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Crystal Structure of Nonaquasamarium(III)bromide-1,4-dioxan Adduct (1:3:2), $Sm(H_2O)_9 \cdot Br_3(C_4H_8O_2)_2$

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Abstract

The title compound has been found to consist of tricapped trigonal prismatic $Sm(H_2O)_9{}^{3+}$ ions in C_{2v} symmetry, sandwiched between expanded 'close packed' layers of bromide ions, with 1,4-dioxan molecules in chair conformation hydrogen bonding between the equatorial water molecules of adjacent cations.

Orthorhombic, *Amm*2, $a = 8.010(3)$, $b = 19.848(4)$, $c = 7.388(3)$ Å, $R = 0.022$ for 992 unique reflexions.

Introduction

The literature contains reference to a very large number of compounds $MX_l(H_2O)_n(dx)_m$ where X is a singly charged anion and dx is 1,4-dioxan. Lynch *et al.* [1] made phase studies of several of these systems showing the existence of well characterised solvates. In recent years crystal structures have shown that the usual role of dioxan in these compounds is to form H-bonded bridges between coordinated water molecules. Among others, this behaviour is found for $InCl_3 \cdot 3H_2O \cdot 3dx$ [2], $SnBr_4 \cdot 2H_2O \cdot 2dx$ [3], $NiBr_2 \cdot 4H_2O \cdot 2dx$ [3] and $MgCl_2 \cdot 6H_2O \cdot dx$ [3] whereas $LiCl \cdot H_2O \cdot dx$ [4] and $NaI \cdot 3dx$ [5] have coordinated dioxan. $NaI \cdot 3dx$ [5] is crystallised water free from aqueous dioxan.

Several lanthanide complexes of this type have been reported. These are particularly difficult to handle since they lose or gain water very readily on exposure, depending on humidity. $Ln(ClO_4)_3 \cdot 9H_2O \cdot 4dx$ (Ln = La–Sm) are the best characterised [6]. For the halides and nitrates the stoichiometry of crystalline compounds is far from well established [7].

No crystal structure has been available for these lanthanide compounds because the crystals have been too poor in quality to allow data collection [8]. Suitable crystals of $SmBr_3 \cdot 9H_2O \cdot 2dx$ have now been obtained which gave a very high quality diffraction pattern. The structure of this compound is reported below.

Experimental

A saturated solution of samarium bromide hydrate in 1,4-dioxan which had been set aside for some twelve years yielded small well shaped pale yellow crystals suitable for X-ray study. These were transferred rapidly to Lindemann glass capillaries, along with a little mother liquor. Preliminary oscillation and Weissenberg photographs showed a centred orthorhombic lattice.

Data were collected from a crystal 0.3 × 0.4 × 0.3 mm using an Enraf-Nonius CAD4-F diffractometer (S.E.R.C. Service at Edinburgh University). Intensities were collected for the $h\ k \pm l$ quadrant of a monoclinic cell ($a = 8.010(3)$, $b = 7.388(3)$, $c = 10.70(4)$ Å, $\beta = 112.09(3)°$) to a θ limit of 30° ($\sin\theta/\lambda = 0.70$) using Mo-K$\alpha$ radiation. The intensities of 2 standard reflexions were checked every hour and the crystal orientation verified every 200 reflexions. Data were corrected for a drift of 8.7% during data collection and for absorption using a ψ scan technique. The minimum and maximum transmission coefficients were 0.80 and 1.35. After Lorentz and polarisation corrections the data were re-indexed to the orthorhombic cell.

Orthorhombic. *Amm*2, $a = 8.010(3)$, $b = 19.848(4)$, $c = 7.388(3)$ Å, $U = 1174.69$ Å^3, $F(000) = 780$, $Z = 2$, $Dx = 2.06$ g cm^{-3}, Mo-Kα radiation, $\lambda = 0.71069$ Å, $\mu = 0.92$ cm^{-1} 1949 measured reflexions (internal consistency 0.028) gave 1002 unique reflexions of which 992 were used in the final refinement.

All calculations were performed on the Dundee University DEC10 computer using the SHELX76 [9], XANADU [10] and PLUTO [11] program packages. Atomic scattering parameters were taken from International Tables [12].

