crystal was used for intensity measurements. The single-crystal nature of the sample was checked and the possible space groups were determined using a precession camera. After careful observation of various diffraction patterns, only *hkl* reflections with $h + k + l = 2n + 1$ were recognized to be systematically absent, indicating the space groups $I\bar{4}2m$, $I\bar{4}m2$, $I422$, $I4mm$ and $I4/mmm$. The space group was determined to be $I4/mmm$ through structure analyses based on all these space groups, as described below. Neither long-range superstructure reflections nor streaking were observed.

Reflections with $2\theta < 80°$ were measured in the full reciprocal sphere and reflections with $80 < 2\theta < 120°$ were measured in half the reciprocal sphere. Reflection data were corrected for Lorentz–polarization effects and absorption. The intensities of symmetrically equivalent reflections were then averaged, giving $R_{\rm int} = 0.13$, indicating the difficulty in correcting for absorption given the very large absorption coefficient and extremely anisotropic shape of the crystal. To reduce the influence of the inadequate absorption correction on the results of structure analyses, reflections were collected in the largest multiplicity as described above.

Full-matrix least-squares refinement was carried out using the $ThCr_2Si_2$ structure (Ban & Sikirica, 1965) as the initial structure model. The Gd, Rh and B atoms were placed at the crystallographic positions of the Th, Cr and Si atoms, *i.e.* the 2*a*, 4*d* and 4*e* sites of the space group $I4/mmm$, respectively, while the C atoms were placed at the 2*b* site in the centre of the Gd plane. By varying the scale factor, the isotropic extinction, the atomic positions and anisotropic displacement parameters for Gd and Rh, the least-squares refinement converged to unweighted and weighted agreement factors, *R* and *wR*, of 0.039 and 0.061, respectively. Furthermore, the occupancy parameter of Rh was refined to 0.934 (2), revealing a slight deviation from full occupancy of the 4*d* sites and leading to further convergence to $R = 0.030$ and $wR = 0.023$. The slight deficiency at the Rh site might suggest partial substitution of Rh by Cu, the presence of which had been revealed by EPMA. Refinements of the occupancies of other sites did not indicate any deficiency and *R* and *wR* were not reduced further. Six strong reflections in the low angle region of $2\theta < 30°$ which might be strongly affected by absorption and extinction were excluded in the final stage of the structure refinement. This refinement resulted in the final *R* and *wR* values of 0.025 and 0.023, and produced an F_o *versus* F_c list in very good agreement. The final difference-electron density map had maxima and minima of 3.62 and -3.72 e Å^{-3} in the vicinity of the Gd atoms.

Possible deviation from centrosymmetry was examined by full-matrix least-squares refinement in all the possible non-centrosymmetric space groups ($I\bar{4}2m$, $I\bar{4}m2$, $I422$ and $I4mm$). No shift in the structural parameters larger than the errors was observed and no significant improvement in the results of the structure analysis were obtained. Therefore, the space group of $GdRh_2B_2C$ was determined as $I4/mmm$, the highest symmetry space group among those possible.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1992). Program(s) used to refine structure: *TEXSAN LS*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *TEXSAN FINISH*.

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: BR1145). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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$Na_8H_{18}[\{Er_3O(OH)_3(H_2O)_3\}_2Al_2(Nb_6O_{19})_5].40.5H_2O$

HARUO NARUKE AND TOSHIHIRO YAMASE

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226, Japan. E-mail: hnaruke@res.titech.ac.jp

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Abstract

The $[\{Er_3O(OH)_3(H_2O)_3\}_2Al_2(Nb_6O_{19})_5]^{26-}$ anion in the title compound, octadecahydrogen octasodium dialuminopentanonacontaoxobis(triaquatrihydroxooxotrierbio)triacontaniobate(26−)–water (1/40.5), is com-

posed of a central $[\{Er_3O(OH)_3(H_2O)_3\}_2]^{8+}$ cluster surrounded by three equatorial $[Nb_6O_{19}]^{8-}$ anions and two axial Al^{3+} cations within $[Al(Nb_6O_{19})]^{5-}$ moieties with approximate D_3 symmetry. A comparison of the geometry of this anion with that of the anion in the isomorphous Eu complex reveals that the smaller ionic radius of the Er atom induces a contraction of the central $\{[Ln_3O(OH)_3(H_2O)_3]_2\}^{8+}$ cluster (Ln = Er, Eu) with a resultant attraction of the equatorial and axial $[Nb_6O_{19}]^{8-}$ anions toward the centre of the complex by 0.09 and 0.07 Å, respectively.

Comment

In the course of our studies on the synthesis and photoluminescence of polyoxometalloeuropates, we have prepared and structurally characterized three multinuclear europate complexes with new structures: $[Eu_3(H_2O)_3(SbW_9O_{33})(W_5O_{18})_3]^{18-}$ (Yamase, Naruke & Sasaki, 1990), $[Eu_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4]^{14-}$ (Naruke, Ozeki & Yamase, 1991) and $[\{Eu_3O(OH)_3(H_2O)_3\}_2Al_2(Nb_6O_{19})_5]^{26-}$ (Ozeki, Yamase, Naruke & Sasaki, 1994). The first anion comprises a central $[Eu_3(H_2O)_3]^{9+}$ core in which the three Eu^{3+} cations are bridged by H_2O molecules with approximate C_{3v} symmetry. The second anion comprises a central $[Eu_4(MoO_4)(H_2O)_{16}]^{10+}$ core in which each Eu^{3+} cation is coordinated by nine O atoms belonging to H_2O, MoO_4 and Mo_7O_{24} units with approximate D_{2d} symmetry. The third complex has two trinuclear $[Eu_3O(OH)_3(H_2O)_3]^{4+}$ clusters in the centre, where each Eu^{3+} cation is coordinated by eight O atoms belonging to H_2O, OH^- and $[Nb_6O_{19}]^{8-}$ units with approximate D_3 symmetry. The shortest Eu···Eu distance in the third complex [3.740 (7) Å] is much shorter than in the first and second complexes [5.015 (5) and 6.158 (2) Å, respectively].

