Short Communications

Structural Studies on the Rare Earth Carboxylates. 27. The Crystal Structure of Erbium Tris(oxydiacetato)erbate Hexahydrate, Containing Eight- and Nine-coordinated Erbium Ions

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In lanthanoid compounds with bidentate carboxylate ligands, the coordination number of the lanthanoid ion most often is nine for the largest and eight or nine for the smallest ions. The earlier reported lanthanoid compounds with the tridentate oxydiacetate ligand have the mononuclear nine-coordinate tris(oxydiacetato)lanthanoidate(III) complex through the whole lanthanoid series.[1-3] When preparing oxydiacetate compounds of composition M_2L_3, several phases were found. The crystals formed in the first part of the lanthanoid series were not stable, but the erbium compound, isostructural with the terbium one, could be investigated with X-ray diffraction methods.

Single crystals of erbium oxydiacetate were prepared by dissolving erbium hydroxide in a water solution of oxydiacetic acid (molar ratio 2:3) and evaporating at room temperature at pH 5 − 7. Addition of solutions of erbium chloride or sodium hydroxide to the solution resulted in identical crystals.

The crystal data are: $Er[Er(C_4H_4O_5)_3].6H_2O$; F.W. 918.8. Orthorhombic system; space group $C222_1$; $a = 8.744(1)$, $b = 17.685(2)$, and $c = 14.922(1)$ Å. $Z = 4$; $D_m = 2.32$ and $D_x = 2.41$ g cm^{-3}. $\mu(CuK\alpha) = 142$ cm^{-1}. Elemental analyses for Er, C, and H gave: Er 39.5; C 17.1; H 3.20. Calc. for $Er_2C_{12}H_{24}O_{26}$: Er 39.9; C 17.2; H 2.88. The unit cell dimensions were determined from powder photographs recorded at 23°C by a Guinier-Hägg camera.

The reflexions $hk0 − hk12$ were recorded at room temperature with nonintegrated Weissenberg multiple-film technique using Ni-filtered CuKα-radiation. A pink crystal, tabular b, with approximate dimensions $0.2 \times 0.2 \times 0.1$ mm^3 was used. The intensities of 1041 independent reflexions were estimated visually by com-

parison with a calibrated scale and corrected for Lorentz, polarization and absorption effects.

A three-dimensional vector map revealed the erbium ions in two fourfold positions, resulting in a false mirror plane at $z = 1/4$ in the difference map based only on erbium. The two images of the structure were slightly resolved by placing an oxygen atom in one of the highest peaks apart from the mirror plane. The atomic coordinates and temperature factors together with the interlayer scale factors were refined using a least-squares programme, minimizing $\sum w(|F_o| - |F_c|)^2$, and with weights according to Cruickshank.[4] The final value of R was 0.10 and of R_w 0.13. The atomic parameters and temperature factors are given in Table 1. The scattering factors were taken from Refs. 5 − 7. The Er scattering factor was corrected for anomalous dispersion.

The structure is composed of layers parallel to the ac-plane in which the coordination polyhedra around the two nonequivalent erbium ions are held together through coordination to Er(2) of outer carboxylate oxygen atoms of the tris(oxydiacetato)erbate complex around Er (1). Each Er (1) ion is thus linked to four Er (2) and vice versa, Fig. 1. Between these layers there seem to be only van der Waals forces. An indication of a fourth water oxygen in a fourfold position (which would give 7 H_2O in the formula) was obtained in the first difference map, but in later calculations this peak was both weakened and located too close to C(3), 2.4 Å. Furthermore, the temperature coefficient of the tentative atom refined to high values. Therefore it was excluded from this model of erbium oxydiacetate.