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Since there were no systematic absences apart from the lattice centring there was considerable difficulty in establishing the correct space group. After trials with *Cmm*2 and *C*222 had given no model the symmetry was reduced to triclinic *C*1. The direct methods routine TANG then revealed several peaks which were assigned as Sm and Br atoms. The relationships between these were sufficient to reveal the correct space group as *Amm*2, (No. 38) (after conversion to standard setting). An electron density map at $R = 0.12$ with anisotropic Sm and Br atoms revealed all other non-hydrogen atoms. Convergence was obtained at $R = 0.022$ with all non-hydrogen atoms anisotropic. The hydrogen atoms of the dioxan molecule were included in calculated positions but water hydrogen atoms were not visible on a difference synthesis and were not included.

It is interesting that this structure has atoms on each of the Wyckoff positions *a* to *f* which can arise in this space group.

TABLE Ia. Nonaquasamarium(III) Bromide Dioxan (1:2:3) Coordinates $\times 10^{-4}$ for Non-hydrogen Atoms with e.s.d.s in Parentheses. $U_{eq}/U \times 10^{-3}$.

Atom	*x/a*	*y/b*	*z/c*	U_{eq}/U[a]
Sm1	0	0	5000	16(1)
Br2	5000	8633(1)	6782(1)	35(1)
Br3	5000	0	1176(2)	36(1)
O4W	12340(5)	762(2)	3898(5)	30(1)
O5W	12286(7)	0	7263(7)	31(1)
O6W	0	0	1832(11)	23(2)
O7W	0	1076(2)	6498(7)	25(1)
O11D	10000	8740(2)	−48(12)	42(1)
C12D	8477(9)	8373(3)	429(8)	43(2)
C13D	8462(9)	7687(3)	−389(9)	44(2)
O14D	10000	7325(2)	66(13)	44(1)

[a] $U_{eq} = 1/3\ \Sigma_i \Sigma_j U_{ij} a_i^* a_j^* a_i \cdot a_j$.

TABLE Ib. Nonaquasamarium(III) Bromide Dioxan (1:2:3) Anisotropic Temperature Factors $\times 10^{-3}$ with e.s.d.s in Parentheses.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Sm1	17(1)	17(1)	13(1)	0	0	0
Br2	30(1)	36(1)	38(1)	8(1)	0	0
Br3	31(1)	53(1)	23(1)	0	0	0
O4W	34(2)	33(2)	24(2)	3(2)	4(2)	−8(2)
O5W	29(3)	35(3)	29(3)	0	−9(3)	0
O6W	17(3)	33(4)	20(4)	0	0	0
O7W	27(3)	19(2)	29(3)	−4(2)	0	0
O11D	72(4)	24(2)	29(4)	1(4)	0	0
C12D	60(4)	38(3)	31(4)	−1(2)	8(3)	9(3)
C13D	48(4)	39(3)	46(5)	4(3)	−1(4)	−4(3)
O14D	63(4)	23(2)	46(4)	9(4)	0	0

TABLE II. Nonaquasamarium(III) Bromide Dioxan (1:2:3) Interatomic distances (Å) and angles (°).

O4W---Sm1	2.461(3)	O5W–Sm1–O4W	77.5(1)
O5W---Sm1	2.477(5)	O6W–Sm1–O4W	69.0(1)
O6W---Sm1	2.538(8)	O6W–Sm1–O5W	137.0(1)
O7W---Sm1	2.449(5)	O7W–Sm1–O4W	68.9(1)
Br3---Br2	4.445(1)	O7W–Sm1–O5W	69.0(1)
O5W---Br2	3.396(3)	O7W–Sm1–O6W	119.3(1)
O4W---Br3	3.302(4)	O5W–Br2–Br3	54.7(1)
C12D---O11D	1.394(7)	Br2–Br3–Br2	75.3(0)
C13D---O11D	2.394(7)	Br2–O5W–Br2	106.1(1)
C13D---C12D	1.510(8)	O4W–Br3–Br2	143.4(1)
O14D---C12D	2.383(7)	Br3–O4W–Sm1	111.9(1)
C12D---C12D	2.251(13)	O4W–Sm1–O4W	75.9(2)
O14D---C13D	1.393(6)	O4W–Br3–O4W	54.5(1)
C13D---C13D	2.272(13)	Br2–O5W–Sm1	108.6(1)