The crystal structure of the title compound is isomorphous with that of $Na_7H_{19}[\{Eu_3O(OH)_3(H_2O)_3\}_2Al_2(Nb_6O_{19})_5].47H_2O$ (Ozeki, Yamase, Naruke & Sasaki, 1994) as the atomic positions of the anion (Table 1) correspond to those of the Eu complex when the cell parameters are transformed according to ($a' = a + b + c$, $b' = -b$, $c' = -c$) and a symmetry operation of ($-x + 1/2$, $-y + 1/2$, $-z + 1/2$) is applied. The structure of the anion is illustrated in Fig. 1. The anion has approximate D_3 point symmetry and consists of two $[Er_3O(OH)_3(H_2O)_3]^{4+}$ clusters, two Al^{3+} cations and

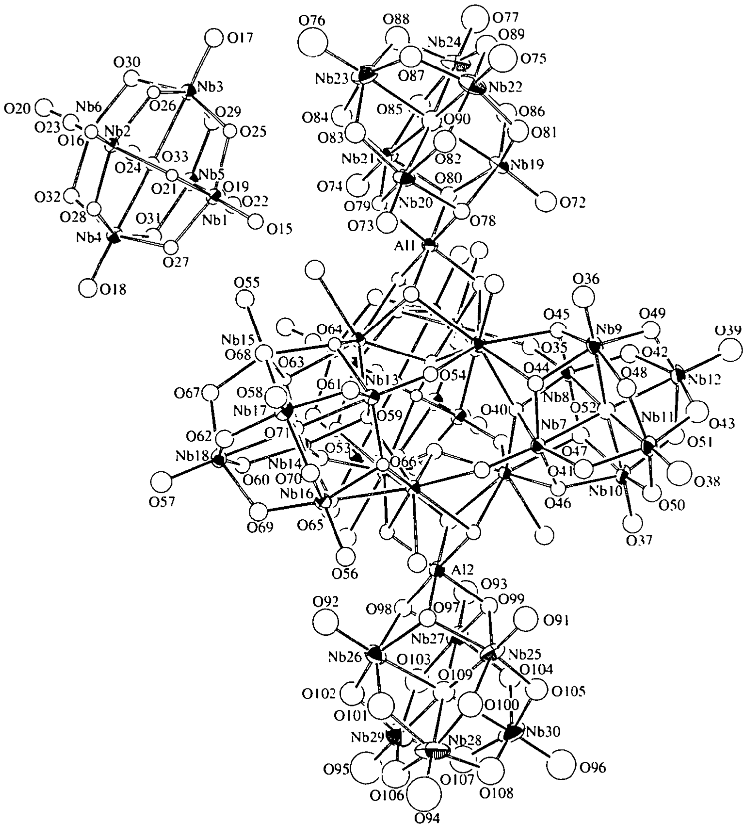


Fig. 1. An *ORTEPII* (Johnson, 1976) plot of the $[\{Er_3O(OH)_3(H_2O)_3\}_2Al_2(Nb_6O_{19})_5]^{26-}$ anion. An $[Nb_6O_{19}]^{8-}$ group behind the molecule is re-illustrated at the top left. Atoms are only labelled for the $[Nb_6O_{19}]^{8-}$ groups and the two Al atoms for clarity. For other atom labels refer to Fig. 2. Displacement ellipsoids are shown at the 50% probability level for Er, Nb and Al atoms.

five hexaniobate $[Nb_6O_{19}]^{8-}$ anions. Three of the five $[Nb_6O_{19}]^{8-}$ anions are located on three molecular C_2 axes and the other two anions are located on a molecular C_3 axis. For convenience, the first three $[Nb_6O_{19}]^{8-}$ anions will be referred to as equatorial and the latter two as axial in the following discussion. Each of the two Al^{3+} cations, which lie on the C_3 axis, is octahedrally coordinated by six O atoms: three from the $[Er_3O(OH)_3(H_2O)_3]^{4+}$ cluster and three from an axial $[Nb_6O_{19}]^{8-}$ anion.

Fig. 2 shows the two trinuclear $[Er_3O(OH)_3(H_2O)_3]^{4+}$ clusters together with the O atoms (shown by the shaded circles) belonging to the equatorial $[Nb_6O_{19}]^{8-}$ anions. Each of the six Er atoms is coordinated by eight O atoms: one μ_3-O atom (O1/O2), two μ_2-O atoms (O3–O5/O6–O8), one terminal O atom (O9–O11/O12–O14) and four O atoms from the equatorial $[Nb_6O_{19}]^{8-}$ anions. The bond-valence sums (Brown & Altermatt, 1985) are 1.48–1.52 for O1/O2, 1.15–1.22 for O3–O5/O6–O8, and 0.22–0.33 for O9–O11/O12–O14, suggesting that the O atoms belong to O^{2-}, OH^- and H_2O units, respectively. It should be noted that the aqua ligands containing O9–O11/O12–O14 are located 2.62 (5)–2.78 (3) Å from the O atoms belonging to the equatorial and axial $[Nb_6O_{19}]^{8-}$ anions, suggesting the presence of intramolecular hydrogen bonds which would stabilize the anion framework. Table 2 lists the interatomic distances in the cluster. The Er···Er (average 3.66 Å) and Er—O [2.21 (3)–2.48 (2) Å] distances are shorter than the corresponding Eu···Eu (average 3.76 Å) and Eu—O [2.29 (3)–2.54 (3) Å] distances, indicating a contraction of the central $[\{Er_3O(OH)_3(H_2O)_3\}_2]^{8+}$ cluster.

