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Tris(hydrogen oxydiacetato)dysprosium(III) oxydiacetic acid monohydrate

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Key indicators

Single-crystal X-ray study
T = 297 K
Mean σ(C–C) = 0.005 Å
Disorder in main residue
R factor = 0.028
wR factor = 0.072
Data-to-parameter ratio = 12.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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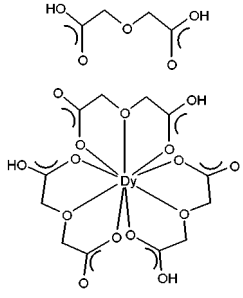
The title compound, $Dy(Hoda)_3.H_2oda\cdot H_2O$ (H_2oda: oxydiacetic acid) or $[Dy(C_4H_5O_5)_3]\cdot C_4H_6O_5\cdot H_2O$, crystallizes in the monoclinic space group $P2_1/n$ and is isostructural with the homologous Y, Gd, and Tb compounds. The structure is described in terms of $Dy(Hoda)_3$ layers connected by H_2oda molecules and intermolecular hydrogen bonds.

Comment

Because of their applicability in absorption, separation and catalysis, attention has been extensively focused on pillared structures (Mitchell, 1990). These are based on transition metal compounds with layered structural motifs, connected by organic molecules of variable length and/or type (Pan *et al.*, 2001). The object of our work was to investigate pillared structures with rare-earth carboxylates. For the versatile rare-earth–oxydiacetic acid system, the isostructural compounds formulated as $[Ln(Hoda)_3\cdot H_2oda\cdot H_2O]$ for Ln = Gd (Baggio *et al.*, 1997), Y (Baggio *et al.*, 1998) and Tb (Barja *et al.*, 2003) have been reported. These consist of $Ln(Hoda)_3$ layers, connected by neutral oxydiacetic acid as the pillar molecule. Due to the lanthanide contraction, a number of neighboring homologous compounds of the lanthanide elements with different electronic and magnetic properties may present essentially the same crystal structures. The study of these families allows us to compare and understand the roles of the individual rare-earth atoms and to verify theories in a wider range of situations. Attempts to prepare a homologous (and potentially isostructural) compound for the slightly lighter element europium in the Eu, Gd, Tb, Dy lanthanide series afforded a radically different structure, *viz*. $[Eu(oda)(Hoda)(H_2O)]\cdot 2H_2O]$ (Aramendia *et al.*, 2000). On the other hand, for the slightly heavier element dysprosium, a new member of the isostructural series, $[Dy(Hoda)_3\cdot H_2oda\cdot H_2O]$, (I), was successfully obtained and its crystal structure is reported here.



(I)

The building block of the extended structure is shown in Fig. 1. It consists of three different groups, *viz*. a compact

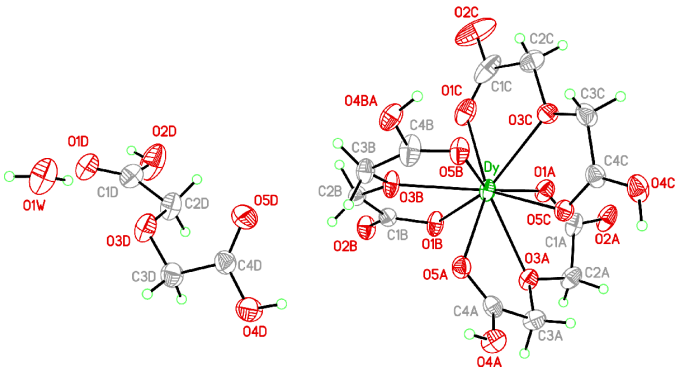


Figure 1
A molecular diagram showing the atom-numbering scheme used. Only one of the two disordered O4*B* positions has been represented, for clarity. Displacement ellipsoids drawn at a 40% probability level.

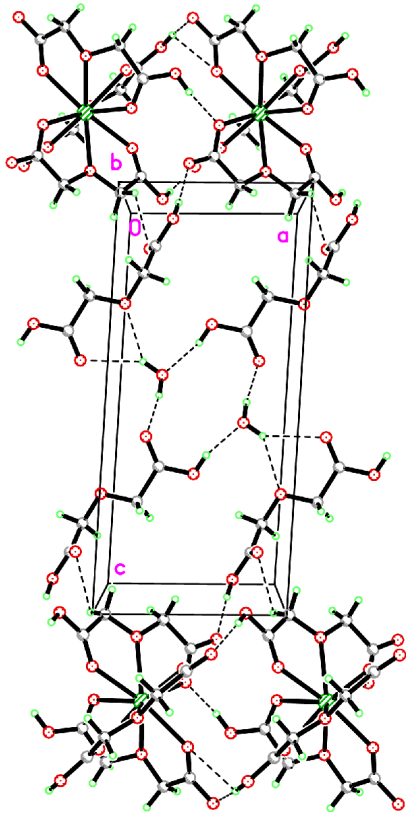


Figure 2
Packing view showing the layered structure of alternating Dy(Hoda)$_3$ and (H_2oda+H_2O) planes, and the main hydrogen-bonding interactions linking them.

