Molecular Structure and Photoluminescence of Square-anitiprismatic Europium Octahydrate Cations in $[Eu(H_2O)_8]_2[V_{10}O_{28}]\cdot 8H_2O$ Crystallines

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$[Eu(H_2O)_8]^{3+}$ cations in $[Eu(H_2O)_8]_2[V_{10}O_{28}]\cdot 8H_2O$ form an approximately square-antiprismatic configuration. This configuration provides another model for the Eu^{3+} aqua ion in aqueous solutions. The lifetime of the $^5D_0$ state for $[Eu(H_2O)_8]^{3+}$ is 0.13 ± 0.01 ms at 4.2K, leading to a validity of the luminescence lifetime method for the determination of the number of bonded water molecules (within the Eu-O distances of 2.5Å).

Luminescence lifetime determinations for trivalent europium ions allow one to evaluate the number (n) of water molecules directly bonded to Eu^{3+}.[1,2] Vibronic coupling of the Eu^{3+} ion excited states with OH oscillators provides an easy path for radiationless deexcitation and all experimental observations tend to demonstrate that the OH oscillators act independently. Since radiationless deexcitation exhibits a large isotopic effect, the study of systems in the presence of H_2O and D_2O leads to an estimate of n. Several hydrated crystalline solids and solutions have been invesitagated by this method and the following relationship between n and the difference in reciprocal $^5D_0$ excited-state lifetimes, $\tau_{H2O}^{-1} - \tau_{D2O}^{-1} = \Delta\tau^{-1}$ was proposed.

$$n=1.05\ (\tau_{H2O}^{-1} - \tau_{D2O}^{-1})=1.05\Delta\tau^{-1} \qquad (1)$$

where τ^{-1} value is in $msec^{-1}$. The method has been applied to various polyoxometalloeuropate complexes where the number of Eu^{3+} ion-coordinated water molecules is known from X-ray-crystallography, and a plot of the deviation of the reciprocal $^5D_0$ lifetime from that ($(3.7\ msec)^{-1}$ at 4.2 K) of the anhydrous Eu^{3+} site-contained $Na_9[Eu(W_5O_{18})_2]\bullet 32H_2O$ crystallines versus total number of aqua and hydroxo ligands coordinating Eu^{3+} indicates a good linearity irrespective of the coordination geometry, if the average distance between Eu^{3+} and aqua or hydroxo oxygen atoms is less than 2.5Å.[3] The $^5D_0$-luminescence lifetime method is increasingly being used both in coordination chemistry and biochemistry for species not amenable to study by single-crystal X-ray method. The Eu^{3+} aqua cation in aqueous solutions has been assigned as $[Eu(H_2O)_9]^{3+}$ with a D_{3h} tricapped-trigonal-prismatic configuration based on the crystal structure of $[Eu(H_2O)_9][(C_2H_5SO_4)_3]$.[4] However, it should be noted that n value (9.6) for the Eu^{3+} aqua ion calculated by the luminescence lifetime method was larger, although the deviation in the uncertainity range is proposed to be ±0.5 water molecule. In our recent preparation and x-ray structural analysis of the Eu^{3+} salt of decavanadate, $[Eu(H_2O)_8]^{3+}$ as another Eu^{3+} aqua cation was found. This is the first example for the octaaquoeuropium(III) which is X-ray crystallographically characterized. In this communication, we report a molecular structure of $[Eu(H_2O)_8]^{3+}$ in $[Eu(H_2O)_8]_2[V_{10}O_{28}]\cdot 8H_2O$ crystals as well as the luminescence lifetime, and discuss a validity of the luminescence lifetime method for the determination of n for the hydrated Eu^{3+} ion.

$[Eu(H_2O)_8]_2[V_{10}O_{28}]\cdot 8H_2O$ was prepared as follows: an aqueous solution of sodium metavanadate (0.27 g) in water (20 ml) was acidified by nitric acid to pH 4.1 and then $EuCl_3\bullet 6H_2O$ (0.15 g) in 5 ml water was added with a ratio of Eu:V=1:5. The orange solution was kept at room temperature in an open vessel for slow evaporation, to provide orange single crystals of $[Eu(H_2O)_8]_2[V_{10}O_{28}]\cdot 8H_2O$.