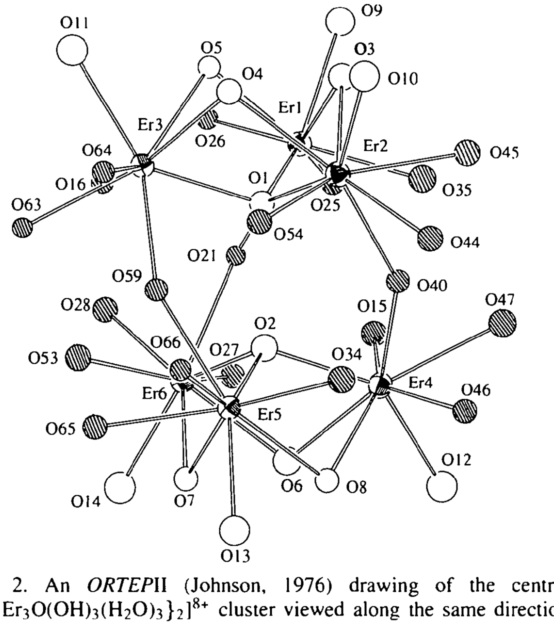
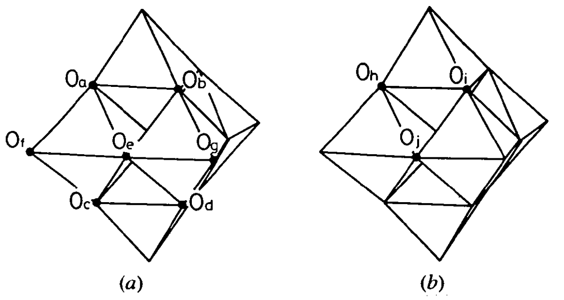


Fig. 2. An *ORTEP*II (Johnson, 1976) drawing of the central $[\{Er_3O(OH)_3(H_2O)_3\}_2]^{8+}$ cluster viewed along the same direction as the anion in Fig. 1. Other O atoms shown by the shaded circles belong to the equatorial $[Nb_6O_{19}]^{8-}$ anions. Displacement ellipsoids are shown at the 50% probability level for Er atoms.

The O atoms in the $[Nb_6O_{19}]^{8-}$ anions can be structurally classified as three species: six terminal O atoms, 12 bridging O atoms and one central O atom. Fig. 3 represents the O-atom sites (O_a–O_j) which bind to the Er and Al atoms in the equatorial and axial $[Nb_6O_{19}]^{8-}$ anions, respectively. The equatorial anion has seven O-atom sites for coordination to Er atoms, five of which are bridging O atoms (O_a–O_e) and two of which are terminal O atoms (O_f and O_g). Two sets ($O_{a,b}$ and $O_{c,d}$) of four bridging O_a–O_d atoms coordinate to two different Er atoms, respectively. The other bridging O_e atom links the two Er atoms. The terminal O_f and O_g atoms each coordinate to other, different Er atoms. As a result, the Nb—O_{a-d} and Nb—O_e distances [1.96 (2)–2.07 (2) and 2.03 (2)–2.08 (2) Å, respectively] are slightly longer than the other bridging Nb—O distances [1.88 (3)–2.04 (2) Å]. Similarly, the terminal Nb—O_f and Nb—O_g distances of 1.80 (3)–1.84 (2) Å are longer than the other terminal Nb—O bonds of 1.71 (3)–1.81 (4) Å. Furthermore, the distances between the two Nb atoms coordinated by O_f and O_g are 3.443 (4)–3.458 (5) Å, and are longer than the other Nb···Nb distances [3.313 (7)–3.386 (5) Å] within the same $[Nb_6O_{19}]^{8-}$ anion. Thus, the point symmetry of the equatorial $[Nb_6O_{19}]^{8-}$ anion is reduced to C_{2v} from the idealized O_h symmetry. Three bridging O atoms (O_h, O_i and O_j) in the axial $[Nb_6O_{19}]^{8-}$ anion coordinate to the same Al atom. The distances [2.06 (2)–2.12 (2) Å] of Nb—O_h, Nb—O_i and Nb—O_j are longer than other bridging Nb—O distances [1.89 (3)–2.05 (2) Å]. The Nb···Nb distances [3.459 (6)–3.473 (8) Å] for the Nb_3 triad linked by O_h, O_i and O_j are longer than in the other triad [3.310 (6)–3.355 (8) Å]. Such elongation of the *M*—O and *M*···*M* distances, induced by the coordination of the $[M_6O_{19}]^{n-}$ (*M* = Nb and W) anion, has been also observed for $[Mn(Nb_6O_{19})_2]^{12-}$ (Flynn & Stucky, 1969) and $[\{(CH_3)_5C_5\}Rh(cis\text{-}Nb_2W_4O_{19})]^{2-}$ (Besecker, Day, Klemperer & Thompson, 1984), where the $[M_6O_{19}]^{n-}$ anion is a tridentate ligand as shown in Fig. 3(*b*). Thus, the axial $[Nb_6O_{19}]^{8-}$ anions are



(*a*) (*b*)

Fig. 3. Polyhedral drawing of the (*a*) equatorial and (*b*) axial $[Nb_6O_{19}]^{8-}$ groups. The O atoms labelled as O_{a-g} and O_{h-j} are the coordination sites to Er^{3+} and Al^{3+} cations, respectively. O_{a-d} correspond to O25–O28, O44–O47 and O63–O66, O_e corresponds to O21, O40 and O59, $O_{f,g}$ correspond to O15, O16, O34, O35, O53 and O54, and O_{h-j} correspond to O78–O80 and O97–O99.

distorted to C_{3v} symmetry by the attachment to the Al^{3+} cations.