C13D–O11D–C12D	36.1(3)
C13D–C12D–O11D	111.0(6)
O14D–C12D–O11D	92.4(4)
O14D–C12D–C13D	33.3(3)
C12D–O11D–C12D	107.7(7)
C12D–O14D–C12D	56.4(1)
C12D–C13D–O11D	32.9(3)
O14D–C13D–O11D	91.9(4)
O14D–C13D–C12D	110.3(6)
C13D–O11D–C13D	56.7(3)
C13D–O14D–C13D	109.3(6)
C13D–O14D–C12D	36.5(3)

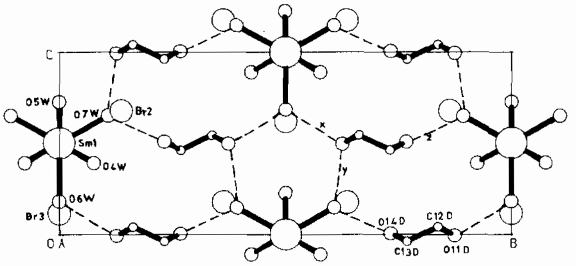

Fig. 1. Unit cell of $Sm(H_2O)_9Br_3(dioxan)_2$ viewed down *a*. Hydrogen bonds are dotted: x, 2.920(4); y, 2.791(4); z, 2.731(3) A.

Final refinement (minimising $\Sigma w|F_o - |F_c||^2$), 74 refined parameters, $wR = 0.022$, $w = 0.0002/(\sigma_F)^2$, mean shift/e.s.d. = 0.062, max shift/e.s.d. = 0.896, max difference peak = 1.4 e/Å^3 (close to Sm).

Discussion

Atomic coordinates and equivalent isotropic thermal parameters are given in Table I. Table II contains the bond lengths and bond angles. Figure 1 shows a projection of the unit cell. The structure contains $Sm(H_2O)_9^{3+}$ ions in the familiar tricapped trigonal prism geometry. These are linked in the *bc* plane by dioxan molecules each forming three hydrogen bonds. The non-crystallographic 3-fold axis of the $Sm(H_2O)_9^{3+}$ cation lies parallel to *a*. The three Br^- ions are also arranged about this 3-fold axis, half a cell removed from the Sm atom and in a triangular cluster packed tightly between the cations. Br···OH_2 = 3.32(3) Å (average) compared with the sum of ionic and van der Waals radii 3.45 Å.

The structure is derived from hexagonal close-packing with *a* as the unique axis. All of the close-packed sites are occupied by either Br^- or H_2O with the sequence of layers perpendicular to *a*: Br(A), H_2O(B), H_2O(A), H_2O(B), Br(A). Figure 2 shows the distortion from ideality of the layer of Br^- ions. The packing within the layer is quite open, *c* = 8.01 Å compared with 6.75 Å for a close packed layer, an expansion of 19%. The structure is further elongated in the *b* direction to give room for the dioxan molecules. *b*/*c* = 2.478 in this lattice compared with 1.732 for a close packed net expressed in terms of these axes. The shortest Br···Br contact is 4.445(1) Å, Br···Br contacts in the triangle of atoms above a Sm atom average 5.31 Å, Fig. 2.

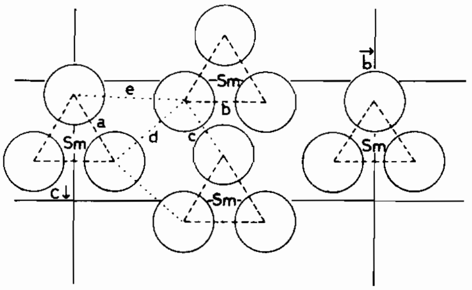

Fig. 2. Layer of bromide ions at *x* = 0.5 showing distortion from an ideal close packed layer. Br···Br distances: a, 5.246(1); b, 5.429(1); c, 4.445(1); d, 6.023(1); e, 7.227(1) Å.

