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Tetrakis(μ-4-chlorobenzoato)bis[(4-chlorobenzoato)(1,10-phenanthroline)dysprosium(III)]

Bi-Song Zhang

Normal College, Jinhua University, Jinhua, Zhejiang 321017, People's Republic of China

Correspondence e-mail: zbs_jy@163.com

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Key indicators

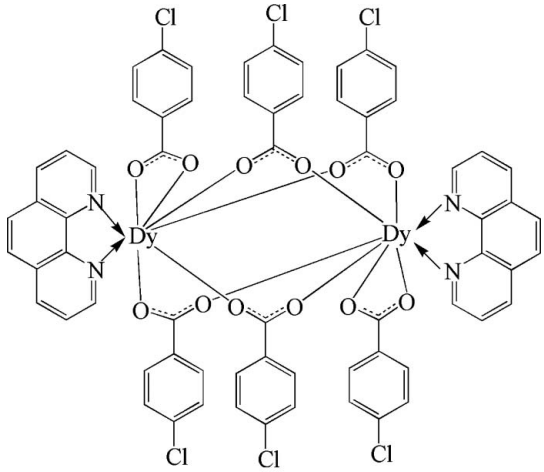
Single-crystal X-ray study
T = 290 K
Mean σ(C–C) = 0.009 Å
R factor = 0.047
wR factor = 0.080
Data-to-parameter ratio = 17.0

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

In the title dinuclear centrosymmetric compound, $[Dy_2(C_7H_4ClO_2)_6(C_{12}H_8N_2)_2]$, the Dy^{III} atom is coordinated in a distorted square-antiprismatic geometry by two N atoms from one bidentate chelating phenanthroline ligand and six O atoms from five 4-chlorobenzoate anions. The dinuclear molecules are linked into a three-dimensional network through weak hydrogen bonds and π–π stacking interactions.

Comment

Lanthanide complexes play an important role in specialty materials (Daiguebonne *et al.*, 2000; Farrugia *et al.*, 2000). The crystal structures of compounds of the general formula $[Ln_2(C_{12}H_8N_2)_2(C_6H_5COO)_6]$ have been reported for La, Eu and Tb (Shi *et al.*, 2001); the related compounds $[Eu_2(C_{12}H_8N_2)_2\{(CH_3)_2C_6H_3COO\}_6]$ (Wang *et al.*, 1999) and $[Tb_2(C_{12}H_8N_2)_2(CH_3C_6H_4COO)_6]\cdot H_2O$ (Wang *et al.*, 2002) are also known. The varied coordination modes of lanthanide elements and halobenzoate groups also stimulated our interest in this work; we reported $[Ho(BrC_6H_4COO)(phen)(\mu\text{-}BrC_6H_4COO)_{4/2}]_2$ (Zhang *et al.*, 2005). We have now synthesized the title new dinuclear Dy^{III} compound $[Dy(ClC_6H_4COO)(phen)(\mu\text{-}ClC_6H_4COO)_{4/2}]_2$, (I).



(I)

In (I), two Dy atoms are bridged by four 4-chlorobenzoate anions to form a binuclear cage structure. Two of these 4-chlorobenzoate anions also behave as chelating ligands. Another 4-chlorobenzoate anion and a 1,10-phenanthroline molecule chelate to the Dy atom (Fig. 1). The eight-coordinate environment of Dy is defined by six O and two N atoms. The chelating phen ligand is planar, and the phen ligands are sandwiched by two phen ligands from two neighboring

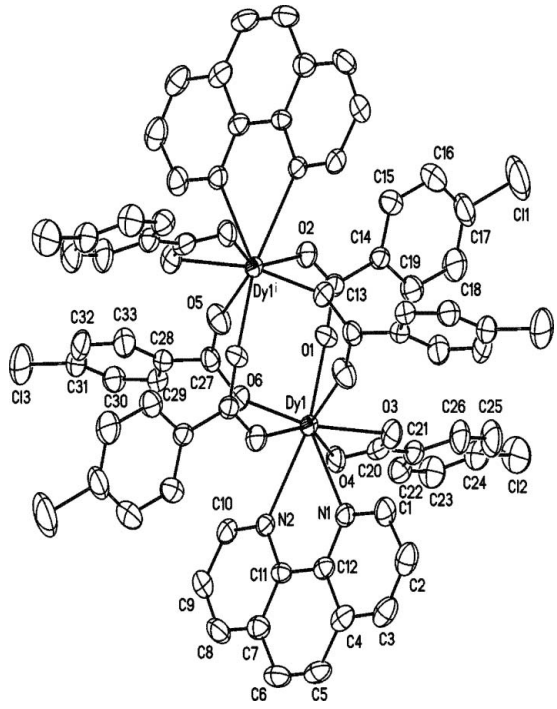


Figure 1
Molecular structure (40% probability displacement ellipsoids) of the title compound (H atoms have been omitted). Symmetry code: (i) $2-x$, $1-y$, $-z$; unlabelled atoms are also related to labelled atoms by this symmetry operation.

