Crystal Structure and Luminescence Site of $Na_9[EuW_{10}O_{36}]\cdot 32H_2O$

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$Na_9[EuW_{10}O_{36}]\cdot 32H_2O$, obtained from aqueous solutions, crystallizes in space group Cc with $a=11.484(5)$, $b=23.020(7)$, $c=23.581(6)$ Å, $\beta=91.71(3)°$, $V=6231(3)$ Å^3, $M_r=3349.4$, $D_x=3.57$ Mg m^{-3}, and $Z=4$. A full-matrix least-squares refinement finally yields $R=0.070$ and $R_w=0.086$ for 6473 independent reflections. The local symmetry around Eu^{3+} for the $[EuW_{10}O_{36}]^{9-}$ anion is approximately square antiprismatic. Photoexcitation into the oxygen-to-tungsten charge transfer bands of a solid sample leads to red emission due to f–f transitions within Eu^{3+}, as a result of an intramolecular energy transfer from the W_5O_{18} group to the Eu atom. The spectral transitions of photoluminescence recorded at 4.2 K can be interpreted based on the assumption of a C_{4v} point group for Eu^{3+}, which is consistent with the co-ordination geometry for the Eu atom.

Three X- ray crystallographic structural studies concerning polyoxotungstolanthanoate complexes, $Na_6H_2[Ce(W_5O_{18})_2]\cdot 30H_2O$,[1] $K_{16}[Ce(P_2W_{17}O_{61})_2]\cdot 50H_2O$,[2] and $K_{15}H_3[Eu_3(H_2O)_3(W_5O_{18})_3(SbW_9O_{33})]\cdot 25.5H_2O$,[3] have been reported. The former two complexes comprise lacunary W_5O_{18} and $P_2W_{17}O_{61}$ units, which derive from the removal of one tungsten atom and its unshared oxygen atom in Lindqvist-typed $[W_6O_{19}]^{2-}$ and Dawson-typed $[P_2W_{18}O_{62}]^{6-}$, respectively. The latter includes a photoluminescent $[Eu_3(H_2O)_3(W_5O_{18})_3(SbW_9O_{33})]^{18-}$ anion, which has a central trinuclear $Eu_3(H_2O)_3$ core linked tetrahedrally by one B-α SbW_9O_{33} and three W_5O_{18} units. Studies concerning the photoluminescence of such polyoxometaloeuropates are interesting for an understanding of the intramolecular energy transfer from the oxygen-to-metal charge-transfer (O→M LMCT) state of polyoxometalate ligands to the emitting $^5D_0$ level of Eu^{3+} in the lattice. Although a detailed description of the crystal structure is essential for a better understanding of the luminescence properties, the only photoluminescent polyoxotungstoeuropate of known crystal structure is $K_{15}H_3[Eu_3(H_2O)_3(W_5O_{18})_3(SbW_9O_{33})]\cdot 25.5H_2O$.[3] The luminescence spectrum of Eu^{3+} in polyoxometaloeuropate lattices is very sensitive to the crystal field around Eu^{3+}. The photoluminescence of $[Eu(W_5O_{18})_2]^{9-}$ has been discussed based on the assumption of the overall point symmetry being D_{4d}, which is identical with the one for $[Ce(W_5O_{18})_2]^{8-}$.[4] However, the number of luminescence peaks within each of the $^5D_0\rightarrow{}^7F_J$ band systems observed for $[Eu(W_5O_{18})_2]^{9-}$(=$[EuW_{10}O_{36}]^{9-}$) disagrees with the prediction made on the basis of the D_{4d} symmetry. In an attempt to elucidate the observable number of peaks within each of the $^5D_0\rightarrow{}^7F_J$ transitions, this paper describes the crystal structure and the photoluminescence site of $Na_9[EuW_{10}O_{36}]\cdot 32H_2O$.

Experimental

$Na_9EuW_{10}O_{36}\cdot 32H_2O$ was prepared in a manner analogous to that for $Na_6H_2[CeW_{10}O_{36}]\cdot 30H_2O$;[5] 8.3 g of $Na_2WO_4\cdot 2H_2O$ was dissolved in 20 ml of water and the solution pH was adjusted to 7.0—7.5 with CH_3COOH. An aqueous solution (2 ml) containing 1.1 g of $Eu(NO_3)_3\cdot 6H_2O$ was added dropwise to the above-mentioned solution with stirring at 80—90°C. Cooling the solution at room temperature yielded colorless crystals of $Na_9[EuW_{10}O_{36}]\cdot 32H_2O$ which were filtered off and dried in air (Found: Na, 5.9; Eu, 4.1; W, 54.9; H_2O, 15.7. Calcd for $Na_9H_{64}EuW_{10}O_{68}$: Na, 6.2; Eu, 4.5; W, 54.9; H_2O, 17.2 %).

