Synthesis and Structure of Dialuminiohexaeuropiopentakis(hexaniobate): a High-Nuclearity Oxoniobate Complex

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We have reported two photoluminescent polyoxolanthaniometalates with completely new structures, namely $K_{15}H_3[Eu_3(H_2O)_3(SbW_9O_{33})(W_5O_{18})_3]\cdot25.5H_2O$[2] and $(NH_4)_{12}H_2[Eu_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4]\cdot13H_2O$.[3] In these complexes, Eu^{3+} cations are found to form hydrated clusters, $[Eu_3(H_2O)_3]^{9+}$ and $[Eu_4(MoO_4)(H_2O)_{16}]^{10+}$, stabilized by the coordination of polyoxometalate units to them. In order to expand our investigation on the photoluminescence and electroluminescence properties of polyoxolanthaniotungstates and polyoxolanthaniomolybdates to polyoxolanthanioniobates, and also to contribute to the stereochemistry of polyoxoniobates, where only small number of examples have been accumulated compared with those of tungstates and molybdates, synthetic approach to the polyoxolanthanioniobates has been undertaken. Here we report synthesis and crystal structure analysis of dialuminiohexaeuropiopentakis(hexaniobate), $\{[Eu_3O(OH)_3(OH_2)_3]_2Al_2(Nb_6O_{19})_5\}^{26-}$ (**1**), which possesses an unprecedented structure with two trimeric oxohydroxoaquo europium clusters coordinated by two Al^{3+} cations and five $[Nb_6O_{19}]^{8-}$ anions.

A 0.326-g sample of Eu_2O_3 was dissolved in 0.5 mL of concentrated HNO_3 and was diluted with 10 mL of water. 0.60 g of $[H_2edta]Na_2\cdot2H_2O$ was added to the solution, whose pH was then brought to 10–11 with concentrated NaOH aqueous solution. This solution was added dropwise to 60 mL of an aqueous solution dissolving 1.2 g of $Na_7H[Nb_6O_{19}]\cdot15H_2O$[4] at 353 K with vigorous agitation. A 10 mL aqueous solution of 0.90 g $Al(NO_3)_3\cdot9H_2O$ whose pH was adjusted at 10–11 was added to the mixture, which was then concentrated to 50 mL by heating. The solution was cooled to 273 K, until a white powder precipitated, which was removed by filtering it off. The filtrate, which was still turbid, was brought to clearness by heating with an additional minimum amount of water. The solution was filtered again and the filtrate was kept at room temperature, from which the colorless crystals were obtained after several weeks. This compound is not specific to Eu^{3+} but presumably can form for various kinds of trivalent lanthanide elements. An attempt to prepare a Tb^{3+} derivative by a similar procedure gave colorless single crystals containing the isostructural $[Tb_6Al_2(Nb_6)_5]$ framework.[5]

X-ray crystal structure analysis[6] of the sodium salt of **1** showed that **1** has the structure illustrated in Figure 1. The anion is comprised of two $[Eu_3O(OH)_3(OH_2)_3]^{4+}$ clusters, two Al^{3+} cations, and five hexaniobate anions, $[Nb_6O_{19}]^{8-}$. The anion **1** has an approximate D_3 point symmetry. Three hexaniobate anions are on the 2-fold axes, which will be referred to as equatorial $[Nb_6O_{19}]^{8-}$ anions. The other two hexaniobate anions are on the 3-fold axis, which will be called as axial $[Nb_6O_{19}]^{8-}$ anions hereafter. Each Al^{3+} cation is on the molecular 3-fold axis in a trigonally distorted octahedral coordination field, with one basal triangle being shared with a central $[Eu_3O(OH)_3(OH_2)_3]^{4+}$ cluster and the other with an axial $[Nb_6O_{19}]^{8-}$ anion. The coordination of the axial $[Nb_6O_{19}]^{8-}$ anions to the Al atoms is achieved by the three adjacent μ_2-(Nb_2) oxygen atoms and is similar to that observed in the $[Mn(Nb_6O_{19})_2]^{12-}$ anion.[7] The coordination of the equatorial $[Nb_6O_{19}]^{8-}$ anion to the Eu^{3+} atoms is also achieved by the three adjacent μ_2-(Nb_2) oxygen atoms, which indicates the high coordinating ability of this triad of O atoms, presumably

