

The Geometry of the Nonaqualanthanoid(3+) Complex in the Solid Bromates and Ethyl Sulphates

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The structures of $[\text{Ln}(\text{H}_2\text{O})_9](\text{BrO}_3)_3$ and $[\text{Ln}(\text{H}_2\text{O})_9](\text{C}_2\text{H}_5\text{SO}_4)_3$, $\text{Ln} = \text{Pr}$ and Yb , have been determined by X-ray diffraction. The structures were refined to $R = 0.025\text{--}0.040$. Accurate cell dimensions for the bromates and ethyl sulphates of all the trivalent Ln ions except Pm were determined at 23°C with Guinier–Hägg powder photographs. The bromates crystallize in the space group $P6_3/mmc$ with $Z = 2$, $a = 11.8395$ (11), $c = 6.8012$ (9) Å for Pr and $a = 11.7056$ (13), $c = 6.6474$ (9) Å for Yb. The ethyl sulphates crystallize in space group $P6_3/m$ with $Z = 2$, $a = 14.0454$ (8), $c = 7.1207$ (6) Å for Pr and $a = 13.8991$ (8), $c = 7.0247$ (6) Å for Yb. Tricapped trigonal prisms of water O atoms with symmetry D_{3h} in the bromates and C_{3h} in the ethyl sulphates surround the nine-coordinated Ln ions. The complex ions form columns about the $\bar{6}$ axes. The anions are hydrogen-bonded to the complex ions and form columns about the 6_3 axes. The decrease in the prismatic Ln–O bonds between the Pr and Yb structures is what is expected from the lanthanoid contraction, 0.155 Å, but van der Waals repulsions between prismatic and equatorial O atoms make the decrease in the equatorial Ln–O bonds about half this value. The variation in cell dimensions through the Ln series for both types of compounds has been related to this repulsion and to the hydrogen-bond systems.

Introduction

The nonaqualanthanoid bromates and ethyl sulphates form two isostructural series with hexagonal symmetry, which are very similar to each other. Helmholz (1939) determined the structure of Nd bromate from two-dimensional X-ray data and Sikka (1969) that of Sm bromate by neutron diffraction. The structures of some ethyl sulphates were first studied by Ketelaar (1937) and later by Fitzwater & Rundle (1959) who refined the Pr and Er compounds, the former with two-dimensional data. Hubbard, Quicksall & Jacobson (1974) have determined the structure of Ho ethyl sulphate with neutron data. In both bromates and ethyl sulphates the Ln ion coordinates nine water O atoms which form a tricapped trigonal prism (TCTP).

Distorted TCTP's are rather common among the solid Ln compounds but the nonaqua complex in the Ln bromates has the symmetry D_{3h} , *i.e.* one of the two idealized ground-state geometries for nine-coordination, the other being the C_{4v} monocapped square antiprism (Day & Hoard, 1970). The TCTP's in the ethyl sulphates are only slightly distorted, to the symmetry C_{3h} . Accurately known TCTP geometries in the bromate and ethyl sulphate series should therefore be of considerable value when discussing the stereochemistry of nine-coordinate Ln complexes.

In a single-crystal study the structures of the Pr and Yb compounds in the two series have been determined.

In order to correlate the change in the Ln–O and O–O distances in the Ln complexes with the change in cell dimensions through the series, a powder investigation of all the Ln bromates and ethyl sulphates (except the Pm compounds) has also been undertaken.

Experimental

Preparation

The bromates of all the trivalent lanthanoids except Pm were prepared by adding solid KBrO_3 to hot water solutions of the respective perchlorates (Kremers & Moeller, 1944). After cooling to about 15°C the precipitated KClO_4 was filtered off. The ethyl sulphates were prepared by adding a concentrated Ba ethyl sulphate solution to water solutions of the Ln sulphates (Nathans, 1961) and filtering off the BaSO_4 precipitate. For both compounds slow evaporation at room temperature gave hexagonal crystals (prismatic *c*) which were recrystallized several times from water. A slow decomposition of the ethyl sulphates was observed, but the crystals were sufficiently stable to use for X-ray experiments for at least some weeks at room temperature. The Ce^{III} bromate decomposed after some days to Ce^{IV} and bromine, but the other bromates were stable.

Powder photographs

Powder photographs of all prepared compounds were recorded at 23 °C by the Guinier–Hägg technique with Cu $K\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$) for the bromates in a camera with radius 40 mm and Cu $K\alpha_1$ radiation ($\lambda = 1.54051 \text{ \AA}$) for the ethyl sulphates in a camera with radius 50 mm. Al powder (cubic, $a = 4.04953 \text{ \AA}$ at 23 °C) was used as an internal standard. A scale was photographed on each film before the X-ray exposure. All the bromates gave the same powder pattern, as did all the ethyl sulphates. The positions of about 50 lines for the bromates and 70 for the ethyl sulphates with $\sin^2 \theta < 0.25$ were measured.

The values of a and c , obtained from the previous determinations (Sikka, 1969; Fitzwater & Rundle, 1959), were refined by least squares, minimizing $\sum w(\sin^2 \theta_o - \sin^2 \theta_c)^2$ with $w = 1/\sin^2 2\theta_o$. Only unambiguously indexed lines were used. Table 1 gives the final cell dimensions and volumes.* Mayer & Glasner (1967) have also determined the cell dimensions of the bromates. As they used data obtained with a powder diffractometer the precision of the parameters was only 0.01–0.02 Å but within these wide limits their results agree with ours.