A parallelepiped single crystal of 0.4×0.4×0.4 mm was sealed in a glass capillary and mounted on a Rigaku AFC-5R four-circle diffractometer. Graphite-monochromated Mo $K\alpha$ radiation ($\lambda=0.71069$ Å) was used as the X-ray source. The lattice parameters were determined by a least-squares calculation from 25 reflections. Crystal data for $Na_9[EuW_{10}O_{36}]\cdot 32H_2O$ at 298 K were $M_r=3349.4$, monoclinic, space group Cc, $a=11.484(5)$, $b=23.020(7)$, $c=23.581(6)$ Å, $\beta=91.71(3)°$, $V=6231(3)$ Å^3, $Z=4$, $D_x=3.57$ Mg m^{-3}, $\mu=199.56$ cm^{-1}, $F(000)=6024$, $R=0.070$ and $Rw=0.086$ for 6473 independent reflections. Intensity data were collected over the range of $5°\leq 2\theta\leq 55°$ using the ω-2θ scanning technique with a scan rate of 8° min^{-1}; $\Delta\omega=(0.75+0.14\tan\theta)°$, $[\sin\theta/\lambda]_{max}=0.70$ Å^{-1}, and the range of indices was $0\leq h\leq 14$, $0\leq l\leq 26$, $-30\leq k\leq 30$. The intensities of four standard reflections measured every 100 reflections exhibited only a slight variation throughout the collection; 7708 independent reflections were measured, of which 6777 were observed with $I>3\sigma(I)$; 6473 independent data were used for a refinement of the structure. Lorenz and polarization factors were applied and an absorption correction was made using the program DIFABS.[6] The correction factors were from 0.003 to 0.046. All of the calculations were carried out using the TEXSAN program suite,[7] which incorporates MITHRIL[8] for a structure solution by a direct method. Na and O atoms were found from difference Fourier syntheses. Eu and W atoms were refined with anisotropic thermal parameters. The atomic-scattering factors were taken from "International Tables for X-Ray Crystallography".[9] Refinements were carried out using the full-matrix least-squares method for 493 parameters. The quantity minimized was $\Sigma w(|F_o|-|F_c|)^2$. The refinement converged to $R=0.070$ and $R_w=0.086$; the weighting scheme employed was $w^{-1}=\sigma^2(F_o)$, where $\sigma^2(F_o^2)=\sigma^2(I)+(0.05I)^2$. $S=\Sigma w^{-1}(|F_o|-|F_c|)/(n-m)=3.08$, and $(\Delta/\sigma)_{max}=0.14$; the residual maximum and minimum Fourier peaks was +7.08 and −11.1 eÅ^{-3}, respectively.

Table 1. Atomic Coordinates and Isotropic Temperature Parameters with Estimated Standard Deviations in Parentheses

