Structure and thermal decomposition of poly[[triaqua(μ_4-oxydiacetato)-lanthanum(III)] nitrate]

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In the title lanthanum complex, $\{[La(C_4H_4O_5)(H_2O)_3]NO_3\}_n$, the lanthanum cation is immersed in a nine-coordinate environment provided by a tridentate oxydiacetate (oda) ligand (through two carboxylate and one ether O atoms), three carboxylate O atoms from neighbouring oda ligands and three aqua ligands. The LaO$_9$ polyhedra are interlinked into a tight three-dimensional framework, which leaves holes where the nitrate anions lodge. The links to the polymeric framework are by an extensive hydrogen-bonding scheme utilizing all the water H atoms. Thermogravimetric analysis shows that the three coordinated water molecules leave the structure in two well differentiated steps.

Comment

During the past few years, lanthanide manganese oxides have attracted scientific attention because of their unusual magnetic and transport properties and their technological importance as probable candidates for cathode materials in high-temperature solid oxide fuel cells (Fergus, 2006; Zhang *et al.*, 2007; Piao *et al.*, 2006). The interest in such ceramic materials has prompted a considerable growth in the development of alternative routes of synthesis, looking for the attainment of highly dispersed mixed oxides and oxide solid solutions with improved properties, low processing temperatures, better homogeneity and finer particles. Ln^{III} carboxylate complexes have received much attention (Vanhoyland *et al.*, 2005; Kumar *et al.*, 2006; Grazyna & Przemyslaw, 2005) because they have been found to be convenient precursors for the thermal preparation of the corresponding oxides. In previous work, we investigated the crystal structure and thermal behaviour of several copper and alkaline earth mixed formates, used as precursors in the chemical preparation of ceramic compounds (Polla *et al.*, 1995, 2000; Perazzo *et al.*, 1997). We also reported the preparation and the thermal and magnetic properties of

yttrium(III) and lanthanide(III) complexes with oxydiacetate as a connecting ligand in various mono- and heterometallic extended solids. Pursuing our interest in the obtainment and characterization of new lanthanide precursors, we report here the synthesis, crystal structure and thermal behaviour of $\{[La(oda)(H_2O)_3]NO_3\}_n$ (oda is oxydiacetate), (I). Although some monocationic La complexes containing either oda or nitrate ions have been reported so far in the literature (see discussion below), (I) is the first compound to be associated with both anions simultaneously.
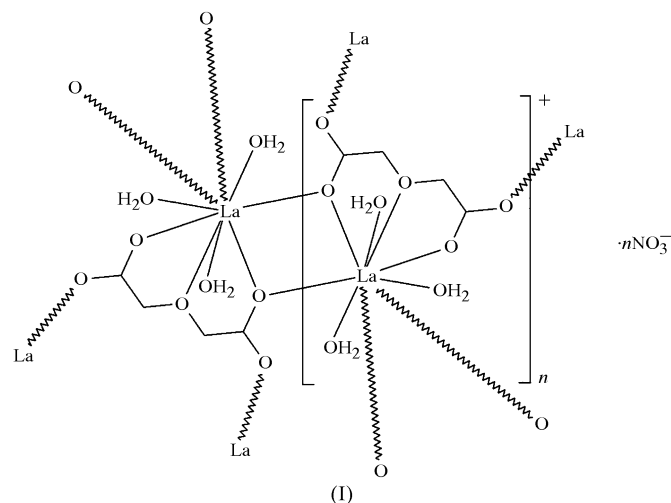

(I)

Fig. 1 shows the molecular structure of (I). The lanthanum cation is immersed in a nine-coordination environment provided by a tridentate oda ligand, through two carboxylate (O11 and O51) and one ether (O31) O atoms, three aqua ligands (O1W–O3W), and three carboxylate O atoms from three neighbouring oda ligands (O21^i, O41^{ii} and O11^{iii}; symmetry codes as in Table 1). The resulting coordination polyhedron has the shape of a distorted monocapped square antiprism with a capping O3W atom, a first plane being defined by O2W and the three carboxylate O atoms from neighbouring units, and a second plane by O1W and the tridentate oda bite, the angle between the planes being 8.6 (1)°. The molecule forms a dimer around the symmetry centre at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, through a double La—O—La bridge defined by the shared O11 atom and its symmetry-related atom. The
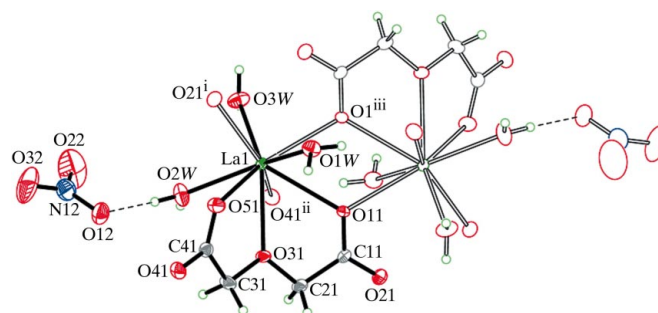

