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Photoluminescent Samarium Octamolybdate

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Abstract

The structure of bis(hexaaquasamarium) octamolybdate hexahydrate, $\text{Sm}_2(\text{H}_2\text{O})_{12}[\text{Mo}_8\text{O}_{27}]\cdot 6\text{H}_2\text{O}$, consists of $[(\text{Mo}_8\text{O}_{27})^{6-}]_\infty$ chains supported by hydrated Sm^{3+} cations. Sm^{3+} has tricapped trigonal prismatic coordination with $\text{Sm}-\text{O}$ distances of 2.38–2.66 Å. $\text{Mo}-\text{O}$ distances in the octamolybdate unit are 1.68–2.49 Å.

Comment

Photo-excitation of the oxygen-to-metal charge-transfer ($\text{O} \rightarrow \text{Mo}/\text{W}$ ligand-to-metal charge-transfer) band of polyoxomolybdo- and polyoxotungstoeuropates causes activation of the f electrons of the Eu atoms to the emitting levels *via* intramolecular energy transfer from the polyoxometalate group to the Eu atoms. The luminescence properties have been discussed in conjunction with the crystal and molecular structure for various metalloeuropates, such as $\text{Eu}_2(\text{H}_2\text{O})_{12}[\text{Mo}_8\text{O}_{27}]\cdot 6\text{H}_2\text{O}$ (Yamase & Naruke, 1991), $(\text{NH}_4)_2\text{H}_2[\text{Eu}_4(\text{MoO}_4)(\text{H}_2\text{O})_{16}(\text{Mo}_7\text{O}_{24})_4]\cdot 13\text{H}_2\text{O}$ (Naruke & Yamase, 1991; Naruke, Ozeki & Yamase, 1991), $\text{K}_{15}\text{H}_3[\text{Eu}_3(\text{H}_2\text{O})_3(\text{SbW}_9\text{O}_{33})(\text{W}_5\text{O}_{18})_3]\cdot 25.5\text{H}_2\text{O}$ (Yamase, Naruke & Sasaki, 1990) and $\text{Na}_9[\text{EuW}_{10}\text{O}_{36}]\cdot 32\text{H}_2\text{O}$ (Sugeta & Yamase, 1993). In order to understand the photoluminescence properties of polyoxometallosamarates in general, we investigated the photoluminescence of polyoxometallosamarates, subsequently to those of the europium compounds. We prepared $\text{Sm}_2(\text{H}_2\text{O})_{12}[\text{Mo}_8\text{O}_{27}]\cdot 6\text{H}_2\text{O}$, (1), as an analogue of $\text{Eu}_2(\text{H}_2\text{O})_{12}[\text{Mo}_8\text{O}_{27}]\cdot 6\text{H}_2\text{O}$, (2) (Yamase & Naruke, 1991). (1) is much less efficient with respect to intermolecular energy transfer than (2). This paper describes the crystal structure of (1) and compares it with that of (2).

Fig. 1 shows an ORTEPII (Johnson, 1976) drawing of the octamolybdate unit and the coordination spheres of the Sm atoms in (1). O1–O6 are the O atoms of water molecules coordinating to the Sm atom,

O7–O20 are the O atoms of the octamolybdate moiety, of which O7–O9 also coordinate to the Sm atom. The octamolybdate unit comprises eight edge-shared MoO_6 octahedra to form a centrosymmetric $[\text{Mo}_8\text{O}_{28}]^{8-}$ unit. The configuration of the octamolybdate unit is the same as that of the discrete $[\text{Mo}_8\text{O}_{26}(\text{OH})_2]^{6-}$ anion in $(\text{NH}_3^+\text{Pr})_6[\text{Mo}_8\text{O}_{26}(\text{OH})_2]\cdot 2\text{H}_2\text{O}$ (Isobe, Marumo, Yamase & Ikawa, 1978) and that of the repeat unit of the infinite $[(\text{Mo}_8\text{O}_{27})^{6-}]_\infty$ chain in $(\text{NH}_4)_6[\text{Mo}_8\text{O}_{27}]\cdot 4\text{H}_2\text{O}$ (Böschchen, Buss & Krebs, 1974). As shown in Fig. 2, the $[\text{Mo}_8\text{O}_{28}]^{8-}$ unit in (1) is connected to another unit in the next cell, sharing one common O atom, O15, at the crystallographic inversion centre to form the condensation polymer of the octamolybdate $[(\text{Mo}_8\text{O}_{27})^{6-}]_\infty$ parallel to the crystallographic c axis. This chain is isostructural with that observed in $(\text{NH}_4)_6[\text{Mo}_8\text{O}_{27}]\cdot 4\text{H}_2\text{O}$