Atom	x	y	z	B_{eq}[a)]/Å^2
Eu(1)	0.9771(2)	0.1322(1)	0.15218(8)	1.17(7)
W(1)	1.0343	0.29641(7)	−0.0104	1.39(6)
W(2)	1.1924(1)	0.24697(7)	0.10125(7)	1.28(6)
W(3)	0.9273(1)	0.29278(7)	0.11924(7)	1.22(6)
W(4)	0.8302(1)	0.20085(7)	0.02413(7)	1.20(6)
W(5)	1.0950(1)	0.15534(7)	0.00491(7)	1.27(6)
W(6)	1.1191(1)	0.00879(7)	0.23823(7)	1.12(5)
W(7)	0.9797(1)	0.10584(7)	0.31181(7)	1.13(5)
W(8)	0.7362(1)	0.07223(7)	0.24367(7)	1.22(6)
W(9)	0.8747(1)	−0.02567(7)	0.17107(7)	1.25(6)
W(10)	0.8876(1)	−0.03128(7)	0.31227(7)	1.28(6)
O(1)	1.051(3)	0.348(2)	−0.066(1)	2.8(6)
O(2)	1.177(2)	0.301(1)	0.033(3)	1.2(4)
O(3)	0.961(2)	0.338(1)	0.049(1)	1.2(4)
O(4)	0.884(2)	0.226(1)	−0.027(1)	1.4(5)
O(5)	1.095(3)	0.229(1)	−0.044(1)	1.9(5)
O(6)	1.329(2)	0.269(1)	0.123(1)	0.8(4)
O(7)	1.092(2)	0.307(1)	0.135(1)	1.4(4)
O(8)	0.868(3)	0.350(1)	0.156(1)	1.7(5)
O(9)	0.794(2)	0.264(1)	0.074(1)	1.4(5)
O(10)	0.694(3)	0.185(1)	−0.009(1)	1.9(5)
O(11)	0.931(3)	0.152(1)	−0.019(1)	1.9(5)
O(12)	1.162(2)	0.110(1)	−0.044(1)	1.4(5)
O(13)	1.229(2)	0.190(1)	0.041(1)	1.1(4)
O(14)	1.011(3)	0.230(1)	0.059(1)	1.6(5)
O(15)	1.156(2)	0.191(1)	0.150(1)	1.1(4)
O(16)	0.919(2)	0.232(1)	0.165(1)	1.3(4)
O(17)	0.930(2)	0.151(1)	0.079(1)	1.2(4)
O(18)	1.070(3)	0.109(1)	0.065(1)	1.7(5)
O(19)	1.123(2)	0.064(1)	0.186(1)	1.6(5)
O(20)	1.006(3)	0.153(1)	0.253(1)	1.6(5)
O(21)	0.786(2)	0.124(1)	0.193(1)	1.0(4)
O(22)	0.908(2)	0.035(1)	0.127(1)	1.4(5)
O(23)	1.259(3)	−0.020(1)	0.242(1)	2.2(5)
O(24)	1.126(3)	0.062(1)	0.298(1)	1.6(5)
O(25)	1.016(3)	0.148(1)	0.369(1)	2.2(5)
O(26)	0.813(3)	0.118(1)	0.303(1)	1.7(5)
O(27)	0.590(3)	0.092(2)	0.245(1)	2.8(6)
O(28)	0.724(2)	0.010(1)	0.190(1)	1.5(5)
O(29)	0.833(3)	−0.080(2)	0.125(1)	2.6(6)
O(30)	1.037(2)	−0.046(1)	0.186(1)	1.0(4)
O(31)	0.927(3)	0.038(1)	0.245(1)	1.8(5)
O(32)	1.049(2)	−0.045(1)	0.295(1)	1.5(5)
O(33)	0.941(3)	0.035(1)	0.355(1)	1.7(5)
O(34)	0.744(2)	0.007(1)	0.301(1)	1.2(4)
O(35)	0.851(3)	−0.072(1)	0.243(1)	1.9(5)
O(36)	0.859(3)	−0.084(2)	0.364(1)	2.6(6)
Ow(1)	0.125(4)	0.255(2)	0.276(2)	4.1(8)
Ow(2)	0.277(3)	0.170(2)	0.379(2)	2.9(6)
Ow(3)	0.287(3)	0.147(2)	0.242(1)	2.8(6)
Ow(4)	0.532(3)	0.194(2)	0.311(2)	3.3(7)
Ow(5)	0.400(3)	0.305(1)	0.234(1)	2.3(6)
Ow(6)	0.379(5)	0.299(3)	0.368(2)	7.(1)
Ow(7)	0.626(4)	0.344(2)	0.319(2)	4.4(9)
Ow(8)	0.594(4)	0.206(2)	0.162(2)	4.2(9)
Ow(9)	0.792(3)	0.239(2)	0.261(2)	3.1(7)
Ow(10)	0.626(3)	0.343(2)	0.166(1)	2.6(6)
Ow(11)	1.016(3)	0.467(2)	0.314(1)	2.7(6)
Ow(12)	0.907(4)	0.389(2)	0.457(2)	4.1(8)
Ow(13)	0.983(3)	0.485(1)	0.167(1)	2.4(6)
Ow(14)	0.862(3)	0.349(2)	0.306(1)	2.6(6)
Ow(15)	1.119(3)	0.373(2)	0.231(1)	2.6(6)
Ow(16)	1.077(3)	0.282(2)	0.384(1)	2.9(6)
Ow(17)	0.961(3)	0.279(2)	0.519(2)	3.2(7)
Ow(18)	0.798(5)	0.233(2)	0.404(2)	6.(1)
Ow(19)	1.137(3)	0.174(2)	0.504(1)	2.7(6)
Ow(20)	0.874(3)	0.137(2)	0.515(2)	2.9(7)
Ow(21)	0.416(4)	0.116(2)	0.112(2)	4.2(8)
Ow(22)	0.706(3)	0.058(1)	0.419(1)	2.4(6)
Ow(23)	0.856(4)	−0.027(2)	0.506(2)	4.3(9)
Ow(24)	1.097(3)	0.058(2)	0.477(2)	3.5(7)
Ow(25)	0.627(3)	0.063(2)	0.563(2)	3.4(7)
Ow(26)	0.455(4)	0.008(2)	0.472(2)	4.0(7)
Ow(27)	0.637(3)	−0.073(2)	0.579(2)	3.0(7)
Ow(28)	0.661(3)	−0.088(1)	0.427(1)	2.4(6)
Ow(29)	1.195(3)	−0.012(2)	0.394(2)	2.9(7)
Ow(30)	1.145(3)	−0.008(2)	0.079(2)	3.1(7)
Ow(31)	0.861(3)	0.454(2)	0.066(2)	3.4(7)
Ow(32)	0.380(5)	0.057(3)	0.358(2)	6.(1)
Na(1)	0.328(2)	0.2315(9)	0.2983(8)	2.4(3)
Na(2)	0.596(2)	0.273(1)	0.246(1)	3.2(4)
Na(3)	0.554(3)	0.279(1)	0.089(1)	4.9(6)
Na(4)	0.925(2)	0.4164(9)	0.2346(8)	2.4(3)
Na(5)	1.001(2)	0.380(1)	0.372(1)	3.3(4)
Na(6)	0.978(2)	0.214(1)	0.445(1)	3.4(4)
Na(7)	0.398(2)	0.066(1)	0.210(1)	4.0(5)
Na(8)	0.901(2)	0.060(1)	0.4503(9)	2.9(4)
Na(9)	0.653(2)	−0.008(1)	0.4942(8)	2.8(4)

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

The photoluminescence spectrum at 4.2 K were measured using an Oxford Instruments CF 204 cryostat and a Questek 2320 XeCl excimer-laser (100 mJ/pulse) as the light source. The emission was monochromatized through a Spex 1702 spectrometer and detected by a Hamamatsu Photonix R928 photomultiplier. The output signal was amplified by a lock-in (NFLI-575 lock-in amplifier) technique, and recorded. The emission decay was measured on a Tektronics 2230 digital storage oscilloscope.

