–2θ scan technique ($\Delta\omega = (1.0+0.40 \tan\theta)^\circ$) at a rate of 4° min^{-1}, of which 9854 were unique ($R_{\mathrm{int}} = 0.044$). Lorentz and polarization factors were applied and an absorption correction of Ψ-scan[17] was made: the transmission factors were from 0.78 to 1.00. The structure was solved by the direct method SIR88[18] and refined by full-matrix least-squares for 6769 observed reflections with $I > 2\sigma(I)$. Hydrogen atoms were not included in the calculation, and all other atoms were refined anisotropically. The final discrepancy factors were $R = 0.067$ and $wR = 0.053$ for 577 parameters. The function minimized was $\Sigma w(|F_{\mathrm{obsd}}|-|F_{\mathrm{calcd}}|)^2$. The weighting scheme was $w^{-1} = \sigma^2(F_{\mathrm{obsd}})+(0.003|F_{\mathrm{obsd}}|)^2$. The goodness of fit parameter was $S = [\{\Sigma w(|F_{\mathrm{obsd}}|-|F_{\mathrm{calcd}}|)^2/(n-m)\}]^{1/2} = 2.48$. The maximum shift/error was 0.01. The maximum positive and negative difference Fourier peaks were 2.52 and -2.64 eÅ^{-3}, respectively. All of the calculations were made using the TEXSAN[19] software package. The positional and thermal parameters are listed in Table 1. Figures 1 and 2 represent ORTEP[20] plots of two crystallographically independent $[V_{10}O_{28}]^{6-}$ anions and two $[Eu(H_2O)_8]^{3+}$ cations, respectively. A packing diagram of **1** drawn by CHARON[21] is shown in Fig. 3(a).

Results and Discussion

Structure of $[V_{10}O_{28}]^{6-}$. Compound **1** consists of

Table 1. Positional and Equivalent Isotropic Thermal Parameters (Å^2)