Single-crystal study

Table 2 gives information concerning crystal data, the collection and reduction of the intensity data sets, and the refinements based on them. The Pr bromate crystal (PRBR) was mounted in a glass capillary and

* Tables of observed and calculated $\sin^2 \theta$, structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32278 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

the Yb ethyl sulphate crystal (YBET) was coated with Apiezon oil to prevent possible decomposition. The Yb bromate crystal (YBBR) was mounted along c on a linear single-crystal diffractometer and the independent reflexions ($h \geq k$) in the layers $hk0$ – $hk5$ were measured. Coincidence losses were negligible. The stability of the crystal and the electronics was checked by measuring one standard reflexion for each layer. Variations less than 2% were observed over each 24 h period. The other crystals were arbitrarily mounted with respect to the φ axis on a CAD-4 to avoid multiple diffraction. The background was measured for 25% of the scan time at each end of the interval. Two reference reflexions were measured at regular intervals. The variation in their intensities was negligible in PRBR, 6% and independent of exposure time in PRET, and 9% and a linearly increasing function of the exposure time in YBET. The values of I and $\sigma_c(I)$ were corrected for Lorentz, polarization and absorption effects [$\sigma_c(I)$ is based on counting statistics]. The expression used in the polarization correction of the CAD-4 data was $p = (1 + \cos^2 2\theta_M \cos^2 2\theta)/(1 + \cos^2 2\theta_M)$ with $\theta_M = 6.08^\circ$ for Mo $K\alpha$ and 13.28° for Cu $K\alpha$ radiation. The Paired data were corrected according to Arndt & Willis (1966).

Refinement of the structures

The nonaqualanthanoid bromates have the diffraction symmetry $6/mmm$, and the systematically absent reflexions are hhl , $l \neq 2n$ giving the possible space groups $P6_3mc$, $P\bar{6}2c$ and $P6_3/mmc$. Helmholz (1939) assumed that the crystal structure of $[\text{Nd}(\text{H}_2\text{O})_9]-(\text{BrO}_3)_3$ belonged to the space group $P6_3mc$ but Sikka (1969) found that the space group of $[\text{Sm}(\text{H}_2\text{O})_9]-(\text{BrO}_3)_3$ was the centrosymmetric $P6_3/mmc$. Since all the Ln bromates are isostructural, both PRBR and

Table 1. Unit-cell dimensions with estimated standard deviations in nonaqualanthanoid bromates and ethyl sulphates

Ln	$r(\text{\AA})$	Bromates			Ethyl sulphates		
		$a(\text{\AA})$	$c(\text{\AA})$	$V(\text{\AA}^3)$	$a(\text{\AA})$	$c(\text{\AA})$	$V(\text{\AA}^3)$
La	1.061	11.8828 (6)	6.8462 (5)	837.18	14.1084 (8)	7.1491 (6)	1232.35
Ce	1.034	11.8523 (9)	6.8204 (8)	829.74	14.0706 (6)	7.1346 (4)	1223.27
Pr	1.013	11.8395 (11)	6.8012 (9)	825.63	14.0454 (8)	7.1207 (6)	1216.53
Nd	0.995	11.8224 (7)	6.7858 (6)	821.38	14.0275 (5)	7.1130 (4)	1212.12
Sm	0.964	11.7885 (12)	6.7511 (11)	812.50	13.9884 (5)	7.0909 (4)	1201.64
Eu	0.950	11.7750 (10)	6.7371 (9)	808.95	13.9742 (7)	7.0827 (5)	1197.80
Gd	0.938	11.7658 (8)	6.7257 (7)	806.33	13.9645 (7)	7.0742 (5)	1194.71
Tb	0.920	11.7503 (8)	6.7080 (6)	802.10	13.9444 (5)	7.0645 (4)	1189.63
Dy	0.908	11.7453 (9)	6.7016 (6)	800.65	13.9287 (6)	7.0537 (4)	1185.13
Ho	0.894	11.7308 (10)	6.6859 (8)	796.79	13.9221 (5)	7.0473 (4)	1182.95
Er	0.881	11.7239 (11)	6.6733 (8)	794.35	13.9110 (5)	7.0371 (4)	1179.36
Tm	0.869	11.7162 (12)	6.6570 (8)	791.38	13.9026 (4)	7.0308 (3)	1176.87
Yb	0.858	11.7056 (13)	6.6474 (9)	788.80	13.8991 (8)	7.0247 (6)	1175.25
Lu	0.848	11.6973 (8)	6.6316 (7)	785.82	13.8870 (7)	7.0153 (5)	1171.65

YBBR were refined in $P6_3/mmc$. Preliminary values of the atomic parameters were taken from Sikka (1969).

The nonaqualanthanoid ethyl sulphates have the diffraction symmetry $6/m$ with systematically absent reflexions $00l$, $l \neq 2n$. Thus the space group is $P6_3$ or $P6_3/m$. Both Ketelaar (1937) and Fitzwater & Rundle (1959) assume the centrosymmetric space group $P6_3/m$. We have also chosen this space group. Our preliminary parameters for the non-hydrogen atoms were those given by Fitzwater & Rundle (1959).

The parameters were refined by full-matrix least squares. The function minimized was $\sum w(|F_o| - |F_c|)^2$, with w calculated from $1/w = \sigma_c(|F_o|^2)/4|F_o|^2 + C_1|F_o|^2$

+ C_2 , where C_1 and C_2 are adjustable constants. The refinement was first performed with individual isotropic temperature factors together with two scale factors for PRBR, six for YBBR (one for each layer measured on the linear diffractometer) and one for each of PRET and YBET. In a following step, anisotropic temperature factors were assigned to all atoms. The six scale factors for YBBR were then constrained so that only one overall scale factor was refined. The convergence was followed by R and R_w . Compared with the isotropic case the anisotropic refinements improved the R 's significantly (Hamilton, 1965).

The H positional parameters given by Sikka (1969)

Table 2. Crystal data for praseodymium and ytterbium bromate (PRBR and YBBR) and praseodymium and ytterbium ethyl sulphate (PRET and YBET)

Unit-cell dimensions are in Table 1. Details of data collection and reduction and the least-squares refinements are given.