Results and Discussion

The atomic coordinates and thermal parameters for nonhydrogen atoms are listed in Table 1.[10] Figure 1 shows an ORTEP plot of $[EuW_{10}O_{36}]^{9-}$ with atom numbering. The space group of $Na_9[EuW_{10}O_{36}]\cdot 32H_2O$ is Cc (No 9), different from $C2/c$ (No 15) for $Na_6H_2[CeW_{10}O_{36}]\cdot 30H_2O$. Eu^{3+} in the center of the anion, which achieves eight-fold co-ordination by attachment of two W_5O_{18} ligands, constituting a distorted square antiprism. There are no aqua ligands in the first co-ordination sphere of Eu^{3+}.

A pseudo plane containing Eu(1), W(2), W(1), and W(4) atoms in the anion intersects with one containing Eu(1), W(7), W(10), and W(9) atoms at an angle of 49°(47° for $Na_6H_2[CeW_{10}O_{36}]\cdot 30H_2O$). In addition, a pseudo plane containing W(2), W(3), W(4), and W(5) atoms intersects with one containing W(6), W-

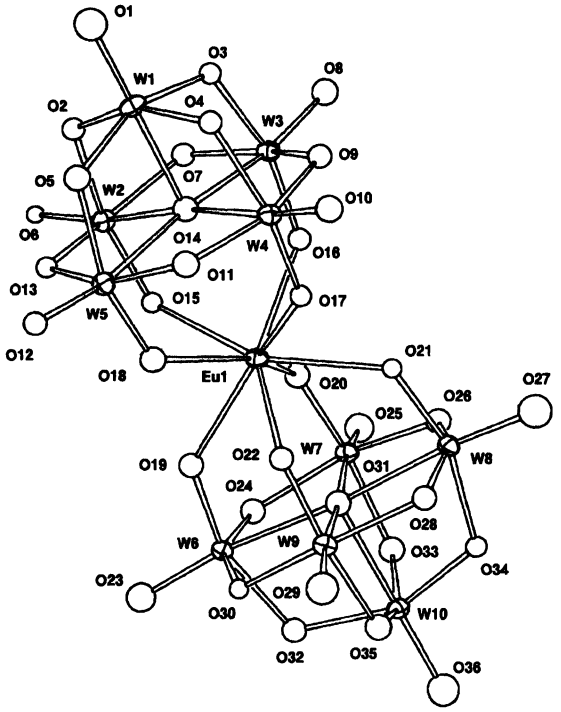

Fig. 1. ORTEP plot of the $[EuW_{10}O_{36}]^{9-}$ with atom numbering.

(7), W(8), and W(9) atoms at an angle of 4.2°(0.1° for $Na_6H_2[CeW_{10}O_{36}]\cdot 30H_2O$). These results indicate a lowering of the site symmetry of the anion from D_{4d} for $[CeW_{10}O_{36}]^{8-}$. Table 2 gives the bond distances for both the W–O and Eu–O bonds. Each of the W-O bond distances is similar to the corresponding distance for $[CeW_{10}O_{36}]^{8-}$,[1] as expected from the similarity of the ionic radius between Eu^{3+} (1.07 Å) and Ce^{4+} (0.97 Å).[11] However, the reduced electrostatic attractive force between the Eu^{3+} and oxygen atoms, compared with that between the Ce^{4+} and oxygen atoms, gives rise to Eu–O distances which are longer than the Ce–O distances; the Eu–O distances of 2.41(3)—2.45(3) Å (mean 2.43 Å) for the EuO_8 group are slightly longer than the Ce–O distances of 2.38(4)—2.40(4) Å (mean 2.38 Å) for the CeO_8 group of $[CeW_{10}O_{36}]^{8-}$. Furthermore, the second-nearest O(14) and O(31) atoms are positioned at 3.18(3) and 3.14(3) Å from the Eu atom, respectively, whereas the corresponding oxygen atoms are at 3.09 Å from the Ce atom. Figure 2 shows the co-ordination geometries of EuO_8 for $[EuW_{10}O_{36}]^{9-}$ and CeO_8 for $[CeW_{10}O_{36}]^{8-}$, together with their frameworks projected onto the square-antiprism square plane. The dihedral angle between the square-antiprism square planes were 3.8 and 1.3° for EuO_8 and CeO_8 sites, respectively. As shown in Fig. 2, the Eu^{3+} ion in $Na_9[EuW_{10}O_{36}]\cdot 32H_2O$ occupies approximately a site of C_{4v} symmetry, while the Ce^{4+} ion in $Na_6H_2[CeW_{10}O_{36}]\cdot 30H_2O$ occupies a site of D_{4d} symmetry.[1]

Figure 3 shows the unit-cell packing of the anion.

