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Key indicators

Single-crystal X-ray study
 T = 293 K
 Mean $\sigma(C-C)$ = 0.009 Å
 R factor = 0.035
 wR factor = 0.112
 Data-to-parameter ratio = 17.8

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

Hexa- μ - α -methylacrylato-bis[(1,10-phenanthroline)-lanthanum(III)] dihydrate

The title compound, $[La_2(C_4H_5O_2)_6(C_{12}H_8N_2)_2] \cdot 2H_2O$, is a discrete centrosymmetric homodinuclear complex, which is structurally very similar to a previously studied analogue. The La^{III} atoms are bridged by two bidentate and two tridentate carboxylate groups, with an $La \cdots La$ separation of 4.0807 (4) Å. Each La^{III} atom exhibits a distorted tricapped trigonal prismatic coordination formed by seven O atoms of bridging methylacrylate groups and two N atoms of the bidentate chelating 1,10-phenanthroline ligands.

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Comment

Molecular magnetic compounds, such as molecular ferro- and ferrimagnets, organic magnets, single-molecule magnets and high-spin molecules, have recently attracted attention (Miller & Drillon, 2001*a,b*, 2002; Christou *et al.*, 2000). Efforts to obtain molecular magnets containing rare-earth ions have been less numerous because the interactions between pairs of *f* electrons are expected to be small, producing measurable effects only at extremely low temperatures, but the number of new reported compounds in which rare-earth ions are magnetically coupled to transition-metal ions and/or organic radicals is rapidly increasing. In recent years, we have pursued a project on the structures and properties of heteronuclear complexes of rare-earth and transition metals bridged by carboxyl groups (Wu *et al.*, 2002, 2003, 2004; Zhu *et al.*, 2005). The title complex, (I), was unexpectedly obtained during the preparation of a lanthanum-iron complex.

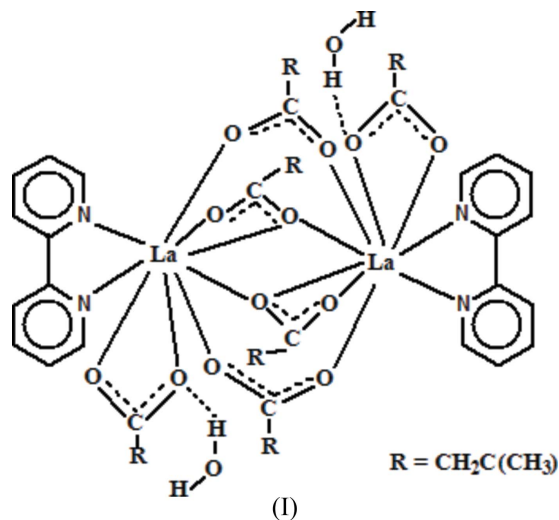


Fig. 1 shows the molecular structure of the title complex; selected bond distances are listed in Table 1.

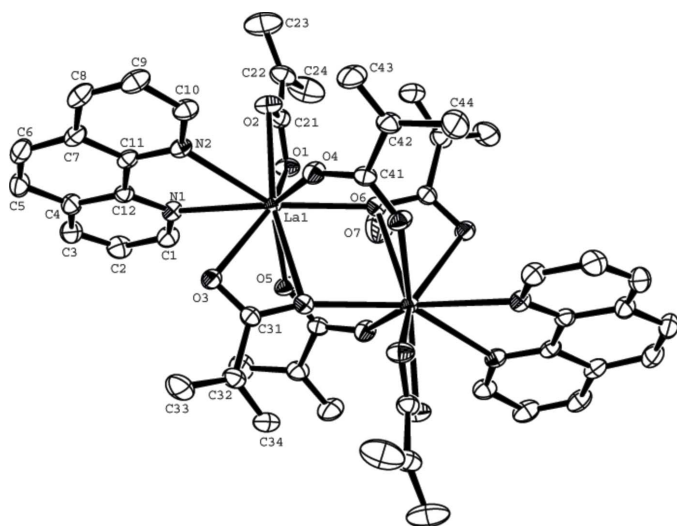


Figure 1

The molecule of the title complex, with displacement ellipsoids drawn at the 30% probability level. H atoms have been omitted. Unlabelled atoms are related to labelled atoms by the symmetry operator $(2-x, 1-y, 1-z)$.