	PRBR	YBBR	PRET	YBET
Formula	Pr(H ₂ O) ₉ (BrO ₃) ₃	Yb(H ₂ O) ₉ (BrO ₃) ₃	Pr(H ₂ O) ₉ (C ₂ H ₅ SO ₄) ₃	Yb(H ₂ O) ₉ (C ₂ H ₅ SO ₄) ₃
FW	686.81	718.80	678.45	710.56
Crystal system	Hexagonal	Hexagonal	Hexagonal	Hexagonal
Space group	$P6_3/mmc$	$P6_3/mmc$	$P6_3/m$	$P6_3/m$
Z	2	2	2	2
D_m (g cm ⁻³)	—	3.00	1.84	—
D_x (g cm ⁻³)	2.762	3.026	1.852	2.008
Crystal size (mm)	0.10 × 0.10 × 0.40	0.15 × 0.15 × 0.30	0.06 × 0.06 × 0.15	0.07 × 0.08 × 0.15
Diffractometer	CAD-4 four-circle	Paired linear	CAD-4 four-circle	CAD-4 four-circle
Radiation	Graphite-monochromated Mo K α (0.71069 Å)	Graphite-monochromated Mo K α (0.71069 Å)	Graphite-monochromated Cu K α (1.54178 Å)	Graphite-monochromated Cu K α (1.54178 Å)
Scan	$\omega-2\theta$	ω	$\omega-2\theta$	$\omega-2\theta$
ω interval (°)	1	3	0.8 + 0.5 tan θ	0.8 + 0.5 tan θ
θ interval (°)	3–30	3–25	5–70	5–70
Take-off angle (°)	5	6	5	5
Minimum number of counts in a scan	3000	4000	3000	3000
Maximum recording time (min)	3	9	3	3
μ (cm ⁻¹)	107 (Mo K α)	144 (Mo K α)	175 (Cu K α)	108 (Cu K α)
Range of the transmission factor	0.233–0.340	0.197–0.235	0.221–0.489	0.447–0.592
Temperature (°C)	22	25.0 ± 0.2	22	22
Number of measured reflexions	318	254	930	893
Number of reflexions given zero weight	40 (<3 σ_c)	66 (<3 σ_c)	36 (<2 σ_c)	34 (<2 σ_c)
Number of independent reflexions in the refinements, m	278	188	894	859
Number of parameters refined, n	35	29	72	72
$R = \sum F_o - F_c / \sum F_o $	0.034	0.040	0.025	0.039
$R_w = [\sum w(F_o - F_c)^2 / \sum w F_o ^2]^{1/2}$	0.041	0.053	0.030	0.050
$S = [\sum w(F_o - F_c)^2 / (m - n)]^{1/2}$	0.92	0.92	0.92	0.73
C_1 (weighting function)	0.0009	0.0025	0.0005	0.0036
C_2 (weighting function)	2.0	0	0.25	0.5
$g \times 10^{-4}$	—	—	0.13 (3)	0.78 (9)
Mosaic spread (")	—	—	43	7.5
Domain size (cm)	—	—	0.21 × 10 ⁻⁴	0.12 × 10 ⁻³
Range of correction on F_o	—	—	1.00–1.05	1.00–1.29

were included in our model of PRBR. Indications of the H positions in YBBR, PRET and YBET were obtained from a difference map computed from the data with $\sin \theta/\lambda < 0.5 \text{ \AA}^{-1}$. The positional parameters of the methylene H atoms were fixed at calculated positions (C—H 1 Å, tetrahedral C angles) and the thermal parameters of all the H atoms at $B = 5.0 \text{ \AA}^2$. The YBBR data did not permit a refinement of the H parameters; for the other three structures the decrease in R values was insignificant. The positions found for the H atoms are compatible with those determined by neutron diffraction for the Sm bromate and Ho ethyl sulphate structures [Sikka (1969) and Hubbard, Quicksall & Jacobson (1974) respectively].

An isotropic extinction parameter was included in the refinement of PRET and YBET (Zachariasen, 1967). The values of C_1 and C_2 were varied until a good constancy of $\langle w(|F_o| - |F_c|)^2 \rangle$ in different $|F_o|$ and $\sin \theta$ intervals was obtained. The final difference maps for the four structures were featureless.

Scattering factors for Pr and Yb were obtained from Cromer, Larson & Waber (1964), those for Br, S, O and C from Hanson, Herman, Lea & Skillman (1964), and those for H from Stewart, Davidson & Simpson (1965). Correction for anomalous dispersion was

included for Pr, Yb, Br and S (Cromer & Liberman, 1970).

Table 3 gives the final positional parameters for

Table 4. *The r.m.s. components R_i ($\times 10^3 \text{ \AA}$) along the principal axes of the ellipsoids of thermal vibration*

	R_1	R_2	R_3	R_1	R_2	R_3
(A) Bromates	Ln = Pr			Ln = Yb		
Ln	127	132	132	66	127	127
O(1)	242	133	182	224	121	169
O(2)	260	166	170	153	146	151
Br	260	145	159	232	138	154
O(3)	206	162	195	204	138	195
O(4)	453	174	233	431	145	219
(B) Ethyl sulphates						
Ln	140	140	148	130	130	140
O(1)	165	175	222	146	153	197
O(2)	156	181	224	155	166	193
S	149	173	196	127	163	164
O(3)	156	199	242	132	186	222
O(4)	182	201	276	158	167	244
O(5)	179	196	246	160	180	223
C(1)	209	275	333	193	250	286
C(2)	183	226	385	149	189	362

Table 3. *Atomic coordinates with estimated standard deviations in PRBR, YBBR, PRET and YBET*

H(1) and H(2) in YBBR and H(5) were not refined.