Table 2. Metal–Oxygen Bond Distances (Å)

W(1)– O(1)	1.77(4)	W(6)– O(19)	1.77(3)
– O(2)	1.91(3)	– O(23)	1.74(3)
– O(3)	1.90(3)	– O(24)	1.87(3)
– O(4)	1.90(3)	– O(30)	2.00(3)
– O(5)	1.89(3)	– O(31)	2.31(3)
– O(14)	2.26(3)	– O(32)	2.01(3)
W(2)– O(2)	2.04(3)	W(7)– O(20)	1.80(3)
– O(6)	1.71(2)	– O(24)	2.00(3)
– O(7)	1.99(3)	– O(25)	1.70(3)
– O(13)	1.98(3)	– O(26)	1.94(3)
– O(14)	2.32(3)	– O(31)	2.29(3)
– O(15)	1.78(3)	– O(33)	1.97(3)
W(3)– O(3)	2.00(3)	W(8)– O(21)	1.79(3)
– O(7)	1.94(3)	– O(26)	1.93(3)
– O(8)	1.73(3)	– O(27)	1.74(4)
– O(9)	1.95(3)	– O(28)	1.91(3)
– O(14)	2.27(3)	– O(31)	2.33(3)
– O(16)	1.77(3)	– O(34)	2.03(3)
W(4)– O(4)	2.04(3)	W(9)– O(22)	1.79(3)
– O(9)	1.93(3)	– O(28)	1.98(3)
– O(10)	1.77(3)	– O(29)	1.72(3)
– O(11)	1.93(3)	– O(30)	1.94(3)
– O(14)	2.31(3)	– O(31)	2.34(3)
– O(17)	1.73(3)	– O(35)	2.03(3)
W(5)– O(5)	2.04(3)	W(10)– O(31)	2.31(3)
– O(11)	1.95(3)	– O(32)	1.93(3)
– O(12)	1.75(3)	– O(33)	1.93(3)
– O(13)	1.91(3)	– O(34)	1.88(3)
– O(14)	2.36(3)	– O(35)	1.93(3)
– O(18)	1.81(3)	– O(36)	1.77(4)
Eu(1)– O(15)	2.46(3)	Eu(1)– O(19)	2.41(3)
– O(16)	2.43(3)	– O(20)	2.43(3)
– O(17)	2.42(3)	– O(21)	2.43(3)
– O(18)	2.40(3)	– O(22)	2.45(3)

Nine Na (1—9) atoms are connected to anion O atoms (at the range of 2.38(4)—2.81(4) Å) and lattice water O_w atoms (at the range of 2.31(4)—2.70(4) Å). The bond lengths for the sodium-oxygen polyhedra are listed in Table 3. Four (Na(1), Na(2), Na(6), and Na(9)) of the nine structurely distinct sodium atoms are present as $Na(H_2O)^{6+}$, one (Na(5)) as $Na(H_2O)^{5+}$. The other two (Na(3) and Na(8)) are bonded to one terminal oxygen atom of an anion, one bridging oxygen atom of the same (for Na(8)), or a neighboring anion, and four water molecules each. The others (Na(4) and Na(7)) are connected to two terminal oxygen atoms which belong to the neighboring two anions, (one bridging oxygen atom of a neighboring anion for Na(7), and four (or three for Na(7)) water molecules. Since in $[CeW_{10}O_{36}]^{8-}$ none of the Na atoms bridges a pair of anions,[1] the linking of adjacent anions by three Na cations (Na(3), Na(4), and Na(7) can be associated with the anionic high charge of $[EuW_{10}O_{36}]^{9-}$, compared with that of $[CeW_{10}O_{36}]^{8-}$.

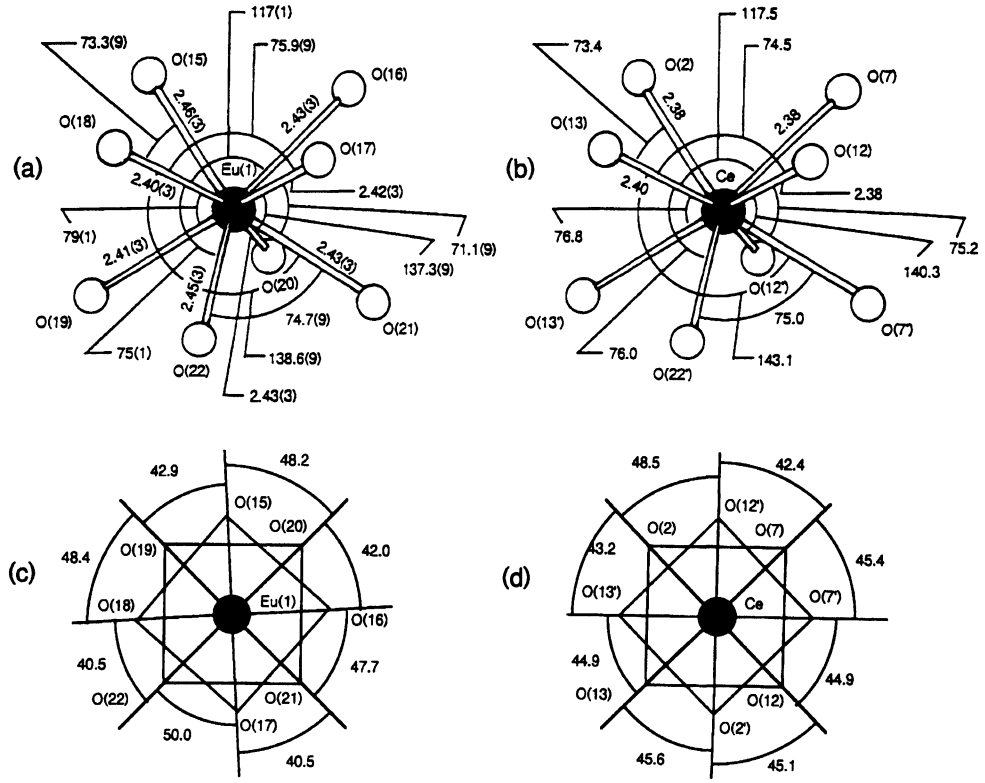

Fig. 2. Co-ordination geometries ((a) and (b)) for Eu^{3+} and Ce^{4+} with selected interatomic distances (Å) and bond bond angles (°). The frameworks of EuO_8 and CeO_8, projected on the square-antiprism square plane, are also represented in (c) and (d), respectively. For CeO_8 the atom numbering system and the calculation are made according to Ref. 1.

