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## Structure of Photoluminescent Polyoxomolybdoeuropate (NH<sub>4</sub>)<sub>12</sub>H<sub>2</sub>[Eu<sub>4</sub>(MoO<sub>4</sub>)(H<sub>2</sub>O)<sub>16</sub>(Mo<sub>7</sub>O<sub>24</sub>)<sub>4</sub>].13H<sub>2</sub>O

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**Abstract.** Dodecaammonium dihydrogen hexadecaqua-29-molybdotetraeuropate(14-) tridecahydrate, (NH<sub>4</sub>)<sub>12</sub>H<sub>2</sub>[Eu<sub>4</sub>Mo<sub>29</sub>O<sub>100</sub>(H<sub>2</sub>O)<sub>16</sub>].13H<sub>2</sub>O, *M<sub>r</sub>* = 5731.0, monoclinic, *C2/c*, *a* = 19.539 (6), *b* = 43.31 (1), *c* = 20.358 (6) Å, β = 117.88 (2)°, *V* = 15229 (8) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 2.47 Mg m<sup>-3</sup>, λ(Mo Kα) = 0.71069 Å, μ = 3.97 mm<sup>-1</sup>, *F*(000) = 10424, *T* = 298 K, *R* = 0.065 and *wR* = 0.080 for 6705 independent reflections. The title compound is obtained from aqueous methanolic solutions containing [Mo<sub>7</sub>O<sub>24</sub>]<sup>6-</sup> and Eu<sup>3+</sup>. The central [Eu<sub>4</sub>(MoO<sub>4</sub>)(H<sub>2</sub>O)<sub>16</sub>]<sup>10+</sup> core of the anion is coordinated by four heptamolybdate groups in the location of *D<sub>2d</sub>* symmetry. Each Eu<sup>3+</sup> atom in the core exhibits ninefold coordination by O atoms belonging to H<sub>2</sub>O, MoO<sub>4</sub> and Mo<sub>7</sub>O<sub>24</sub> units.

**Introduction.** There have been three structural studies of lanthanide polyoxotungstate complexes, Na<sub>6</sub>H<sub>2</sub>[Ce(W<sub>5</sub>O<sub>18</sub>)<sub>2</sub>].30H<sub>2</sub>O (Iball, Low & Weakley, 1974), K<sub>16</sub>[Ce(P<sub>2</sub>W<sub>17</sub>O<sub>61</sub>)<sub>2</sub>].50H<sub>2</sub>O (Molchanov, Kazanskii, Torchenkova & Simonov, 1979), and K<sub>15</sub>H<sub>3</sub>[Eu<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub>(W<sub>5</sub>O<sub>18</sub>)<sub>3</sub>(SbW<sub>9</sub>O<sub>33</sub>)].25.5H<sub>2</sub>O (Yamase, Naruke & Sasaki, 1990). The former two complexes contain lacunary units of W<sub>5</sub>O<sub>18</sub> and P<sub>2</sub>W<sub>17</sub>O<sub>61</sub> which are prepared by removing a WO<sub>6</sub> octahedron from the Lindqvist and Dawson structures, respectively. The latter is a potassium salt of the luminescent mixed-polyoxotungstates anion [Eu<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub>-

(W<sub>5</sub>O<sub>18</sub>)<sub>3</sub>(SbW<sub>9</sub>O<sub>33</sub>)]<sup>18-</sup> in which the central Eu<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub> core is coordinated by a *B*-type α-SbW<sub>9</sub>O<sub>33</sub> and three W<sub>5</sub>O<sub>18</sub> units with tetrahedral conformation. The polyoxometalloeuropates are interesting from the point of view of the intramolecular energy transfer from the oxygen-to-metal charge transfer state of polyoxometallate lattices to the emitting <sup>5</sup>D<sub>0</sub> level of the Eu<sup>3+</sup> atoms. Our recent interest has been focused on the crystal structure of luminescent polyoxometalloeuropates. There have been few studies of their crystal structures, although luminescence properties for [Eu(W<sub>5</sub>O<sub>18</sub>)<sub>2</sub>]<sup>9-</sup>, [Eu-(P<sub>2</sub>W<sub>17</sub>O<sub>61</sub>)<sub>2</sub>]<sup>17-</sup> and [Eu(XW<sub>11</sub>O<sub>39</sub>)<sub>2</sub>]<sup>*n-*</sup> (*n* = 13 and *n* = 15 for *X* = Si and B, respectively) (Stillman & Thomson, 1976; Blasse, Dirksen & Zonnevijlle, 1981; Ballardini, Chiorboli & Balzani, 1984) have been reported and discussed in relation to their structures. This paper describes the crystal structure of the luminescent (NH<sub>4</sub>)<sub>12</sub>H<sub>2</sub>[Eu<sub>4</sub>(MoO<sub>4</sub>)(H<sub>2</sub>O)<sub>16</sub>(Mo<sub>7</sub>O<sub>24</sub>)<sub>4</sub>].13H<sub>2</sub>O in the course of our extension of the structural study of polyoxotungstoeuropates to that of the polyoxomolybdoeuropates. Very recently, a similar structure of non-luminescent dimeric [Pr<sub>4</sub>(MoO<sub>4</sub>)(Mo<sub>7</sub>O<sub>24</sub>)<sub>4</sub>]<sup>28-</sup> was reported (Kazansky, 1988). However, no further information on its detailed structure has been published.