Figure 1
The dimeric unit in (I), showing the La coordination environment (displacement ellipsoids are shown at the 40% probability level). Only one of the hydrogen bonds linking the uncoordinated nitrate ion to the cation is shown (in broken lines). (The symmetry codes are as in Table 1.)

dinuclear unit thus defined (Fig. 1) constitutes the real building block in the structure.

The other two interactions have rather different well defined structural functions. Atom O41 links the reference dimer with its four nearest neighbours to form a two-dimensional structure parallel to the $(\bar{1}01)$ plane. These structures stack in a slanted fashion along [100], being in turn connected by O21 atoms into a three-dimensional array. Fig. 2(a) shows the packing of (I) along [101], where the compact two-
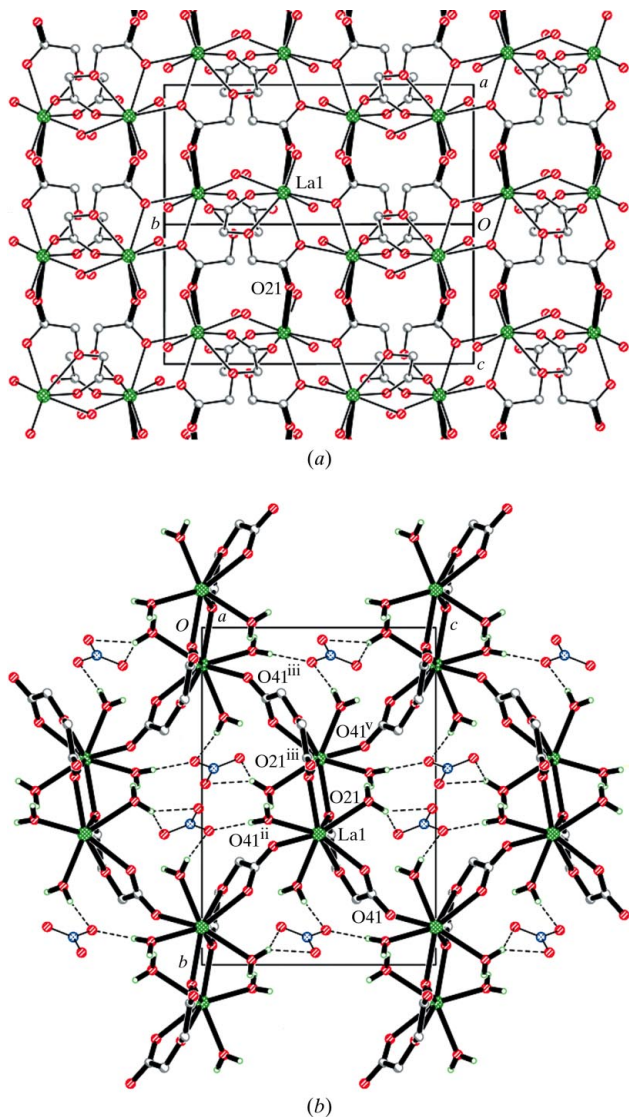

(a)

(b)

Figure 2
The packing of (I). (a) [101] view, showing in projection the two-dimensional substructures as well as their linkage. (b) [100] view, showing the same two-dimensional substructures (in heavy lines), this time along the stacking direction at 20.6 (1)° to the $[\bar{1}01]$ planes. The water-padded channels lodging the nitrate anions (in light lines) are clearly seen, as well as the hydrogen-bonding interactions (in broken lines) linking the latter to the polymeric framework. The four O41 atoms linking the reference dimer to its four nearest neighbours are labelled, as are some O21 atoms pointing (almost vertically in the picture) upwards and downwards, to serve as linkage to neighbouring planes. (The symmetry codes are as in Tables 1 and 2.)

dimensional structures are clearly seen in projection (as horizontal compact zones in light lines), as is their linkage through atoms O21 (heavy lines). The [100] projection shown in Fig. 2(b) clarifies the way in which the planes build up, through a four-nearest-neighbours interaction by way of atoms O41. The packing is quite compact along b and c, but leaves empty columnar spaces parallel to a, towards which the aqua ligands direct their H atoms. These hydrogen-padded channels are the locii where the nitrate anions locate. From this projection, and having the c axis as a reference, a conservative estimate of the internal H···H diameter of these channels is 0.4c, or about 4 Å. The simultaneous convergence of potentially good donors and acceptors for hydrogen bonding results in a complex interaction scheme, involving all six aqua H atoms (Table 2).