Atom	x	y	z	B_{eq} [a)]	Atom	x	y	z	B_{eq} [a)]
Eu1	0.37822(8)	0.49627(8)	0.62027(3)	1.50(2)	O21	0.698(1)	1.0709(9)	0.4888(4)	1.9(2)
Eu2	0.93039(8)	1.02361(7)	0.87721(3)	1.39(2)	O22	0.936(1)	1.2218(8)	0.4825(4)	1.3(2)
V1	0.4765(3)	0.4615(2)	1.1497(1)	1.53(5)	O23	1.179(1)	1.3865(9)	0.4661(4)	2.1(2)
V2	0.7765(3)	0.5311(2)	1.0782(1)	1.43(5)	O24	1.092(1)	1.0176(9)	0.4518(4)	1.4(2)
V3	0.5195(3)	0.7165(2)	1.0550(1)	1.28(5)	O25	1.330(1)	1.1650(9)	0.4422(4)	2.1(2)
V4	0.6615(2)	0.5361(2)	0.9623(1)	1.10(5)	O26	0.885(1)	1.1070(9)	0.3910(4)	1.8(2)
V5	0.3955(3)	0.7221(2)	0.9393(1)	1.36(5)	O27	1.117(1)	1.2561(9)	0.3820(4)	1.7(2)
V6	0.9016(3)	0.9079(2)	0.6481(1)	1.86(6)	O28	1.134(1)	1.1404(9)	0.5387(4)	1.6(2)
V7	0.9347(3)	1.1926(2)	0.5691(1)	1.54(5)	O29	0.176(1)	0.386(1)	0.6850(4)	2.4(3)
V8	0.6621(3)	1.0122(3)	0.5768(1)	1.76(6)	O30	0.251(1)	0.675(1)	0.6689(4)	2.8(3)
V9	1.1466(3)	1.2328(2)	0.4565(1)	1.63(5)	O31	0.565(1)	0.620(1)	0.6625(5)	3.3(3)
V10	0.8703(3)	1.0518(2)	0.4616(1)	1.39(5)	O32	0.466(1)	0.333(1)	0.6935(4)	2.8(3)
O1	0.407(1)	0.432(1)	1.2164(4)	2.5(3)	O33	0.339(1)	0.288(1)	0.5794(4)	2.3(2)
O2	0.664(1)	0.4967(9)	1.1524(4)	1.4(2)	O34	0.180(1)	0.550(1)	0.5653(4)	1.8(2)
O3	0.440(1)	0.6498(9)	1.1288(4)	1.5(2)	O35	0.449(1)	0.693(1)	0.5506(4)	2.3(2)
O4	0.934(1)	0.556(1)	1.0922(4)	1.8(2)	O36	0.606(1)	0.426(1)	0.5723(4)	2.1(2)
O5	0.705(1)	0.7100(9)	1.0683(4)	1.1(2)	O37	0.731(1)	1.149(1)	0.8322(4)	2.0(2)
O6	0.484(1)	0.876(1)	1.0508(4)	1.8(2)	O38	0.799(1)	0.862(1)	0.8297(4)	2.7(3)
O7	0.8144(9)	0.5606(9)	0.9891(4)	1.3(2)	O39	1.106(1)	0.940(1)	0.8048(4)	2.3(2)
O8	0.5851(9)	0.7146(9)	0.9690(4)	1.2(2)	O40	1.038(1)	1.223(1)	0.8137(4)	2.5(3)
O9	0.361(1)	0.8822(9)	0.9388(4)	1.8(2)	O41	1.143(1)	1.063(1)	0.9202(4)	2.0(2)
O10	0.6574(9)	0.3411(8)	0.9745(4)	1.1(2)	O42	0.989(1)	0.798(1)	0.9274(4)	2.4(2)
O11	0.446(1)	0.5025(8)	0.9498(4)	1.0(2)	O43	0.729(1)	0.947(1)	0.9482(4)	2.0(2)
O12	0.2246(9)	0.6540(8)	0.9276(4)	1.2(2)	O44	0.879(1)	1.215(1)	0.9301(4)	2.4(3)
O13	0.705(1)	0.5628(9)	0.8896(4)	1.7(2)	O45	1.326(1)	1.252(1)	0.7997(4)	2.3(2)
O14	0.486(1)	0.7165(9)	0.8675(4)	1.5(2)	O46	0.742(1)	1.248(1)	0.7068(4)	2.9(3)
O15	0.919(1)	0.854(1)	0.7133(4)	2.4(3)	O47	0.484(1)	1.023(1)	0.8244(5)	3.5(3)
O16	0.949(1)	1.095(1)	0.6402(4)	1.9(2)	O48	0.924(1)	0.487(1)	0.8023(4)	2.7(3)
O17	0.714(1)	0.946(1)	0.6475(4)	2.1(2)	O49	0.200(1)	1.092(1)	0.6982(5)	3.8(3)
O18	0.970(1)	1.347(1)	0.5711(4)	2.1(2)	O50	0.154(1)	0.671(1)	0.7841(4)	2.5(3)
O19	0.738(1)	1.1848(9)	0.5773(4)	1.7(2)	O51	0.909(1)	0.497(1)	0.6875(5)	2.7(3)
O20	0.494(1)	1.037(1)	0.5895(5)	3.4(3)	O52	0.464(2)	0.905(1)	0.7282(7)	8.1(5)