**Experimental.** 0.93 g of (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>.4H<sub>2</sub>O was dissolved in 9 ml of water, to which 1 ml of CH<sub>3</sub>OH was added. An aqueous solution (1 ml) containing

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0.17 g of  $\text{Eu}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$  was added dropwise to the above solution with stirring at room temperature. Resulting solution (pH ~ 5) was kept in the dark at 278 K in a capped container for 24 h. Colorless single crystals were obtained from the solution. Found: H, 2.25; N, 3.27; Mo, 47.2; Eu, 10.1%. Calculated for  $(\text{NH}_4)_{12}\text{H}_2[\text{Eu}_4(\text{MoO}_4)(\text{H}_2\text{O})_{16}(\text{Mo}_7\text{O}_{24})_4]\cdot 13\text{H}_2\text{O}$ : H, 1.90; N, 2.93; Mo, 48.5; Eu, 10.6%.

A parallelepiped single crystal of  $0.15 \times 0.10 \times 0.05$  mm was sealed in a glass capillary and mounted on a Rigaku AFC-5R four-circle diffractometer. The systematic extinction showed the space group to be  $C2/c$ . Graphite-monochromated  $\text{Mo K}\alpha$  radiation was used as the X-ray source. Lattice parameters were determined by least squares from 25 reflections ( $5 < 2\theta < 30^\circ$ ). Intensity data were collected with the following conditions:  $2\theta$ - $\omega$  scanning technique with a scan rate of  $8^\circ \text{ min}^{-1}$ ,  $\Delta\omega = (0.75 + 0.14\tan\theta)^\circ$ ,  $2\theta_{\text{max}} = 60.1^\circ$ ,  $(\sin\theta/\lambda)_{\text{max}} = 0.70 \text{ \AA}^{-1}$ ,  $0 \leq h \leq 27$ ,  $0 \leq k \leq 58$ ,  $-27 \leq l \leq 27$ . Four standard reflections measured every 100 reflections exhibited intensity variations within  $\pm 1\%$  throughout the data collection. 23 127 independent reflections were measured, of which 6935 were observed with  $I > 3\sigma(I)$ . 6705 independent data were used for structure determination and refinement. Lorentz and polarization corrections were applied and an analytical absorption correction (de Meulenaer & Tompa, 1965) was made. The transmission factors were from 0.666 to 0.825. All calculations were carried out by the use of the *TEXSAN* program suite (Molecular Structure Corporation, 1989), incorporating *MITHRIL* (Gilmore, 1984) for the structure solution. N and O atoms were found from the difference Fourier syntheses. Anisotropic thermal parameters for Eu and Mo atoms were refined. The distance between the lattice water O atom of  $\text{Ow}(9)$  and its symmetry related position is very short (2.2 Å), which may be brought about by the disordered structure of these atoms. Thus, the site occupancy of  $\text{Ow}(9)$  was fixed at 0.5 through the structure refinements. Refinements were made by the full-matrix least-squares method for 434 parameters;  $R = 0.065$ ,  $wR = 0.080$ ,  $1/w = \{[\sigma^2(I) + 0.0025I^2]^{1/2}\} / 2F_o$ ,  $S = \sum w(|F_o| - |F_c|) / (n - m) = 1.42$ ,  $\Delta/\sigma = 0.13$ ,  $(\Delta\rho)_{\text{max}} = 4.59$ ,  $(\Delta\rho)_{\text{min}} = -4.86 \text{ e \AA}^{-3}$ . The complex atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).

