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Key indicators

Single-crystal X-ray study
 $T = 293$ K
Mean $\sigma(\text{C}-\text{C}) = 0.008$ Å
 R factor = 0.030
 wR factor = 0.077
Data-to-parameter ratio = 14.3For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Tetra- μ - α -methacrylato-bis[(methacrylato)-
(1,10-phenanthroline)gadolinium(III)] dihydrate

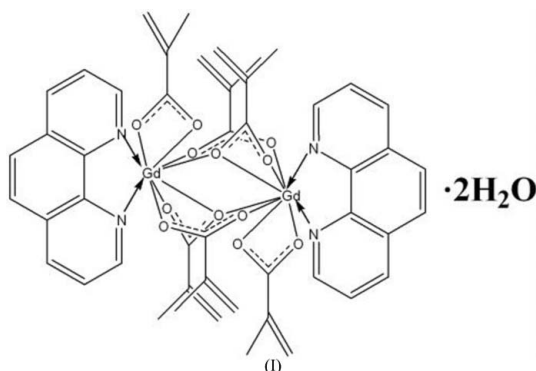
The title compound, $[\text{Gd}_2(\text{C}_4\text{H}_5\text{O}_2)_6(\text{C}_{12}\text{H}_8\text{N}_2)_2] \cdot 2\text{H}_2\text{O}$, is a discrete centrosymmetric dinuclear complex. The Gd^{III} atoms are bridged by two bidentate and two tridentate carboxylate groups, with a $\text{Gd} \cdots \text{Gd}$ separation of 3.957 (1) Å. Each Gd^{III} atom exhibits a distorted tricapped trigonal prismatic coordination, formed by seven O atoms of methacrylate groups and two N atoms of the bidentate chelating 1,10-phenanthroline ligand. The crystal packing is stabilized by π - π stacking interactions and van der Waals forces.

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Comment

The chemistry of rare-earth complexes containing O atoms and N atoms is an interesting field because of the potential uses of such luminescent compounds (Costes *et al.*, 2000; Mullica *et al.*, 1999). In the present work, the title gadolinium complex, (I), with α -methacrylato and 1,10-phenanthroline as ligands, was prepared and the crystal structure determined.



The structure of (I) consists of a centrosymmetric, dimeric arrangement of Gd^{III} ions bridged by two bidentate and two tridentate carboxylate groups, together with two water molecules. Three α -methacrylate groups adopt different coordination modes. One acts as a conventional bidentate bridging ligand, bonding to Gd through O5 and Gd^i through O6 [symmetry code: (i) $1 - x, 1 - y, 1 - z$]. The other is chelated to Gd through O3 and O4ⁱ, with O4ⁱ also linked to Gd^i . The third carboxylate group (O1/C13/O2) forms a chelate ring with a Gd ion. The $\text{Gd} \cdots \text{Gd}^i$ separation is 3.957 (1) Å. The coordination geometry around the Gd atom may be described as distorted tricapped trigonal prismatic. Atoms N1, O1, O4, O6, O3 and O5 form the prism, while atoms N2, O2 and O4ⁱ cap the rectangular faces. Dihedral angles between the rectangular faces are 55.3 (2), 62.2 (2) and 62.4 (2)°.

The crystal packing is stabilized by π - π stacking interactions and van der Waals forces. The shortest distance

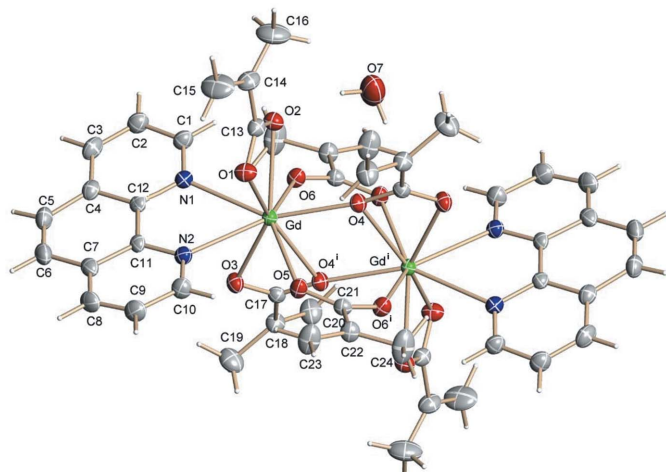


Figure 1
View of the molecular structure, including the uncoordinated water molecule, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry code: (i) $1 - x, 1 - y, 1 - z$.]

between C atoms of stacked ring systems is 3.307 (4) Å for $C8 \cdots C10^i$ [symmetry code: (ii) $-x, 2 - y, 1 - z$].