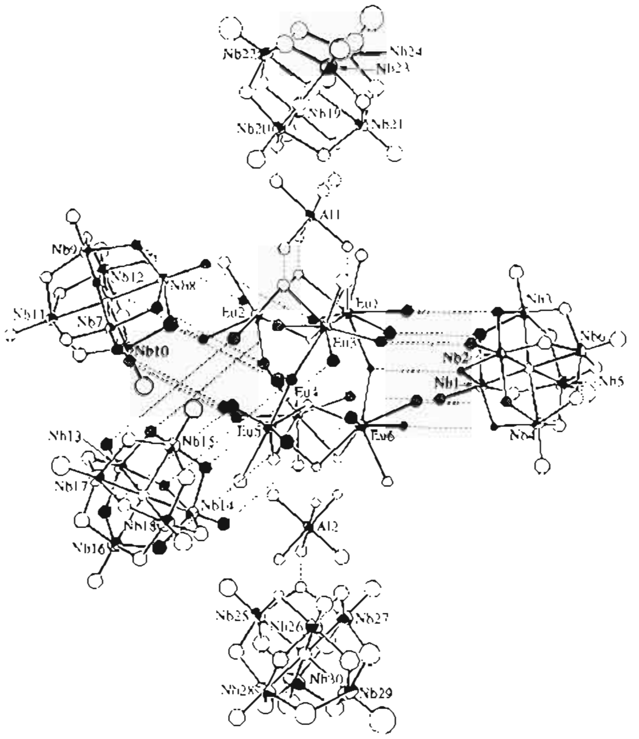

Figure 1. ORTEP drawing of anion **1**. Two AlO_6 octahedra and five hexaniobate anions are shown displaced to show the crowded central $[Eu_3O(OH)_3(OH_2)_3]^{4+}$ cores. Shaded circles represent O atoms of the equatorial hexaniobate anions which coordinate to the central Eu atoms.

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(1) (a) Tokyo Institute of Technology. (b) Chiba University.

(2) Yamase, T.; Naruke, H.; Sasaki, Y. *J. Chem. Soc., Dalton Trans.* **1990**, 1687–1696.

(3) Naruke, H.; Ozeki, T.; Yamase, T. *Acta Crystallogr.* **1991**, *C47*, 489–492.

(4) Flynn, C. M., Jr.; Stucky, G. D. *Inorg. Chem.* **1969**, *8*, 332–334.

(5) A similar procedure, using 0.345 g of Tb_4O_7 instead of Eu_2O_3 as the starting material gives colorless crystals of the Tb derivative of **1**, whose X-ray crystal structure analysis is in progress, and the same $Tb_6Al_2(Nb_6)_5$ framework has already been confirmed, with the crystallographic data being as follows: triclinic space group $P\bar{1}$ with $a = 20.60(1)$ Å, $b = 18.05(1)$ Å, $c = 27.52(2)$ Å, $\alpha = 110.63(5)°$, $\beta = 91.22(6)°$, $\gamma = 117.05(4)°$, $V = 8325(13)$ Å^3, and $Z = 2$. Diffraction data were collected on a Rigaku AFC5R diffractometer at 298 K, using graphite-monochromatized Mo Kα radiation, to a maximum $2\theta = 50°$, giving 30 027 reflections. The Tb positions were determined by direct methods using the program MITHRIL (Gilmore, G. J. *J. Appl. Crystallogr.* **1984**, *17*, 42–46) and Nb positions were obtained by the program DIRDIF (Parthasarathi, V.; Beurskens, P. T.; Slot, H. J. B. *Acta Crystallogr.* **1983**, *A39*, 860–864). The current discrepancy indices are $R = 0.199$ and $R_w = 0.188$ for 340 parameters and 5671 independent reflections with $I > 3\sigma(I)$.