Atom	Position	Ln = Pr			Ln = Yb		
		x	y	z	x	y	z
<i>(A) Bromates</i>							
Ln	2(c)	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$
O(1)	12(k)	0.4226 (3)	0.8452 (3)	0.0021 (9)	0.4178 (5)	0.8356 (5)	0.0143 (18)
O(2)	6(h)	0.2104 (5)	0.4208 (5)	$\frac{1}{4}$	0.2135 (6)	0.4269 (6)	$\frac{1}{4}$
Br	6(h)	0.8703 (1)	0.7406 (1)	$\frac{1}{4}$	0.8693 (1)	0.7386 (1)	$\frac{1}{4}$
O(3)	12(j)	0.9307 (6)	0.6398 (6)	$\frac{1}{4}$	0.9321 (10)	0.6383 (10)	$\frac{1}{4}$
O(4)*	12(k)	0.9054 (9)	0.8109 (9)	0.0546 (36)	0.9070 (14)	0.8140 (14)	0.0531 (65)
H(1)	24(l)	0.3861 (77)	0.8716 (73)	-0.0661 (12.5)	0.3662	0.8613	-0.0248
H(2)	12(j)	0.1378 (124)	0.3662 (125)	$\frac{1}{4}$	0.1416	0.3939	$\frac{1}{4}$
<i>(B) Ethyl sulphates</i>							
Ln	2(c)	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$
O(1)	12(i)	0.3330 (2)	0.7913 (2)	0.0055 (3)	0.3321 (2)	0.7843 (2)	0.0167 (4)
O(2)	6(h)	0.3525 (3)	0.4925 (3)	$\frac{1}{4}$	0.3526 (3)	0.4959 (3)	$\frac{1}{4}$
S	6(h)	0.6831 (1)	0.6289 (1)	$\frac{1}{4}$	0.6808 (1)	0.6287 (1)	$\frac{1}{4}$
O(3)	6(h)	0.7545 (3)	0.5817 (3)	$\frac{1}{4}$	0.7498 (4)	0.5774 (4)	$\frac{1}{4}$
O(4)	6(h)	0.7703 (3)	0.7561 (3)	$\frac{1}{4}$	0.7699 (3)	0.7564 (3)	$\frac{1}{4}$
O(5)	12(i)	0.6184 (2)	0.6057 (2)	0.0814 (4)	0.6154 (2)	0.6062 (3)	0.0792 (5)
C(1)	6(h)	0.8139 (7)	0.9426 (6)	$\frac{1}{4}$	0.8177 (8)	0.9464 (7)	$\frac{1}{4}$
C(2)	6(h)	0.7280 (5)	0.8308 (5)	$\frac{1}{4}$	0.7273 (6)	0.8324 (5)	$\frac{1}{4}$
H(1A)	12(i)	0.2747 (35)	0.7791 (34)	-0.0746 (66)	0.2886 (51)	0.7765 (56)	-0.0621 (101)
H(1B)	12(i)	0.3525 (38)	0.8449 (38)	0.0181 (77)	0.3577 (61)	0.8549 (61)	0.0384 (119)
H(2)	12(i)	0.3601 (36)	0.4601 (35)	0.1754 (62)	0.3753 (54)	0.4779 (58)	0.1651 (93)
H(3)	6(h)	0.8005 (54)	0.9971 (58)	$\frac{1}{4}$	0.8052 (85)	1.0051 (78)	$\frac{1}{4}$
H(4)	12(i)	0.8589 (36)	0.9552 (38)	0.1465 (59)	0.8379 (58)	0.9598 (59)	0.1458 (81)
H(5)	12(i)	0.6821	0.8171	0.1350	0.6810	0.8191	0.1334

* Occupancy 0.5.

PRBR, YBBR, PRET and YBET. Table 4 gives the root-mean-square components along the principal axes of the ellipsoids of vibration.*

Description of the structures

Figs. 1 and 2 show stereoscopic pairs of drawings of the unit cells of PRBR and PRET respectively. Both structures are composed of columns of nonaqua complexes about the 6 axes along $x = \frac{1}{3}, y = \frac{2}{3}$ and $x = \frac{2}{3}, y = \frac{1}{3}$ and by the anions about the 6₃ axis through the origin. These columns are linked by hydrogen bonds. Fig. 3 shows projections of the structures on the *ab* plane. Selected interatomic distances and angles are given in Table 5 for the bromates and in Table 6 for the ethyl sulphates.

The coordination polyhedra

In the bromates the coordination polyhedron of $[\text{Ln}(\text{H}_2\text{O})_9]^{3+}$ is a regular tricapped trigonal prism (TCTP) of symmetry D_{3h} , as indicated by Fig. 3(a). In the ethyl sulphates the six O(1) atoms form a regular trigonal prism about Ln^{3+} . The three equatorial O(2) atoms are located in the mirror plane at $z = \frac{1}{2}$, but the equilateral triangle formed by them, completing the TCTP, is slightly rotated from the D_{3h} position resulting in the symmetry C_{3h} (cf. Fig. 3b). This distortion is probably caused by the hydrogen bonds $\text{O}(2) \cdots \text{O}(5)$ to the ethyl sulphate groups.

* See footnote p. 1461.

In all the compounds the prismatic Ln—O(1) is shorter than the equatorial Ln—O(2) bond. Ln—O(1) is 0.17 (2) Å shorter in YBBR than in PRBR and 0.15 (1) Å shorter in YBET than in PRET which is compatible with the decrease in ionic radius, 0.155 Å (Templeton & Dauben, 1954), between Pr^{3+} and Yb^{3+} . The contraction of the equatorial Ln—O(2) is, on the other hand, only about half the contraction of the Ln—O(1) bond: 0.09 (2) Å in the bromates and 0.07 (2) Å in the ethyl sulphates. This is probably caused by repulsions between O(1) and O(2) as the O(1)—O(2) contact distances are very short, 2.67 Å in YBBR and 2.65 Å in YBET.

To compare the coordination polyhedra in the four compounds, some quantities are collected in Table 7. The contraction of the Ln—O lengths is of course reflected by the contraction of the TCTP. The average decrease, Δ , in the edge of the prismatic triangle and the height of the prism between the Pr and Yb compounds is what is expected from the decrease in ionic radius between Pr^{3+} and Yb^{3+} .

As the symmetry of the coordination polyhedron in the ethyl sulphates does not deviate much from D_{3h} , we can compare the shape of the TCTP in both the bromates and ethyl sulphates with the model calculated from ligand—ligand repulsions for monatomic ligands by Kepert (1965). The distance quotients $\rho = \text{Ln—O}(2)/\text{Ln—O}(1)$ and the angles θ between the Ln—O(1) bonds and the threefold axis of the prism are given in Table 7 together with the corresponding θ values for the hard-sphere model (HSM). Our result is in agreement with Kepert's prediction, that a more stable structure is obtained for 'real' ligands if θ is

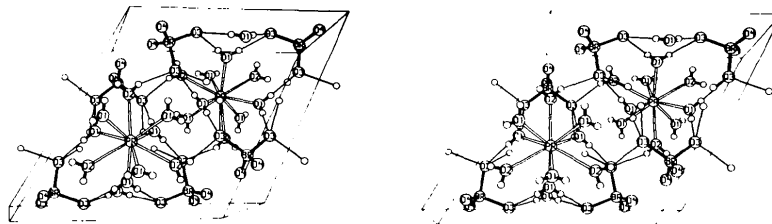


Fig. 1. A stereoscopic pair of drawings of the unit cell of praseodymium bromate.

