

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: KH1001). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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catena-Diaquatris(α -methacrylato)-lanthanum(III)

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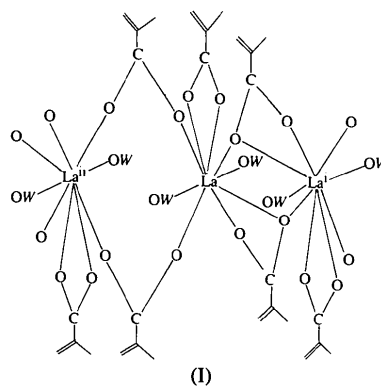
Abstract

The structure of *catena*-poly[{diaqua(methacrylato-*O*, *O'*)lanthanum-bis- μ -methacrylato-*O*, *O'*:*O*; *O*:*O*, *O'*:*O*, *O'*}lanthanum]-bis- μ -methacryl-

ato-*O*:*O'*; *O*:*O'*], [La₂(C₄H₅O₂)₆(H₂O)₄], has been determined by single-crystal X-ray diffraction. Each La³⁺ ion is coordinated by seven O atoms from the methacrylato groups and by two water molecules which define a distorted tricapped trigonal prism. Each of the three independent methacrylato ligands bonds to the La^{III} ions in a different way. The crystal contains infinite chains running parallel to the **ab** direction.

Comment

The stereochemistry of complexes of rare earth ions with unsaturated carboxylic acids is of interest because of their potential use as extracting agents; in this context the effect of an α -C=C double bond on the coordination of the carboxylate group to rare earth ions may be significant. However, only a few molecular structures are known (Xue, Zhu & Yang, 1992; Hansson, 1975). The structure determination of the title complex, (I), was undertaken as part of a program of studies on rare earth metal complexes containing unsaturated carboxylic acids. Each complex contains a single independent La³⁺ ion which is coordinated by seven O atoms from five methacrylato groups and by two water molecules. The coordination polyhedron is a distorted tricapped trigonal prism.



Rare earth metal-carboxylate complexes are very often polymeric in the solid state, with the COO⁻ group bridging two or three metal ions. However, other bonding modes of the carboxyl groups also occur. Bidentate carboxyl groups are the least common because of the strained nature of the four-membered chelate ring. For this reason, cases where bridging and chelating carboxylate ligands occur in the same complex are very rare indeed. Unlike other polymeric Ln³⁺-carboxylate complexes which contain either bidentate bridging ligands only (Ma, Li, Lin & Xi, 1993) or chelating and bidentate bridging ligands (Ma, Jin & Ni, 1993), the present compound contains pairs of La³⁺ ions linked by two distinctly different types of carboxylate bridge. One methacrylato group acts as a conventional bidentate bridging ligand, bonding to La

through atom O(22) and to Laⁱⁱ through atom O(21ⁱⁱ) [Laⁱ··Laⁱⁱ 5.524 (1) Å; symmetry code: (ii) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$]. The other is chelated to La through atoms O(11ⁱ) and O(12), with atom O(11ⁱ) also linked to Laⁱ [Laⁱ··Laⁱ 4.268 (2) Å; symmetry code: (i) $1 - x, 1 - y, 1 - z$] (Fig. 1). Pairs of symmetrically related ligands link Laⁱ··Laⁱ and Laⁱ··Laⁱⁱ, thus forming infinite chains running parallel to the **ab** direction. The four-atom [La, O(11), Laⁱ, O(11ⁱ)] and eight-atom [La, O(21), C(21), O(22ⁱⁱ), Laⁱⁱ, O(21ⁱⁱ), C(21ⁱⁱ), O(22)] mean planes make a dihedral angle of 63.71 (5)° with each other. The third carboxylate group [O(31), C(31), O(32)] forms a chelate ring with La.