The Er(1) ion is nine-coordinated, surrounded by a distorted tricapped trigonal prism(TCTP) of carboxylate and ether oxygen atoms. The coordination is similar to that in the other oxydiacetates.[1-3] The distances from the erbium ion to the six carboxylate oxygens are in the range 2.33 − 2.36 Å (mean 2.35 Å) and the distances to the ether oxygens significantly longer, 2.49 − 2.50 Å. Compared to the cerium-oxygen distances in the other investigated oxydiacetates,[3] the former distance is 0.12 Å shorter, compatible with the decrease in ionic radius of 0.15 Å between cerium and erbium, while the latter distance is only 0.07 Å shorter. Using the same parameters as those defined in Table 5 of Ref. 3 to describe the TCTP polyhedron of Er(1) we obtain: $\varrho = 1.06$; $\theta = 47.8°$, torsion of prism 16.3°; tilt of triangular
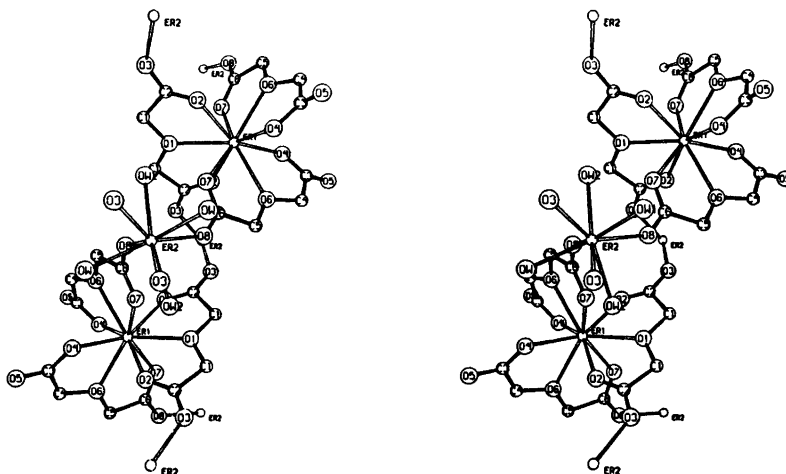
Fig. 1. A stereoscopic pair of drawings showing the coordination around the erbium ions looking down the *a*-axis. *b* is to the right and *c* upwards.

Table 1. Atomic parameters with estimated standard deviations in parentheses. *B* denotes the isotropic temperature factor.

Atom	x/a ($\times 10^4$)	y/b ($\times 10^4$)	z/c ($\times 10^4$)	B (Å^2)
Er(1)	0	1151(1)	2500	*a*
Er(2)	5078(2)	0	0	*a*
O(1)	0	−263(15)	2500	3.3 (5)
O(2)	1727(27)	518(13)	3420(17)	3.2 (4)
O(3)	2849(23)	−416(11)	4172(15)	2.6 (3)
O(4)	−1877(22)	2093(10)	2298(13)	2.4 (3)
O(5)	−3134(45)	3063(20)	1628(27)	5.9 (8)
O(6)	116(24)	1865(8)	1061(13)	2.5 (3)
O(7)	1798(19)	732(10)	1429(13)	2.1 (3)
O(8)	2939(24)	796(13)	119(16)	3.4 (4)
C(1)	1050(64)	−691(30)	3095(36)	6.1 (11)
C(2)	1893(26)	−114(13)	3628(19)	2.1 (4)
C(3)	−1812(39)	2624(19)	1748(25)	2.8 (6)
C(4)	− 706(40)	2557(19)	1043(26)	4.4 (6)
C(5)	1025(36)	1692(17)	386(24)	3.2 (6)
C(6)	2008(37)	1014(19)	674(25)	3.1 (6)
OW(1)	5921(21)	1148(10)	655(14)	2.6 (3)
OW(2)	4169(27)	−265(12)	1486(17)	3.7 (4)
OW(3)	4208(34)	2258(17)	1434(21)	5.3 (5)

a The anisotropic thermal parameters, calculated from the expression exp $[-(h^2\beta_{11}+2hk\beta_{12}+\ldots)]$, are for Er(1): $\beta_{11}=0.0047(4)$, $\beta_{22}=0.0014(1)$, $\beta_{33}=0.0021(3)$, $\beta_{12}=0$, $\beta_{13}=0.00020(2)$, $\beta_{23}=0$ and for Er(2): $\beta_{11}=0.0031(4)$, $\beta_{22}=0.0016(1)$, $\beta_{33}=0.0018(3)$, $\beta_{12}=0$, $\beta_{13}=0$, $\beta_{23}=0.00034(1)$.

faces to the equatorial plane: 3°, to each other: 5°; height of trigonal prism: 3.15 Å; edge of prismatic triangle: 2.99 − 3.07 Å, of equatorial triangle: 4.30 − 4.34 Å.