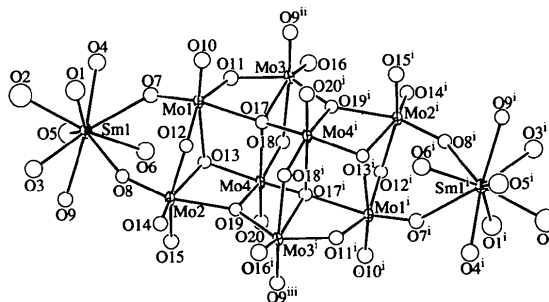


Fig. 1. ORTEPII (Johnson, 1976) drawing of the octamolybdate unit and the coordination spheres of the Sm atoms in (1). Displacement ellipsoids for the Sm and Mo atoms are drawn at the 50% probability level. [Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $x, y, 1 + z$; (iii) $1 - x, 1 - y, -z$.]

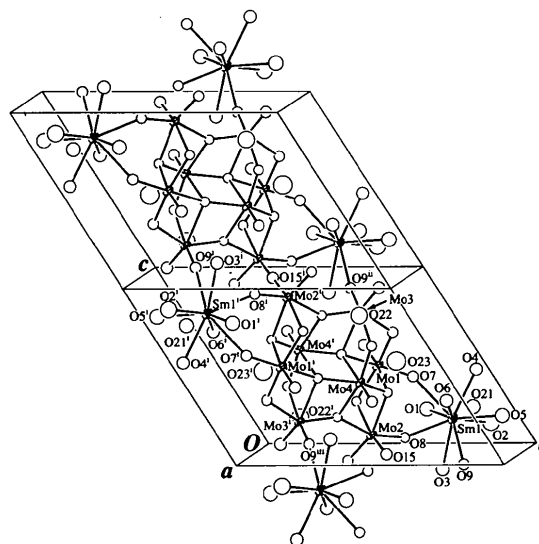


Fig. 2. Packing diagram of two unit cells viewed down the a axis. Symmetry codes are the same as those in Fig. 1.

(Bösch, Buss & Krebs, 1974). O21–O23 are the O atoms of water molecules of crystallization which do not coordinate to any metal atoms.

Two Sm³⁺ cations bridge the octamolybdate units by sharing two O atoms with the octamolybdate moiety in the original cell and one O atom of the unit in the next cell. Each Sm³⁺ cation achieves tricapped trigonal prismatic coordination, with O1, O2 and O4 forming one base triangle, O6, O8 and O9 forming the other, and O3, O5 and O7 capping the side faces. The Sm—O distances range from 2.38 to 2.66 Å. The local symmetry of the SmO₉ coordination sphere is C₁, as was crystallographically and spectroscopically observed for the Eu analogue (Yamase & Naruke, 1991). The average Sm—O distance is 2.50 (8) Å, which is slightly longer than the average Eu—O distance of 2.48 (7) Å observed in (2), although the difference is not significant when taking into account their standard deviations. This difference may have originated from the larger ionic radius of Sm³⁺ compared with Eu³⁺, resulting from the lanthanide contraction. The effect of the lanthanide contraction on the Ln—O bond distances in the polyoxometallolanthanoates has been demonstrated for the structures of the [LnW₁₀O₃₆]⁹⁻ anions (Ozeki & Yamase, 1994). Each Mo atom has two short Mo—O bonds of 1.68–1.78 Å, two intermediate Mo—O bonds of 1.88–2.04 Å and two long Mo—O bonds of 2.13–2.49 Å. Each short Mo—O bond has a long Mo—O bond in its *trans* position and the two intermediate Mo—O bonds are *trans* to each other. The water O atoms, O21–O23, have four or five contacts to other O atoms with O...O distances of 2.70–2.96 Å, probably extending the hydrogen-bond network across the [Sm₂(H₂O)₁₂(Mo₈O₂₇)]_∞ chains. As described above, the structures of (1) and (2) are essentially identical, which would indicate that the differences in their photoluminescence properties originate from the differences in their electronic states.