These distortions of the $[Nb_6O_{19}]^{8-}$ anions have also been pointed out for the Eu complex (Ozeki, Yamase, Naruke & Sasaki, 1994) where the Nb—O, Nb···Nb and Al—O distances are almost identical with the corresponding distances in the Er complex. However, the contraction of the central $[\{Er_3O(OH)_3(H_2O)_3\}_2]^{8+}$ cluster results in a shift of the equatorial and axial $[Nb_6O_{19}]^{8-}$ groups towards the centre of the complex by about 0.09 and 0.07 Å, respectively, compared with the Eu complex. Hence, replacing Eu^{3+} by Er^{3+} in the $[\{Ln_3O(OH)_3(H_2O)_3]_2Al_2(Nb_6O_{19})_5]^{26-}$ anion induces a contraction of the central $[\{Ln_3O(OH)_3(H_2O)_3\}_2]^{8+}$ cluster, resulting in an attraction of the five $[Nb_6O_{19}]^{8-}$ anions towards the anion centre.

Experimental

The compound was synthesized and recrystallized by the same procedure reported for the Eu complex (Ozeki, Yamase, Naruke & Sasaki, 1994) except for replacement of Eu_2O_3 with Er_2O_3 (> 99.9%).

Crystal data

$Na_8H_{18}[\{Er_3O(OH)_3(H_2O)_3\}_2Al_2(Nb_6O_{19})_5].40.5H_2O$
$M_r = 6538.47$
Triclinic
$P\overline{1}$
$a = 28.01\ (1)$ Å
$b = 28.22\ (2)$ Å
$c = 19.24\ (1)$ Å
$\alpha = 107.04\ (6)°$
$\beta = 93.75\ (6)°$
$\gamma = 130.71\ (2)°$
$V = 10\ 308\ (14)$ Å^3
$Z = 2$
$D_x = 2.11$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 20 reflections
$\theta = 10.9–15.1°$
$\mu = 4.121$ mm^{-1}
$T = 298$ K
Prism
0.3 × 0.3 × 0.2 mm
Pale pink

Data collection

Rigaku AFC-5*S* diffractometer
$2\theta/\omega$ scans
Absorption correction: refined from ΔF (*DIFABS*; Walker & Stuart, 1983)
$T_{min} = 0.20$, $T_{max} = 0.44$
49 151 measured reflections
47 664 independent reflections

24 061 observed reflections [$I > 3\sigma(I)$]
$R_{int} = 0.03$
$\theta_{max} = 30°$
$h = -39 \rightarrow 36$
$k = -36 \rightarrow 38$
$l = 0 \rightarrow 24$
3 standard reflections monitored every 100 reflections intensity decay: 2.1%

Refinement

Refinement on *F*
$R = 0.076$
$wR = 0.098$
$S = 3.53$
24 061 reflections
1174 parameters
H atoms not located
$w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{max} = 0.29$
$\Delta\rho_{max} = 3.56$ e Å^{-3}
$\Delta\rho_{min} = -3.13$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)*

U_{iso} for Na and O, $U_{eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ for Er, Nb and Al.