**Discussion.**  $(\text{NH}_4)_{12}\text{H}_2[\text{Eu}_4(\text{MoO}_4)(\text{H}_2\text{O})_{16}(\text{Mo}_7\text{O}_{24})_4]\cdot 13\text{H}_2\text{O}$  is prepared by a similar procedure to that for  $\text{Eu}_2\text{Mo}_7\text{O}_{24}\cdot 6\sim 8\text{H}_2\text{O}$  (*Gmelin Handbook of Inorganic Chemistry*, 1985), although  $\text{Eu}_2\text{Mo}_7\text{O}_{24}\cdot 6\sim 8\text{H}_2\text{O}$  solids are obtained from more acidic solution at pH ~ 3 adjusted by  $\text{HNO}_3$ . The IR and photoemission spectra of  $(\text{NH}_4)_{12}\text{H}_2[\text{Eu}_4$

$(\text{MoO}_4)(\text{H}_2\text{O})_{16}(\text{Mo}_7\text{O}_{24})_4]\cdot 13\text{H}_2\text{O}$  were different from those of  $\text{Eu}_2\text{Mo}_7\text{O}_{24}\cdot 6\sim 8\text{H}_2\text{O}$ .

Atomic coordinates and thermal parameters for non-H atoms are listed in Table 1,\* and an *ORTEP* (Johnson, 1965) plot of the anion in  $(\text{NH}_4)_{12}\text{H}_2[\text{Eu}_4(\text{MoO}_4)(\text{H}_2\text{O})_{16}(\text{Mo}_7\text{O}_{24})_4]\cdot 13\text{H}_2\text{O}$  with the atom numbering is shown in Fig. 1. The anion exhibits a point symmetry of  $D_{2d}$ , one of whose dihedral axes is the  $C_2$  axis of the crystal. The anion contains four  $[\text{Mo}_7\text{O}_{24}]^{6-}$  moieties which are located in  $D_{2d}$  symmetry. The two  $[\text{Mo}_7\text{O}_{24}]^{6-}$  moieties of  $\text{Mo}(2)\text{--}\text{Mo}(8)$  and  $\text{Mo}(9)\text{--}\text{Mo}(15)$  are crystallographically independent and isostructural with the 'paramolybdate' consisting of seven edge-shared  $\text{MoO}_6$  octahedra. Table 2 shows the range of bond distances for each metal in the anion. Each O atom of the central tetrahedral  $\text{MoO}_4$  is bound to a Eu atom. Each Eu atom achieves ninefold coordination with the O atoms approximating a tricapped trigonal prism, by attachment of one O atom from the  $[\text{MoO}_4]^{2-}$  unit, four O atoms from three  $[\text{Mo}_7\text{O}_{24}]^{6-}$  units, and four O atoms from four aqua ligands. The  $\text{Mo}(1)$  atom of the central  $\text{MoO}_4$  unit lies on the crystallographic  $C_2$  axis. There is no significant difference in the average Eu—O distance between the  $\text{Eu}(1)\text{O}_9$  and  $\text{Eu}(2)\text{O}_9$  sites: the bond distances between  $\text{Eu}(1)$  and  $\text{Ow}(1\text{--}4)$  atoms are in the range of 2.43–2.52 Å and those between  $\text{Eu}(2)$  and  $\text{Ow}(5\text{--}8)$  atoms in the range of 2.47–2.59 Å. These distances are comparable to the Eu—Ow distances for  $[\text{Eu}(\text{H}_2\text{O})_9]^{3+}$  in  $\text{Eu}(\text{C}_2\text{H}_5\text{SO}_4)_3\cdot 9\text{H}_2\text{O}$  (Gerkin & Peppart, 1984) where the Eu—Ow distances of 2.415 (1)–2.542 (3) Å provided the idealized symmetry of a tricapped trigonal prism.