The nitrate O atoms enter into these types of interactions in a fairly uneven way, which correlates with the internal geometry of the anion as well as with its vibrational behaviour. Thus, atom O12, which is involved in stronger hydrogen bonds with two rather short O···H contacts towards two different dimers, has an (equivalent) isotropic displacement parameter that is very small for an uncoordinated O atom (0.03 Å^2), as well as the longest N—O distance. Atom O32, in turn, which interacts with a third binuclear unit through a single medium-strength hydrogen bond, has a medium-size displacement parameter and an intermediate N—O bond length. Finally, atom O22, which makes a couple of very weak contacts with small interaction angles (O—H···O < 130°, not presented in Table 2), shows the largest ellipsoid, typical for a terminal unbound O atom, and a shorter bond to the central N atom.

Two monocationic La(oda) complexes have already been reported in the literature, viz. La$_2$oda$_3$ (Baggio et al., 1998), which is isostructural with a whole lanthanide family of homologous compounds and contains two independent La units with coordination numbers 9 and 10, and (LaH$_2$O)$_2$(C$_2$O$_4$)-(oda)$_2$ (Trombe & Romero, 2000), where the oxalate anion is included in the coordination polyhedron and where the La
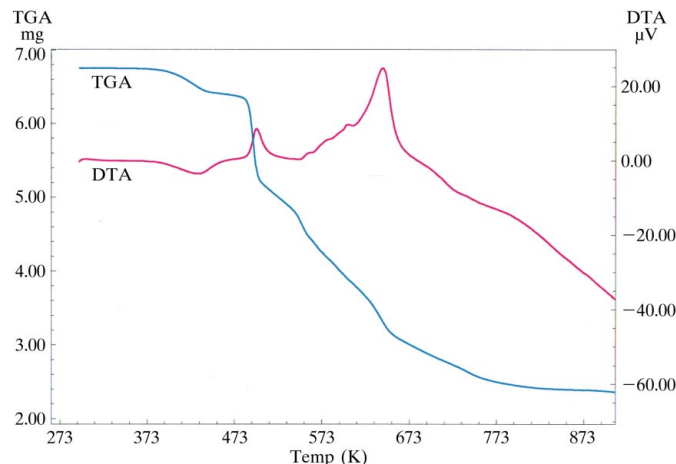

Figure 3
Combined TGA (mg)/DTA (μV) curves, representing the thermal decomposition data for (I).

atom has a coordination number of 10. Both complexes are [like (I)] three-dimensional polymers, confirming the unusual bridging capacity of the oda anion through its five O atoms. A search of the Cambridge Structural Database (CSD; Allen, 2002) for the different coordination modes known for oda confirms that almost all the reported cases share the chelating tridentate character of the anion towards some central cation (only four do not show coordination involving the central ether atom O31). The great diversity of binding modes arises from the extra bonds that the carboxylate O atoms can make, both those already involved in the central binding and the remaining 'external' O atoms. In this respect, the binding mode adopted by oda in the present structure [one bridging 'internal' (O11) and two monocoordinated 'external' (O21 and O41) carboxylate O atoms] is a novel one.

Regarding the La—$O_{carboxy}$ distances, a search of the CSD for LaO_9 cores with at least one O atom pertaining to a carboxylate group provided 316 entries with a mean La—$O_{carboxy}$ bond length of 2.51 (6) Å, slightly shorter than (though not significantly different from) the value found here [2.57 (6) Å].

The dehydration process takes place in two well differentiated stages (Fig. 3). The first step, between 370 and 450 K, corresponds to the release of one water molecule (theoretical weight loss: 5.0%; experimental: 4.9%), with an endothermic peak at about 420 K. After this, the two remaining water molecules are lost in the range 450–520 K, partially overlapping the decomposition of the nitrate ligand. These two simultaneous processes (the first slightly endothermic, the second largely exothermic) appear in the DTA curve as an integrated exothermic peak centred at about 490 K and take place *via* an oxydiacetic acid intermediate; this is not uncommon, and similar cases can be found in the literature [*e.g.* the hydrazinium analogues reported by Yasodhai & Govindarajan (2000)].