	x	*y*	*z*	U_{iso}/U_{eq}
Er1	0.37705 (7)	0.07094 (7)	0.31095 (7)	0.0183 (4)
Er2	0.31978 (7)	0.14356 (7)	0.25110 (8)	0.0200 (4)
Er3	0.36788 (6)	0.07056 (7)	0.11987 (7)	0.0173 (4)
Er4	0.14770 (7)	−0.07335 (7)	0.24143 (8)	0.0203 (4)
Er5	0.13650 (6)	−0.07001 (7)	0.05292 (7)	0.0177 (4)
Er6	0.19199 (6)	−0.14591 (7)	0.10344 (7)	0.0182 (4)
Nb1	0.2631 (1)	−0.0977 (1)	0.2924 (1)	0.0187 (8)
Nb2	0.3607 (1)	−0.0536 (1)	0.1776 (1)	0.0162 (8)
Nb3	0.4282 (1)	−0.0017 (1)	0.3679 (1)	0.0208 (8)
Nb4	0.2451 (1)	−0.2188 (1)	0.1533 (2)	0.0210 (8)
Nb5	0.3134 (1)	−0.1658 (1)	0.3410 (2)	0.0236 (8)
Nb6	0.4097 (1)	−0.1217 (1)	0.2300 (2)	0.0215 (8)
Nb7	0.1556 (1)	0.0517 (1)	0.2385 (1)	0.0214 (8)
Nb8	0.2678 (1)	0.0931 (1)	0.3922 (1)	0.0215 (8)
Nb9	0.2776 (1)	0.2156 (2)	0.3819 (2)	0.0275 (9)
Nb10	0.1055 (1)	−0.0039 (2)	0.3758 (2)	0.0295 (9)
Nb11	0.1173 (2)	0.1185 (2)	0.3663 (2)	0.0334 (9)
Nb12	0.2270 (2)	0.1593 (2)	0.5161 (2)	0.0328 (9)
Nb13	0.2635 (1)	0.0751 (1)	0.0282 (1)	0.0186 (8)
Nb14	0.2309 (1)	−0.0741 (1)	−0.0474 (1)	0.0178 (8)
Nb15	0.3591 (1)	0.0688 (1)	−0.0637 (2)	0.0233 (8)
Nb16	0.1262 (1)	−0.0676 (1)	−0.1290 (1)	0.0229 (8)
Nb17	0.2546 (1)	0.0740 (2)	−0.1451 (2)	0.0273 (9)
Nb18	0.2214 (1)	−0.0723 (2)	−0.2187 (1)	0.0255 (9)
Nb19	0.5730 (1)	0.3529 (1)	0.4434 (2)	0.0288 (9)
Nb20	0.5675 (1)	0.3490 (1)	0.2613 (2)	0.0289 (9)
Nb21	0.6261 (1)	0.2886 (2)	0.3290 (2)	0.0297 (9)
Nb22	0.6772 (2)	0.4979 (2)	0.4226 (2)	0.045 (1)
Nb23	0.7296 (2)	0.4372 (2)	0.3127 (2)	0.0482 (9)
Nb24	0.7346 (2)	0.4397 (2)	0.4879 (2)	0.045 (1)
Nb25	−0.1089 (1)	−0.2802 (2)	0.0578 (2)	0.037 (1)
Nb26	−0.0735 (2)	−0.3501 (2)	−0.0829 (2)	0.040 (1)
Nb27	−0.0534 (2)	−0.3531 (2)	0.0948 (2)	0.033 (1)
Nb28	−0.2307 (2)	−0.4271 (2)	−0.1012 (2)	0.074 (1)
Nb29	−0.1778 (2)	−0.4973 (2)	−0.0657 (2)	0.063 (1)
Nb30	−0.2109 (2)	−0.4296 (2)	0.0702 (2)	0.056 (1)
Al1	0.4814 (4)	0.2209 (5)	0.2907 (5)	0.021 (3)
Al2	0.0305 (4)	−0.2217 (5)	0.0715 (5)	0.022 (3)
Na1	0.3601 (7)	0.0153 (8)	0.6153 (8)	0.055 (4)
Na2	0.4124 (9)	0.1809 (9)	0.718 (1)	0.082 (5)
Na3	0.7902 (8)	0.0474 (9)	0.5554 (9)	0.075 (5)
Na4	0.6183 (8)	0.0792 (9)	0.3537 (9)	0.077 (5)
Na5	0.070 (1)	0.058 (1)	0.688 (1)	0.103 (6)
Na6	0.746 (1)	0.335 (1)	0.657 (1)	0.124 (8)
Na7	0.598 (1)	0.286 (1)	0.651 (1)	0.134 (8)
Na8	1	0	1	0.097 (9)
Na9†	0.649 (2)	0.326 (2)	1.012 (2)	0.12 (1)
O1	0.3189 (8)	0.0593 (9)	0.211 (1)	0.017 (4)
O2	0.1951 (9)	−0.0620 (9)	0.151 (1)	0.023 (5)
O3	0.4149 (9)	0.1823 (9)	0.336 (1)	0.021 (4)
O4	0.4103 (9)	0.1790 (9)	0.202 (1)	0.022 (4)
O5	0.4511 (8)	0.1328 (9)	0.2503 (9)	0.017 (4)
O6	0.1048 (9)	−0.185 (1)	0.153 (1)	0.025 (5)
O7	0.0941 (8)	−0.1803 (9)	0.021 (1)	0.018 (4)
O8	0.0640 (8)	−0.1306 (9)	0.123 (1)	0.018 (4)
O9	0.4814 (9)	0.158 (1)	0.419 (1)	0.028 (5)
O10	0.3918 (9)	0.263 (1)	0.289 (1)	0.030 (5)
O11	0.4782 (9)	0.144 (1)	0.116 (1)	0.031 (5)
O12	0.0555 (9)	−0.161 (1)	0.265 (1)	0.029 (5)
O13	0.0229 (9)	−0.140 (1)	−0.021 (1)	0.029 (5)
O14	0.1141 (9)	−0.267 (1)	0.019 (1)	0.030 (5)
O15	0.2071 (9)	−0.0864 (9)	0.306 (1)	0.021 (4)
O16	0.3738 (8)	−0.0040 (9)	0.1240 (9)	0.017 (4)
O17	0.4971 (9)	0.081 (1)	0.444 (1)	0.029 (5)