Experimental

Compound (1) was prepared following the preparative procedure described for Eu₂(H₂O)₁₂[Mo₈O₂₇].6H₂O (Yamase & Naruke, 1991) with a slight modification. 2.4 g of K₂MoO₄ was dissolved in 450 ml of H₂O and the pH adjusted to 3.0 with HClO₄. To this solution 0.1 g of Sm(CH₃COO)₃.4H₂O was added dropwise with vigorous stirring. The pH of the solution was kept between 2.9 and 3.1 with HClO₄ throughout the mixing. Pale yellow thin plate crystals were obtained after keeping the solution at room temperature for 3 d.

Crystal data

Sm₂(H₂O)₁₂[Mo₈O₂₇].6H₂O Mo Kα radiation
M_r = 1824.6 λ = 0.71069 Å

Triclinic

P $\bar{1}$

a = 10.114 (3) Å

b = 12.013 (9) Å

c = 9.368 (4) Å

α = 122.59 (4)°

β = 90.11 (3)°

γ = 98.31 (4)°

V = 945 (1) Å³

Z = 1

D_x = 3.21 Mg m⁻³

Data collection

Rigaku AFC-5S diffractometer

ω/2θ scans

Absorption correction:

empirical *via* ψ scan

(North, Phillips &

Mathews, 1968)

T_{min} = 0.718, T_{max} =

1.000

4605 measured reflections

4339 independent reflections

Refinement

Refinement on F

R = 0.061

wR = 0.061

S = 2.11

2496 reflections

135 parameters

H atoms not located

w = 1/σ²(F)

Cell parameters from 23

reflections

θ = 7.5–10.0°

μ = 5.75 mm⁻¹

T = 298 K

Thin plate

0.30 × 0.10 × 0.01 mm

Pale yellow

2496 observed reflections

[I > 3σ(I)]

R_{int} = 0.047

θ_{max} = 27.5°

h = -13 → 13

k = -15 → 13

l = 0 → 12

3 standard reflections

monitored every 100

reflections

intensity decay: 6.7%

(Δ/σ)_{max} = 0.002

Δρ_{max} = 3.49 e Å⁻³

Δρ_{min} = -2.19 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 (Å²)

U_{iso} for O atoms; $U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^*$; a_i, a_j for Sm and Mo.

	x	y	z	U_{iso}/U_{eq}
Sm1	0.1889 (1)	0.7782 (1)	0.1627 (2)	0.0214(4)
Mo1	0.2473 (2)	0.6384 (2)	0.4734 (3)	0.0192(5)
Mo2	0.3449 (2)	0.4642 (2)	0.0899 (2)	0.0180(5)
Mo3	0.4468 (2)	0.7377 (2)	0.8084 (2)	0.0179(5)
Mo4	0.5815 (2)	0.5886 (2)	0.4162 (2)	0.0167(5)
O1	-0.032 (2)	0.667 (2)	0.191 (2)	0.042 (5)
O2	0.019 (2)	0.882 (2)	0.119 (3)	0.056 (6)
O3	0.054 (2)	0.596 (2)	-0.138 (2)	0.034 (4)
O4	0.160 (2)	0.980 (2)	0.439 (2)	0.032 (4)
O5	0.313 (2)	0.993 (2)	0.195 (2)	0.044 (5)
O6	0.420 (2)	0.837 (2)	0.292 (2)	0.033 (4)
O7	0.194 (1)	0.733 (2)	0.402 (2)	0.024 (4)
O8	0.247 (1)	0.564 (1)	0.062 (2)	0.020 (3)
O9	0.313 (1)	0.732 (2)	-0.081 (2)	0.024 (4)
O10	0.117 (2)	0.615 (2)	0.575 (2)	0.028 (4)
O11	0.362 (1)	0.793 (1)	0.675 (2)	0.023 (3)
O12	0.226 (1)	0.468 (1)	0.267 (2)	0.019 (3)
O13	0.439 (1)	0.641 (1)	0.341 (2)	0.018 (3)
O14	0.280 (1)	0.303 (1)	-0.060 (2)	0.022 (3)
O15	1/2	1/2	0	0.026 (5)
O16	0.551 (2)	0.881 (2)	0.949 (2)	0.029 (4)
O17	0.384 (1)	0.553 (1)	0.554 (2)	0.019 (3)
O18	0.612 (1)	0.725 (1)	0.628 (2)	0.020 (3)
O19	0.476 (1)	0.402 (1)	0.209 (2)	0.017 (3)
O20	0.718 (1)	0.611 (2)	0.325 (2)	0.024 (4)