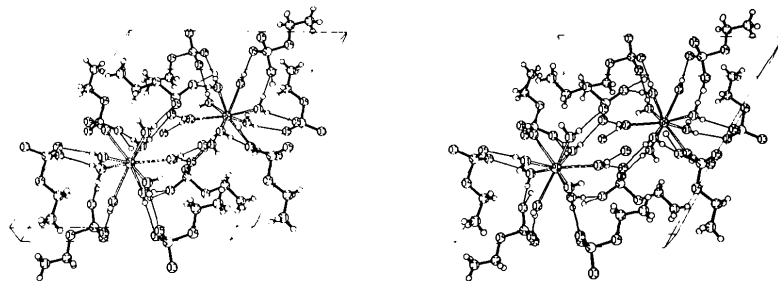


Fig. 2. A stereoscopic pair of drawings of the unit cell of praseodymium ethyl sulphate.

increased from the HSM value. We find the increases 5.4° in PRBR, 4.3° in YBBR and 2.7° in both PRET and YBET.

The bromate ions

In the bromate group (Fig. 4) O(4) is statistically distributed above and below the mirror plane $z = \frac{1}{4}$, on

Table 5. Selected interatomic distances (Å) and angles ($^\circ$) with estimated standard deviations in PRBR and YBBR

The superscripts (i)–(viii) indicate the following equivalent sites in the structure:

(i)	$y - x, 1 - x, z$	(v)	$y, x, -z$
(ii)	$x, y, \frac{1}{2} - z$	(vi)	$1 - y, x - y, z$
(iii)	$1 + y - x, y, z$	(vii)	$x - y, x, -z$
(iv)	$y - x, y, z$	(viii)	$x - 1, x - y, z$

(a) The coordination polyhedron

Distances	PRBR	YBBR
Ln—O(1)	2.49 (1)	2.32 (1)
Ln—O(2)	2.52 (1)	2.43 (1)

(b) The bromate group

Distances	PRBR	YBBR
Br—O(3)	1.67 (1)	1.67 (1)
Br—O(4)	1.51 (2)	1.52 (4)
O(3)—O(3 ⁱⁱⁱ)	2.62 (1)	2.64 (2)
O(3)—O(4)	2.56 (2)	2.58 (3)

Angles	PRBR	YBBR
O(3)—Br—O(3 ⁱⁱⁱ)	103.6 (5)	104.9 (8)
O(3)—Br—O(4)	107.2 (6)	107.9 (9)

(c) The water molecule

Distances	PRBR	YBBR
O(1)—H(1)	0.80 (8)	0.84
O(2)—H(2)	0.78 (14)	0.73

Angles	PRBR	YBBR
H(1)—O(1)—H(1 ^{iv})	95 (13)	128
H(2)—O(2)—H(2 ^{iv})	88 (19)	125

(d) The hydrogen-bond system

Distances	PRBR	YBBR
O(1) ... O(3 ^v)	2.82 (1)	2.85 (1)
O(2) ... O(3 ^{vi})	2.87 (1)	2.85 (1)

Angles	PRBR	YBBR
O(3 ^v) ... O(1) ... O(3 ^{vii})	94.0 (3)	91
O(3 ^{vi}) ... O(2) ... O(3 ^{viii})	125.2 (4)	124
O(1)—H(1) ... O(3 ^{vii})	177 (9)	151
O(2)—H(2) ... O(3 ^{viii})	155 (13)	179

Table 6. Selected interatomic distances (Å) and angles ($^\circ$) with estimated standard deviations in PRET and YBET

The superscripts (i)–(vi) indicate the following equivalent sites in the structure:

(i)	$y - x, 1 - x, z$	(iv)	$x - y, x, -z$
(ii)	$x, y, \frac{1}{2} - z$	(v)	$1 - x, 1 - y, -z$
(iii)	$1 - y, 1 + x - y, z$	(vi)	$1 - x, 1 - y, \frac{1}{2} + z$

(a) The coordination polyhedron

Distances	PRET	YBET
Ln—O(1)	2.470 (2)	2.321 (3)
Ln—O(2)	2.592 (3)	2.518 (4)

(b) The ethyl sulphate group

Distances	PRET	YBET
S—O(3)	1.453 (3)	1.453 (4)
S—O(4)	1.582 (4)	1.577 (4)
S—O(5)	1.441 (2)	1.441 (3)
O(3)—O(4)	2.347 (5)	2.360 (6)
O(3)—O(5)	2.420 (3)	2.416 (4)
O(4)—O(5)	2.438 (4)	2.434 (5)
O(5)—O(5 ⁱⁱ)	2.401 (5)	2.400 (7)
O(4)—C(2)	1.441 (6)	1.447 (7)
C(1)—C(2)	1.424 (9)	1.448 (11)

Angles

	PRET	YBET
O(3)—S—O(4)	101.2 (2)	102.2 (2)
O(3)—S—O(5)	113.5 (1)	113.1 (1)
O(4)—S—O(5)	107.4 (1)	107.4 (2)
O(5)—S—O(5 ⁱⁱ)	112.8 (2)	112.7 (3)
S—O(4)—C(2)	117.0 (3)	116.4 (4)
O(4)—C(2)—C(1)	112.0 (5)	110.6 (6)

(c) The water molecule

Distances	PRET	YBET
O(1)—H(1A)	0.94 (4)	0.79 (7)
O(1)—H(1B)	0.67 (5)	0.87 (7)
O(2)—H(2)	0.74 (4)	0.77 (6)

Angles

	PRET	YBET
H(1A)—O(1)—H(1B)	97 (5)	97 (7)
H(2)—O(2)—H(2 ⁱⁱ)	92 (7)	101 (10)