O18	0.1762 (9)	−0.300 (1)	0.073 (1)	0.030 (5)
O19	0.296 (1)	−0.210 (1)	0.398 (1)	0.033 (5)
O20	0.4627 (9)	−0.133 (1)	0.205 (1)	0.030 (5)
O21	0.2955 (8)	−0.0507 (8)	0.2196 (9)	0.012 (4)
O22	0.2580 (9)	−0.143 (1)	0.351 (1)	0.027 (5)
O23	0.4140 (9)	−0.0733 (9)	0.168 (1)	0.021 (4)
O24	0.3765 (9)	−0.1663 (9)	0.299 (1)	0.022 (4)
O25	0.3534 (8)	−0.0046 (9)	0.3686 (9)	0.014 (4)
O26	0.4259 (8)	0.0270 (9)	0.2829 (9)	0.014 (4)
O27	0.2025 (8)	−0.1841 (9)	0.194 (1)	0.020 (4)
O28	0.2760 (8)	−0.1494 (9)	0.107 (1)	0.019 (4)
O29	0.3899 (9)	−0.067 (1)	0.411 (1)	0.025 (5)
O30	0.4702 (9)	−0.0299 (9)	0.322 (1)	0.023 (5)
O31	0.2430 (9)	−0.242 (1)	0.238 (1)	0.025 (5)
O32	0.3209 (8)	−0.2078 (9)	0.146 (1)	0.019 (4)
O33	0.3357 (8)	−0.1084 (9)	0.260 (1)	0.018 (4)
O34	0.1343 (9)	0.005 (1)	0.136 (1)	0.023 (5)
O35	0.3251 (9)	0.083 (1)	0.390 (1)	0.026 (5)
O36	0.342 (1)	0.297 (1)	0.384 (1)	0.043 (6)
O37	0.041 (1)	−0.086 (1)	0.373 (1)	0.033 (5)
O38	0.060 (1)	0.128 (1)	0.356 (1)	0.054 (7)
O39	0.252 (1)	0.196 (1)	0.620 (1)	0.048 (6)
O40	0.2243 (8)	0.0479 (9)	0.2731 (9)	0.016 (4)
O41	0.1006 (9)	0.070 (1)	0.254 (1)	0.031 (5)
O42	0.2806 (9)	0.136 (1)	0.498 (1)	0.031 (5)
O43	0.160 (1)	0.158 (1)	0.480 (1)	0.044 (6)
O44	0.2389 (9)	0.1506 (9)	0.267 (1)	0.022 (4)
O45	0.3222 (9)	0.1809 (9)	0.382 (1)	0.022 (4)
O46	0.0988 (8)	−0.0291 (9)	0.261 (1)	0.018 (4)
O47	0.1828 (9)	0.001 (1)	0.376 (1)	0.025 (5)
O48	0.201 (1)	0.203 (1)	0.366 (1)	0.032 (5)
O49	0.2906 (9)	0.235 (1)	0.490 (1)	0.028 (5)
O50	0.0593 (9)	0.026 (1)	0.362 (1)	0.031 (5)
O51	0.1505 (9)	0.058 (1)	0.487 (1)	0.030 (5)
O52	0.1924 (9)	0.103 (1)	0.376 (1)	0.027 (5)
O53	0.2208 (9)	−0.1246 (9)	0.002 (1)	0.020 (4)
O54	0.2805 (8)	0.1242 (9)	0.129 (1)	0.019 (4)
O55	0.4455 (9)	0.119 (1)	−0.038 (1)	0.027 (5)
O56	0.0395 (9)	−0.117 (1)	−0.152 (1)	0.030 (5)
O57	0.205 (1)	−0.126 (1)	−0.312 (1)	0.038 (6)
O58	0.264 (1)	0.128 (1)	−0.181 (1)	0.041 (6)
O59	0.2504 (8)	0.0000 (9)	0.0496 (9)	0.015 (4)
O60	0.2185 (9)	−0.1162 (9)	−0.152 (1)	0.021 (4)
O61	0.2670 (9)	0.118 (1)	−0.033 (1)	0.029 (5)
O62	0.2354 (9)	0.001 (1)	−0.235 (1)	0.031 (5)
O63	0.3299 (8)	−0.0002 (9)	−0.0183 (9)	0.013 (4)
O64	0.3528 (8)	0.1102 (9)	0.0353 (9)	0.015 (4)
O65	0.1403 (8)	−0.1106 (9)	−0.074 (1)	0.019 (4)
O66	0.1628 (8)	−0.0008 (9)	−0.0160 (9)	0.015 (4)
O67	0.3207 (9)	−0.0034 (9)	−0.167 (1)	0.022 (4)
O68	0.3469 (9)	0.116 (1)	−0.107 (1)	0.025 (5)
O69	0.1322 (9)	−0.114 (1)	−0.217 (1)	0.028 (5)
O70	0.1582 (9)	0.005 (1)	−0.160 (1)	0.028 (5)
O71	0.2414 (9)	−0.001 (1)	−0.094 (1)	0.021 (4)
O72	0.511 (1)	0.316 (1)	0.486 (1)	0.038 (6)
O73	0.504 (1)	0.312 (1)	0.182 (1)	0.040 (6)
O74	0.602 (1)	0.209 (1)	0.293 (1)	0.046 (6)
O75	0.696 (1)	0.572 (1)	0.457 (1)	0.068 (8)
O76	0.787 (1)	0.468 (1)	0.262 (1)	0.071 (8)
O77	0.798 (1)	0.474 (1)	0.573 (1)	0.068 (8)
O78	0.5118 (9)	0.310 (1)	0.331 (1)	0.024 (5)
O79	0.5518 (9)	0.2628 (9)	0.248 (1)	0.020 (4)
O80	0.5541 (9)	0.2648 (9)	0.380 (1)	0.020 (4)
O81	0.605 (1)	0.441 (1)	0.464 (1)	0.036 (5)
O82	0.600 (1)	0.438 (1)	0.322 (1)	0.040 (6)
O83	0.646 (1)	0.388 (1)	0.232 (1)	0.035 (5)