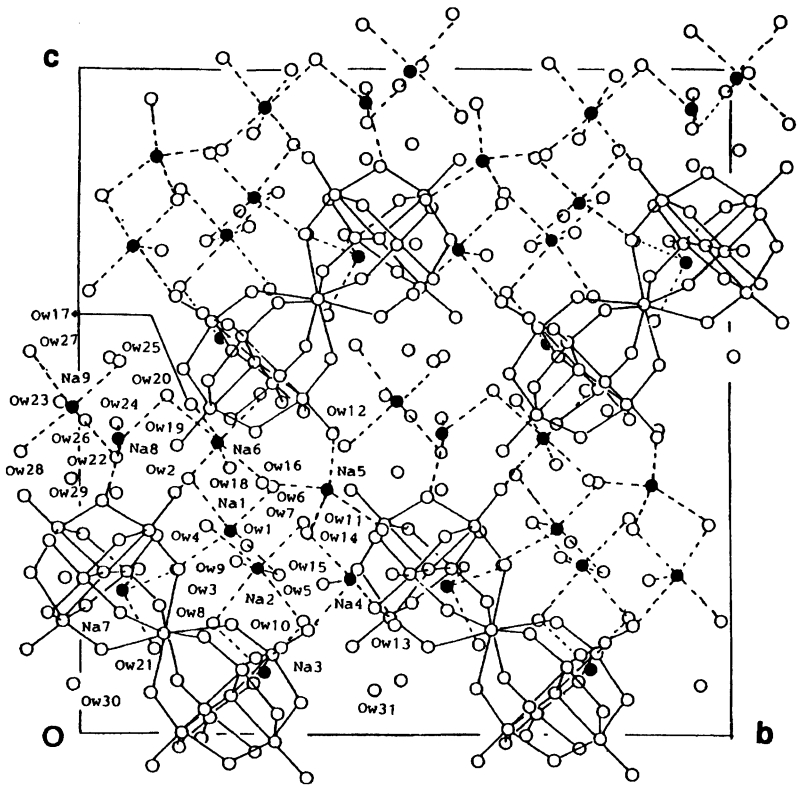

Fig. 3. Crystal structure viewed along *a*-axis. The hydrogen bonds are indicated by broken lines.

Table 3. Na–O and –O_w bond Distances (Å)

Na(1)– O_w(1)	2.43(5)	Na(6)– O_w(16)	2.44(4)
– O_w(2)	2.46(4)	– O_w(17)	2.31(4)
– O_w(3)	2.39(4)	– O_w(18)	2.31(6)
– O_w(4)	2.51(4)	– O_w(19)	2.43(4)
– O_w(5)	2.44(4)	– O_w(20)	2.70(4)
– O_w(6)	2.32(6)	– O_w(25)	2.40(4)
Na(2)– O_w(4)	2.49(5)	Na(7)– O_w(3)	2.39(5)
– O_w(5)	2.38(4)	– O_w(13^{iv})	2.35(4)
– O_w(7)	2.39(5)	– O(19^{i})	3.19(4)
– O_w(8)	2.50(5)	– O_w(21)	2.38(5)
– O_w(9)	2.41(5)	– O(23^{i})	2.66(4)
– O_w(10)	2.51(4)	– O(27)	2.41(4)
Na(3)– O(6^{i})	2.73(4)	Na(8)– O_w(20)	2.37(4)
– O_w(8)	2.44(5)	– O_w(22)	2.34(4)
– O(9)	2.81(4)	– O_w(23)	2.46(5)
– O_w(10)	2.48(5)	– O_w(24)	2.33(4)
– O_w(17^{ii})	2.34(5)	– O(25)	3.12(4)
– O_w(19^{ii})	2.49(5)	– O(33)	2.38(4)
Na(4)– O(8)	2.47(4)	Na(9)– O_w(22)	2.43(4)
– O_w(11)	2.41(4)	– O_w(23)	2.38(5)
– O_w(13)	2.35(4)	– O_w(25)	2.34(4)
– O_w(14)	2.41(4)	– O_w(26)	2.35(5)
– O_w(15)	2.45(4)	– O_w(27)	2.50(4)
– O(23^{iii})	2.41(4)	– O_w(28)	2.42(4)
Na(5)– O_w(11)	2.42(4)		
– O_w(12)	2.32(5)		
– O_w(14)	2.32(4)		
– O_w(16)	2.45(4)		
– O_w(28)	2.34(4)		

(i) $x-1$, y, z; (ii) $x-1/2$, $-y+1/2$, $z-1/2$; (iii) $x-1/2$, $y+1/2$, z; (iv) $x-1/2$, $y-1/2$, z.

