P1*A*—Pt3*A*—B4*A*	164.8 (5)	P1*B*—Pt3*B*—B4*B*	165.3 (4)
P1*A*—Pt3*A*—C2*A*	100.7 (4)	P1*B*—Pt3*B*—C2*B*	100.8 (3)
B8*A*—Pt3*A*—P1*A*	138.0 (4)	B8*B*—Pt3*B*—P1*B*	136.5 (4)
B7*A*—Pt3*A*—P1*A*	99.9 (4)	B7*B*—Pt3*B*—P1*B*	99.3 (4)

The cage C atoms were initially refined as B atoms, being subsequently identified by inspection of the relevant interatomic distances and displacement parameters. The two crystallographically independent molecules appear to be related by the symmetry operation $\frac{3}{4}-x$, $0.068+y$, $\frac{1}{2}-z$; however, attempts to impose this symmetry on the structure solution or refinement caused the model to become unstable, suggesting that this is merely pseudosymmetry. The need for an absorption correction became apparent when residual peaks of up to 2.46 e Å^{-3} persisted near the Pt atom; the only available method was a refined correction using *DIFABS* (Walker & Stuart, 1983), which resulted in transmission factors consistent with the observed crystal dimensions. After this was applied, a final electron-density map showed a maximum residual electon-density peak of 0.95 e Å^{-3} near Pt3*A*. The H atoms were constrained to ride on the atoms to which they were bonded (C_{aryl}—H = 0.95, C_{alkyl}—H = 0.98 and B—H = 1.08 Å), with displacement parameters set at $1.2U_{eq}$ of that atom (1.5 for CH_3 groups). All alkyl C atoms were constrained to be tetrahedral.

Data collection: *CAD*-4 *Software* (Enraf-Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *CADABS* (Gould & Smith, 1986). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL*/*PC* (Sheldrick, 1994). Software used to prepare material for publication: *SHELXTL*/*PC*.

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Triaquatris(μ-oxydiacetato)europium(III)-lanthanum(III) Pentahydrate

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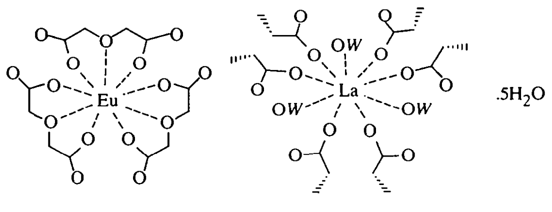
Abstract

The new heterobimetallic complex $[\{LaEu(oda)_3(H_2O)_3.5H_2O\}_n]$ (oda = $^-O_2CCH_2OCH_2CO_2^-$) has been synthesized and structurally characterized. Three tridentate oda ligands are coordinated to the smaller Eu^{III} cation, while six adjacent outer carboxylate O atoms and three metal-bound water O atoms are bonded to the larger La^{III} cation. The structure consists of a three-dimensional network with the metal centers bridged by oda carboxylate groups, with Eu···La separations of 6.95 (1) Å.

Comment

Heterometallic carboxylates containing lanthanides are of current interest with regard to chemical processing of lanthanide-containing ceramic materials (Segal, 1989). Among oxodicarboxylic acid derivatives, two heterobimetallic oxydiacetates, $[\{LaLn(oda)_3(H_2O)_3.6H_2O\}_n]$ (Ln = Gd or Y; oda = $^-O_2CCH_2OCH_2CO_2^-$), have been structurally characterized (Baggio *et al.*, 1998). These have been shown to be isomorphous with the reported homometallic complex $[\{La_2(oda)_3(H_2O)_3.5H_2O\}_n]$ (Baggio *et al.*, 1996). In this report, we present the preparation and results of the crystal structure analysis of the related europium–lanthanum heterobimetallic complex $[\{LaEu(oda)_3(H_2O)_3.5H_2O\}_n]$, (1).