It is worth mentioning that the splitting of the water loss process is in line with the difference in binding strength of the water molecules, as measured by their corresponding bond valence (Brown & Altermatt, 1985) [0.334 for O1W (first step), and 0.396 and 0.389 for O2W and O3W (second step)]. Finally, the very steep process beginning at about 520 K and continuing smoothly up to about 820 K (centred at the exothermic peak at 650 K) corresponds to the decomposition of the oda ligand, yielding La_2O_3 oxide in a pure phase.

Experimental

Compound (I) was obtained by treating an equimolar aqueous solution of lanthanum nitrate and oxydiacetic acid in a refluxing system at 470 K for a period of 2 d; the pH of the solution was initially 2 but was adjusted to 5 using sodium hydroxide. After cooling, the solution was filtered and small colourless needle-shaped single crystals of the La complex were grown by slow evaporation at room temperature. In the thermal behaviour study, the total weight loss observed (57.9–58.1%, for repeated TGA measurements) is in good agreement with the theoretical loss (57.8%) required to obtain the corresponding La_2O_3 oxide.

Crystal data

[La(C$_4$H$_4$O$_5$)(H$_2$O)$_3$]NO$_3$	$V = 1039.49$ (13) Å^3
$M_r = 387.04$	$Z = 4$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 7.0510$ (5) Å	$\mu = 4.17$ mm^{-1}
$b = 14.5981$ (11) Å	$T = 295$ (2) K
$c = 10.6214$ (8) Å	$0.28 \times 0.08 \times 0.08$ mm
$\beta = 108.046$ (2)°	

Data collection

Bruker SMART CCD area-detector diffractometer	8490 measured reflections
	2328 independent reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)	2066 reflections with $I > 2\sigma(I)$
$T_{min} = 0.50$, $T_{max} = 0.72$	$R_{int} = 0.033$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.028$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.063$	
$S = 1.06$	
2328 reflections	$\Delta\rho_{max} = 1.05$ e Å^{-3}
172 parameters	$\Delta\rho_{min} = -0.55$ e Å^{-3}
9 restraints	

Table 1
Selected bond lengths (Å).

La1—O21^i	2.475 (3)	La1—O11^{iii}	2.604 (3)
La1—O3W	2.516 (3)	La1—O51	2.622 (3)
La1—O2W	2.521 (3)	La1—O11	2.633 (2)
La1—O41^{ii}	2.550 (3)	N12—O22	1.206 (6)
La1—O31	2.559 (3)	N12—O32	1.222 (6)
La1—O1W	2.576 (3)	N12—O12	1.259 (5)

Symmetry codes: (i) $x + 1, y, z$; (ii) $x - \frac{1}{2}, -y + \frac{3}{2}, z - \frac{1}{2}$; (iii) $-x + 1, -y + 1, -z + 1$.

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1W—H1$WA\cdots$O32^{iv}	0.86 (5)	2.29 (5)	3.015 (6)	141 (3)
O1W—H1$WB\cdots$O41^v	0.85 (4)	2.08 (4)	2.929 (4)	175 (4)
O2W—H2$WA\cdots$O51^{ii}	0.85 (4)	2.00 (4)	2.813 (4)	158 (4)
O2W—H2$WB\cdots$O12	0.85 (5)	1.93 (5)	2.773 (5)	169 (4)
O3W—H3$WA\cdots$O12^{ii}	0.84 (4)	1.91 (4)	2.742 (5)	166 (4)
O3W—H3$WB\cdots$O1W^{vi}	0.84 (4)	2.20 (4)	2.969 (4)	151 (4)

Symmetry codes: (ii) $x - \frac{1}{2}, -y + \frac{3}{2}, z - \frac{1}{2}$; (iv) $x - \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$; (v) $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$; (vi) $-x + 2, -y + 1, -z + 1$.

H atoms attached to carbon were positioned geometrically and treated as riding (C—H = 0.97 Å); those in the water molecules were found in a difference Fourier map and refined with restrained O—H [0.85 (3) Å] and H$\cdots$H [1.35 (4) Å] distances. In all cases, U_{iso}(H) values were taken as 1.2U_{eq}(C,O).

Data collection: *SMART-NT* (Bruker, 2001); cell refinement: *SAINT-NT* (Bruker, 2001); data reduction: *SAINT-NT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-NT* (Bruker, 2001); software used to prepare material for publication: *SHELXTL-NT* and *PLATON* (Spek, 2003).

metal-organic compounds

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