

Di- μ -*trans*-2-butenato- κ^3 O,O,O'-di- μ -*trans*-2-butenato- κ^2 O,O'-bis[(*trans*-2-butenato- κ^2 O,O')(1,10-phenanthroline- κ^2 N,N')]dysprosium(III)] dihydrate

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Key indicators

Single-crystal X-ray study

$T = 297$ K

Mean $\sigma(\text{C}-\text{C}) = 0.008$ Å

H-atom completeness 93%

Disorder in solvent or counterion

R factor = 0.036

wR factor = 0.092

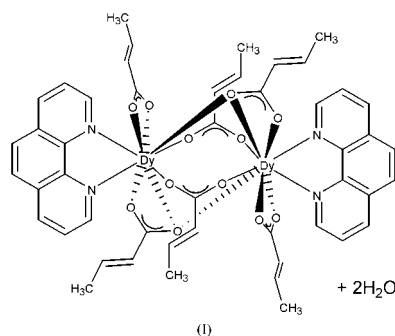
Data-to-parameter ratio = 14.8

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

The title compound, $[\text{Dy}_2(\text{C}_4\text{H}_5\text{O}_2)_6(\text{C}_{12}\text{H}_8\text{N}_2)_2]\cdot 2\text{H}_2\text{O}$, crystallizes as dimeric units with an inversion center. Each Dy atom is nine-coordinate, by seven O atoms from *trans*-2-butenato groups and two N atoms from a phenanthroline molecule. The dimer is quadruply bridged by *trans*-2-butenates (two $\eta^1:\eta^1:\mu_2$ and two $\eta^2:\eta^1:\mu_2$ bridges). The intradimer Dy...Dy separation is 3.9003 (5) Å.

Comment

The characterization of carboxylate-bridged 4*f*-4*f* homodinuclear compounds is attracting growing interest in the field of materials science due to their luminescent, sensory and magnetic properties (Kahn *et al.*, 2000). Until recently pure and well characterized complexes of this type have been scarce and mostly limited to carboxylate compounds containing gadolinium for its orbital non-degeneracy. Homodinuclear Ln carboxylates with a quadruply bridged core with two $\eta^1:\eta^1:\mu_2$ and two $\eta^2:\eta^1:\mu_2$ bridges were reported for $[\text{Gd}_2(\text{CH}_3\text{CO}_2)_6(\text{phen})_2]\cdot 2\text{H}_2\text{O}$ (Panagiotopoulos *et al.*, 1995) and for $[\text{Ln}(\text{HL})_3(\text{H}_2\text{O})_2]$ (Ln = Er, Gd; H_2L = salicylic acid) (Costes *et al.*, 2002). Recently, three new compounds with similar quadruply bridged cores have been reported for $[\text{Ln}_2(\text{L})_6(\text{phen})_2]\cdot 2\text{H}_2\text{O}$ (Ln = Gd (Rizzi *et al.*, 2003) and Eu and Tb (Barja *et al.*, 2003; HL = *trans*-2-butenic acid).



The lanthanide contraction phenomenon results in close similarities in the chemical properties of homologous compounds in the series. In particular, investigations within a group of isostructural compounds are of interest since they allow a chosen physical property to be examined (*e.g.* the magnetic behavior), avoiding any change due to structural differences.

We now report a new isostructural member of this $[\text{Ln}_2(\text{L})_6(\text{phen})_2]\cdot 2\text{H}_2\text{O}$ series, *viz.* $[\text{Dy}(\text{C}_4\text{H}_5\text{O}_2)_3(\text{C}_{12}\text{H}_8\text{N}_2)]_2\cdot 2\text{H}_2\text{O}$, (I). Its molecular structure is shown in Fig. 1; it is a dimer built up around a symmetry center; its asymmetric unit (drawn as full displacement ellipsoids) is composed of a nine-