(d) The hydrogen-bond system

Distances	PRET	YBET
O(1) ... O(3 ^{iv})	2.734 (3)	2.757 (4)
O(1) ... O(5 ⁱⁱⁱ)	2.833 (3)	2.832 (4)
O(2) ... O(5 ^v)	2.864 (3)	2.862 (4)

Angles

	PRET	YBET
O(3 ^{iv}) ... O(1) ... O(5 ⁱⁱⁱ)	96.0 (1)	94.0 (1)
O(5 ^v) ... O(2) ... O(5 ^{vi})	111.0 (1)	107.8 (2)
O(1) ... H(1A) ... O(3 ^{iv})	173 (4)	177 (7)
O(1)—H(1B) ... O(5 ⁱⁱⁱ)	172 (6)	172 (7)
O(2)—H(2) ... O(5 ^v)	167 (4)	162 (7)

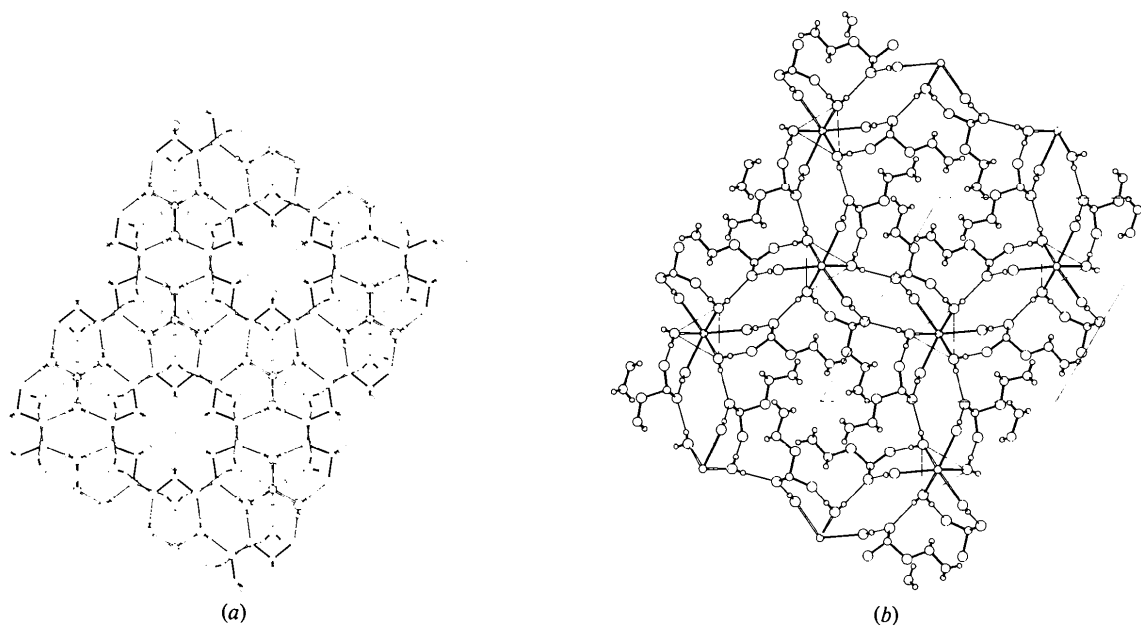


Fig. 3. Projections of (a) praseodymium and (b) praseodymium ethyl sulphate on the plane (001).

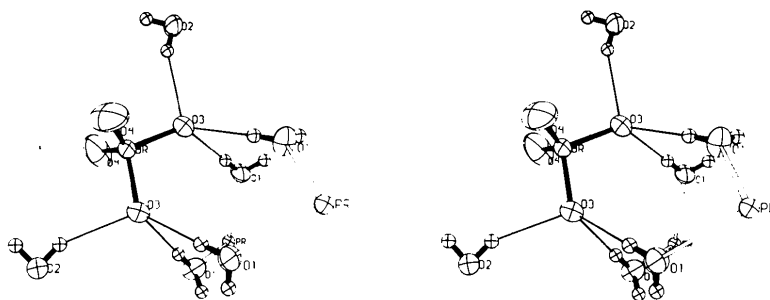


Fig. 4. A stereoscopic pair of drawings of the vicinity of a bromate ion in PRBR showing the hydrogen-bond system. The thermal ellipsoids (except H) are scaled to include 50% probability.

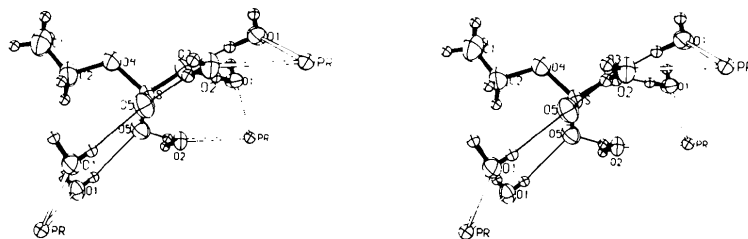


Fig. 5. A stereoscopic pair of drawings of the vicinity of an ethyl sulphate molecule in PRET showing the hydrogen-bond system. The thermal ellipsoids are scaled as in Fig. 4.

Table 7. A comparison of the coordination polyhedra (TCTP) in PRBR, PRET, YBBR and YBET

The quantities ρ and θ are defined in the text. For superscripts (i) and (ii), see Tables 5 (the bromates) and 6 (the ethyl sulphates).

Quantity	PRBR	PRET	YBBR	YBET	Δ (average)
Edge of the prismatic triangles, O(1)–O(1') (Å)	3.17 (1)	3.036 (4)	2.97 (2)	2.847 (5)	0.20
Edge of the equatorial triangle, O(2)–O(2') (Å)	4.37 (2)	4.489 (5)	4.21 (2)	4.361 (7)	0.14
Height of the prism, O(1)–O(1'') (Å)	3.38 (1)	3.482 (5)	3.13 (1)	3.278 (6)	0.22
Rotation of the equatorial triangle (°)	–	5.0	–	4.7	0.3
Shortest contact distance, O(1')–O(2) (Å)	2.82 (1)	2.757 (3)	2.67 (1)	2.648 (5)	0.13
ρ	1.01	1.05	1.05	1.08	–
θ (°)	47.4	45.1	47.5	45.1	–
θ (HSM) (°)	42.0	42.9	42.9	43.5	–

which the Br and O(3) atoms are located (Fig. 3a). The distances and angles within the group are the same in PRBR and YBBR. The distance Br–O(4) is short. When it is corrected for thermal motion [O(4) riding on Br] it becomes somewhat longer, 1.57 Å, in both structures.