The $Sm(H_2O)_9^{3+}$ has C_{2v} symmetry. The maximum deviations from ideal D_{3h} symmetry are seen in the equatorial plane where Sm(1)–O(6W) (2.537(8)) is almost 0.1 Å larger (12σ) than Sm(1)–O(7W) (2.449(5) Å)) and O(7W)–Sm(1)–O(7W)′ (121.4(1)°) is 1.7° larger than O(6W)–Sm(1)–O(7W) (119.3(1)°). The larger angle allows a reduction in prism height O(5W)···O(5W)″ to 3.378(4) Å compared with 3.456(4) Å for O(4W)···O(4W)″*.

Albertsson and Elding [13] have discussed the geometry of $Ln(H_2O)_9^{3+}$ as seen in precise redeterminations of Pr and Yb bromates where the cation has D_{3h} symmetry and Pr and Yb ethyl sulphates where the symmetry is C_{3v}. Table III shows that, allowing for the lower symmetry, $Sm(H_2O)_9^{3+}$ is generally similar to the other ions. The distance quotient ρ = (Ln–O(equatorial))/(Ln–O(prism)) is close to unity for the present compound, corresponding to Sm–O(equatorial) being about 0.02 Å less and Sm–O(prism) about 0.02 Å greater than the interpolated values assuming conventional ionic radii. In consequence the prism is narrower and taller than predicted from the bromates using formulae in ref. 13, with an average equatorial O···O contact of 4.284 Å against a predicted 4.33 Å and an average prism height 3.431 Å against a predicted 3.31 Å. The angle between the Sm–O(prism) vector and the '3-fold' axis, θ, is 45.0° compared with 47.4° for the bromates. The prism height and θ agree better with the ethyl sulphate series, where the predicted values are 3.41 Å and 45.1°. However, the equatorial O···O distance predicted from the ethyl sulphate series is 4.45 Å. A hard sphere model gives θ as 43° but Kepert [14] has predicted that larger values of θ, corresponding to flattened prisms, will be more stable in real compounds.

The explanation of these changes in shape must be a combination of packing forces, interactions of anions and cations and hydrogen bonding. In the bromates and ethyl sulphates the hydrogen bonding

TABLE III. Comparison of Coordination Polyhedra in the Title Compound and in $Ln(H_2O)_9(BrO_3)_3$.

	Title Compound		Wt. Av.	$Pr^{3+\,a}$	$Yb^{3+\,a}$
Edge of prismatic triangle (Å)	3.027(4)	3.092(3)	3.070	3.17	2.97
Edge of equatorial triangle (Å)	4.299(4)	4.254(4)	4.284	4.37	4.21
Height of prism (Å)	3.378(3)	3.457(4)	3.431	3.38	3.13
Contact distance O(prism)···O(equator) (Å)	2.778(4) 2.831(3)	2.790(4)	2.800	2.82	2.67
θ (°)	47.09	45.31	45.90	47.4	47.5
Ln–O(prism) (Å)			2.466	2.49	2.32
Ln–O(equator) (Å)			2.478	2.52	2.43
Distance quotient ρ			1.005	1.01	1.05

[a] From Ref. [13].

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*Atom O(7W)′ is related to O(7W) by *x*, −*y*, *z* and atom O(5W)″ is related to O(5W) by −*x*, *y*, *z*.

o the $Ln(H_2O)_9^{3+}$ unit is much more extensive than in the present compound and involves the interaction of water protons with anionic oxygen atoms. In the present compound the equatorial water molecules form hydrogen bonds to dioxan oxygen atoms (O(6W···O(11D) 2.920(4) Å, O(7W)···O(11D) 2.791(4) Å and O(7W)···O(14D) 2.731(3) Å). The prismatic oxygen atoms could only form hydrogen bonds to Br^-, the $Br\cdots OH_2$ distance (3.32(3) Å average) is equally compatible with a riding model or a hydrogen bond and since the water protons were not located there is no evidence on this point.

The dioxan molecules have typical dimensions. Their role of hydrogen bonding between coordinated water molecules is exactly the same as in $MgCl_2(6H_2O)\cdot dx$ and in $NiBr_2\cdot 4H_2O\cdot 2dx$ [3].