Compound (I) is structurally very similar to another La analogue, (II), in which the water molecule is replaced by an α -methylacrylic acid molecule (Lu, *et al.*, 1996). As one would expect, the surroundings of the central atoms in the two complexes are the same. This means that the La^{III} atoms, with the coordination geometry of a distorted tricapped trigonal prism, are linked to each other by bidentate and tridentate carboxylate groups to form a centrosymmetric dimeric unit. Each La^{III} atom is nine-coordinated by two N atoms of the phenanthroline ligand and seven O atoms from three different coordination modes of six carboxylate groups. The detailed coordination modes of α -methylacrylate groups in (II) are also fully applicable to the title complex. The La^{III}–La^{III} separation [4.0807 (4) Å; symmetry code as in Table 1] in the dimer just exceeds the sum of two atomic radii and is slightly longer than that [4.0456 (4) Å] in (II).

The structure of the title complex has two distinct La–O distances; the average La–O_{bridging} bond length is 2.498 Å and La–O_{chelating} is 2.606 Å, which are similar to those (2.494 and 2.612 Å) of (II). The La–O_{chelating} distance is significantly larger than the sum of the covalent radii of the two atoms, as is to be expected because the (O–La–O)_{chelating} angles of about 50° indicate ring strain. The phenanthroline ligands possess local C_{2v} symmetry. The average La–N bond distance is 2.708 Å and is nearly the same as the corresponding La–N distance (2.709 Å) in (II). A water molecule is connected to atom O1 by a hydrogen bond.

Comparison of structures (I) and (II) shows that it is uncertain whether water or a free α -methylacrylic acid molecule will be included in the complex during the growth of the crystal.

Experimental

LaL₃·2H₂O [430 mg, 1.0 mmol; HL = CH₂C(CH₃)COOH] was dissolved in water (5 ml). A 1 M solution of Fe(NO₃)₃ (1.0 ml) was

added and the pH was adjusted to 4.1 with 0.1 M HL. An ethanol solution (5 ml) of 1,10-phenanthroline (200 mg, 1.0 mmol) was added to the mixture with stirring. The filtrate was allowed to stand at room temperature, and colourless single crystals suitable for X-ray diffraction precipitated after a few days. Analysis calculated for C₄₈H₅₀La₂N₄O₁₄: C 49.41, H 4.15, N 4.80, La 23.81%; found: C 49.56, H 4.18, N 4.76, La 23.63%.

Crystal data

[La₂(C₄H₅O₂)₆(C₁₂H₈N₂)₂].2H₂O
M_r = 1184.74
 Triclinic, *P* $\bar{1}$
a = 10.8815 (4) Å
b = 11.0081 (5) Å
c = 11.7412 (7) Å
 α = 69.229 (2)°
 β = 77.892 (4)°
 γ = 68.091 (2)°
V = 1215.16 (10) Å³

Z = 1
D_x = 1.619 Mg m⁻³
 Mo *K* α radiation
 Cell parameters from 6732 reflections
 θ = 2.5–27.5°
 μ = 1.80 mm⁻¹
T = 293 (2) K
 Chunk, colourless
 0.21 × 0.18 × 0.14 mm

Data collection

Rigaku R-Axis RAPID diffractometer
 ω scans
 Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
 T_{\min} = 0.703, T_{\max} = 0.786
 11677 measured reflections

5471 independent reflections
 5112 reflections with $I > 2\sigma(I)$
 R_{int} = 0.045
 θ_{\max} = 27.5°
 h = -13 → 14
 k = -13 → 14
 l = -15 → 15

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)]$ = 0.035
 $wR(F^2)$ = 0.112
 S = 1.24
 5471 reflections
 307 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0611P)^2 + 0.7074P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max}$ = 0.001
 $\Delta\rho_{\max}$ = 0.81 e Å⁻³
 $\Delta\rho_{\min}$ = -1.21 e Å⁻³

Table 1

Selected bond lengths (Å).

La1–O1	2.584 (3)	La1–O6	2.457 (3)
La1–O2	2.532 (3)	La1–O6 ⁱ	2.718 (3)
La1–O3	2.592 (3)	La1–N1	2.699 (4)
La1–O4	2.493 (3)	La1–N2	2.719 (3)
La1–O5	2.495 (3)		

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

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
O7–HW1...O1	0.99	1.88	2.863 (5)	174

All H atoms were placed in calculated positions (C–H = 0.93–0.96 Å and O–H = 0.94–0.99 Å) and included in the final cycles of refinement in a riding model, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ [$U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C}, \text{O})$ in the case of the methyl and water H atoms]. The deepest hole is located 1.0 Å from atom La1.

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *CrystalStructure* (Rigaku/MSO, 2002); data reduction: *CrystalStructure*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick,

1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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