The difference between the models used by Helmholtz (1939) and by us appears in the bromate ion. In our model the space-group symmetry forces the occupancy of the O(4) sites to be one half in each position above and below the mirror plane. In Helmholtz's (1939) model this O atom is disordered in the same way, but he found the best fit to the data when the occupancy for the two positions was one third and two thirds respectively. He also assumed that the Br atom had a z coordinate that differed by 0.02 from $z = \frac{1}{4}$ and that it was disordered in the same way as O(4). In our model Br is in the mirror plane at $z = \frac{1}{4}$.

The ethyl sulphate ions

In the ethyl sulphate group (Fig. 5) the S atom, O(3) and O(4), and the C atoms are located in the mirror plane at $z = \frac{1}{4}$, while O(5) is above and below this plane (Fig. 2). Probability plot analysis has been used to compare the geometries of the ethyl sulphate ion in the two structures. Ordered values of $\delta d_i = |d(1)_i - d(2)_i| / [\sigma^2 d(1)_i + \sigma^2 d(2)_i]^{1/2}$ are compared with values expected for a half-normal distribution of zero mean and unit variance (De Camp, 1973; Albertsson & Schultheiss, 1974). Interatomic distances less than 4.5 Å are used corresponding to a comparison of bond lengths, bond angles and torsion angles. The result is shown in Fig. 6. The plot is linear for points with $\delta d_i < 2.50$ Å with intercept 0.02 and slope 1.54. The few points with high values of δd_i correspond to distances to H atoms. The plot indicates that there are no systematic differences between the ethyl sulphate geometries in the two structures but that the standard deviations of the interatomic distances have on average been underestimated by a factor of 1.5 in the two structures.

The hydrogen bonds

The hydrogen-bond systems in the bromates and the ethyl sulphates can be compared in Figs. 1–3. Figs. 4

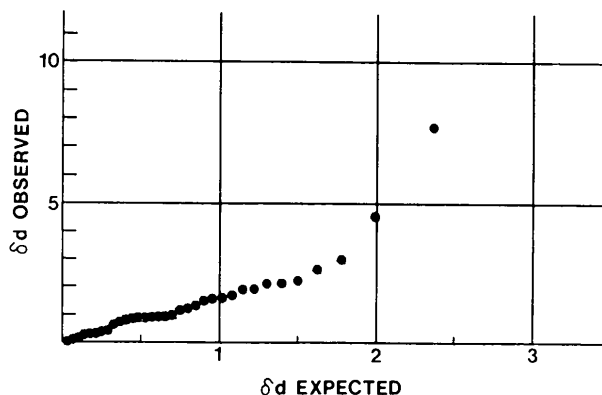


Fig. 6. A δd half-normal probability plot comparison of interatomic distances less than 4.65 Å in the ethyl sulphate molecule in PRET and YBET. Slope: 1.54, intercept: 0.02.

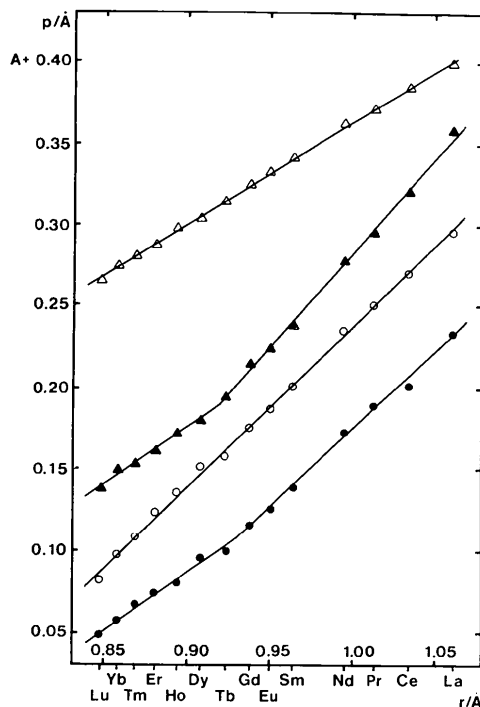


Fig. 7. The variation in the unit-cell dimensions ρ in the lanthanoid bromates and ethyl sulphates as a function of the ionic radius, r , of the six-coordinated lanthanoid ions. Legend: bromates a (●), $A = 11.65$; c (○), $A = 6.55$; ethyl sulphates a (▲), $A = 13.75$; c (△), $A = 6.75$.

and 5 provide a closer view of each bond. In the bromates all the water molecules are hydrogen-bonded to the bromate O(3) atoms which are acceptors of three hydrogen bonds each. This means that the plane of the O(2) water molecule coincides with the equatorial plane. In the ethyl sulphates the plane of this water molecule is perpendicular to the equatorial plane. Its hydrogen atoms, H(2), donate bonds to the sulphate O(5) atoms. H(1A) and H(1B), belonging to O(1) in the ethyl sulphates, donate bonds to O(3) and O(5) respectively. These sulphate O atoms are acceptors of two hydrogen bonds each (Fig. 5).

The hydrogen-bond lengths in PRBR and YBBR vary between 2.82 and 2.87 Å with no significant differences between the two structures. The O—H...O angles are in the range 150–180°. In both the ethyl sulphates the O(1)...O(3) bonds are about 0.1 Å shorter than the O(1)...O(5) and O(2)...O(5) bonds. The O—H...O angles vary between 162 and 177°.

Discussion

Fig. 7 shows a plot of the variations in the cell dimensions a and c vs the ionic radii of the lanthanoids (Templeton & Dauben, 1954). These radii are valid for coordination number (CN) 6 found in cubic oxides but can also be used to compare isostructural series of compounds internally, if CN differs from 6 (Shannon, 1976).