(6) Crystallographic data for $Na_7H_{19}\{[Eu_3O(OH)_3(OH_2)_3]_2Al_2(Nb_6O_{19})_5\}\cdot47H_2O$: Empirical formula based on diffraction data is $Al_2Eu_6H_{131}Na_7Nb_{30}O_{156}$, space group $P\bar{1}$ with $a = 23.15(2)$ Å, $b = 28.31(2)$ Å, $c = 19.32(2)$ Å, $\alpha = 107.03(6)°$, $\beta = 113.44(10)°$, $\gamma = 100.81(8)°$, $V = 10418(25)$ Å^3, and $Z = 2$. Diffraction data were collected on a Rigaku AFC5R diffractometer at 298 K, using graphite-monochromatized MoKα radiation, to a maximum $2\theta = 50°$, giving 37 474 reflections. The structure was solved by direct methods using the program SHELXS86 (Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467–473). The final discrepancy indices were $R = 0.087$ and $R_w = 0.086$ for 1006 parameters and 12 275 independent reflections with $I > 3\sigma(I)$.

(7) Flynn, C. M., Jr.; Stucky, G. D. *Inorg. Chem.* **1969**, *8*, 335–344.

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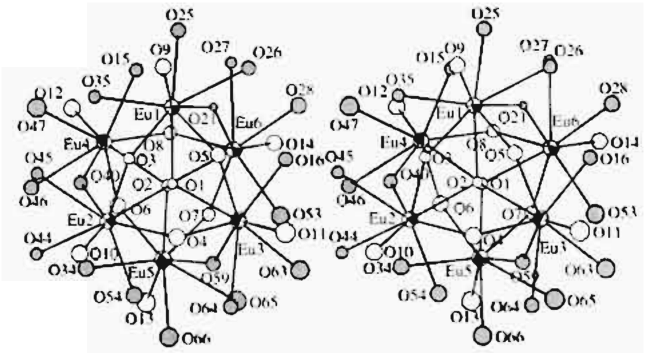

Figure 2. Stereoscopic drawing of the central $\{[Eu_3O(OH)_3(OH_2)_3]_2\}^{8+}$ cluster viewed along its 3-fold axis. O1 and O2 are O^{2-} triply shared by three Eu^{3+}, O3–O8 are OH^- shared by two Eu^{3+} and one Al^{3+}, and O9–O14 are OH_2 groups. Other O atoms shown in shaded circles are those of the three equatorial $[Nb_6O_{19}]^{8-}$ anions. Eu—Eu distances (Å) are as follows: Eu1···Eu2 = 3.762(4), Eu2···Eu3 = 3.777(5), Eu3···Eu1 = 3.771(7), Eu4···Eu5 = 3.741(7), Eu5···Eu6 = 3.740(7), Eu6···Eu4 = 3.743(5), Eu1···Eu4 = 4.650(5), Eu2···Eu5 = 4.646(7), Eu3···Eu6 = 4.609(6), Eu1···Eu6 = 4.753(7), Eu2···Eu4 = 4.763(6), and Eu3···Eu5 = 4.717(5).

due to the high negative charge of the $[Nb_6O_{19}]^{8-}$ anion. An isostructural oxovanadate anion, $[V_6O_{19}]^{8-}$, behaves as a tridentate ligand chelating to four organometallic groups,[8] and $[Nb_2W_4O_{19}]^{4-}$ also serves as a tridentate ligand to some organometallic groups.[9] In contrast, an isostructural oxotungstate anion, $[W_6O_{19}]^{2-}$, which possesses a smaller negative charge, barely chelates to cationic fragments with a similar mode of coordination but serves as a tetradentate ligand by forming a lacunary $[W_5O_{18}]^{6-}$ moiety as found in $[LnW_{10}O_{36}]^{n-}$ [10] and $[Eu_3(H_2O)_3(SbW_9O_{33})(W_5O_{18})_3]^{18-}$.[2]