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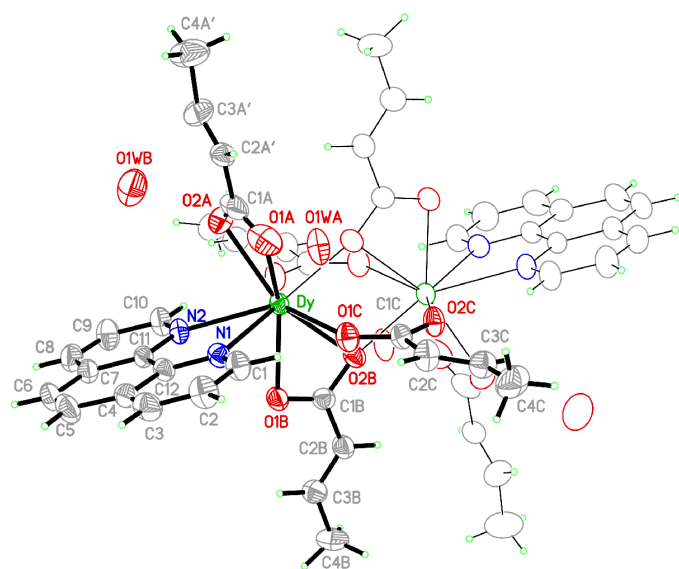


Figure 1
The molecular structure of the dimer with the symmetry-independent part enhanced. Only the main component of the disordered *trans*-2-butenoate 'A' is shown, for clarity. Displacement ellipsoids are drawn at the 40% probability level.

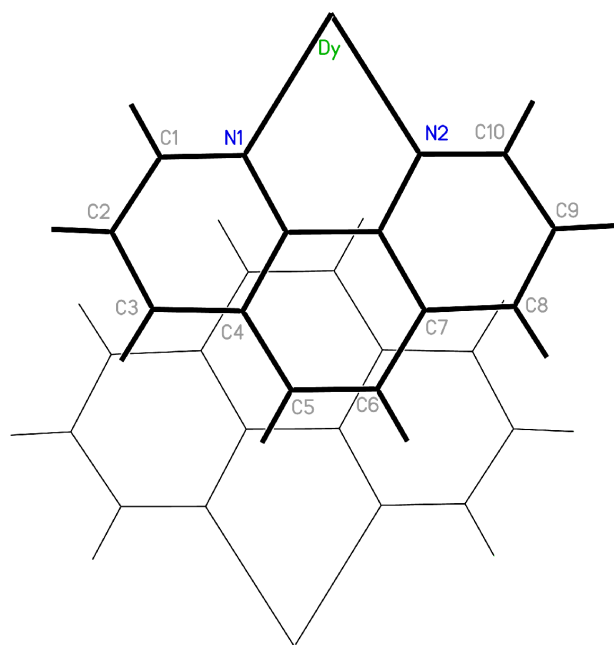


Figure 2
Schematic view normal to the interacting phen groups, showing their partial overlap.

coordinate dysprosium cation surrounded by seven O atoms from five *trans*-2-butenoates (one partially disordered over two almost equally populated sites) and two N atoms from a phenanthroline molecule. The *trans*-2-butenoate units display three different coordination modes: *O,O'*-chelating, μ_2 -*O,O'*-bridging and μ_2 -*O,O,O'*-tridentate bridging. The bridging core consists of two pairs of bridges (two $\eta^2:\eta^1:\mu_2$ and two $\eta^1:\eta^1:\mu_2$) which define two closed loops around the same symmetry center, their mean planes subtending a dihedral angle of 89.2 (1)°. The Dy...Dy separation is 3.900 (1) Å, compared to

3.953 (1), 3.937 (2) and 3.911 (1) Å for the isostructural Eu^{III}, Gd^{III} and Tb^{III} dimers.

A search in the CSD (November 2002 and updates; Allen, 2002) showed this structure to be the first fully reported dysprosium carboxylate complex with a quadruply bridged core. Only three other carboxylate-bridged structures are listed, which display the double μ_2 -*O,O'*-bridging mode built around symmetry centers. As expected, the latter compounds with only two μ_2 -*O,O'*-carboxylate bridges showed larger Dy...Dy distances (4.14–4.6 Å).