Although concentrated aqueous solutions of $LnCl_3$ and $Ln(ClO_4)_3$ are known to contain $Ln(H_2O)_9^{3+}$ cations from diffraction studies [15–17] there is no evidence for crystalline hydrates of these salts or the corresponding bromides with more than six H_2O [17, 18]. $LnBr_3\cdot 6H_2O$ are isostructural with $LnCl_3\cdot 6H_2O$ where the type structure shows $GdCl_2(H_2O)_6^+$, 8-coordinate, and Cl^- [19]. $Ln(ClO_4)_3\cdot 6H_2O$ contains octahedral $Ln(H_2O)_6^{3+}$ [17]. Each of these structures is found over a large part of the lanthanide series. It is not obvious why the presence of dioxan should preserve the $Sm(H_2O)_9^{3+}$ ion into the crystal and exclude the Br^- from the coordination sphere. There is no evidence of similar behaviour in the other metal halide–dioxan–water systems studied. $MgCl_2\cdot 6H_2O\cdot 2dx$ contains the sme $Mg(H_2O)_6^{2+}$ ions as $MgCl_2\cdot 6H_2O$ whereas $NiBr_2\cdot 4H_2O\cdot 2dx$ contains *trans* $NiBr_2\cdot(H_2O)_4$ units. On the present evidence $Ln(ClO_4)_3\cdot 9H_2O\cdot 4dx$ will also contain $Ln(H_2O)_9^{3+}$ ions with hydrogen bonding dioxan but $La(NO_3)_3\cdot 2H_2O\cdot dx$ probably contains coordinated nitrate groups as found in hydrated $Ln(NO_3)_3$ species [20, 21].

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References

1 J. A. Weicksel and C. C. Lynch, *J. Am. Chem. Soc., 72,* 2632 (1950).

2 S. H. Whitlow and E. J. Crabe, *Acta Crystallogr., Sect. B:, 31,* 2534 (1975).

3 J. C. Barnes and T. J. R. Weakley, *J. Chem. Soc., Dalton Trans.,* 1786 (1976).

4 F. Durant and M. Griffe, *Bull. Soc. Chim. Belg., 77,* 557 (1968).

5 J. C. Barnes and C. S. Duncan, *J. Chem. Soc., Dalton Trans.,* 1732 (1972).

6 G. Vicentini, M. Perrier and E. Giesbrecht, *Chem. Ber., 94,* 1153 (1961).

7 J. C. Barnes and P. A. Bristow, unpublished observations.

8 W. G. R. de Camargo and J.V. Valarelli, *Acta Crystallogr., 16,* 321 (1963).

9 G. M. Sheldrick, 'SHELX76', Program for Crystal Structure Determination, University of Cambridge, 1976.

10 P. Roberts and G. M. Sheldrick, 'XANADU', Program for Crystallographic Calculations, University of Cambridge, 1975.

11 S. Motherwell and W. Clegg, 'PLUTO', Program for Molecular Drawings, University of Cambridge, 1978.

12 'International Tables for X-ray Crystallography, Vol. IV', Kynock Press, Birmingham, 1974.

13 J. Albertsson and I. Elding, *Acta Crystallogr., Sect. B:, 33,* 1460 (1977).

14 D. L. Kepert, *J. Chem. Soc.,* 4736 (1965).

15 A. Habenschuss and F. H. Spedding, *J. Chem. Phys., 70,* 3758 (1979).

16 A. Habenschuss and F. H. Spedding, *J. Chem. Phys., 70,* 3797 (1979).

17 J. Glaser and G. Johansson, *Acta Chem. Scand., Ser. A:, 35,* 639 (1981).

18 D. Brown, S. Fletcher and D. H. Holah, *J. Chem. Soc. A:,* 1889 (1968).

19 M. Marezio, H. A. Plettinger and W. H. Zachariasen, *Acta Crystallogr., 14,* 234 (1961).

20 B. Eriksson, L. O. Larsson, L. Niinisto and J. Valkonen, *Inorg. Chem., 19,* 1207 (1980).

21 B. Eriksson, *Acta Chem. Scand., Ser. A:, 36,* 186 (1982).