$[Eu(H_2O)_8]_2[V_{10}O_{28}]\bullet 8H_2O$ crystallizes in the $P\bar{1}$ triclinic space group.[5] A view of the unit cell is presented in Figure 1. The structure consists of two octacoordinate cations $[Eu(H_2O)_8]^{3+}$ and $[V_{10}O_{28}]^{6-}$ anions with eight additional water molecules bonded to both cation and anion through hydrogen bonds. The eight water molecules for $[Eu(H_2O)_8]^{3+}$ coordinate the Eu atom at Eu-O distances 2.38(1)-2.54(1)Å (average 2.44 ± 0.02 Å) to form an approximately square-antiprismatic configuration. Figure 2 shows the coordination geometries of crystallographically two independent $[Eu(H_2O)_8]^{3+}$ cations. There is no significant difference in the structural configuration between the two $[Eu(H_2O)_8]^{3+}$cations. Similar arrangements were observed for the anhydrous $Ce(IV)O_8$ and $Eu(III)O_8$ sites of $Na_6H_2[Ce(W_5O_{18})_2]\bullet 30H_2O$[6] and $Na_9[Eu(W_5O_{18})_2]\bullet 32H_2O$[7] where the site symmetries are approximately D_{4d} and C_{4V} respectively, and the Eu-O distances for the latter are 2.40(3)-2.46(3) Å. $[V_{10}O_{28}]^{6-}$ consists of an arrangement of ten edge-

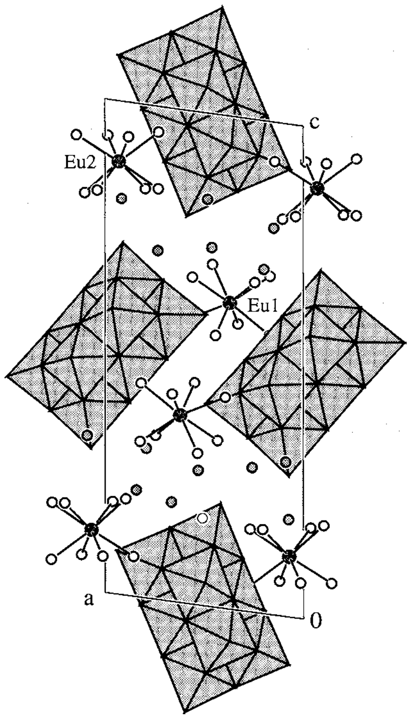

Figure 1. Crystal structure of $[Eu(H_2O)_8]_2[V_{10}O_{28}]\cdot 8H_2O$.

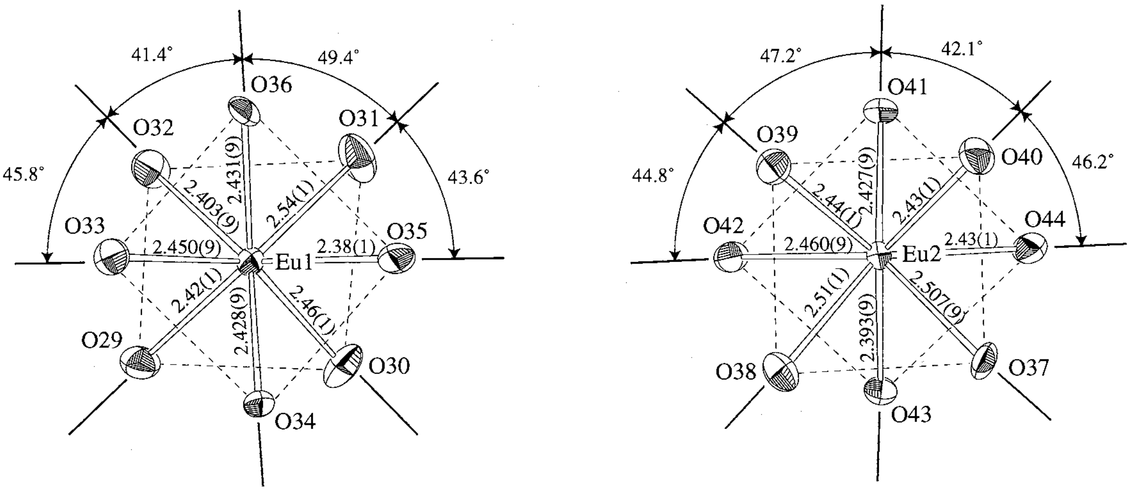

Figure 2. Coordination geometries of two $[Eu(H_2O)_8]^{3+}$ cations projected on the square-antiprism square plane.