(1)

The reaction of equimolar amounts of La_2O_3 and Eu_2O_3 with oxydiacetic acid in water and subsequent work-up gave colorless crystals of (1) in good yield. The IR spectrum shows strong absorption bands at 1593 cm^{-1}, and at 1443 and 1422 cm^{-1}, which may be assigned to the asymmetric and symmetric vibrations of the RCO_2^- groups (Nakamoto, 1986). The low Δ values found [$\Delta = \nu_{asym}(CO_2^-) - \nu_{sym}(CO_2^-)$] of *ca* 150 cm^{-1} suggest bridging coordination of the carboxylate groups (Deacon & Phillips, 1980). Absorptions in the 3600–3200 and 1640–1610 cm^{-1} regions correspond to coordinated- and lattice-water modes, respectively. The IR spectrum closely resembles those of the aforementioned lanthanum polymers, suggesting a similar structure, as confirmed by the X-ray study described below.

Complex (1) is a stable colorless crystalline solid and can be stored in a dry atmosphere at room temperature. The thermal gravimetric analysis (TGA) carried out under an oxygen atmosphere showed a weight loss of 17.0% in the range 323–493 K, which corresponds to the loss of eight water molecules in (1) (calculated 17.3%).

A structural diagram and the atomic numbering scheme are shown in Fig. 1. Five out of the ten independent atoms in the structure lie on special positions, *viz.* La (on a $\bar{6}$ center), Eu (on the intersection of a threefold and a twofold axis), both O1*W* and the disordered O2*W* (on a mirror plane), and O3 (on a twofold axis). The structure is built up from two nine-coordinate metal ions, each of which is surrounded by an O_9 donor set. The polyhedron around each metal atom can be described as a tricapped trigonal prism (TCTP) formed by the stacking of three triangular layers. The outer layers are symmetry related, resulting in two sets of independent *M*—O distances: one set of six *M*—O prismatic bonds and a second set of three *M*—O capping bonds (*M* = La or Eu).

Selected bond lengths and angles are listed in Table 2. The six La—O1 distances of 2.502 (4) Å and the three La—O1*W* bonds of 2.667 (7) Å are comparable to those found for the LaO_9 units in the three aforementioned complexes [average 2.474 (2) and 2.704 (4) Å, respectively]. Also, the six Eu—O2 prismatic distances of 2.427 (4) Å and the three Eu—O3 capping distances of 2.488 (6) Å are in good agreement with the respective values found in $Na_3[Eu(oda)_3].2NaClO_4.6H_2O$ (Sen *et al.*, 1981), $Na_3[Eu(oda)_3].2NaBF_4.6H_2O$ (Fronczek *et al.*, 1981) and $Na_3[Eu(oda)_3].6H_2O$ (Albin *et al.*, 1985).

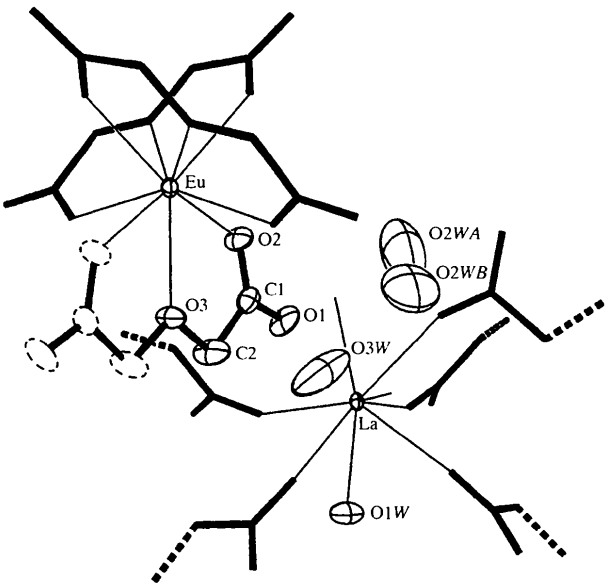


Fig. 1. A partial view of the title structure, showing schematically the interactions among different units. Displacement ellipsoids are drawn at the 50% probability level.