The anion has structurally two gutters: one surrounded by two  $\text{Mo}_7\text{O}_{24}$  of  $\text{Mo}(2\text{--}8)$  and  $\text{Mo}(9\text{--}15)$ ,  $\text{Ow}(4)$ , and  $\text{Ow}(6')$ , and the other by two  $\text{Mo}_7\text{O}_{24}$  of  $\text{Mo}(2\text{--}8')$  and  $\text{Mo}(9\text{--}15)$ ,  $\text{Ow}(4')$  and  $\text{Ow}(6)$ . Ammonium N atoms  $\text{N}(3)$  and  $\text{N}(6)$  [or  $\text{N}(3')$  and  $\text{N}(6')$ ] lying on the  $S_4$  axis of the anion are located inside and outside of the gutter, respectively. The two N atoms  $\text{N}(3,6)$  and the eight terminal O atoms  $\text{Ow}(1\text{--}8)$  at the two  $\text{Eu}(1)$  and  $\text{Eu}(2)$  sites exhibit hydrogen bonds with the O atoms belonging to  $\text{Mo}_7\text{O}_{24}$  units, supporting that these eight  $\text{Ow}(1\text{--}8)$  atoms are aqua ligands. The lifetime (0.2 ms) of the emission from the  $^5D_0$  state of  $\text{Eu}^{3+}$  for the complex was much shorter than that (~ 2ms) for  $[\text{Eu}(\text{W}_5\text{O}_{18})_2]^{9-}$  and  $[\text{Eu}(\text{SiW}_{11}\text{O}_{39})_2]^{13-}$  which have no aqua ligands in the first coordination sphere of

\* Lists of structure factors, anisotropic thermal parameters, bond angles, metal–oxygen bond distances and hydrogen bond distances have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53458 (73 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates and thermal parameters ( $\text{\AA}^2$ ) for non-H atoms

