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Crystal structure of diaquadidysprosium triglutarate tetrahydrate, $Dy_2(H_2O)_2[O_2C(CH_2)_3CO_2]_3 \cdot 4H_2O$

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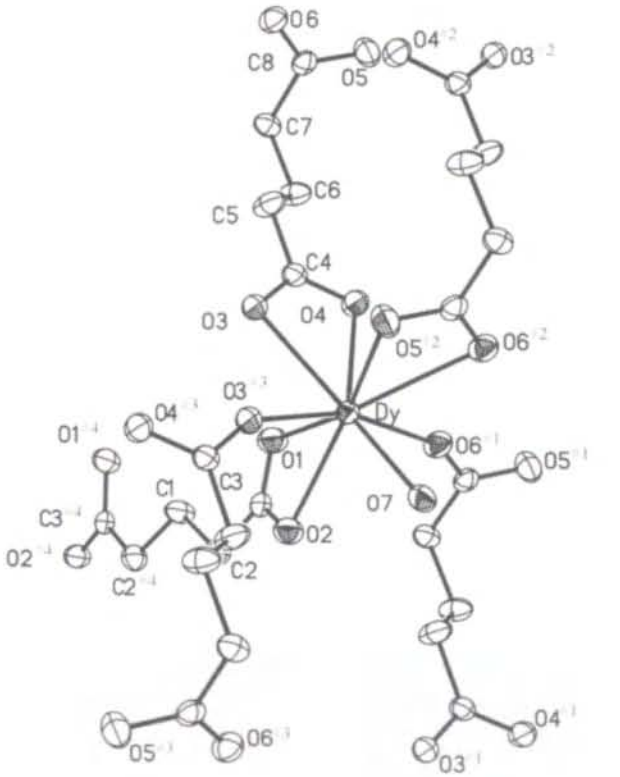

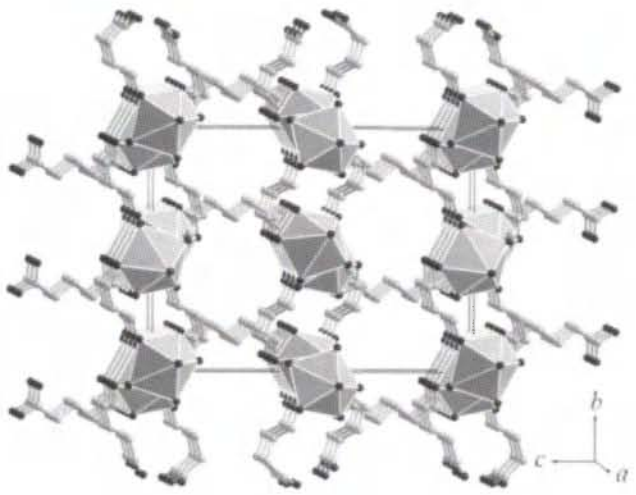

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Abstract

$C_{15}H_{26}Dy_2O_{18}$, monoclinic, $C12/c1$ (no. 15), a = 7.918(2) Å, b = 14.912(3) Å, c = 19.617(4) Å, β = 94.66(3)°, V = 2308.6 Å^3, Z = 4, $R_{gt}(F)$ = 0.027, $wR_{ref}(F^2)$ = 0.066, T = 293 K.

Source of material

0.0396 g (0.30 mmol) glutaric acid and 0.0595 g (0.30 mmol) 1,10-phenanthroline monohydrate were added to a stirred aqueous solution of $Dy(NO_3)_3 \cdot 5H_2O$ (0.1316 g, 0.30 mmol) in 10 ml doubly-distilled water. The resulting mixture (pH = 5.0) was loaded into a 23 ml Teflon-lined stainless steel autoclave, which was heated at 170 °C for three days, affording colorless crystals. The composition was confirmed by thermogravimetric analyses (weight loss for six moles of H_2O molecules per formula unit: calc. 13.13 %, obs. 12.8 % over 25 °C – 188 °C).

Discussion

The title compound was initially reported by Serpaggi and Férey [1] to be isostructural with $[Ln(H_2O)]_2[O_2C(CH_2)_3CO_2]_3 \cdot 4H_2O$ with *Ln* = Nd, Eu [2].

The asymmetric unit of the present dysprosium glutarate contains a Dy^{3+} cation, one and a half glutarate anions, an aqua ligand and two lattice H_2O molecules. The hydrogen atoms of the lattice water molecules were not localized. One glutarate anion (O1, O2, C1 to C3) is located on the twofold rotation axis passing through C3 atom and assumes an *anti/anti* conformation with non-hydrogen atoms nearly coplanar, while the other dicarboxylate ion (O3 to O6, C4 to C8) adopts an *anti/gauche* conformation. One lattice H_2O molecule (O8) is disordered over four sites with equal occupancies. The large temperature displacement parameters for O9 atom suggest that the water molecules of O9 are disordered ones. The Dy atoms are each coordinated by nine oxygen atoms of one aqua ligand, one *anti/anti* and four *anti/gauche* conformational glutarate anions to form distorted mono-capped tetragonal antiprism DyO_9 with d(Dy—O) = 2.344 Å–2.669 Å, ∠O–Dy–O = 65.9° – 162.3° being comparable with those observed in the literature [3,4]. The *anti/anti* conformational dicarboxylate bischelate two Dy atoms, and as far as the *anti/gauche* one is concerned, each terminal carboxylate group chelates one Dy atom with one oxygen atom additionally bonded to second metal atom. Through O3, O6 and their symmetry related partners, the DyO_9 polyhedra are edge-shared to generate 1D metal-oxygen chains extending in the [100] direction and the resulting chains are then bridged by the *anti/gauche* conformational glutarate anions into 2D brick-wall parallel to (001), which are further linked by the bischelating dicarboxylate anions to form 3D framework with the tunnels in the [100] direction filled with the lattice H_2O molecules. The glutarate anions exhibit normal bonding values comparable with those reported in the literature [5-7].