The crystal structure of (1) is a three-dimensional network of two distinct TCTP polyhedra with the carboxylate groups of the oxydiacetate ligands bridging pairs of La/Eu atoms in a bidentate *anti–anti* mode (Cotton & Wilkinson, 1988). Each La ion is linked to six different Eu ions and *vice versa* at non-interacting distances of 6.95 (1) Å. The shortest La···La and Eu···Eu distances are 10.35 (1) and 8.85 (1) Å, respectively. A common feature in the isomorphous series formed by the La/La, La/Gd, La/Y and La/Eu oda polymers (hexagonal, $P\bar{6}2c$) is the LaO_9 polyhedron formed by six outer carboxylate and three water molecules. The second polyhedron in the asymmetric unit is formed by the tris-tridentate $[Ln(oda)_3]^{3-}$ unit (Ln = La, Gd, Y or Eu). In the two other reported homometallic oda complexes of lanthanides of smaller atomic radii, $[\{Ln_2(oda)_3(H_2O)_4.2H_2O\}_n]$ (Ln = Er and Y; orthorhombic, $C222_1$) (Elding, 1977; Baggio *et al.*, 1998), the interactions are between nine-coordinate $[Ln(oda)_3]^{3-}$ and eight-coordinate LnO_8 polyhedra, which generate a two-dimensional sheet structure in which each Ln atom in the former polyhedra is linked to four Ln atoms in the latter, and *vice versa*. These significant structural differences illustrate the size effect of the lanthanide cation on the nature of the solid complex formed.

The water molecules of hydration lie in the vicinity of the La—O1 capping bonds, close enough to suggest hydrogen-bonding interactions among themselves [O1*W*···O2*WB* 2.57 (5) Å], as well as with the carboxylate atoms [O3*W*···O2 2.88 (7) Å]. However, uncertainty in the H-atom positions precluded a detailed analysis of this subject.

Experimental

To a boiling solution of oxydiacetic acid (0.80 g, 6.0 mmol) in water (200 ml) was added a solid mixture of Eu_2O_3 (0.35 g, 1.0 mmol) and La_2O_3 (0.33 g, 1.0 mmol) in portions of 50 mg. The reaction mixture was stirred under reflux for 10 h, allowed to cool to room temperature and then passed through a glass filter. After 10 d, colorless crystals of the product suitable for X-ray diffraction were filtered off and dried *in vacuo* for 5 h. Yield 1.15 g; 70% based on Eu_2O_3. Elemental analysis found C 17.10, H 3.45%; $C_{12}H_{28}O_{23}EuLa$ requires C 17.30, H 3.40%. FT-IR (KBr disc, $\nu_{\rm max}$/cm^{-1}): 3440 (*vs*), 2917 (*w*), 1593 (*vs*), 1466 (*s*), 1442 (*vs*), 1421 (*vs*), 1360 (*m*), 1312 (*vs*), 1240 (*w*), 1127 (*s*), 1057 (*s*), 941 (*m*), 735 (*m*), 598 (*m*), 569 (*s*), 355 (*w*) and 316 (*w*). The reagents were of analytical or reagent-grade purity and used as received. Water was purified by a Millipore Milli-Q system yielding 18 MΩ cm water. Elemental analysis (C, H) was performed with a Carlo Erba EA 1108 analyzer. The IR spectrum was recorded as a KBr pellet with a Nicolet 510P FT-IR spectrophotometer. Thermogravimetric analysis was recorded on a Mettler TG-50 thermal analyzer in a dynamic atmosphere of oxygen at a heating rate of 5 K min^{-1}.