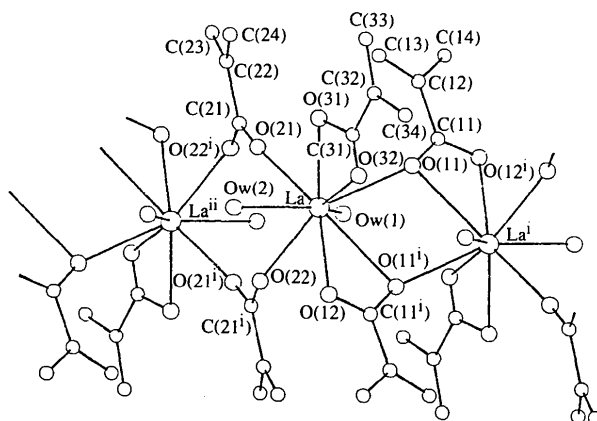


Fig. 1. A drawing of the title complex showing the atomic numbering scheme. H atoms are omitted for clarity.

The structure has two distinct La—O distances involving methacrylate groups. The average La—O length is 2.616 Å for the four-membered rings and 2.429 Å for the eight-membered ring. The former is to be expected because the angles O(12)—La—O(11ⁱ) and O(31)—La—O(32) of less than 50° indicate ring strain. The presence of the α -C=C double bonds may have a bearing on the shortness of the La—O bonds in the eight-membered ring. The average La—OW bond length is 2.568 Å.

The carboxyl groups give rise to very strong IR absorptions at 1545.0 and 1430.0 cm^{-1} . These values can be used to distinguish between the different coordination modes of the ligands (*i.e.* ionic, monodentate or bidentate) (Deacon & Phillips, 1980). In this compound, the band separation of 115.0 cm^{-1} is less than the value for sodium methacrylate (146.0 cm^{-1}) and is consistent with the observed structure.

Experimental

Freshly prepared $\text{La}_2(\text{CO}_3)_3 \cdot n\text{H}_2\text{O}$ (2.10 mmol) was added to an aqueous solution of methacrylic acid at 331–333 K with continuous stirring for 2 h. The solution was filtered and allowed to evaporate slowly at the same temperature. The dry

residues were recrystallized from water and subsequently from ethanol/water (4:1 *v/v*) solution. Single crystals suitable for X-ray work were obtained after a few days by slow evaporation. Analysis: calculated C 33.50, H 4.45, La 32.29%; found C 33.23, H 4.38, La 32.23%.

Crystal data

$[\text{La}_2(\text{C}_4\text{H}_5\text{O}_2)_6(\text{H}_2\text{O})_4]$
 $M_r = 860.37$
 Monoclinic
 C2/c
 $a = 10.060 (2) \text{ \AA}$
 $b = 13.953 (5) \text{ \AA}$
 $c = 23.804 (4) \text{ \AA}$
 $\beta = 95.27 (1)^\circ$
 $V = 3327 (1) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.718 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 25 reflections
 $\theta = 10\text{--}12^\circ$
 $\mu = 2.611 \text{ mm}^{-1}$
 $T = 293 \text{ K}$
 Plate
 $0.5 \times 0.3 \times 0.1 \text{ mm}$
 Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: ψ scans (SDP; Frenz, 1985)
 $T_{\min} = 0.324$, $T_{\max} = 0.999$
 3201 measured reflections
 3078 independent reflections

2738 observed reflections [$I > 3\sigma(I)$]
 $R_{\text{int}} = 0.021$
 $\theta_{\max} = 25^\circ$
 $h = 0 \rightarrow 11$
 $k = 0 \rightarrow 16$
 $l = -28 \rightarrow 28$
 3 standard reflections
 frequency: 60 min
 intensity decay: <12%

Refinement

Refinement on F
 $R = 0.0471$
 $wR = 0.0560$
 $S = 5.991$
 2738 reflections
 266 parameters
 H atom parameters not refined