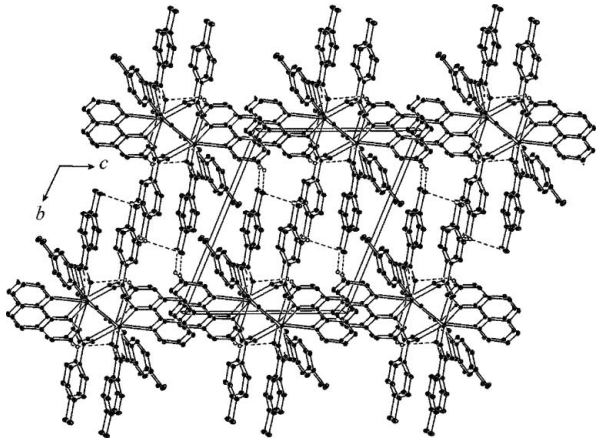


Figure 2
The hydrogen bonds and π–π stacking form a two-dimensional structure (the dashed lines indicate the hydrogen bonds).

dinuclear molecules. The mean interplanar distances are 3.20 and 3.29 Å, which are indicative of π–π stacking interactions along [100] (Fig. 2). Such weak interactions and an intermolecular C9—H9···O4^{iii} [symmetry code: (iii) $1-x$, $1-y$, $-z$; Table 2] hydrogen bond are apparently responsible for the supramolecular assembly of the complex molecules to generate two-dimensional layers parallel to (001). Between adjacent layers, atom C2 acts as a donor to atom Cl2^{ii} [symmetry code: (ii) $2-x$, $2-y$, $1-z$] to form interlayer C—H···Cl hydrogen bonds. Through the interlayer hydrogen bonds, the resulting two-dimensional layers are held together into a three-dimensional framework.

Experimental

The dysprosium(III) complex was obtained from the reaction of freshly prepared $Dy_2(CO_3)_3$, phen and 4-chlorobenzoic acid in CH_3OH/H_2O (1:2 *v*/*v*), freshly prepared for an optimal synthesis. 1 *M* Na_2CO_3 (6 ml) was added dropwise to a 5.0 ml aqueous solution of $Dy(NO_3)_3$ (0.086 g, 0.251 mmol). The resulting white $Dy_2(CO_3)_3$ precipitate was separated out, washed with doubly distilled water until no NO_3^- anions remained and added with continuous stirring to CH_3OH/H_2O (15 ml, 1:2 *v*/*v*) containing 1,10-phenanthroline monohydrate (0.050 g, 0.253 mmol) and 4-chlorobenzoic acid (0.040 g, 0.255 mmol). The mixture was stirred for *ca* 2.0 h. Subsequently, the resulting suspension was heated in a 25 ml Teflon-lined stainless steel autoclave at 423 K for 7 d. After the autoclave was cooled to room temperature, brown needle crystals were obtained.

Crystal data

$[Dy_2(C_7H_4ClO_2)_6(C_{12}H_8N_2)_2]$
M_r = 1618.72
Triclinic, $P\overline{1}$
a = 10.071 (2) Å
b = 11.840 (2) Å
c = 14.300 (3) Å
α = 111.02 (3)°
β = 96.58 (3)°
γ = 101.56 (3)°
V = 1526.6 (7) Å^3
Z = 1
D_x = 1.761 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 2.76 mm^{-1}
T = 290 (2) K
Needle, brown
0.29 × 0.12 × 0.08 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.679, T_{max} = 0.802
15082 measured reflections
6889 independent reflections
5256 reflections with $I > 2\sigma(I)$
R_{int} = 0.055
θ_{max} = 27.5°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.081
S = 1.08
6889 reflections
406 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0001P)^2 + 3.4415P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.98 e Å^{-3}
$\Delta\rho_{min}$ = −1.15 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Dy1—O5^i	2.276 (4)	Dy1—O4	2.357 (4)
Dy1—O2^i	2.316 (4)	Dy1—O3	2.476 (4)
Dy1—O6	2.320 (4)	Dy1—N1	2.552 (4)
Dy1—O1	2.321 (4)	Dy1—N2	2.622 (4)
O5^i—Dy1—O2^i	79.15 (14)	O4—Dy1—O3	54.20 (13)
O5^i—Dy1—O6	123.94 (15)	O5^i—Dy1—N1	85.72 (15)
O2^i—Dy1—O6	78.48 (14)	O2^i—Dy1—N1	80.82 (14)
O5^i—Dy1—O1	75.84 (15)	O6—Dy1—N1	138.98 (13)
O2^i—Dy1—O1	124.73 (13)	O1—Dy1—N1	143.52 (13)
O6—Dy1—O1	76.23 (13)	O4—Dy1—N1	89.15 (14)
O5^i—Dy1—O4	131.98 (13)	O3—Dy1—N1	70.51 (13)
O2^i—Dy1—O4	146.69 (12)	O5^i—Dy1—N2	139.99 (14)
O6—Dy1—O4	89.13 (14)	O2^i—Dy1—N2	71.52 (13)
O1—Dy1—O4	80.76 (13)	O6—Dy1—N2	76.39 (13)
O5^i—Dy1—O3	79.33 (14)	O1—Dy1—N2	143.77 (14)
O2^i—Dy1—O3	145.14 (14)	O4—Dy1—N2	75.55 (12)
O6—Dy1—O3	136.37 (14)	O3—Dy1—N2	110.53 (13)
O1—Dy1—O3	75.25 (13)	N1—Dy1—N2	63.54 (14)

Symmetry code: (i) $-x+2$, $-y+1$, $-z$.

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

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2···Cl2^{ii}	0.93	2.73	3.565 (7)	150
C9—H9···O4^{iii}	0.93	2.51	3.153 (9)	127
C10—H10···O6	0.93	2.47	3.065 (7)	122

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

H atoms were included at calculated positions and treated as riding atoms [C—H = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(C)]. The largest peak in the final difference map is 1.24 Å from atom O6 and the deepest hole is 0.80 Å from Dy1.

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXL97*; software used to prepare material for publication: *SHELXL97*.

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