Crystal data

$[EuLa(C_4H_4O_5)_3(H_2O)_3].5H_2O$
M_r = 831.2
Hexagonal
$P\bar{6}2c$
a = 9.295 (1) Å
c = 17.689 (3) Å
V = 1323.5 (3) Å^3
Z = 2
D_x = 2.09 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 7.5–12.5°
μ = 4.04 mm^{-1}
T = 293 (2) K
Polyhedron
0.22 × 0.20 × 0.18 mm
Colorless

Data collection

Siemens *R*3*m* diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (*XEMP*; Sheldrick, 1991)
$T_{\rm min}$ = 0.40, $T_{\rm max}$ = 0.48
1672 measured reflections
808 independent reflections
740 reflections with $I > 2\sigma(I)$

$R_{\rm int}$ = 0.019
$\theta_{\rm max}$ = 24.97°
$h = -11 \rightarrow 0$
$k = 0 \rightarrow 11$
$l = 0 \rightarrow 21$
2 standard reflections every 98 reflections intensity decay: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.023
$wR(F^2)$ = 0.065
S = 1.09
808 reflections
73 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o^2) + (0.039P)^2 + 1.975P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max}$ = −0.006
$\Delta\rho_{\rm max}$ = 0.46 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.95 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.00 (4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^ia^j\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
La	2/3	1/3	1/4	0.0117 (2)
Eu	0	0	0	0.0121 (2)
C1	0.3444 (7)	0.1842 (16)	0.1050 (3)	0.0242 (15)
C2	0.3972 (9)	0.0916 (10)	0.0531 (4)	0.042 (2)
O1	0.4416 (6)	0.2683 (6)	0.1557 (2)	0.0351 (12)
O2	0.2062 (5)	0.1727 (6)	0.0932 (3)	0.0293 (10)
O3	0.2677 (7)	0	0	0.027 (2)
O1*W*	0.4485 (9)	0.0084 (9)	1/4	0.047 (2)
O2*WA*†	0.091 (5)	−0.099 (6)	1/4	0.156 (8)
O2*WB*†	0.129 (4)	−0.163 (5)	1/4	0.117 (7)
O3*W*‡	0.221 (1)	−0.282 (1)	0.136 (1)	0.109 (6)

† Site occupancy = 0.50. ‡ Site occupancy = 0.33.

Table 2. *Selected geometric parameters (Å, °)*

La—O1	2.502 (4)	C1—O2	1.252 (9)
La—O1*W*	2.667 (7)	C1—C2	1.499 (13)
Eu—O2	2.427 (4)	C2—O3	1.426 (7)
Eu—O3	2.488 (6)	O3—C2$^{\rm i}$	1.426 (7)
C1—O1	1.235 (8)		
O1$^{\rm ii}$—La—O1	80.4 (2)	O2—Eu—O2$^{\rm viii}$	78.9 (2)
O1$^{\rm iii}$—La—O1	136.23 (8)	O2—Eu—O3$^{\rm ix}$	136.52 (12)
O1—La—O1$^{\rm iv}$	83.6 (2)	O2—Eu—O3$^{\rm viii}$	74.54 (10)
O1$^{\rm ii}$—La—O1*W*	66.4 (2)	O2—Eu—O3	62.68 (10)
O1$^{\rm v}$—La—O1*W*	138.14 (12)	O1—C1—O2	124.7 (10)
O1—La—O1*W*	69.9 (2)	O1—C1—C2	117.5 (7)
O2—Eu—O2$^{\rm vi}$	149.1 (2)	O2—C1—C2	117.7 (6)
O2—Eu—O2$^{\rm i}$	125.4 (2)	O3—C2—C1	109.0 (5)
O2—Eu—O2$^{\rm vii}$	87.0 (2)	C2—O3—C2$^{\rm i}$	113.9 (7)

Symmetry codes: (i) $x - y, -y, -z$; (ii) $1 - y, x - y, z$; (iii) $1 - y, x - y, \frac{1}{2} - z$; (iv) $x, y, \frac{1}{2} - z$; (v) $1 - x + y, 1 - x, \frac{1}{2} - z$; (vi) $-x, -x + y, -z$; (vii) $y, x, -z$; (viii) $-y, x - y, z$; (ix) $-x + y, -x, z$.