The Er(2) ion is eight-coordinated, surrounded by a distorted square antiprism of oxygen atoms, four of which are outer carboxylate oxygens (O(3) and O(8)), belonging to the four nearest Er(1)-polyhedra, and the others the water oxygen atoms OW(1) and OW(2) (*cf.* Fig. 1). The distances from the erbium ion to the oxygen atoms of the poly-

hedra are in the range 2.31−2.40 Å (mean 2.36 Å). The value of θ (angle between the erbium-oxygen bonds and the pseudo eightfold rotation inversion axis) is in the range 53.7−59.7° (mean 56.7°), in agreement with that found in erbium glycolate (Table 7 in Ref. 8). The distances along the edges of the square planes are in the range 2.78−2.80 Å, and the distance between these planes 2.59 Å. They are almost parallel with the a-axis and tilted 0.5° to each other.

The distances and angles within the ligand molecules are not far from those found in the other lanthanoid oxydiacetate compounds. The two halves of the ligand containing $O(1)−O(3)$ and $C(1)$, $C(2)$ are planar and the angle between them is 5°. In the other ligand the half containing $O(7)$ and $O(8)$ is planar while the other is more twisted (dihedral angles $O(6)−C(5)−C(6)−O(8)$: −179°, $O(6)−C(4)−C(3)−O(5)$: −151°). Apparently, $O(5)$ has refined to a somewhat erroneous location.

The $OW(3)$ water oxygen atom is not coordinated to erbium. It is within hydrogen bond distance from $O(5)$ (2.74 Å), $O(4)$ (2.80 Å), and $OW(1)$ (2.74 Å).

As this structure contains both eight- and nine-coordinated erbium ions, erbium seems to have a preference for eight-coordination when it is not forced by the ligands to adopt nine-coordination as in the tris(oxydiacetato)-erbate complex.

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Preparation and Structure of Stoichiometric δ-NbN

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The cubic phase of niobium nitride, δ-NbN, can be obtained in a reaction between niobium and nitrogen. A rod pressed isostatically from niobium powder was heated by induction in pure nitrogen gas at 2.0 MPa in an ADL MP crystal growth furnace. For experimental details see Ref. 1. The sample was 15 cm long and 10 mm in diameter. When the sample was red-hot, a violent and fast exothermic reaction between niobium and nitrogen started. The sample became incandescent and measurements with a disappearing filament pyrometer indicated that the temperature was at least 1800 °C. After approximately 20 s, the whole volume of the sample had reacted with nitrogen and the temperature of the specimen dropped to the level determined by the power of the induction heater.

A Guinier powder pattern obtained with a Guinier de Wolff camera with Cu$K\alpha_1$ radiation ($\lambda = 1.54051$ Å) and germanium ($a_{Ge} = 5.6576$ Å) as an internal standard showed that a sample treated as described above was cubic δ-NbN with $a = 4.394(3)$ Å. It was recently reported,[1] that zone melting of a specimen of δ-NbN at pressures up to 2 MPa resulted in a sample containing γ-NbN with the composition $NbN_{0.84(1)}$, and β-Nb_2N with the composition $NbN_{0.46(1)}$. A determination of the composition of δ-NbN is reported below.

A neutron diffraction powder pattern of δ-NbN was measured with a double axis neutron spectrometer at the DR3 reactor at Risø. The pattern was obtained with an incident neutron wave length of 0.998 Å, reflected from a (002) plane of a Be crystal. The collimations in front of and behind the sample were defined by Soller slits to be 21 and 30', respectively. The pattern was obtained for scattering angles (2θ) from 20 to 102° in steps of 0.2° and could be indexed with a cubic unit cell with $a = 4.39$ Å.

The structure of the compound was refined using the Rietveld refinement programs [2,3] for powder profile intensities. The scattering lengths [4] (in 10^{-12} cm) were: $b_{Nb} = 0.711$, and $b_N = 0.940$.

The intensities of the diffraction pattern had contributions from 18 reflections. Two of these, (400) and (440), had an additional scattering contribution from an unidentified impurity.

δ-NbN is isostructural with NaCl, space group $Fm3m$, No. 225, with niobium in site $4a$, and nitrogen in site $4b$. The variable parameters used in the refinements are: Two isotropic temperature factors, an occupancy factor for