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Polymeric aqua(nitrilotriacetato)-erbium(III)

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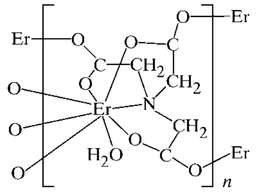
In the structure of the title compound, $[Er(C_6H_6NO_6)(H_2O)]_n$, the Er atoms are eight-coordinated by one N atom and six O atoms from three symmetry-related nitrilotriacetate (NTA) ligands, and by one O atom of a water molecule, adopting a distorted square-antiprismatic geometry. The Er atoms are linked by the NTA ligands into layers, which are interconnected *via* O—H···O hydrogen bonds between the water molecules and the carboxylate O atoms. The asymmetric unit contains one Er atom, one NTA ligand and one water molecule, all of which are located in general positions.

Comment

Owing to the enormous variety of intriguing structural topologies, much effort has been devoted to researching novel coordination materials using multidentate organic ligands to coordinate to metal centres (Philp & Stoddard, 1996; Yaghi *et al.*, 1998; Hagman *et al.*, 1999). The higher coordination numbers of lanthanide ions and the inherent flexibility of their coordination geometries might lead to some unprecedented topological architectures (Long *et al.*, 2000, 2001; Pan *et al.*, 2000). We are currently interested in pursuing synthetic strategies using lanthanide ions as nodes in the construction of polymeric frameworks. The nitrilotriacetate (NTA) ligand, which has six O atoms and one N atom as potential donors, is a rather versatile ligand for the synthesis of polymeric complexes containing lanthanide cations. To date, it is known that the NTA ligand may form at least three kinds of complexes with lanthanide elements, such as mononuclear cluster anions (Belyaeva *et al.*, 1974; Starynowicz, 1987; Chen *et al.*, 1989), polymeric complexes (Belyaeva *et al.*, 1968; Martin & Jacobson, 1972*a*,*b*) and heterometallic polymers (Liu *et al.*, 2000). As part of our investigations of new polycarboxylic-acid-bridged polymeric complexes, the title complex, $[Er(C_6H_6NO_6)(H_2O)]_n$, (I), was obtained as red crystals and its structure is presented here.



(I)

Compound (I) has a two-dimensional framework that is built up by connecting the crystallographically unique Er^{III} atom with its neighbours through bridging NTA ligands. For each NTA ligand, the N atom and one of the two O atoms in each carboxylate group coordinate to the same Er^{III} atom. The remaining three carboxylate O atoms in each ligand coordinate to three adjacent symmetry-related Er^{III} atoms. Six acetate O atoms, one N atom and one water ligand form a distorted square-antiprismatic coordination sphere about each metal centre (Fig. 1). The Er—N distance is about 0.24 Å longer than the average length of an Er—O(carboxylate)

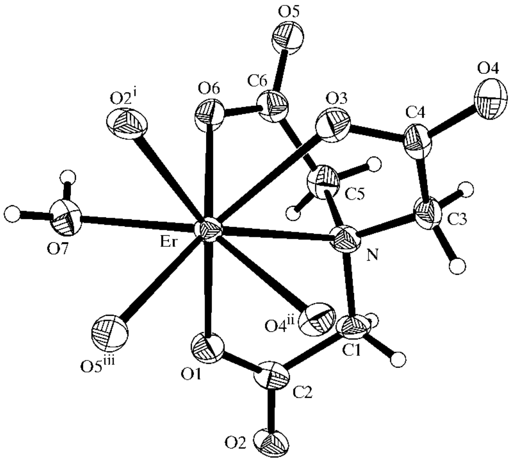


Figure 1
A perspective view of the locally expanded unit for (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii [symmetry codes: (i) $x - 1, y, z$; (ii) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (iii) $x, y - 1, z$].