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

two distinct $[Eu(H_2O)_8]^{3+}$ cations, a $[V_{10}O_{28}]^{6-}$ anion, and eight crystallization waters. Unlike other polyoxometalloeuropates, where Eu^{3+} cations are attached by polyoxometallate ligands, none of the Eu atoms for **1** is bonded to the O atoms of the $[V_{10}O_{28}]^{6-}$ anion. The first determination of the structure of $[V_{10}O_{28}]^{6-}$ anion, which comprises ten edge-sharing VO_6 octahedra with approximate D_{2h} symmetry, was made for $K_2Zn_2[V_{10}O_{28}]\cdot 16H_2O$.[22] Thereafter, the crystal structures of many derivatives have been characterized. Figure 1 shows the structures of the two crystallographically distinct and centrosymmetric $[V_{10}O_{28}]^{6-}$ anions of **1**. The least-squares planes of [V5, V3, V5^{i}, V3^{i}] and [V7, V9, V7^{ii}, V9^{ii}] are nearly perpendicular to those of [V1, V2, V4, V1^{i}, V2^{i}, V4^{i}] and [V6, V8, V10, V6^{ii}, V8^{ii}, V10^{ii}], respectively (dihedral angles are 89.87° and 90.19°, respectively). The V–O distances are listed in Table 2. There are only slight differences in the V–O distances, O–V–O angles, and V$\cdots$V separations between **1** and $K_2Zn_2[V_{10}O_{28}]\cdot 16H_2O$.[22] The bond valence sums[23] for the V and O atoms are 4.9(1)—5.2(1) and 1.67(4)—1.97(5), respectively. No protonation on the $[V_{10}O_{28}]^{6-}$ anion was deduced, since the bond valence sum for the O atoms for $[V_{10}O_{28}]^{6-}$ should be 1.25—1.33[24—26] if protonation occurred.

Structure of $[Eu(H_2O)_8]^{3+}$. Figure 2 shows the coordination geometries of the two crystallographically independent $[Eu(H_2O)_8]^{3+}$ cations, in which the geometry slightly deviates from a D_{4d} square-antiprism. The mean Eu–O distance (2.44±0.02 Å) is similar to that (2.46±0.02 Å) for the tricapped-trigonal-prismatic $[Eu(H_2O)_9]^{3+}$ cation in $[Eu(H_2O)_9][(C_2H_5SO_4)_3]$,[27] and slightly lengthens compared to the mean Yb–O distance (2.33±0.04 Å) in square-antiprismatic $[Yb(H_2O)_8]^{3+}$ [15] due to the lanthanide contraction. The two least-square planes constituting the square-antiprismatic $Eu(H_2O)_8$ site ([O29,O30,O31,O32] and [O33,O34,O35,O36] for Eu1 and [O37,O38,O39,O40] and [O41,O42,O43,O44] for Eu2) are nearly parallel in small dihedral angles of 1.38 and 2.08° for Eu1 and Eu2 sites, respectively. The distances from Eu1 to the least-squares planes of [O29,O30,O31,O32] and [O33,O34,O35,O36] are 1.35 and 1.26 Å, respectively. Similarly, the distances from Eu2 to the planes of [O37,O38,O39,O40] and [O41,O42,O43,O44] are 1.35 and 1.27 Å, respectively. The plausible hydrogen-bonds involving the aqua-ligands are listed in Table 3. All of the aqua-ligands form hydrogen-bonds with surrounding O atoms of crystallization waters and/or $[V_{10}O_{28}]^{6-}$ anions. Such a hydrogen-bonding feature is also observed for the isostructural