sharedVO_6 octahedra with D_{2h} symmetry. The octahedra are distorted in order to maintain approximate valence balance at terminal and bridging oxygen atoms and bond lengths range from 1.578(9)Å for V-O terminal to 2.349((9)Å for V-O central. Four structures of decavanadolanthanoate complexes $[La(H_2O)_7]_2$-$[V_{10}O_{28}]•6H_2O$,[8] $[Nd(H_2O)_9]_2[V_{10}O_{28}]•10H_2O$,[9] $[Er(H_2O)_8]_2$-$[V_{10}O_{28}]•9H_2O$,[10] and $[Yb(H_2O)_8]_2[V_{10}O_{28}]•8H_2O$[11] have been characterized; the former two showed tricapped-trigonal prismatic configuration of $LaO_2(H_2O)_7$ and $Nd(H_2O)_9$ sites, and the latter two square-antiprismatic configuration of $Er(H_2O)_9$ and $Yb(H_2O)_9$ sites. The crystal structure of $[Yb(H_2O)_8]_2$-$[V_{10}O_{28}]•8H_2O$ was isomorphous with that of the present Eu^{3+} complex. There was little difference in the $[V_{10}O_{28}]^{6-}$ structure among these decavanadolanthanoate complexes.

The luminescence spectra and lifetimes of microcrystalline powders were measured at 4.2 K on a previous described instrumental setup.[3] The Eu^{3+} ion was excited at 525.6 nm ($^5D_1$ level) by a LAS 2050 tunable dye(Coumarin 152)-laser pumped by a Questek 2320 XeCl excimer laser. The excitation of the $^7F_0 \rightarrow ^5D_1$ band (525.6 nm) of Eu^{3+} results in the emission bands originating from the $^5D_0$ excited level. Figure 3 shows the emission spectrum at 4.2 K. The emission pattem shows nearly zero $^5D_0 \rightarrow ^7F_0$, two $^5D_0 \rightarrow ^7F_1$, three $^5D_0 \rightarrow ^7F_2$, one $^5D_0 \rightarrow ^7F_3$, and three $^5D_0 \rightarrow ^7F_4$ lines. The luminescence for the $Eu(^5D_0)$ level exponentially decayed and the lifetime at 4.2 K was 0.13 ± 0.01 ms. This assists a linear relationship of $n=1.05\Delta\tau^{-1}$ with uncertainity of 0.5 for n. The integrated and relative intensities of the $^5D_0 \rightarrow ^7F_J$ transitions are ~0, 55, 31, 2, and 11 for J=0, 1, 2, 3, and 4, respectively. Since the rate of the magnetic-dipole $^5D_0 \rightarrow ^7F_1$ transition is 1.35×10^2 s^{-1},[3] which is almost independent of the geometry of the Eu^{3+} surroundings, the radiative rate for the present complex is 2.45×10^2 s^{-1}. Furthermore, the nonradiative rate of the $^5D_0$ state for the $Eu(H_2O)_8$ site can be estimated to be $(7.4 \pm 0.7) \times 10^3$ $[=10^3/(0.13 \pm 0.01) - 2.45 \times 10^2]$ s^{-1}.

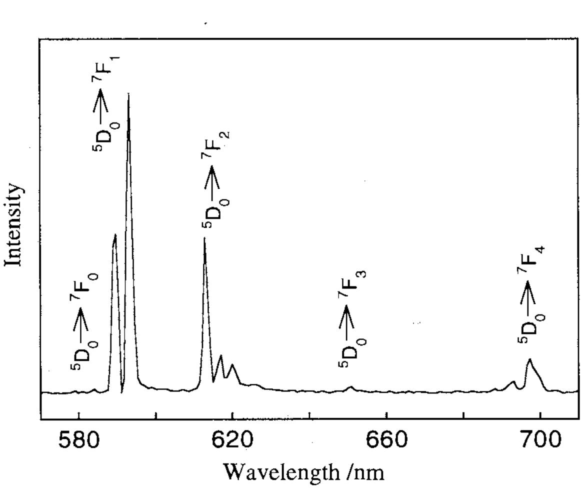

Figure 3. Photoluminescence spectrum at 4.2 K.

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5 Crystal data for $[Eu(H_2O)_8]_2[V_{10}O_{28}]·8H_2O$: $H_{48}Eu_2V_{10}V_{15}O_{52}$, M=1693.68, parallelepiped, space group P$\bar{1}$ (No. 2), a=9.413(1), b=9.885(1), c=23.556(4) Å, α=81.31(2)°, β=82.08(2)°, γ=89.51(2)°, U=2145.8(5) $Å^3$, F(000)=1640, Z=2, D_c=2.621 $g•cm^{-3}$, $\mu(Mo\text{-}K_\alpha)$=50.74 cm^{-1}, intensity data were collected on a Rigaku AFC5S diffractometer employing the ω scan method; absorption corrections (Ψ-scan) were applied. The structure was solved using direct methods (SIR88) and refined using a full-matrix least-squares refinement procedure, 9854 unique reflections, 6769 observed $[I \geq 2\sigma(I)$, $R_1=0.067$, $wR_2=0.053$; 577 refined parameters], $2\theta_{max}=55°$.
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