Dy(Hoda)$_3$ unit, an H_2oda free acid and a molecule of water of crystallization. A detailed discussion of the monomeric structure has already been made in the above-mentioned publication on the gadolinium compound (Baggio *et al.*, 1997) for it will not be repeated here (for slight differences due to disorder see the *Refinement* section). There is, however, a qualitative improvement in the present work, with the possibility of restrained refinement of H-atom positions. This permits a detailed description of the hydrogen-bond interactions in the extended structure built solely by intermolecular hydrogen bonds (Fig. 2). There are nine strong O—H···O and seven weak C—H···O hydrogen bonds in the structure, listed in Table 2. The strong interactions serve mainly to link the Dy(Hoda)$_3$ units into planar structures parallel to (010) at $y \sim 0.25$, 0.75 (entries 1–4 in Table 2) and the H_2oda and water molecules into planes parallel to the former and lying in between, at $y \sim 0$, 0.50 (entries 5–8). A strong interaction O4*D*—H4*D*···O2*B*$(1+x,\ y,\ z)$ links neighboring planes (entry 9). The weak C—H···O interactions operate between planes (entries 10–16), contributing to the stabilization of the structure.

Experimental

Dysprosium carbonate hydrate 99.99% (0.25 g, 0.5 mmol) was added to an aqueous solution (20 ml) of oxydiacetic acid (0.70 g, 5 mmol). After stirring for 2 h under reflux, the solution was filtered and the filtrate was kept at pH = 3 for a week, whereupon colorless crystals of the product suitable for X-ray analysis were collected by filtration and dried in air. Analysis calculated for $C_{16}H_{23}DyO_{21}$: C 26.90, H 3.22%; found: C 27.00, H 3.25%. The IR spectrum showed the presence of acid carbonyl groups (1740–1680 cm^{-1}), carboxylate anions (1597 and 1445 cm^{-1}) and water molecules (1641 and 3550 cm^{-1}).

Crystal data

$[Dy(C_4H_5O_5)_3]\cdot C_4H_6O_5\cdot H_2O$
M_r = 713.84
Monoclinic, $P2_1/n$
a = 6.5585 (5) Å
b = 25.1747 (19) Å
c = 14.6163 (11) Å
β = 93.259 (1)°
V = 2409.4 (3) Å^3
Z = 4
D_x = 1.968 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 146 reflections
θ = 2.4–24.6°
μ = 3.20 mm^{-1}
T = 297 (2) K
Plate, colorless
0.28 × 0.22 × 0.14 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS* in *SAINT-NT*; Bruker, 2002)
T_{min} = 0.44, T_{max} = 0.64
19843 measured reflections
5363 independent reflections
4651 reflections with $I > 2\sigma(I)$
R_{int} = 0.030
θ_{max} = 28.0°
$h = -8 \rightarrow 8$
$k = -31 \rightarrow 32$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.072
S = 0.89
5363 reflections
423 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.045P)^2 + 2.6742P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.004
$\Delta\rho_{max}$ = 0.59 e Å^{-3}
$\Delta\rho_{min}$ = −0.85 e Å^{-3}

Table 1
Selected geometric parameters (Å).

Dy—O1*A*	2.294 (2)	Dy—O5*A*	2.396 (2)
Dy—O1*C*	2.313 (3)	Dy—O3*B*	2.434 (2)
Dy—O5*C*	2.339 (2)	Dy—O3*C*	2.469 (3)
Dy—O5*B*	2.365 (2)	Dy—O3*A*	2.565 (2)
Dy—O1*B*	2.392 (2)		

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

D—H···A	D—H	H···A	D···A	D—H···A
O4A—H4A···O1B^{i}	0.86 (2)	1.77 (2)	2.592 (3)	161 (2)
O4BA—H4BA···O2C^{i}	0.85 (2)	1.89 (2)	2.696 (6)	160 (2)
O4BB—H4BB···O1C^{i}	0.86 (2)	1.62 (3)	2.464 (7)	169 (8)
O4C—H4C···O2A^{i}	0.88 (2)	1.61 (2)	2.488 (4)	173 (3)
O1W—H1WA···O3D	0.85 (2)	2.28 (3)	2.998 (4)	142 (4)
O1W—H1WA···O1D	0.85 (2)	2.32 (3)	3.066 (4)	146 (4)
O1W—H1WB···O1D^{ii}	0.85 (2)	2.07 (2)	2.898 (4)	166 (5)
O2D—H2D···O1W^{iii}	0.83 (2)	1.80 (2)	2.608 (5)	164 (5)
O4D—H4D···O2B^{i}	0.84 (2)	1.78 (2)	2.617 (4)	169 (5)
C2A—H2AB···O2C^{iv}	0.97 (2)	2.32 (2)	3.288 (5)	171 (3)
C2B—H2BA···O4C^{v}	0.97 (2)	2.51 (2)	3.253 (4)	134 (3)
C3B—H3BB···O4C^{v}	0.97 (2)	2.43 (2)	3.127 (4)	129 (2)
C3C—H3CB···O5D^{vi}	0.97 (2)	2.49 (2)	3.375 (5)	153 (3)
C2B—H2BB···O4D^{vii}	0.97 (2)	2.57 (2)	3.381 (4)	141 (3)
C3B—H3BA···O5D	0.97 (2)	2.53 (3)	3.176 (4)	124 (2)
C2D—H2DA···O2B^{viii}	0.97 (2)	2.61 (2)	3.547 (5)	162 (3)

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

H atoms attached to carbon were positioned geometrically, while those attached to oxygen were found in a difference Fourier map. All were refined with restrained bond lengths [C—H = 0.96 (2) Å and O—H = 0.85 (2) Å]. One of the carboxylate O atoms (O4B) appeared disordered over two almost equally populated sites [occupancies: O4BA = 0.571 (4) and O4BB 0.429 (4)]. Related structures were identified by use of version 5.24 (November 2002 and updates) of the Cambridge Structural Database (Allen, 2002).

Data collection: *SMART-NT* (Bruker, 2001); cell refinement: *SMART-NT*; data reduction: *SAINT-NT* (Bruker, 2002); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL-NT* (Sheldrick, 1994); software used to prepare material for publication: *SHELXTL-NT*.

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