O84	0.689 (1)	0.340 (1)	0.282 (1)	0.037 (5)
O85	0.693 (1)	0.342 (1)	0.429 (1)	0.041 (6)
O86	0.651 (1)	0.391 (1)	0.519 (1)	0.033 (5)
O87	0.733 (1)	0.511 (1)	0.360 (1)	0.043 (6)
O88	0.782 (1)	0.463 (1)	0.415 (1)	0.049 (6)
O89	0.737 (1)	0.514 (1)	0.506 (1)	0.045 (6)
O90	0.650 (1)	0.393 (1)	0.377 (1)	0.032 (5)
O91	−0.080 (1)	−0.195 (1)	0.103 (1)	0.055 (7)
O92	−0.017 (1)	−0.315 (1)	−0.133 (1)	0.056 (7)
O93	0.014 (1)	−0.321 (1)	0.165 (1)	0.050 (6)
O94	−0.297 (2)	−0.455 (2)	−0.177 (2)	0.11 (1)
O95	−0.204 (1)	−0.577 (1)	−0.109 (2)	0.086 (9)
O96	−0.265 (1)	−0.462 (1)	0.127 (1)	0.070 (8)
O97	−0.0436 (9)	−0.258 (1)	−0.005 (1)	0.025 (5)
O98	−0.0065 (9)	−0.313 (1)	0.021 (1)	0.026 (5)
O99	−0.0315 (9)	−0.262 (1)	0.124 (1)	0.025 (5)
O100	−0.182 (1)	−0.329 (1)	−0.035 (1)	0.057 (7)
O101	−0.154 (1)	−0.383 (1)	−0.141 (1)	0.060 (7)
O102	−0.111 (1)	−0.442 (1)	−0.113 (1)	0.055 (7)
O103	−0.098 (1)	−0.445 (1)	0.024 (1)	0.052 (7)
O104	−0.124 (1)	−0.389 (1)	0.138 (1)	0.041 (6)
O105	−0.166 (1)	−0.332 (1)	0.109 (1)	0.040 (6)
O106	−0.243 (1)	−0.507 (1)	−0.136 (1)	0.069 (8)
O107	−0.226 (1)	−0.510 (1)	0.008 (1)	0.061 (7)
O108	−0.268 (1)	−0.450 (1)	−0.019 (1)	0.062 (7)
O109	−0.140 (1)	−0.388 (1)	−0.003 (1)	0.037 (6)
O110	0.770 (2)	0.424 (2)	0.102 (2)	0.12 (1)
O111	0.637 (2)	0.400 (2)	0.096 (2)	0.14 (1)
O112	0.945 (2)	0.430 (2)	0.799 (2)	0.14 (1)
O113	0.971 (2)	0.209 (2)	0.358 (3)	0.20 (2)
O114	0.833 (1)	0.372 (2)	0.776 (2)	0.09 (1)
O115	0.738 (3)	0.270 (3)	0.406 (3)	0.24 (2)
O116	0.931 (1)	0.015 (2)	0.272 (2)	0.09 (1)
O117	0.868 (1)	0.053 (2)	0.366 (2)	0.09 (1)
O118	0.682 (2)	0.305 (2)	0.746 (2)	0.10 (1)
O119	0.702 (2)	0.321 (2)	0.931 (2)	0.10 (1)
O120	0.547 (1)	0.218 (1)	0.921 (1)	0.068 (8)
O121	0.651 (1)	0.291 (2)	0.552 (2)	0.088 (9)
O122	0.628 (1)	0.162 (1)	0.457 (1)	0.049 (6)
O123	0.503 (1)	0.246 (1)	0.563 (1)	0.068 (8)
O124	0.432 (2)	0.316 (2)	0.556 (2)	0.12 (1)
O125	0.557 (1)	0.083 (1)	0.266 (1)	0.043 (6)
O126	0.547 (1)	0.167 (1)	0.603 (1)	0.037 (5)
O127	0.579 (1)	0.011 (1)	0.427 (1)	0.043 (6)
O128	0.468 (1)	0.144 (1)	0.691 (1)	0.067 (8)
O129	0.445 (1)	0.213 (1)	0.849 (2)	0.084 (9)
O130	0.397 (1)	0.011 (1)	0.739 (1)	0.054 (7)
O131	0.142 (2)	0.096 (2)	0.917 (2)	0.13 (1)
O132	0.033 (2)	0.090 (2)	0.967 (2)	0.11 (1)
O133	0.025 (1)	0.073 (2)	0.131 (2)	0.09 (1)
O134	0.102 (2)	0.412 (2)	0.743 (2)	0.18 (2)
O135	0.513 (2)	0.077 (2)	0.938 (2)	0.11 (1)
O136	0.386 (1)	0.163 (1)	0.591 (1)	0.074 (8)
O137	0.337 (2)	0.199 (2)	0.733 (2)	0.10 (1)
O138†	0.041 (2)	0.079 (2)	0.805 (2)	0.04 (1)
O139	0.209 (1)	0.018 (2)	0.556 (2)	0.09 (1)
O140	0.334 (1)	0.031 (1)	0.508 (1)	0.049 (6)
O141	0.116 (2)	0.063 (2)	0.043 (2)	0.11 (1)
O142	0.625 (2)	0.278 (2)	0.101 (2)	0.14 (1)
O143	0.313 (1)	0.057 (1)	0.674 (1)	0.066 (8)
O144	0.187 (2)	0.135 (2)	0.720 (2)	0.16 (2)
O145	0.223 (2)	0.322 (2)	0.387 (2)	0.15 (2)
O146	0.666 (2)	0.216 (2)	1.002 (3)	0.20 (2)
O147	0.656 (2)	0.099 (2)	0.174 (2)	0.16 (2)
O148	0.721 (2)	0.107 (2)	0.402 (3)	0.19 (2)
O149†	−0.022 (2)	−0.021 (2)	0.169 (2)	0.05 (1)
O150†	1/2	0	1	0.30 (3)
O151	0.817 (3)	0.343 (4)	0.066 (4)	0.34 (3)