Figure 2 shows the stereoscopic drawing of the central $[Eu_3O(OH)_3(OH_2)_3]^{4+}$ clusters with the atom numbering scheme. Each Eu atom achieves 8-fold coordination, with one terminal O atom, one O atom shared by three Eu atoms, two O atoms shared by two Eu atoms and one Al atom, and four atoms of the equatorial $[Nb_6O_{19}]^{8-}$ anions, three of which are the $\mu_2(Nb_2)$-O atoms of one $[Nb_6O_{19}]^{8-}$ anion while the other is the terminal O atom of another $[Nb_6O_{19}]^{8-}$ anion. Eu1, Eu2, and Eu3 form a doubly bridged trimeric $[Eu_3O(OH)_3(OH_2)_3]^{4+}$ core with a triply shared O atom, O1, and three doubly shared atoms, O3, O4, and O5. O3, O4, and O5 are also linked to Al1. Likewise, Eu4, Eu5, and Eu6 form an $[Eu_3O(OH)_3(OH_2)_3]^{4+}$ cluster with $O2(\mu_3)$, O6, O7, and O8 atoms. O6, O7, and O8 are coordinated to Al2. The bond valence sums[11] at O1 and O2 are 1.51 and 1.72, suggesting that these are O^{2-}, while the six O atoms O3–O8 can be regarded as the O atoms of hydroxy groups judging from their bond valence sum, ranging from 1.11 to 1.23. The terminal O atoms, O9–O14, show bond valence sums from 0.29 to 0.40 and are likely to be the O atoms of water molecules. Six oxygen atoms, O3–O8, are coordinated to the Al atoms to form the basal triangles of the trigonally distorted AlO_6 octahedra. The Eu...Eu distances in these $[Eu_3O(OH)_3(OH_2)_3]^{4+}$ clusters are 3.76(1) Å; this is shorter by about 1.3 Å than that in the singly bridged trimeric $[Eu_3(H_2O)_3]^{9+}$ core in $K_{15}H_3[Eu_3(H_2O)_3(SbW_9O_{33})(W_5O_{18})_3]\cdot25.5H_2O$, where they were 5.067(4) and 5.015(5) Å.[2] The two $[Eu_3O(OH)_3(OH_2)_3]^{4+}$ clusters are linked to each other via the three equatorial $[Nb_6O_{19}]^{8-}$ anions. The Eu—Eu distances among the two Eu atoms in different $[Eu_3O(OH)_3(OH_2)_3]^{4+}$ clusters are 4.75(2) Å for the two Eu atoms sharing a common O atom and 4.64(2) Å elsewhere.

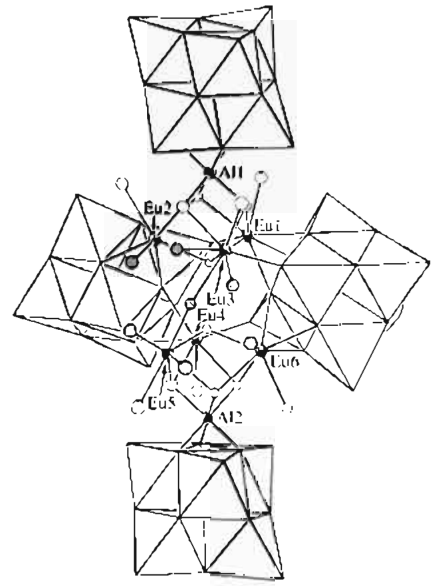

Figure 3. Drawing of anion **1** with the $[Nb_6O_{19}]^{8-}$ groups shown in the polyhedral representations. One of the three equatorial $[Nb_6O_{19}]^{8-}$ anion is not shown to show the central $\{[Eu_3O(OH)_3(OH_2)_3]_2\}^{8+}$ core. Shaded circles represent the O atoms of the hidden $[Nb_6O_{19}]^{8-}$ anion which coordinate to the Eu atoms.