The total water content per formula unit was known to be eight molecules, as found from TGA measurements. The positions of the three coordinated water molecules (O1*W*'s) bound to the La atom were readily obtained and satisfactorily refined. The remaining five hydration water molecules (O2*W*, O3*W*) were located after some effort due to crystallographic disorder. Other space-group assignments of lower symmetry were checked, but the structure was best refined in $P\bar{6}2c$ (No. 190). The H atoms corresponding to water molecules could not be found and correspondingly were not included in the refinement. Those bonded to the C atoms were included at calculated positions and allowed to ride, with C—H = 0.95 Å and an isotropic displacement parameter proportional to $U_{\rm eq}$ of the C carrier.

Data collection: *P3/P4-PC* (Siemens, 1991). Cell refinement: *P3/P4-PC*. Data reduction: *XDISK* in *SHELXTL/PC* (Sheldrick, 1991). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *XP* in *SHELXTL/PC*. Software used to prepare material for publication: *CIFTAB* (Sheldrick, 1993) and *PARST* (Nardelli, 1983). Literature search: *CSD* (Allen *et al.*, 1983).

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(15-Crown-5)caesium Dicopper(I) Triiodide, (15-Crown-5)potassium Dicopper(I) Triiodide and (15-Crown-5)rubidium Dicopper(I) Triiodide

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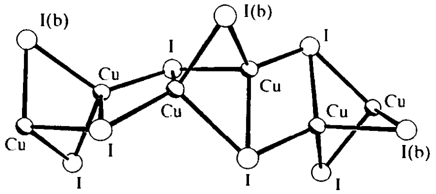
Abstract

(15-Crown-5)caesium triiododicopper(I), [Cs($C_{10}H_{20}O_5$)][Cu_2I_3], (15-crown-5)potassium triiododicopper(I), [K($C_{10}H_{20}O_5$)][Cu_2I_3], and (15-crown-5)rubidium triiododicopper(I), [Rb($C_{10}H_{20}O_5$)][Cu_2I_3], are isostructural. They contain a polymeric $Cu_2I_3^-$ moiety, *catena*-poly[[copper(I)-μ_2-iodo-copper(I)]-di-μ_3-iodo], which may be viewed as a series of opposite edge-sharing Cu_2I_2 rhombs, with alternate units bridged by an additional I atom in an up, up, down, down pattern.

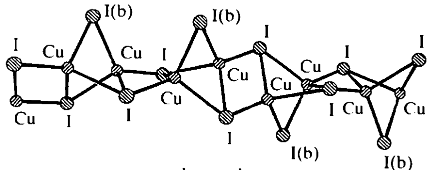
Comment

Copper(I) halide complexes have been observed to exhibit a wide variety of stoichiometries depending upon the identities of halide, counterion, solvent and conditions of synthesis (Rath & Holt, 1986). These complexes may be viewed as composed of rhombs of alternating Cu and halide atoms which may be combined in various ways. While many of these are discrete cluster species (Hu & Holt, 1994*a*,*b*), others such as $Cu_3I_4^-$ (Rath & Holt, 1985) and $Cu_2I_3^-$ are polymeric in nature.

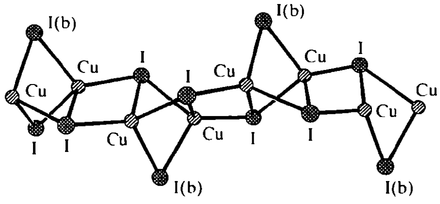
The $Cu_2I_3^-$ polymer may be viewed as a chain of Cu_2I_2 rhombs which share opposite edges, with an additional I atom bridging the Cu atoms of every alternate rhomb. However, the bridging I atoms may show bridging on the same side of the polymeric sheet, bridging in the sequence two up, two down, *etc.*, or bridging on alternating sides of the polymer (Fig. 1).



up, up, up, up



up, up, down, down



up, down, up, down

Fig. 1. Three variations of bridging.

Only one example is known in which all bridging is on the same side of the polymeric sheet: [2,4,6-triphenylthiopyrylium][Cu_2I_3] (Batsanov *et al.*, 1982) crystallizes with a helix-like tertiary structure in which the bridging I atoms project outwards (up, up, up, up; Fig. 1).

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