Water molecules serve to bind the molecules together by a complex system of hydrogen bonds. Table 4 lists the plausible hydrogen-bond distances (2.71—3.18 Å) for the O_w atoms.

The photoexcitation of the O→W LMCT band of $[EuW_{10}O_{36}]^{9-}$ gives the emission of Eu^{3+}, indicating the occurrence of an intramolecular energy transfer from the O→W LMCT states to Eu^{3+} in the polyoxotungstoeuropate lattice. The emission originates from the $^5D_0$ excited state of Eu^{3+} and the luminescent transitions all terminate in the $J=0$—4 levels of the ^7F_J ground state. Figure 4 shows the photoluminescence spectrum of $Na_9[EuW_{10}O_{36}]\cdot 32H_2O$ at 4.2 K. The quantum yield (0.99 at 4.2 K) of the emission on the O→W LMCT photoexcitation is very high.[12] This high quantum yield has been discussed in terms of the localization of the O→W LMCT excitation energy on the edge-sharing WO_6 octahedron in the lattice.[3,13] The decay of the luminescence was exponential and its decay time (3.5 ms at 4.2 K) was longer than that (1.1 ms at 4.2 K)[3] for $[Eu_3(H_2O)_3(SbW_9O_{33})(W_5O_{18})_3]^{18-}$, showing a co-ordination of two aqua ligands around Eu^{3+}. A longer decay time of the emission for the present complex can be attributed to no co-ordination of the aqua ligands to Eu^{3+}, which results in an absence of the nonradiative deactivation process of the $^5D_0$ state due to coupling with the vibrational states of the high-frequency O–H oscillators of the aqua ligands.[13,14]

The Eu^{3+} emission pattern at 4.2 K shows one $^5D_0 \rightarrow {}^7F_0$, two $^5D_0 \rightarrow {}^7F_1$, two $^5D_0 \rightarrow {}^7F_2$, two

Table 4. Hydrogen Bond Distance (<3.2 Å) for O_w (1—32) Atoms

O(1)	–O_w(4^{i})	3.07(5)	O(12)	–O_w(12^{i})	2.82(5)
	–O_w(22^{i})	2.82(5)	O_w(12)	–O_w(17)	2.99(6)
O_w(1)	–O_w(15^{ii})	2.92(6)		–O_w(26^{vii})	2.79(6)
	–O_w(16^{ii})	2.71(6)		–O_w(28^{vii})	3.06(6)
	–O(20^{ii})	2.77(5)	O(12)	–O_w(29)	2.72(5)
O(2)	–O_w(20^{i})	2.72(5)	O(13)	–O_w(17^{i})	2.82(5)
O_w(2)	–O(4^{iii})	2.89(5)	O_w(13)	–O(23^{iv})	3.16(5)
	–O(25^{ii})	3.05(5)		–O(28^{vii})	2.86(4)
	–O_w(32)	2.90(7)		–O_w(31)	2.83(5)
O_w(3)	–O(15^{ii})	2.80(4)	O_w(15)	–O(35^{vii})	2.95(5)
	–O(19^{ii})	2.97(5)	O_w(16)	–O(25)	3.18(5)
	–O(24^{ii})	3.01(5)	O(17)	–O_w(27^{vi})	2.85(5)
O(3)	–O_w(25^{i})	2.99(5)	O_w(17)	–O_w(19)	3.17(5)
	–O_w(31)	2.94(5)	O(18)	–O_w(30)	2.84(5)
O_w(4)	–O(27)	2.91(5)	O_w(19)	–O_w(20)	3.14(5)
O(4)	–O_w(6^{i})	2.88(7)		–O_w(24)	2.78(5)
O(5)	–O_w(18^{i})	2.82(7)	O(19)	–O_w(30)	3.04(5)
O_w(5)	–O(6^{ii})	2.85(4)	O_w(20)	–O(29^{viii})	2.97(5)
	–O_w(6)	3.18(7)	O_w(21)	–O(27^{vi})	2.94(6)
	–O(35^{iv})	2.88(5)	O(22)	–O_w(23)	2.89(5)
O_w(6)	–O(11^{iii})	2.93(7)		–O_w(30)	3.13(5)
	–O(36^{iv})	2.71(7)	O_w(22)	–O(33)	3.19(5)
O(6)	–O_w(17^{i})	3.11(5)		–O(34^{vi})	3.07(4)
O(7)	–O_w(15)	2.73(4)	O_w(23)	–O_w(28)	3.19(6)
O_w(7)	–O_w(14)	2.74(6)	O(24)	–O_w(29)	2.93(5)
	–O(32^{iv})	2.76(5)	O_w(24)	–O_w(29)	2.79(5)
O_w(8)	–O_w(10)	3.18(6)		–O_w(30^{viii})	2.71(5)
	–O_w(21)	3.03(6)	O_w(25)	–O_w(26)	3.15(6)
	–O(21)	2.98(5)		–O_w(27)	3.16(6)
O(8)	–O_w(10)	2.80(5)		–O(29^{viii})	2.77(5)
O_w(9)	–O_w(14)	2.85(5)		–O_w(31^{iii})	3.08(6)
	–O(16)	2.73(5)	O_w(26)	–O_w(31)	2.64(6)
	–O(20)	3.17(5)		–O_w(32)	3.02(7)
	–O(21)	3.10(5)	O_w(27)	–O(28^{viii})	3.15(5)
	–O(26)	2.96(5)	O_w(28)	–O(36)	2.75(5)
O(9)	–O_w(19^{v})	2.80(4)	O_w(29)	–O(32)	2.94(5)
O(10)	–O_w(16^{v})	2.91(5)		–O_w(32^{ix})	2.79(7)
	–O_w(17^{v})	2.90(5)	O_w(30)	–O(30)	2.98(5)
	–O_w(28^{vi})	2.72(5)		–O_w(31^{x})	2.66(6)
O_w(10)	–O(30^{iv})	2.79(4)			
O(11)	–O_w(23^{vi})	3.06(5)			
O_w(11)	–O_w(15)	3.16(5)			
	–O_w(32^{vii})	2.82(7)			
	–O(34^{vii})	2.80(4)			