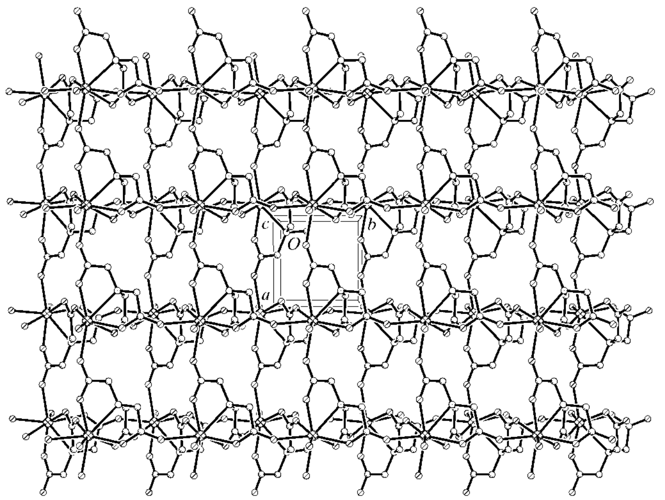


Figure 2
The crystal packing viewed down the *c* axis, showing the extended lamellar structure of (I). H atoms have been omitted for clarity.

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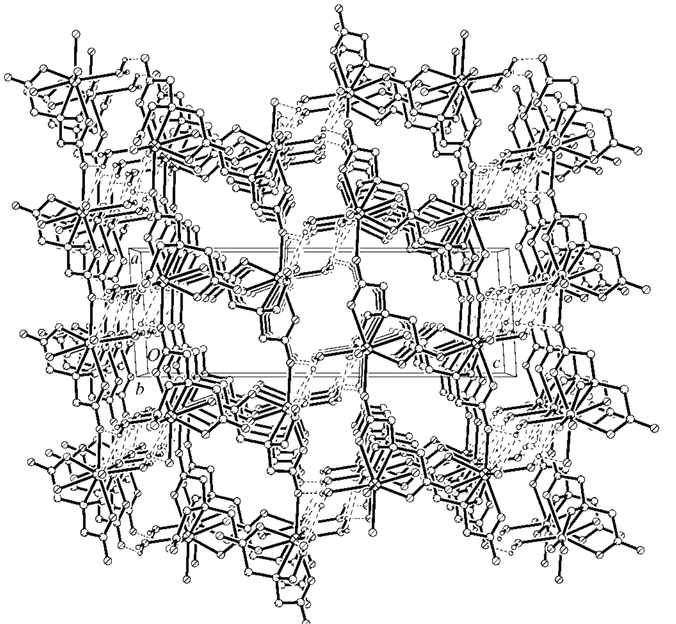

Figure 3
The crystal packing in (I) viewed down the *b* axis. Hydrogen bonding is indicated by dashed lines. For clarity, H atoms on C atoms have been omitted.

bond. The latter bonds show little variation, due to the similar coordination mode of the carboxylate groups (Table 1). The length of the Er—O bond involving the water ligand is similar to the Er—O distances involving the carboxylate groups.

Each NTA ligand acts as a bridging ligand, connecting four Er^{III} ions into a two-dimensional structure (Fig. 2). The two-dimensional polymer of (I) can be described as a trilayer. As shown in Fig. 3, all of the C, H and N atoms are in the middle 'layer', while the two covering 'sheets' are eight-coordinated Er^{III} centres, with all of the water ligands oriented to the outside of the trilayer. Furthermore, all of these trilayers are linked together through weak hydrogen bonding between the water ligands and the carboxylate O atoms of the NTA ligands, thus producing a three-dimensional framework in which the mean O···O hydrogen-bonding distance is 2.942 (9) Å.

Compared with the previously reported three-dimensional polymeric complexes $[Ln(NTA)(H_2O)_2]$ (Ln is Nd, Pr or Dy; Belyaeva *et al.*, 1968; Martin & Jacobson, 1972*a*,*b*), the replacement of one water ligand by one NTA carboxylate O atom causes the structure of (I) to become a two-dimensional lamellar structure. The difference results from the different coordination mode of the NTA ligand in (I), which prevents it from making the additional connections required to build a three-dimensional framework. This also suggests that the products obtained under hydrothermal reaction conditions are quite different from those obtained from syntheses conducted at room temperature.

Experimental

The pH of a mixture of $ErCl_3$ [1.0 mmol, prepared from Er_2O_3 (0.191 g) dissolved in 35% HCl] and nitrilotriacetic acid (0.19 g, 1.0 mmol) in H_2O (18 ml) was adjusted to 4.96 with 10% $NH_3\cdot H_2O$ under vigorous stirring. The reaction mixture was then heated at 443 K for 6 d under autogeneous pressure in a sealed 25 ml Teflon-lined stainless steel vessel. The reaction solution was cooled gradually and washed with water and ethanol, whereupon red crystals of (I) were isolated. Spectroscopic analysis, IR (solid KBr pellet, ν, cm^{-1}): 1599 (*s*), 1468 (*m*), 1429 (*s*), 1396 (*m*), 1338 (*m*), 1315 (*s*), 1300 (*m*), 1228 (*m*), 1132 (*m*), 1117 (*m*), 1024 (*s*), 991 (*m*), 970 (*m*).