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

	x	y	z	$B_{\text{eq}}$
Eu(1)	0.32313 (7)	0.19221 (3)	0.19317 (7)	1.79 (4)
Eu(2)	0.39221 (7)	0.06963 (3)	0.08115 (7)	1.86 (4)
Mo(1)	$\frac{1}{2}$	0.13106 (7)	$\frac{1}{2}$	1.5 (1)
Mo(2)	0.3855 (1)	0.04898 (5)	0.2682 (1)	2.03 (8)
Mo(3)	0.2617 (1)	0.10145 (5)	0.1700 (1)	2.01 (8)
Mo(4)	0.0902 (1)	0.10463 (6)	0.1477 (2)	3.3 (1)
Mo(5)	0.1993 (1)	0.04107 (6)	0.2342 (1)	2.5 (1)
Mo(6)	0.3477 (1)	-0.00692 (6)	0.3461 (1)	3.0 (1)
Mo(7)	0.3050 (1)	0.05064 (6)	0.4217 (1)	2.9 (1)
Mo(8)	0.1815 (1)	0.10425 (6)	0.3259 (1)	3.1 (1)
Mo(9)	0.4770 (1)	0.21348 (5)	0.1209 (1)	1.82 (8)
Mo(10)	0.3543 (1)	0.16062 (5)	0.0236 (1)	1.85 (8)
Mo(11)	0.2770 (2)	0.15680 (6)	-0.1528 (1)	3.3 (1)
Mo(12)	0.3902 (1)	0.21884 (5)	-0.0659 (1)	2.19 (9)
Mo(13)	0.5338 (1)	0.26688 (6)	0.0493 (1)	3.1 (1)
Mo(14)	0.5794 (1)	0.20775 (7)	-0.0182 (1)	3.3 (1)
Mo(15)	0.4551 (2)	0.15469 (6)	-0.1157 (1)	3.3 (1)
O(1)	0.4234 (9)	0.1541 (4)	0.2442 (9)	2.1 (3)
O(2)	0.4682 (8)	0.1077 (3)	0.1699 (8)	1.5 (3)
O(3)	0.4094 (9)	0.0478 (4)	0.1952 (9)	2.1 (3)
O(4)	0.2984 (9)	0.0944 (4)	0.1084 (9)	2.0 (3)
O(5)	0.4748 (8)	0.0519 (3)	0.3491 (8)	1.7 (3)
O(6)	0.368 (1)	0.0045 (4)	0.265 (1)	2.5 (3)
O(7)	0.3553 (9)	0.0914 (4)	0.2602 (8)	1.9 (3)
O(8)	0.258 (1)	0.0501 (4)	0.185 (1)	2.7 (3)
O(9)	0.267 (1)	0.1399 (4)	0.183 (1)	2.9 (4)
O(10)	0.154 (1)	0.0975 (4)	0.100 (1)	3.1 (4)
O(11)	0.089 (1)	0.1442 (5)	0.142 (1)	4.6 (5)
O(12)	0.003 (1)	0.0938 (5)	0.081 (1)	4.8 (5)
O(13)	0.204 (1)	0.0932 (4)	0.2332 (9)	2.3 (3)
O(14)	0.106 (1)	0.0465 (4)	0.164 (1)	3.3 (4)
O(15)	0.322 (1)	0.0419 (4)	0.325 (1)	2.5 (3)
O(16)	0.211 (1)	0.0021 (4)	0.246 (1)	3.2 (4)
O(17)	0.439 (1)	-0.0088 (5)	0.415 (1)	4.2 (4)
O(18)	0.318 (1)	-0.0449 (5)	0.326 (1)	4.2 (4)
O(19)	0.401 (1)	0.0538 (4)	0.482 (1)	3.8 (4)
O(20)	0.300 (1)	0.0054 (4)	0.406 (1)	3.0 (4)
O(21)	0.289 (1)	0.0933 (4)	0.390 (1)	2.7 (3)
O(22)	0.189 (1)	0.0532 (4)	0.3188 (9)	2.4 (3)
O(23)	0.196 (1)	0.1442 (5)	0.322 (1)	4.9 (5)
O(24)	0.079 (1)	0.0996 (4)	0.236 (1)	3.1 (4)
O(25)	0.262 (1)	0.0495 (5)	0.476 (1)	4.2 (4)
O(26)	0.145 (1)	0.1008 (5)	0.388 (1)	4.1 (4)
O(27)	0.424 (1)	0.2156 (4)	0.169 (1)	2.5 (3)
O(28)	0.313 (1)	0.1677 (4)	0.081 (1)	2.4 (3)
O(29)	0.5703 (9)	0.2105 (4)	0.1869 (9)	2.2 (3)
O(30)	0.473 (1)	0.2579 (4)	0.100 (1)	2.7 (3)
O(31)	0.4590 (9)	0.1707 (4)	0.0930 (8)	1.8 (3)
O(32)	0.368 (1)	0.2114 (4)	0.0140 (9)	2.2 (3)
O(33)	0.367 (1)	0.1210 (4)	0.0246 (9)	2.3 (3)
O(34)	0.258 (1)	0.1653 (4)	-0.069 (1)	2.8 (4)
O(35)	0.270 (1)	0.1172 (5)	-0.152 (1)	3.9 (4)
O(36)	0.194 (1)	0.1692 (5)	-0.225 (1)	5.5 (5)
O(37)	0.3883 (9)	0.1671 (4)	-0.0597 (9)	2.0 (3)
O(38)	0.301 (1)	0.2137 (4)	-0.142 (1)	2.7 (3)
O(39)	0.507 (1)	0.2177 (4)	0.0340 (9)	2.4 (3)
O(40)	0.405 (1)	0.2584 (4)	-0.059 (1)	3.1 (4)
O(41)	0.621 (1)	0.2685 (5)	0.126 (1)	4.3 (5)
O(42)	0.506 (1)	0.3043 (5)	0.023 (1)	4.2 (4)
O(43)	0.661 (1)	0.2045 (5)	0.064 (1)	4.3 (4)
O(44)	0.565 (1)	0.2532 (4)	-0.022 (1)	3.6 (4)
O(45)	0.549 (1)	0.1652 (4)	-0.022 (1)	3.4 (4)
O(46)	0.456 (1)	0.2062 (4)	-0.105 (1)	2.8 (4)
O(47)	0.453 (1)	0.1157 (5)	-0.098 (1)	4.1 (4)
O(48)	0.347 (1)	0.1595 (4)	-0.193 (1)	3.3 (4)
O(49)	0.612 (1)	0.2077 (5)	-0.084 (1)	4.5 (5)
O(50)	0.492 (1)	0.1581 (5)	-0.177 (1)	5.3 (5)
Ow(1)	0.265 (1)	0.2290 (4)	0.085 (1)	3.0 (4)
Ow(2)	0.181 (1)	0.1928 (5)	0.136 (1)	4.1 (4)
Ow(3)	0.298 (1)	0.2424 (5)	0.230 (1)	3.9 (4)
Ow(4)	0.299 (1)	0.1795 (4)	0.298 (1)	3.5 (4)
Ow(5)	0.293 (1)	0.0680 (4)	-0.050 (1)	3.5 (4)
Ow(6)	0.466 (1)	0.0788 (4)	0.012 (1)	3.3 (4)
Ow(7)	0.278 (1)	0.0328 (4)	0.058 (1)	3.7 (4)
Ow(8)	0.411 (1)	0.0165 (4)	0.047 (1)	3.3 (4)
Ow(9)	0.443 (3)	0.290 (1)	0.248 (3)	7 (1)
Ow(10)	0.089 (3)	0.040 (1)	0.425 (3)	23 (2)
Ow(11)	0.333 (4)	0.092 (1)	-0.263 (4)	25 (3)
Ow(12)	0.102 (3)	0.155 (1)	0.456 (3)	20 (2)
Ow(13)	0.470 (4)	0.060 (1)	0.641 (3)	23 (2)
Ow(14)	0.143 (4)	0.220 (1)	0.282 (4)	24 (2)
Ow(15)	0.515 (3)	0.282 (1)	-0.156 (3)	19 (2)