(i) $1/2+x$, $1/2-y$, $-1/2+z$; (ii) $x-1$, y, z; (iii) $-1/2+x$, $1/2-y$, $1/2+z$; (iv) $-1/2+x$, $1/2+y$, z; (v) $-1/2+x$, $1/2-y$, $-1/2+z$; (vi) x, $-y$, $-1/2+z$; (vii) $1/2+x$, $1/2+y$, z; (viii) x, $-y$, $1/2+z$; (ix) $1+x$, y, z; (x) $1/2+x$, $-1/2+y$, z.

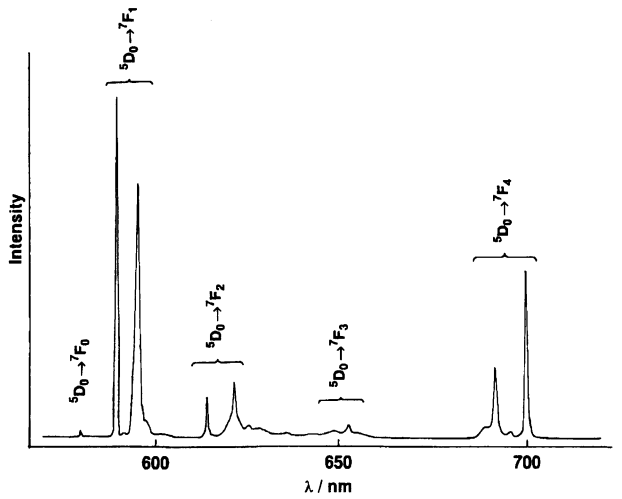

Fig. 4. Photoluminescence spectrum of solid $Na_9[EuW_{10}O_{36}]\cdot 32H_2O$ at 4.2 K. The excitation wavelength is 308 nm.

$^5D_0 \rightarrow ^7F_3$, and four $^5D_0 \rightarrow ^7F_4$ lines, as shown in Fig. 4. Furthermore, the relative intensities of the $^5D_0 \rightarrow ^7F_J$ emissions of Eu^{3+} at 4.2 K are 1:50:17:5:27 with respect to the total intensity of the $^5D_0 \rightarrow ^7F_J$ (J= 0—4) transitions. Since the $^5D_0 \rightarrow ^7F_0$ transition cannot be split by any crystal field, the existence of a single peak at 581 nm (Fig. 4) may be taken as evidence that only a single Eu^{3+} species is responsible for the series of luminescent transitions. The number of peaks within each of the $^5D_0 \rightarrow ^7F_J$ band systems must, therefore, equal the number of true ^7F_J crystal field components. Thus, a correlation of the number of observed luminescence peaks with the number those predicted on the basis of symmetry considerations allows one to determine the molecular point group of the emitting Eu^{3+}. The D_{4d} site symmetry has been postulated for $[EuW_{10}O_{36}]^{9-}$ on the basis of the structure of $[CeW_{10}O_{36}]^{8-}$.[4] The D_{4d} site symmetry should lead to an observation of zero $^5D_0 \rightarrow ^7F_0$ peak, two $^5D_0 \rightarrow ^7F_1$ peaks, zero $^5D_0 \rightarrow ^7F_2$ peak, one $^5D_0 \rightarrow ^7F_3$ peak and two $^5D_0 \rightarrow ^7F_4$ peaks. However, the $^5D_0 \rightarrow ^7F_2$ transition, which should be forbidden completely under D_{4d} symmetry, appears significantly with an $(^5D_0 \rightarrow ^7F_1)/(^5D_0 \rightarrow ^7F_2)$ ratio of 2.9 (Fig. 4). The number of peaks within the $^5D_0 \rightarrow ^7F_J$ band systems (Fig. 4) agrees with the predictions made on the basis of C_{4v} symmetry; for C_{4v}, we expect one $^5D_0 \rightarrow ^7F_0$, two $^5D_0 \rightarrow ^7F_1$, two $^5D_0 \rightarrow ^7F_2$, two $^5D_0 \rightarrow ^7F_3$, and four $^5D_0 \rightarrow ^7F_4$ lines.[4] A C_{4v} point group for Eu^{3+} is in good agreement with the site symmetry of EuO_8 predicted by X-ray crystallography, as shown in Fig. 2. Thus, it may be concluded that the effective crystal field experienced by Eu^{3+} for the $Na_9[EuW_{10}O_{36}]\cdot 32H_2O$ lattice is C_{4v}.

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