† Site occupancy = 0.5.

Table 2. *Selected interatomic distances (Å)*

Er1···Er3	3.664 (2)	Er3—O59	2.43 (2)
Er1···Er2	3.678 (3)	Er3—O63	2.44 (2)
Er2···Er3	3.667 (3)	Er3—O5	2.48 (2)
Er4···Er6	3.652 (3)	Er4—O2	2.22 (2)
Er4···Er5	3.654 (2)	Er4—O15	2.29 (3)
Er5···Er6	3.649 (4)	Er4—O12	2.33 (2)
Er1—O1	2.23 (2)	Er4—O8	2.35 (2)
Er1—O35	2.28 (3)	Er4—O46	2.37 (3)
Er1—O5	2.35 (2)	Er4—O40	2.39 (2)
Er1—O26	2.37 (3)	Er4—O47	2.42 (2)
Er1—O9	2.40 (2)	Er4—O6	2.43 (2)
Er1—O21	2.41 (2)	Er5—O2	2.28 (3)
Er1—O25	2.42 (3)	Er5—O34	2.29 (3)
Er1—O3	2.44 (3)	Er5—O7	2.33 (3)
Er2—O1	2.26 (3)	Er5—O13	2.37 (2)
Er2—O54	2.26 (2)	Er5—O65	2.42 (2)
Er2—O10	2.33 (2)	Er5—O66	2.43 (2)

Er2—O3	2.35 (2)	Er5—O59	2.44 (2)
Er2—O45	2.41 (2)	Er5—O8	2.46 (2)
Er2—O4	2.43 (2)	Er6—O2	2.21 (3)
Er2—O44	2.43 (3)	Er6—O53	2.25 (2)
Er2—O40	2.45 (2)	Er6—O6	2.34 (2)
Er3—O16	2.24 (3)	Er6—O14	2.37 (2)
Er3—O1	2.27 (2)	Er6—O27	2.40 (3)
Er3—O4	2.33 (2)	Er6—O28	2.42 (3)
Er3—O11	2.37 (2)	Er6—O7	2.45 (2)
Er3—O64	2.38 (3)	Er6—O21	2.47 (1)

During the refinement, U_{iso} for Na9 converged to a value which was too large (0.27 Å^2), so the site occupancy was reduced to 0.5. The resulting value of U_{iso}, 0.12 (1) Å^2, is reasonable for an Na^+ cation. The site occupancies of the O138 and O149 atoms, both of which are from waters of crystallization, were fixed at 0.5 because of the short distance (1.6 Å) between them. Although the distance between Nb22 and O75 [1.68 (4) Å] is rather short for a terminal Nb—O bond, the same [1.68 (4) Å] and shorter [1.62 (2) Å] distances have been reported for $Na_7H_{19}[\{Eu_3O(OH)_3(H_2O)_3\}_2Al_2(Nb_6O_{19})_5].47H_2O$ (Ozeki, Yamase, Naruke & Sasaki, 1994) and $AgLaNb_2O_7$ (Sato, Watanabe & Uematsu, 1993), respectively. The maximum Fourier peak (3.56 e Å^{-3}) is 2.20, 2.20 and 2.21 Å from O110, O146 and O151, respectively, all of which are from waters of crystallization. These distances are too short for Na···O or O···O hydrogen-bond distances. Moreover, since U_{iso} for O110 and O146 converged to moderate values [0.12 (1) and 0.20 (2) Å^2, respectively] with site occupancies of 1.0, disorder among O110, O146 and the peak site is not likely to occur. Therefore, the maximum Fourier peak was not identified as an atom. The minimum Fourier peak (−3.13 e Å^{-3}) is a very short distance from Nb28 (0.39 Å), suggesting that it is a ghost of the Nb atom. The high R value of 0.076 is probably due to the rather poor quality of the crystal, which is strongly efflorescent.

Program(s) used to solve structure: *DIRDIF* (Beurskens *et al.*, 1992). Program(s) used to refine structure: *TEXSAN* (Molecular Structure Corporation, 1989).

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Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: OA1001). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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The First Beryllium Periodate: $Be(H_4IO_6)_2.4H_2O$

ZHIBIN ZHANG,[a] HEINZ DIETER LUTZ,[a] MITKO GEORGIEV[b] AND MARIA MANEVA[b]

[a]*Universität-GH Siegen, Anorganische Chemie I, D-57068 Siegen, Germany, and* [b]*Universität für Chemische Technologie und Metallurgie, Lehrstuhl für Anorganische Chemie, Sofia, Bulgaria. E-mail: lutz@chemie.uni-siegen.d400.de*

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Abstract

The title compound, beryllium tetrahydrogenhexaoxoiodate(VII) tetrahydrate, is built up from slightly deformed $Be(OH_2)_4$ tetrahedra (*a*,*b*) and $IO_2(OH)_4$ octahedra (*A*,*B*) with *cis* configuration of the oxo ligands. They are arranged along [001] forming layers with stacking *aBAbABaBAbAB*. The $[H_4IO_6]^-$ and $Be(OH_2)_4^{2+}$ ions are held together by a network of eight independent hydrogen bonds of different strength. Two of the H atoms of $[H_4IO_6]^-$ are disordered over O—H↔H—O split positions.

Comment

The title compound, which is very easily decomposed by exposure to X-rays, was first described as $Be(IO_4)_2.8H_2O$ (Biber, Neiman & Bragina, 1941; Maneva, Georgiev & Pavlova, 1988). This was indicated by IR experiments, but resulted from the strong reaction with KBr used as the matrix. Raman spectroscopic and more careful IR experiments, however, revealed that the compound under study was an orthoperiodate, $Be(H_4IO_6)_2.4H_2O$, rather than a metaperiodate (Maneva, Georgiev, Lange & Lutz, 1991). This has been confirmed by the single-crystal X-ray studies reported in this work.

The crystal structure, which represents a hitherto unknown structure, is built up of layers of $Be(OH_2)_4$ tetrahedra (*a*,*b*) and double layers of H_4IO_6 octahedra