Table 1 (cont.)

	x	y	z	$B_{\text{eq}}$
N(1)	0	0.049 (1)	$\frac{1}{2}$	8 (1)
N(2)	0	0.158 (1)	$\frac{1}{2}$	9 (2)
N(3)	0.417 (1)	0.1293 (5)	0.389 (1)	3.3 (5)
N(4)	0.332 (2)	0.2852 (7)	0.067 (2)	5.5 (7)
N(5)	0.167 (3)	0.022 (1)	-0.107 (3)	13 (1)
N(6)	0.329 (3)	0.129 (1)	0.530 (3)	13 (1)
N(7)	0.298 (3)	-0.029 (1)	0.128 (3)	13 (1)

Table 2. Metal—oxygen bond distances ( $\text{\AA}$ )

Eu(1)—O	2.39 (2)–2.48 (2)	Mo(7)—O	1.69 (2)–2.26 (2)
—Ow	2.43 (2)–2.52 (2)	Mo(8)—O	1.72 (2)–2.23 (2)
Eu(2)—O	2.38 (1)–2.45 (2)	Mo(9)—O	1.69 (2)–2.22 (2)
—Ow	2.47 (2)–2.59 (2)	Mo(10)—O	1.73 (2)–2.23 (2)
Mo(1)—O	1.76 (2)–1.77 (1)	Mo(11)—O	1.69 (2)–2.50 (2)
Mo(2)—O	1.75 (2)–2.26 (2)	Mo(12)—O	1.72 (2)–2.25 (2)
Mo(3)—O	1.68 (2)–2.25 (2)	Mo(13)—O	1.69 (2)–2.47 (2)
Mo(4)—O	1.68 (2)–2.54 (2)	Mo(14)—O	1.69 (2)–2.23 (2)
Mo(5)—O	1.70 (2)–2.26 (2)	Mo(15)—O	1.71 (2)–2.24 (2)
Mo(6)—O	1.68 (2)–2.52 (2)		

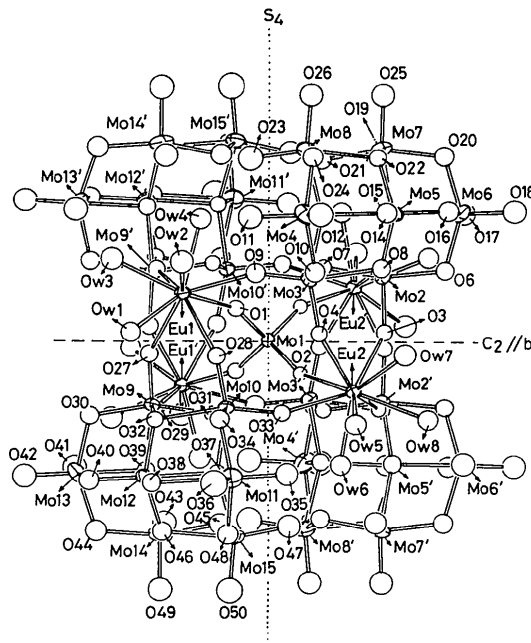


Fig. 1. ORTEP (Johnson, 1965) plot of the anion projected to the plane defined by the  $b$  and the anion's  $S_4$  axes. The  $C_2$  and  $S_4$  axes are drawn by broken and dotted lines, respectively. Parentheses of the atom numbering are omitted for clarity.