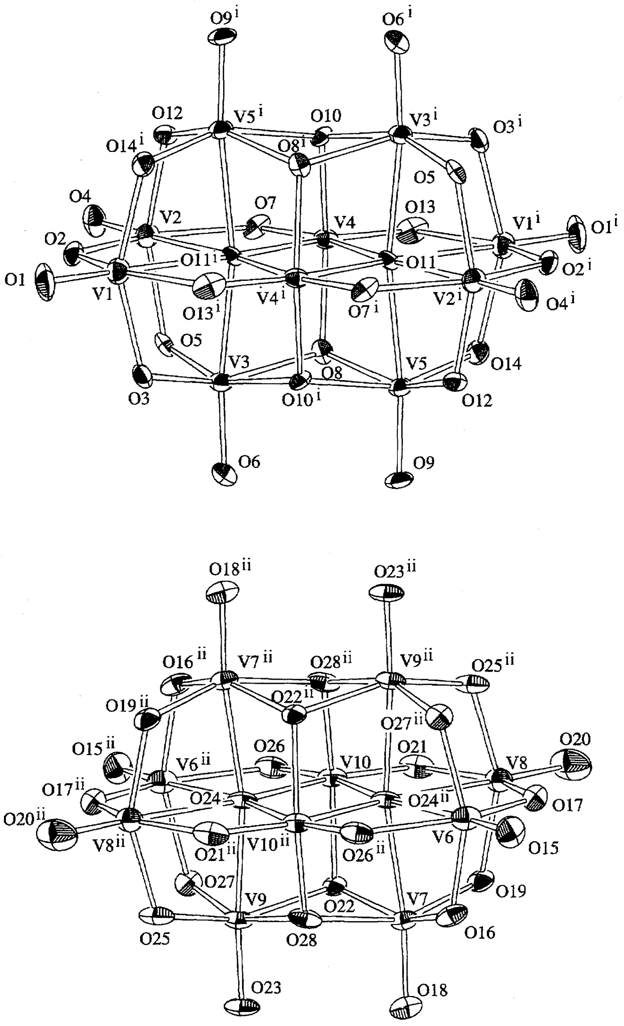


Fig. 1. ORTEP drawing of the two crystallographically independent $[V_{10}O_{28}]^{6-}$ anions. Symmetry codes are as follows: (i) $1-x$, $1-y$, $2-z$; (ii) $2-x$, $2-y$, $1-z$.

$[Yb(H_2O)_8]_2[V_{10}O_{28}]\cdot 8H_2O$.[15]

Of four categories for the lattices of $Ln_2V_{10}O_{28}\cdot nH_2O$, exemplified by $[\{La(H_2O)_7\}_2\{V_{10}O_{28}\}]\cdot 6H_2O$,[12] $[Nd(H_2O)_9]_2[V_{10}O_{28}]\cdot 10H_2O$,[13] $[Er(H_2O)_8]_2[V_{10}O_{28}]\cdot 9H_2O$,[14] and $[Yb(H_2O)_8]_2[V_{10}O_{28}]\cdot 8H_2O$,[15] the La^{3+} cation coordinates two terminal O atoms of a $[V_{10}O_{28}]^{6-}$ group to form a tricapped-trigonal-prismatic $LaO_2(H_2O)_7$ site.[12] Other Ln^{3+} cations coordinate only aqua-ligands, to form a tricapped-trigonal-prismatic site for Nd,[13] and square-antiprismatic sites for Er^{3+} and Yb^{3+}.[14,15] A decrease in the coordination number of Ln^{3+} from 9 (Ln = La and Nd) to 8 (Ln = Eu, Er, and Yb) seems to be ascribed to the lanthanide contraction. All of the $[Ln(H_2O)_9]^{3+}$ cations in $[Ln(H_2O)_9][(C_2H_5SO_4)_3]$ (Ln = La-Lu) have a tricapped-trigonal-prismatic configuration,[27] where each of the nine aqua-ligands is also connected to two $[C_2H_5SO_4]^-$ anions by hydrogen

Table 2. Selected Interatomic Distances (Å) in the $[V_{10}O_{28}]^{6-}$ Anions[a)]

V1–O1	1.60(1)	V6–O15	1.578(9)
V1–O2	1.818(9)	V6–O17	1.81(1)
V1–O14^{i}	1.884(9)	V6–O16	1.883(9)
V1–O3	1.893(9)	V6–O27^{ii}	1.884(9)
V1–O13^{i}	2.080(9)	V6–O26^{ii}	2.11(1)
V1–O11^{i}	2.329(9)	V6–O24^{ii}	2.350(9)
V2–O4	1.587(9)	V7–O18	1.612(9)
V2–O12^{i}	1.855(9)	V7–O16	1.825(9)
V2–O5	1.881(9)	V7–O19	1.834(9)
V2–O2	1.898(9)	V7–O28	2.01(1)
V2–O7	2.055(9)	V7–O22	2.015(9)
V2–O11^{i}	2.325(9)	V7–O24^{ii}	2.230(9)
V3–O6	1.600(9)	V8–O20	1.59(1)
V3–O5	1.812(9)	V8–O17	1.82(1)
V3–O3	1.822(9)	V8–O19	1.858(9)
V3–O10^{i}	2.009(9)	V8–O25^{ii}	1.871(9)
V3–O8	2.037(9)	V8–O21	2.05(1)
V3–O11	2.204(8)	V8–O24^{ii}	2.349(9)
V4–O7	1.683(8)	V9–O23	1.608(9)
V4–O13	1.69(1)	V9–O27	1.796(9)
V4–O10	1.906(8)	V9–O25	1.85(1)
V4–O8	1.921(9)	V9–O22	1.995(9)
V4–O11	2.121(9)	V9–O28	1.999(9)
V4–O11^{i}	2.158(9)	V9–O24	2.215(9)
V5–O9	1.611(9)	V10–O26	1.657(9)
V5–O14	1.792(9)	V10–O21	1.68(1)
V5–O12	1.820(9)	V10–O28^{ii}	1.902(9)
V5–O8	2.002(8)	V10–O22	1.948(9)
V5–O10^{i}	2.027(9)	V10–O24	2.098(9)
V5–O11	2.204(8)	V10–O24^{ii}	2.129(9)