The dinuclear cores in (I) are well separated from each other. A non-bonding interaction operates through the π - π contact between neighboring phen groups related by the symmetry operation (2 - x, 1 - y, 1 - z). As a result, the phen groups are parallel to each other tail-to-head and with their mean planes displaced by 3.38 (1) Å. The central aromatic rings overlap *ca* 60% of their total area, with a slippage between centers of 0.89 (1) Å (Fig. 2). The values are typical for this type of interactions (Janiak, 2000). Otherwise some tentative contacts can be inferred from the short O...O_W distances; however, these are partially occupied sites and no H atoms could be located.

Experimental

To a solution of 1,10-phenanthroline (0.2 g, 1.2 mmol) in water-ethanol (1:1, 50 ml) was added Gd₂O₃ (0.12 g, 0.3 mmol) and *trans*-2-butenoic acid (0.22 g, 2.5 mmol). The mixture was heated under reflux for 8 h, cooled and passed through a glass filter. The filtrate was stored for a few weeks; colorless crystals of the title compound were then filtered off and dried in air (yield 70%).

Crystal data

[Dy₂(C₄H₅O₂)₆(C₁₂H₈N₂)₂].2H₂O
M_r = 1231.92
 Triclinic, *P* $\bar{1}$
a = 10.5490 (8) Å
b = 10.9773 (9) Å
c = 11.4134 (9) Å
 α = 78.9910 (10)°
 β = 71.7230 (10)°
 γ = 77.3540 (10)°
V = 1213.83 (17) Å³

Z = 1
D_x = 1.685 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 217 reflections
 θ = 2.1–22.9°
 μ = 3.12 mm⁻¹
T = 297 (2) K
 Block, colorless
 0.32 × 0.24 × 0.12 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS in S_{AINT}-NT; Bruker, 2002)
T_{min} = 0.42, *T_{max}* = 0.69
 9966 measured reflections

5166 independent reflections
 4598 reflections with *I* > 2σ(*I*)
R_{int} = 0.025
 θ_{max} = 27.9°
h = -13 → 13
k = -14 → 14
l = -14 → 14

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.036
wR(*F*²) = 0.092
S = 1.02
 5166 reflections
 350 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0535P)^2 + 0.5535P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.011$
 $\Delta\rho_{max} = 1.54 \text{ e \AA}^{-3}$
 $\Delta\rho_{min} = -0.84 \text{ e \AA}^{-3}$

Table 1
Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C1—H1A \cdots O1C	0.93	2.43	3.042 (6)	124
C6—H6A \cdots O1WA ⁱ	0.93	2.45	3.318 (14)	155
C10—H10A \cdots O2C ⁱⁱ	0.93	2.35	3.020 (6)	128

Symmetry codes: (i) $x, 1 + y, z$; (ii) $2 - x, -y, 2 - z$.

One of the *trans*-2-butenate groups (*A*) appeared disordered, with three of the C atoms disordered over two almost equally populated sites [primed site 0.57 (4), and double primed site 0.43 (4)]. They were refined with similarity restraints to assure a reasonable geometry. Also, the water molecule appeared split over two sites with occupation factors of 0.27 (3) and 0.73 (3). H atoms attached to carbon were placed at their expected positions and allowed to ride on the host carbon [$C-H = 0.93$ Å and $U_{iso}(H) = 1.2U_{eq}(C)$]. Those belonging to the disordered water molecule were not found and accordingly not included in the model. Full use of the CCDC package was made to search version 5.24 of the CSD Database (November 2002 and updates; Allen, 2002). The largest peaks in the difference Fourier map were found *ca.* 0.85 ÅÅ from the dysprosium atom.

Data collection: *SMART-NT* (Bruker, 2001); cell refinement: *SMART-NT*; data reduction: *SAINT-NT* (Bruker, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular

graphics: *SHELXTL-PC* (Sheldrick, 1994); software used to prepare material for publication: *SHELXL97*.

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