Eu<sup>3+</sup> (Ballardini, Mulazzani, Venturi, Bolletta & Balzani, 1984; Ballardini, Chiorbori & Balzani, 1984). Such a short lifetime of the emission, with a resultant low quantum yield (0.07) of the emission, supports strongly the coordination of the Eu atom with four aqua ligands, since the coupling of the <sup>5</sup>D<sub>0</sub> level for the Eu<sup>3+</sup> site with the vibrational states of the high frequency O—H oscillators would result in the enhancement of the rate of non-radiative decay (Horrocks & Sudnick, 1979). Thus, we conclude that four terminal O atoms at each Eu site are aqua ligand O atoms.

Fig. 2 shows the unit-cell packing of the anion. Ammonium nitrogen N(1,2,4,5,7), aqua ligand

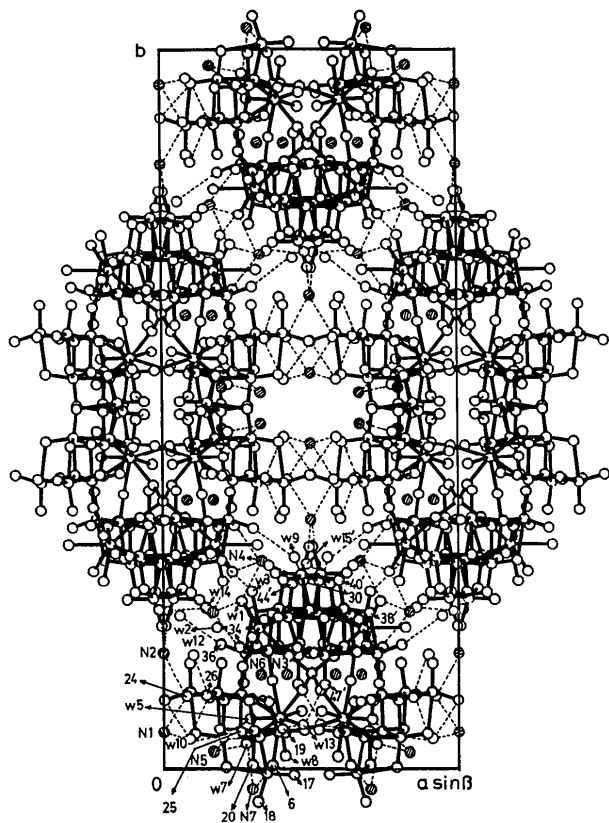


Fig. 2. The crystal structure viewed along the  $c$  axis. The hydrogen bonds are drawn by broken lines. N and W indicate nitrogen and water O atoms, respectively. Other atom numbering is for O atom. Parentheses of the atom numbering are omitted for clarity.

oxygen Ow(1–3,5,8) at the Eu sites, and lattice water oxygen Ow(9,10) atoms indicate the hydrogen bonds with the neighboring anion, leading to a three-dimensional hydrogen bonding network.

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## Diiodinated Derivatives of 1,2-Diarsenadecaborane: $\text{As}_2\text{B}_{10}\text{H}_8\text{I}_2$

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**Abstract.**  $\text{As}_2\text{B}_{10}\text{H}_8\text{I}_2$ ,  $M_r = 519.8$ , monoclinic,  $I2/a$ ,  $a = 14.262$  (3),  $b = 8.128$  (2),  $c = 21.575$  (4) Å,  $\beta = 92.65$  (2)°,  $V = 2498$  (2) Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 2.76$  g cm<sup>-3</sup>,  $\lambda(\text{Mo K}\alpha) = 0.71073$  Å,  $\mu = 101.8$  cm<sup>-1</sup>,  $F(000) =$

1840,  $T = 294$  K,  $R = 0.036$  for 2066 observed reflections. The structure contains a disordered distorted dodecahedron of  $\text{As}_2\text{B}_{10}$  atoms with the As atoms adjacent. Two diiodinated (B–I) isomers (9,12- and 8,12-diiodo forms) are co-crystallized in the asymmetric unit, with the former predominating. The packing of the molecules in the crystal is

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