Figure 3 shows an alternative representation of the anion **1** with one $[Nb_6O_{19}]^{8-}$ group unshown for clarity and the other four shown with polyhedral representations. An $[Nb_6O_{19}]^{8-}$ anion has three kinds of O atoms: six terminal O atoms, 12 bridging μ_2-(Nb_2)–O atoms and one central μ_6-(Nb_6)–O atom. A free $[Nb_6O_{19}]^{8-}$ anion has an O_h point symmetry. The coordination of the $[Nb_6O_{19}]^{8-}$ anions to the central $[Eu_3O(OH)_3(OH_2)_3]^{4+}$ clusters or the Al^{3+} cations reduce the O_h symmetry to C_{2v} and C_{3v} for equatorial and axial $[Nb_6O_{19}]^{8-}$ anions, respectively. The Nb–O distances in the $[Nb_6O_{19}]^{8-}$ anions in **1** tend to correlate with the number of Eu^{3+} or Al^{3+} atoms linked to the concerning O atoms. In each equatorial $[Nb_6O_{19}]^{8-}$ anion, two terminal O atoms are bonded to two Eu^{3+} atmos, resulting in the elongation of the Nb–O distances to 1.82(2) Å compared with the other terminal Nb–O bonds of 1.75(4) Å. One of the 12 bridging μ_2-(Nb_2)–O atom coordinates to two Eu^{3+} atoms resulting in Nb–O distances of 2.09(3) Å, while the four μ_2-(Nb_2)–O atoms linked to one Eu^{3+} atom exhibit Nb–O distances of 2.01(4) Å, and the Nb–O distances for the other μ_2-(Nb_2)–O atoms are 1.95(5) Å. Thus the symmetry of the equatorial $[Nb_6O_{19}]^{8-}$ anions are reduced to C_{2v}. In each axial $[Nb_6O_{19}]^{8-}$ anion in **1**, three $\mu_2(Nb_2)$-O atoms are bonded to the Al atoms, with Nb–O distances of 2.10(4) Å and Al–O distances of 1.89(3) Å. The Nb–O distances for the other μ_2-(Nb_2)–O atoms are 1.95(5) Å. The terminal Nb–O bonds are 1.76(6) Å. Therefore, the symmetry of the axial $[Nb_6O_{19}]^{8-}$ anions is reduced to C_{3v}.

Supplementary Material Available: Tables of experimental details and crystal parameters, tables of atomic positional parameters, anisotropic thermal parameters, bond lengths and angles, and atomic contacts, packing diagram of the unit cell, and a drawing of anion **1** with complete numbering of atoms (38 pages). Ordering information is given on any current masthead page.

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(9) (a) $[(OC)_3M(Nb_2W_4O_{19})]^{3}$ (M = Mn, Re): Besecker, C. J.; Day, V. W.; Klemperer, W. G.; Thompson, M. R. *Inorg. Chem.* **1985**, *24*, 44–50. (b) $\{[(CH_3)_5C_5Rh][Nb_2W_4O_{19}]\}^{2-}$: Besecker, C. J.; Day, V. W.; Klemperer, W. G.; Thompson, M. R. *J. Am. Chem. Soc.* **1984**, *106*, 4125–4136.

(10) (a) Ln = Ce^{IV}: Iball, J.; Low, J. N.; Weakley, T. J. R. *J. Chem. Soc., Dalton Trans.* **1974**, 2021–2024. (b) Ln = Tb^{III}: Ozeki, T.; Takahashi, M.; Yamase, T. *Acta Crystallogr.* **1992**, *C48*, 1370–1374. (c) Ln = Eu^{III}: Sugeta, M.; Yamase, T. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 444–449. (d) Ln = Sm^{III}: Ozeki, T.; Yamase, T. *Acta Crystallogr.* **1993**, *C49*, 1574–1577. (e) Ln = Gd^{III}: Yamase, T.; Ozeki, T. *Acta Crystallogr.* **1993**, *C49*, 1577–1580.

(11) Bond valence sum, V_i, was calculated according to the equation $V_i = \Sigma_j \exp((r_0 - r_{ij})/B)$, where $B = 0.37$ Å and $r_0 = 2.074$ Å for Eu–O bonds, 1.651 Å for Al–O bonds, and 1.911 Å for Nb–O bonds (Brown, I. D.; Altermatt, D. *Acta Crystallogr.* **1985**, *B41*, 244–247).