a) Symmetry codes: (i) $1-x$, $1-y$, $2-z$; (ii) $2-x$, $2-y$, $1-z$.

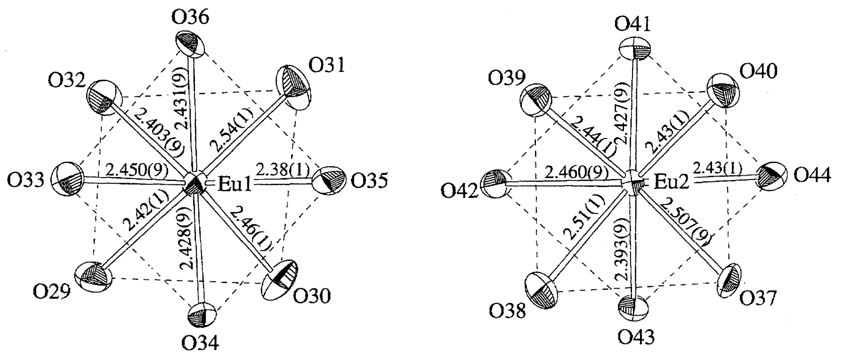
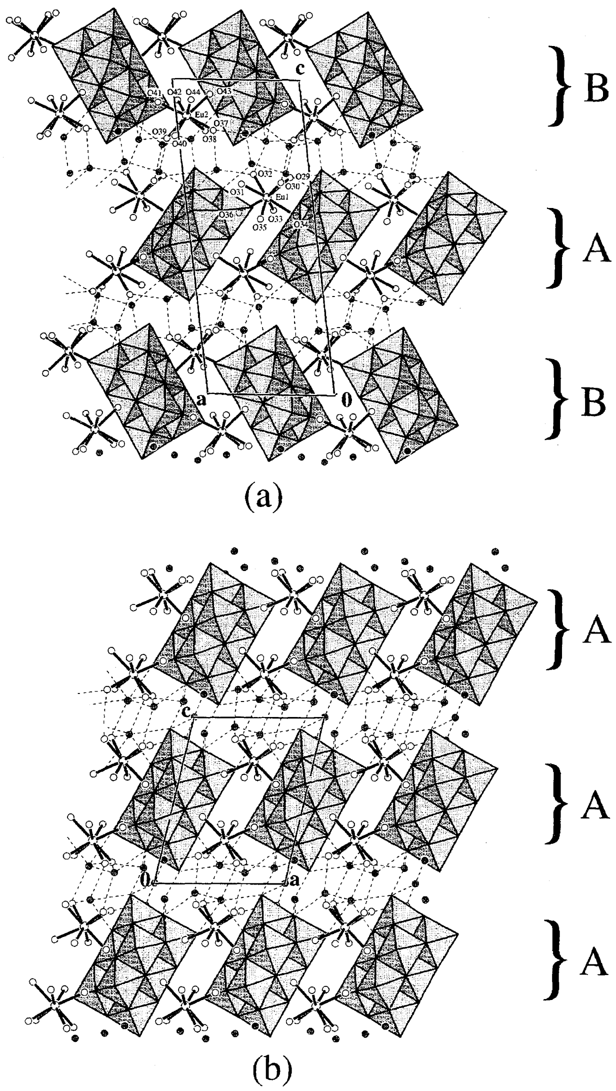


Fig. 2. Structure of the two crystallographically independent $[Eu(H_2O)_8]^{3+}$ cations viewed along the hypothetical S_8-axes of the approximate D_{4d} configrations, together with the Eu–O distances.