Unit weights applied
 $(\Delta/\sigma)_{\max} = 0.01$
 $\Delta\rho_{\max} = 0.85 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.31 \text{ e \AA}^{-3}$
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$B_{\text{eq}} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq} (8)
La	0.48689 (4)	0.35034 (3)	0.51716 (2)	2.399 (8)
OW(1)	0.2491 (7)	0.4224 (4)	0.5017 (3)	4.6 (2)
OW(2)	0.5975 (6)	0.1856 (4)	0.5203 (3)	3.6 (1)
O(11)	0.4751 (6)	0.5166 (4)	0.5606 (2)	3.0 (1)
O(12)	0.6405 (6)	0.3503 (4)	0.4349 (2)	3.3 (1)
O(21)	0.3458 (6)	0.2578 (5)	0.5724 (3)	4.1 (1)
O(22)	0.3711 (6)	0.2626 (6)	0.4373 (3)	4.7 (2)
O(31)	0.6253 (6)	0.3308 (5)	0.6129 (3)	3.8 (1)
O(32)	0.7363 (6)	0.4046 (4)	0.5507 (3)	3.7 (1)
C(11)	0.3954 (8)	0.5706 (6)	0.5854 (3)	2.7 (2)
C(12)	0.3455 (9)	0.5410 (7)	0.6403 (4)	3.7 (2)
C(13)	0.397 (1)	0.4642 (8)	0.6676 (5)	6.9 (3)
C(14)	0.244 (1)	0.6001 (8)	0.6626 (5)	5.4 (3)
C(21)	0.2369 (9)	0.2386 (7)	0.5919 (4)	3.4 (2)
C(22)	0.240 (1)	0.2144 (8)	0.6535 (4)	4.3 (2)
C(23)	0.122 (1)	0.204 (1)	0.6774 (5)	7.8 (4)
C(24)	0.367 (1)	0.205 (1)	0.6853 (5)	6.2 (3)
C(31)	0.7245 (9)	0.3782 (6)	0.6006 (4)	3.4 (2)

C(32)	0.832 (1)	0.4029 (8)	0.6466 (5)	4.8 (2)
C(33)	0.807 (1)	0.389 (1)	0.6999 (5)	8.2 (4)
C(34)	0.955 (1)	0.442 (1)	0.6296 (6)	8.6 (4)

Table 2. Selected geometric parameters (Å, °)

La ⁱ ...La ^j	4.268 (2)	O(21)—C(21)	1.254 (4)
La ⁱ ...La ^h	5.524 (1)	O(22)—C(21 ^h)	1.232 (4)
La—OW(1)	2.590 (7)	O(31)—C(31)	1.253 (4)
La—OW(2)	2.551 (2)	O(32)—C(31)	1.259 (12)
La—O(11)	2.547 (5)	C(11)—C(12)	1.506 (4)
La—O(11 ⁱ)	2.674 (5)	C(12)—C(13)	1.334 (6)
La—O(12)	2.601 (2)	C(12)—C(14)	1.446 (5)
La—O(21)	2.403 (2)	C(21)—C(22)	1.506 (5)
La—O(22)	2.462 (7)	C(22)—C(23)	1.371 (6)
La—O(31)	2.575 (2)	C(22)—C(24)	1.430 (6)
La—O(32)	2.672 (6)	C(31)—C(32)	1.504 (5)
O(11)—C(11)	1.283 (10)	C(32)—C(33)	1.333 (7)
O(12)—C(11 ⁱ)	1.248 (4)	C(32)—C(34)	1.442 (7)
La ⁱ ...La...La ^j	122.37 (1)	O(11)—La—O(21)	102.57 (9)
OW(1)—La—OW(2)	138.50 (8)	O(11)—La—O(22)	136.74 (9)
OW(1)—La—O(11)	68.05 (8)	O(11)—La—O(31)	77.45 (8)
OW(1)—La—O(11 ⁱ)	79.55 (8)	O(11)—La—O(32)	72.47 (8)
OW(1)—La—O(12)	119.65 (9)	O(11 ⁱ)—La—O(12)	49.11 (7)
OW(1)—La—O(21)	72.89 (9)	O(11 ⁱ)—La—O(21)	152.09 (8)
OW(1)—La—O(22)	73.59 (9)	O(11 ⁱ)—La—O(22)	84.2 (2)
OW(1)—La—O(31)	125.8 (1)	O(11 ⁱ)—La—O(31)	125.9 (2)
OW(1)—La—O(32)	139.64 (8)	O(11 ⁱ)—La—O(32)	79.68 (8)
OW(2)—La—O(11)	147.64 (8)	O(12)—La—O(22)	71.99 (9)
OW(2)—La—O(11 ⁱ)	123.8 (2)	O(12)—La—O(31)	110.99 (8)
OW(2)—La—O(12)	74.6 (2)	O(12)—La—O(32)	67.58 (8)
OW(2)—La—O(21)	77.2 (2)	O(21)—La—O(22)	84.1 (1)
OW(2)—La—O(22)	75.6 (1)	O(21)—La—O(31)	75.60 (9)
OW(2)—La—O(31)	71.3 (2)	O(21)—La—O(32)	124.97 (9)
OW(2)—La—O(32)	81.44 (8)	O(22)—La—O(31)	144.0 (1)
O(11)—La—O(11 ⁱ)	70.24 (8)	O(22)—La—O(32)	137.40 (9)
O(11)—La—O(12)	110.80 (8)	O(31)—La—O(32)	49.52 (8)
O(12)—La—O(21)	146.64 (9)		