In both series, c decreases linearly with decreasing ionic radius but with different slopes: 1.00 for the bromates and 0.63 for the ethyl sulphates. Also a decreases with decreasing ionic radius, but here two lines can be drawn; one La–Tb with slope 0.96 for the bromate series and 1.15 for the ethyl sulphate series, and one Tb–Lu with slope 0.71 in both series. If the cell contraction was parallel to the decrease in ionic radius the slopes should be near $\sqrt{3}$ and 1.4 for the a and c curves respectively. (The actual value of the ideal c curve slope depends on the angle θ in Table 7; for strict linearity a constant value of this angle is also required through the whole Ln series, a condition that seems to be approximately fulfilled in the present compounds.)

In the single-crystal investigation we have found that the height of the TCTP's (parallel to c) does decrease as $1.4\Delta r$ between the Pr and Yb compounds (Δr is the lanthanoid contraction). The much smaller slopes of the c lines are probably caused by the obstructing rigidity of other parts of the structures (the packing forces) in the c direction. The different slopes of the two c lines might be due to the different hydrogen-bond systems in the bromates and ethyl sulphates. The hydrogen bonds donated by the O(2) water molecules may oppose the shortening of c in the ethyl sulphates as the bonds are in a plane parallel to c . These bonds are perpendicular to c in the bromates.

The edge of the equatorial triangle decreases, on average, $0.9\Delta r$ between the Pr and Yb compounds. The corresponding decrease in a is $0.86\Delta r$ in the bromates and $0.94\Delta r$ in the ethyl sulphates. For both series the slope of the a curves changes at Tb. In the ab plane the short O(1)–O(2) contacts in the coordination polyhedra around the ions Tb³⁺–Lu³⁺ apparently enhance the obstruction of the lanthanoid contraction caused by packing considerations. Albertsson (1970) reported a similar behaviour of the isostructural series of oxydiacetates Na₃[Ln(C₄H₄O₅)₃]·2NaClO₄·6H₂O, Ln = Ce–Lu. The Ln ion is also surrounded in these compounds by a slightly distorted TCTP of O atoms.

Which is the smallest Ln ion a hard-sphere model of TCTP can use as central ion if we assume 1.50 Å as the radius of the spheres (an estimation of the van der Waals radius of O in water)? For equal prismatic and equatorial metal–ligand distances, $\rho = 1$, the angle θ (Table 7) has the value $\arcsin(\frac{2}{3}) = 41.8^\circ$ in the hard-sphere model resulting in a metal–ligand distance of 2.60 Å. Central ions with radii less than $2.60 - 1.50 = 1.10$ Å would 'rattle' in this model, thus destabilizing the complex. 1.095 Å is the accepted ionic radius for Tb³⁺ with CN 9. This simple calculation thus indicates that van der Waals repulsion should occur between the ligands in a TCTP of O atoms around a Ln ion smaller than Gd³⁺, in agreement with our experimental result.

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Studies on Tellurium–Carbon Bonded Compounds. III.* The Crystal Structure of Acetylacetonone Tellurium(II)

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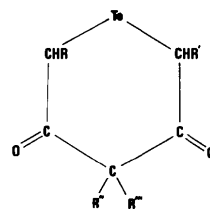
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The structure of the title compound has been determined by the heavy-atom method from 685 reflexions, measured with a diffractometer, and refined by full-matrix least-squares methods to R 3.4%. Crystals are orthorhombic, space group $Iba2$, $a = 22.35$ (3), $b = 10.78$ (2), $c = 5.26$ (1) Å, $Z = 8$. In the molecules of the complex a Te^{II} atom is bonded to one bivalent acetylacetonone ligand *via* the α -C atoms [$\text{Te}-\text{C}$ 2.17 (1), 2.15 (1) Å; $\text{C}-\text{Te}-\text{C}$ 90.8 (4)°] forming a heterocyclic ring of chair conformation. The molecules are arranged into one-dimensional polymers parallel to [001] by associations between the Te atoms; the implications of these associations with regard to the colour of this and related tellurium compounds are discussed in the light of present theories. H atoms could not be located.

Introduction

Many crystal structures of acetylacetonone complexes have been investigated by X-ray analysis in recent years (Anderson, Neuman & Melson, 1973; Dymock & Palenik, 1974; Hon & Pfluger, 1973; Montgomery & Lingafelter, 1964; Morosin, 1965, 1967; Morosin & Montgomery, 1969) and in all of these the ligand bonds *via* the O atoms behaving as a univalent bidentate ligand. The only anomalous examples so far reported are with Pt^{II} , Pt^{IV} and S (Figgis, Lewis, Long, Mason, Nyholm, Pauling & Robertson, 1962; Hazell, Swallow & Truter, 1959; Jones & Power, 1976; Mason, Robertson & Pauling, 1969; Swallow & Truter, 1960, 1962). In these cases the ligand can be either uni- or trifunctional. In the unifunctional case the ligand bonds to the Pt or S atom solely *via* the γ -C atom, and in the trifunctional case the β -diketone bonds *via* the O atoms of the carbonyl groups to one Pt atom and through the γ -C to another Pt atom.

We have previously reported NMR data (Dewan & Silver, 1976*a*) and the crystal structures of 3,3-dimethylacetylacetonone tellurium(II) (*A*) and 1,1'-dimethylacetylacetonone tellurium(II) (*B*) (Dewan & Silver, 1976*b,c*) wherein the β -diketone acts as a bivalent bidentate chelate bonding to the Te^{II} atom *via* the α -C atoms. This is the first time that acetylacetonone derivatives have been shown by X-ray analysis to bind in this manner. These Te compounds were prepared and reported by Morgan and co-workers (Morgan, 1925; Morgan & Drew, 1920, 1922, 1924*a,b*, 1925;



- (A): $\text{R} = \text{R}' = \text{H}$; $\text{R}'' = \text{R}''' = \text{CH}_3$
 (B): $\text{R} = \text{R}' = \text{CH}_3$; $\text{R}'' = \text{R}''' = \text{H}$
 (C): $\text{R} = \text{R}' = \text{H}$; $\text{R}'' = \text{R}''' = \text{H}$

* Part II: Dewan & Silver (1976c).