Table 3. Hydrogen-Bond Distances (< 3.3 Å)$^{a)}$

Between the [V$_{10}$O$_{28}$]$^{6-}$ anions and crystallization water molecules					
O1	O31^{i}	2.87(1)	O14	O38	3.24(1)
O1	O48^{i}	3.28(1)	O15	O38	2.83(1)
O2	O50^{i}	2.80(1)	O15	O39	3.18(1)
O2	O45^{iii}	2.88(1)	O16	O49^{vii}	2.89(1)
O3	O37^{iv}	2.74(1)	O16	O46	2.89(1)
O3	O45^{iii}	3.19(1)	O17	O52	2.80(2)
O4	O44^{iii}	2.82(1)	O18	O34^{viii}	2.78(1)
O4	O48^{v}	2.96(1)	O18	O51^{ix}	3.17(1)
O5	O41^{iii}	2.73(1)	O19	O36^{ix}	2.67(1)
O5	O45^{iii}	3.16(1)	O19	O46	3.21(1)
O6	O43^{iv}	2.66(1)	O20	O33^{ix}	2.86(1)
O6	O43	3.10(1)	O21	O35^{x}	2.81(1)
O6	O37^{iv}	3.17(1)	O22	O34^{x}	2.66(1)
O6	O47^{iv}	3.29(1)	O23	O36^{xi}	2.72(1)
O7	O42	2.94(1)	O23	O34^{viii}	3.04(1)
O8	O43	2.62(1)	O23	O33^{viii}	3.26(1)
O9	O41^{v}	2.75(1)	O25	O35^{xi}	2.56(1)
O9	O47	2.93(1)	O25	O31^{xi}	3.06(1)
O10	O44^{vi}	2.60(1)	O26	O30^{x}	2.79(1)
O12	O42^{v}	2.62(1)	O26	O49^{x}	3.27(1)
O13	O48	2.88(1)	O27	O51^{xi}	2.75(1)
O13	O38	3.16(1)	O27	O31^{xi}	3.23(1)
O14	O47	3.05(1)	O28	O33^{viii}	2.78(1)
Between aqua-ligands of Eu^{3+} and crystallization water molecules					
O29	O51^{v}	2.74(1)	O37	O47	2.69(1)
O29	O49^{vi}	2.88(2)	O37	O46	2.96(1)
O30	O50	2.74(1)	O39	O49^{vii}	2.76(1)
O32	O45^{xii}	2.67(1)	O39	O50^{vii}	2.79(1)
O32	O46^{vi}	2.78(1)	O40	O45	2.70(1)
O33	O49^{vi}	3.27(1)	O40	O48^{ix}	2.80(1)
Among crystallization water molecules					
O45	O47^{vii}	2.73(1)	O48	O51	2.71(1)
O46	O51^{ix}	2.88(1)	O48	O50^{vii}	2.79(1)
O47	O52	2.73(2)	O49	O52	3.18(2)

a) Symmetry codes: (i) $1-x$, $1-y$, $2-z$; (ii) $2-x$, $2-y$, $1-z$; (iii) $2-x$, $2-y$, $2-z$; (iv) $1-x$, $2-y$, $2-z$; (v) $1-x$, y, z; (vi) x, $-1+y$, z; (vii) $1+x$, y, z; (viii) $1+x$, $1+y$, z; (ix) x, $1+y$, z; (x) $1-x$, $2-y$, $1-z$; (xi) $2-x$, $2-y$, $1-z$; (xii) $-1+x$, $-1+y$, z.