Table 1. Data collection and handling.

Crystal:	colorless block, size 0.05 × 0.05 × 0.12 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	65.10 cm^{-1}
Diffractometer, scan mode:	Bruker P4, $\theta/2\theta$
$2\theta_{max}$:	55°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3483, 2653
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2267
$N(param)_{refined}$:	155
Programs:	SHELXS-97 [8], SHELXL-97 [9]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{iso}
H(2A)	8*f*	−0.0131	−0.2337	0.3219	0.032
H(2B)	8*f*	0.1681	−0.2250	0.2960	0.032
H(3A)	8*f*	−0.0877	−0.0966	0.2650	0.034
H(5A)	8*f*	0.0590	0.2650	0.4621	0.038
H(5B)	8*f*	−0.0707	0.2208	0.4076	0.038
H(6A)	8*f*	0.1327	0.2274	0.3265	0.035
H(6B)	8*f*	0.2605	0.2733	0.3811	0.035
H(7A)	8*f*	0.1140	0.3785	0.3028	0.029
H(7B)	8*f*	−0.0537	0.3551	0.3366	0.029
H(7BB)	8*f*	0.4806	−0.1366	0.5671	0.035
H(7AA)	8*f*	0.3621	−0.2008	0.5566	0.035
H(9BB)	8*f*	0.6268	0.0578	0.2576	0.284
H(9AA)	8*f*	0.6787	0.0398	0.1940	0.284

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Dy	8*f*		0.24288(2)	−0.03725(1)	0.48756(1)	0.0167(1)	0.0164(1)	0.0231(1)	−0.00010(8)	0.00214(7)	0.00041(8)
O(1)	8*f*		0.1445(5)	−0.0537(2)	0.3696(2)	0.035(2)	0.023(2)	0.031(2)	0.002(1)	−0.002(2)	−0.000(1)
O(2)	8*f*		0.1666(4)	−0.1776(2)	0.4290(2)	0.033(2)	0.023(2)	0.028(2)	−0.001(1)	−0.002(1)	0.002(1)
C(1)	8*f*		0.1292(5)	−0.1374(3)	0.3725(2)	0.015(2)	0.022(2)	0.031(2)	0.000(2)	0.001(2)	0.000(2)
C(2)	8*f*		0.0724(6)	−0.1911(3)	0.3101(2)	0.028(2)	0.027(2)	0.025(2)	0.001(2)	−0.003(2)	0.002(2)
C(3)	4*e*		0	−0.1346(4)	¼	0.037(4)	0.022(3)	0.025(3)	0	−0.008(3)	0
O(3)	8*f*		0.0126(4)	0.0778(2)	0.4670(2)	0.020(2)	0.021(2)	0.035(2)	−0.002(1)	0.003(1)	0.001(1)
O(4)	8*f*		0.2675(4)	0.1131(2)	0.4419(2)	0.021(2)	0.022(2)	0.044(2)	−0.001(1)	0.007(1)	0.005(2)
C(4)	8*f*		0.1126(5)	0.1345(3)	0.4444(2)	0.021(2)	0.017(2)	0.027(2)	−0.002(2)	0.004(2)	−0.001(2)
C(5)	8*f*		0.0487(7)	0.2254(3)	0.4227(3)	0.030(2)	0.019(2)	0.047(3)	0.007(2)	0.013(2)	0.007(2)
C(6)	8*f*		0.1414(7)	0.2670(3)	0.3659(3)	0.035(3)	0.021(2)	0.033(3)	0.003(2)	0.015(2)	−0.001(2)
C(7)	8*f*		0.0685(6)	0.3593(3)	0.3449(2)	0.029(2)	0.021(2)	0.023(2)	−0.002(2)	0.001(2)	0.001(2)
C(8)	8*f*		0.1128(6)	0.4267(3)	0.4001(2)	0.023(2)	0.018(2)	0.024(2)	0.003(2)	0.000(2)	0.006(2)
O(5)	8*f*		0.2616(4)	0.4535(2)	0.4091(2)	0.025(2)	0.036(2)	0.035(2)	−0.006(2)	0.004(1)	−0.010(2)
O(6)	8*f*		0.0036(4)	0.4551(2)	0.4392(2)	0.025(2)	0.026(2)	0.031(2)	0.004(1)	0.007(1)	−0.001(1)
O(7)	8*f*		0.3819(4)	−0.1442(2)	0.5602(2)	0.027(2)	0.021(2)	0.039(2)	−0.005(1)	−0.005(1)	0.006(1)
O(8AA)	8*f*	0.25	0.9166(4)	0.0882(2)	0.3005(2)	0.06(1)	0.054(4)	0.066(4)	−0.016(6)	0.004(6)	−0.005(4)
O(8AB)	8*f*	0.25	0.9710(4)	0.0936(2)	0.2952(2)	0.06	0.054	0.066	−0.016	0.004	−0.005
O(8BA)	8*f*	0.25	0.8657(4)	0.0929(2)	0.3032(2)	0.06	0.054	0.066	−0.016	0.004	−0.005
O(8BB)	8*f*	0.25	0.7996(4)	0.0888(2)	0.2964(2)	0.06	0.054	0.066	−0.016	0.004	−0.005
O(9)	8*f*		0.6198(4)	0.0710(2)	0.2153(2)	0.31(2)	0.20(1)	0.22(2)	−0.04(1)	0.13(1)	−0.08(1)

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