O21	0.667 (2)	0.966 (2)	0.288 (2)	0.041 (5)
O22	0.864 (2)	0.795 (2)	0.831 (3)	0.058 (6)
O23	0.958 (2)	0.839 (2)	0.583 (3)	0.073 (7)

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Cs₂Ga₂O(BO₃)₂

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Table 2. Selected bond lengths (Å)

Sm1—O8	2.38 (1)	Mo2—O15	1.885 (2)
Sm1—O2	2.42 (2)	Mo2—O12	2.04 (1)
Sm1—O9	2.44 (1)	Mo2—O19	2.17 (1)
Sm1—O6	2.46 (2)	Mo2—O13	2.23 (1)
Sm1—O4	2.47 (2)	Mo3—O16	1.68 (2)
Sm1—O1	2.52 (2)	Mo3—O9 ⁱ	1.72 (1)
Sm1—O5	2.56 (2)	Mo3—O19 ⁱⁱ	1.89 (1)
Sm1—O7	2.57 (1)	Mo3—O11	1.94 (1)
Sm1—O3	2.66 (2)	Mo3—O17	2.21 (1)
Mo1—O10	1.70 (2)	Mo3—O18	2.34 (1)
Mo1—O7	1.74 (1)	Mo4—O20	1.69 (1)
Mo1—O12	1.89 (1)	Mo4—O18	1.75 (1)
Mo1—O11	1.99 (2)	Mo4—O13	1.92 (1)
Mo1—O17	2.19 (1)	Mo4—O17 ⁱⁱ	1.94 (1)
Mo1—O13	2.31 (1)	Mo4—O19	2.13 (1)
Mo2—O14	1.69 (1)	Mo4—O17	2.49 (1)
Mo2—O8	1.78 (1)		

Symmetry codes: (i) $x, y, 1 + z$; (ii) $1 - x, 1 - y, 1 - z$.

Data collection: *RCRYSTAN85* (Rigaku Corporation, 1985). Data reduction: *TEXSAN* (Molecular Structure Corporation, 1989). Program(s) used to solve structure: *SAP91* (Fan, 1991). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEPII* (Johnson, 1976).

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Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: AS1146). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Abstract

The structure of dicaesium digallium diorthoborate oxide constitutes a new type of oxide borate. It consists of a three-dimensional gallium–oxide–orthoborate lattice with Cs atoms occupying large cavities in the lattice. This lattice is made from pairs of Ga atoms connected through a shared O atom along the [001] direction; these Ga dimers are interconnected through shared O vertices to trigonal BO₃ groups along the [010], [110] and $\bar{1}10$ directions, completing the tetrahedral coordination environment of each Ga atom.

Comment

Solid-state borates have been shown to crystallize with a wide variety of structures (Heller, 1986) as a result of the vast number of possible ways of combining the borate anions with the metal-atom polyhedra. The metal-atom polyhedra may be octagonal, tetrahedral or square planar, and the borate anions may be trigonal or tetrahedral orthoborates, pyroborates or combinations thereof, linear chains, or fused rings, thus affording vast numbers of structural types. Partly in order to study such new structural types and partly to search for new non-linear optical materials (of which several examples of borates exist), we recently surveyed the Cs₂O–Ga₂O₃–B₂O₃ phase diagram, the compounds in which have not been reported previously. Among the compounds discovered in this system is an oxide borate of a new structural type, Cs₂Ga₂O(BO₃)₂.

A unit cell of the title compound is depicted in Fig. 1. The structure consists of a three-dimensional gallium–oxide–orthoborate lattice that affords large vacancies within which Cs atoms are located. The lattice is built from pairs of Ga atoms that are interconnected through an O(7) atom and which lie roughly along the [001] direction. O(7) is an oxide anion since it is not bonded to either of the two crystallographically distinct B atoms. Each Ga atom completes its tetrahedral coordination by bonding to O atoms that constitute the two crystallographically distinct trigonal orthoborate groups. These orthoborate groups connect the Ga–O–Ga dimers roughly along the [010], [110] and $\bar{1}10$ directions. Because the Ga–O–Ga bond angle is relatively large [140.8(4)°], large cavities are created