(a)

(b)

Fig. 3. Packing diagrams of [Eu(H$_2$O)$_8$]$_2$[V$_{10}$O$_{28}$]·8H$_2$O (**1**) (a) and [Er(H$_2$O)$_8$]$_2$[V$_{10}$O$_{28}$]·9H$_2$O[14] (b) viewed along the *b*-axes. The [V$_{10}$O$_{28}$]$^{6-}$ anions are represented polyhedrally. Crystallization water oxygens are shown in shaded circles. For clarity, only the hydrogen-bonds involving the crystallization waters are denoted by broken lines.

bonds to yield a bulky (H$_2$O)(C$_2$H$_5$SO$_4$)$_{1/3}$ ligand which rationalizes a tricapped-trigonal-prismatic crystal field to the Ln^{3+} site. Unlike [Ln(H$_2$O)$_9$][(C$_2$H$_5$SO$_4$)$_3$], on the other hand, all of the aqua-ligands for Ln^{3+} in the Ln$_2$V$_{10}$O$_{28}$·nH$_2$O are not always hydrogen-bonded with the [V$_{10}$O$_{28}$]$^{6-}$ anions. For example, two (O29 and O32) aqua-ligands for the Eu1 site and one (O40) for the Eu2 site in **1** are hydrogen-bonded with lattice water molecules (Table 3). Similarly, two aqua-ligands for each site of the Nd(H$_2$O)$_9$ and Er(H$_2$O)$_8$ sites in Nd- and Er-complexes[13,14] form hydrogen bonds with lattice waters. Thus, the decrease in the bulkiness associated with the hydrogen-bonds for the aqua-ligand allows simply the coordination number of Ln^{3+} in the Ln$_2$V$_{10}$O$_{28}$·nH$_2$O to be governed by the lanthanide contraction.

Structural Comparison among 1, Er-, and Yb-Complexes. **1** is isostructural with [Yb(H$_2$O)$_8$]$_2$[V$_{10}$O$_{28}$]·8H$_2$O rather than [Er(H$_2$O)$_8$]$_2$[V$_{10}$O$_{28}$]·9H$_2$O. Therefore, it seems to be difficult to understand the structural relationship among these three complexes only based on the lanthanide contraction of the ionic radius of Ln^{3+} (1.066 Å (Eu^{3+}) > 1.004 Å (Er^{3+}) > 0.985 Å (Yb^{3+})).[28] The crystal structures of **1** and [Er(H$_2$O)$_8$]$_2$[V$_{10}$O$_{28}$]·9H$_2$O[14] are shown in Fig. 3, where neutral [Ln(H$_2$O)$_8$]$_2$[V$_{10}$O$_{28}$] layers (classified in two differently arranged layers A and B) are parallel to the *ab*-plane and piled up along the *c*-axis. The crystallization water molecules are located between the adjacent layers. The arrangement of the layer packing is different between the two compounds. The repeating pattern of the lattice of **1** is ···ABABA··· (Fig. 3(a)), while that of [Er(H$_2$O)$_8$]$_2$[V$_{10}$O$_{28}$]·9H$_2$O is ···AAAA··· (Fig. 3(b)). Since the layer packing of [Yb(H$_2$O)$_8$]$_2$[V$_{10}$O$_{28}$]·8H$_2$O is identical with that of **1** (Fig. 3(a)), it is reasonable to assume that the number (eight and nine for **1** and $[Er(H_2O)_8]_2[V_{10}O_{28}]\cdot 9H_2O$, respectively) of the crystallization water molecules affects the repeating patten of the layers, if we consider that the water molecules link adjacent layers with hydrogen-bonds, as denoted by the broken lines in Fig. 3. This suggests that a hypothetical Eu-complex with the same packing as $[Er(H_2O)_8]_2[V_{10}O_{28}]\cdot 9H_2O$ is possible to be prepared under a low concentration of the vanadate, considering that **1** was isolated by the slow evaporation of a highly concentrated solution of the vanadate (0.01 M $[V_{10}O_{28}]^{6-}$) (1 M = 1 mol dm^{-3}), compared to the solution (0.004 M $[V_{10}O_{28}]^{6-}$) for the preparation of $[Er(H_2O)_8]_2[V_{10}O_{28}]\cdot 9H_2O$.[11,14]

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