Experimental

α -Methylacrylic acid (130 mg, 1.5 mmol) and $Gd(NO_3)_3 \cdot 6H_2O$ (135 mg, 0.3 mmol) were dissolved in water (12 ml) and the pH was adjusted to 4.1 by the addition of 10% NaOH solution. An ethanol solution (3 ml) of 1,10-phenanthroline (60 mg, 0.3 mmol) was added with stirring. After filtration, the filtrate was evaporated at room temperature and single crystals suitable for X-ray work were obtained after a few days. Analysis calculated for $C_{48}H_{50}Gd_2N_4O_{14} \cdot 2C_{47.20}, H\ 4.13, N\ 4.60\%$; found $C\ 47.24, H\ 4.11, N\ 4.51\%$.

Crystal data

$[Gd_2(C_4H_5O_2)_6(C_{12}H_8N_2)_2] \cdot 2H_2O$	$V = 1183.7 (4) \text{ \AA}^3$
$M_r = 1221.42$	$Z = 1$
Triclinic, $P\bar{1}$	$D_x = 1.713 \text{ Mg m}^{-3}$
$a = 10.783 (2) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 10.894 (2) \text{ \AA}$	$\mu = 2.85 \text{ mm}^{-1}$
$c = 11.628 (2) \text{ \AA}$	$T = 293 (2) \text{ K}$
$\alpha = 69.59 (2)^\circ$	Plate, colorless
$\beta = 77.14 (2)^\circ$	$0.33 \times 0.23 \times 0.06 \text{ mm}$
$\gamma = 68.44 (2)^\circ$	

Data collection

Rigaku R-AXIS RAPID diffractometer	10058 measured reflections
ω scans	4527 independent reflections
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	4159 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.471, T_{\max} = 0.848$	$R_{\text{int}} = 0.040$
	$\theta_{\text{max}} = 25.8^\circ$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0379P)^2 + 0.5838P]$
$R[F^2 > 2\sigma(F^2)] = 0.030$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.077$	$(\Delta/\sigma)_{\text{max}} = 0.002$
$S = 1.06$	$\Delta\rho_{\text{max}} = 1.21 \text{ e \AA}^{-3}$
4527 reflections	$\Delta\rho_{\text{min}} = -0.81 \text{ e \AA}^{-3}$
316 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (Å, °).

Gd—O1	2.415 (3)	Gd—O5	2.377 (3)
Gd—O2	2.505 (3)	Gd—O6	2.387 (3)
Gd—O3	2.456 (3)	Gd—N1	2.573 (3)
Gd—O4	2.343 (3)	Gd—N2	2.610 (3)
Gd—O4 ⁱ	2.644 (3)		
O1—Gd—O2	52.79 (10)	O3—Gd—O5	87.10 (11)
O1—Gd—O3	140.15 (10)	O3—Gd—O6	81.26 (10)
O1—Gd—O4	90.63 (11)	O3—Gd—N1	74.03 (10)
O1—Gd—O4 ⁱ	159.53 (10)	O3—Gd—N2	70.99 (10)
O1—Gd—O5	88.41 (11)	O4—Gd—O4 ⁱ	75.10 (10)
O1—Gd—O6	126.20 (11)	O4—Gd—O5	73.13 (10)
O1—Gd—N1	84.04 (11)	O4—Gd—O6	79.69 (10)
O1—Gd—N2	69.45 (11)	O4—Gd—N1	146.80 (11)
O2—Gd—O3	142.66 (10)	O4—Gd—N2	144.12 (10)
O2—Gd—O4	76.87 (10)	O5—Gd—O4 ⁱ	73.58 (9)
O2—Gd—O4 ⁱ	134.22 (9)	O5—Gd—O6	136.08 (9)
O2—Gd—O5	130.06 (10)	O5—Gd—N1	139.09 (11)
O2—Gd—O6	73.54 (10)	O6—Gd—N1	77.31 (10)
O2—Gd—N1	73.86 (10)	O6—Gd—N2	136.17 (10)
O2—Gd—N2	109.78 (10)	N1—Gd—N2	63.01 (11)
O3—Gd—O4	125.45 (10)	N1—Gd—O4 ⁱ	115.92 (9)
O3—Gd—O4 ⁱ	50.44 (9)	N2—Gd—O4 ⁱ	114.21 (10)

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

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O7—H72 ⁱ ···O4	0.865 (17)	2.44 (6)	3.084 (6)	132 (7)
O7—H71 ⁱ ···O2	0.87 (8)	2.01 (8)	2.838 (6)	161 (8)

All methyl H atoms were constrained to an ideal geometry, with $C-H = 0.96 \text{ \AA}$ and $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C)$, but each group was allowed to rotate freely about its $C-C$ bond. The $=CH_2$ and aromatic H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with $C-H = 0.93-0.96 \text{ \AA}$ and $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C)$. Water H atoms were restrained, with $O-H = 0.85 (1) \text{ \AA}$ and $H \cdots H = 1.39 (1) \text{ \AA}$. The $C14-C16$ distance is short [1.413 (8) Å], perhaps because of unresolved disorder of the α -methacrylate group. The highest residual density peak is located near the α -methacrylate group.

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MS, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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