Crystal data

$[Er(C_6H_6NO_6)(H_2O)]$
$M_r = 373.39$
Monoclinic, $P2_1/n$
$a = 6.7262\ (6)$ Å
$b = 6.5427\ (4)$ Å
$c = 19.800\ (2)$ Å
$\beta = 93.444\ (4)°$
$V = 869.8\ (1)$ Å^3
$Z = 4$

$D_x = 2.852$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 920 reflections
$\theta = 2.1$–$25.1°$
$\mu = 9.67$ mm^{-1}
$T = 293\ (2)$ K
Prism, red
0.16 × 0.08 × 0.06 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.328$, $T_{max} = 0.560$
2640 measured reflections

1520 independent reflections
1340 reflections with $I > 2\sigma(I)$
$R_{int} = 0.033$
$\theta_{max} = 25.1°$
$h = -5 \rightarrow 7$
$k = -7 \rightarrow 5$
$l = -23 \rightarrow 23$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.072$
$S = 1.09$
1520 reflections
137 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0119P)^2 + 12.9152P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.83$ e Å^{-3}
$\Delta\rho_{min} = -1.04$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0110 (5)

H atoms on C atoms were generated geometrically. The H atoms of the water ligand were clearly visible in difference maps, and these were placed in the difference map positions and constrained to ride on their parent O atom. All H atoms were assigned fixed isotropic displacement parameters, with $U_{iso}(H) = 1.2U_{eq}$(parent atom). The -1.04 e Å^{-3} hole in the final difference map is 0.83 Å from the Er atom.

Table 1
Selected geometric parameters (Å, °).

Er—O1	2.336 (6)	Er—O5^{iii}	2.309 (6)
Er—O2^{i}	2.359 (6)	Er—O6	2.312 (6)
Er—O3	2.373 (6)	Er—O7	2.343 (6)
Er—O4^{ii}	2.310 (6)	Er—N	2.575 (7)
O4^{ii}—Er—O1	86.3 (2)	O5^{iii}—Er—O4^{ii}	75.8 (2)
O5^{iii}—Er—O1	81.7 (2)	O4^{ii}—Er—O6	139.2 (2)
O6—Er—O1	100.3 (2)	O5^{iii}—Er—O6	144.8 (2)
O1—Er—O2^{i}	151.1 (2)	O1—Er—O7	78.7 (2)
O4^{ii}—Er—O2^{i}	105.4 (2)	O4^{ii}—Er—O7	147.9 (2)
O5^{iii}—Er—O2^{i}	75.9 (2)	O5^{iii}—Er—O7	74.1 (2)
O6—Er—O2^{i}	88.1 (2)	O6—Er—O7	71.9 (2)
O7—Er—O2^{i}	77.7 (2)	O1—Er—N	66.2 (2)
O1—Er—O3	130.5 (2)	O2^{i}—Er—N	141.8 (2)
O2^{i}—Er—O3	78.5 (2)	O3—Er—N	65.3 (2)
O4^{ii}—Er—O3	73.2 (2)	O4^{ii}—Er—N	76.3 (2)
O5^{iii}—Er—O3	132.4 (2)	O5^{iii}—Er—N	138.4 (2)
O6—Er—O3	72.1 (2)	O6—Er—N	70.2 (2)
O7—Er—O3	137.1 (2)	O7—Er—N	121.3 (2)

Symmetry codes: (i) $x-1, y, z$; (ii) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$; (iii) $x, y-1, z$.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O7—H7B···O2^{i}	0.90	2.30	2.983 (8)	133
O7—H7B···O5^{ii}	0.90	2.15	2.912 (9)	142
O7—H7A···O6^{ii}	0.82	2.42	2.932 (9)	122

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

Data collection: *SMART* (Siemens, 1996); cell refinement: *SMART* and *SAINT* (Siemens, 1994); data reduction: *SMART* and *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Siemens, 1994); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1137). Services for accessing these data are described at the back of the journal.

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