D—H...A	D...A	D—H...A
OW(1)—HW(11)...O(32 ⁱ)	2.735 (3)	149.7 (2)

Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$.

Data collection was performed using *CAD-4 Software* (Enraf-Nonius, 1989). All non-H atoms were located by Patterson and Fourier techniques and refined by full-matrix least-squares methods with anisotropic displacement parameters. Most H atoms were located by the same methods and the remainder were placed in calculated positions. All H atoms were assigned a B_{iso} of 4.0 Å² and their parameters were not refined. All calculations were performed using *SDP* (Frenz, 1985), on a VAX II computer.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and least-squares-planes data, together with three packing diagrams, have been deposited with the IUCr (Reference: MU1143). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Bimetallic Complex Between Uranyl and *p*-*tert*-Butylcalix[8]arene

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Abstract

UO₂(NO₃)₂ reacts with *p*-*tert*-butylcalix[8]arene, deprotonated with triethylamine as base, in acetonitrile to give the bimetallic complex μ -hydroxo-1:2 κ^2 O- μ -[5,11,17,23,29,35,41,47-octa-*tert*-butylnonacyclo[43.3.1.1^{3,7}.1^{9,13}.1^{15,19}.1^{21,25}.1^{27,31}.1^{33,37}.1^{39,43}]hexapentaconta-1(49),3,5,7(56),9,11,13(55),15,17,19(54),-21,23,25(53),27,29,31(52),33,35,37(51),39,41,43(50),-45,47-tetracosae-49,50,51,52,53,54,55,56-octolato-1 κ^4 O^{49,50,51,52}:2 κ^4 O^{53,54,55,56}]bis[dioxouranium(VI)] with bis(triethylammonium) hydroxide bis(triethylamine) trihydrate tetraacetonitrile solvate, (C₆H₁₆N)₂[(UO₂)₂(C₈₈H₁₀₈O₈)(OH)](OH).2C₆H₁₅N.3H₂O.4C₂H₃N. The two uranyl ions are included in the fourfold deprotonated macrocycle, each of them being bonded to four phenolic O atoms, with a bridging hydroxyl ion ensuring the five-coordinate equatorial environment usual for a uranyl ion. A protonated triethylamine molecule is hydrogen bonded to one O atom of each uranyl moiety.

Comment

The ability of calixarenes to complex metallic cations has been the subject of extensive research in recent years (for reviews see: Gutsche, 1989; Bünzli & Harrowfield, 1991). Among large-metal-ion complexes, those containing lanthanides have been investigated particularly, both structurally and spectroscopically, while structurally characterized actinide complexes remain scarce, being limited to the complex of uranyl with bis(homooxa)-*p*-*tert*-butylcalix[4]arene (Harrowfield, Ogden & White, 1991a) and the bimetallic complex of thorium(IV) with *p*-*tert*-butylcalix[8]arene