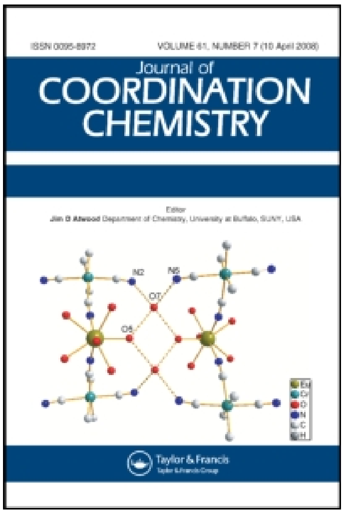

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SYNTHESIS AND STRUCTURE OF A THREE-DIMENSIONAL LANTHANUM(III) COORDINATION POLYMER WITH MELLITATE, $\{La_2[C_6(COO)_6](H_2O)_9\} \cdot 2H_2O$

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SYNTHESIS AND STRUCTURE OF A THREE-DIMENSIONAL LANTHANUM(III) COORDINATION POLYMER WITH MELLITATE, $\{La_2[C_6(COO)_6](H_2O)_9\}\cdot 2H_2O$

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The crystal and molecular structure of a lanthanum(III) mellitate, $La_2C_{12}H_{22}O_{23}$, has been determined by X-ray structural analysis using a combination of direct and heavy atom methods. The complex crystallizes in the monoclinic space group $P2_1/n$ with unit-cell dimensions of $a = 6.723(4)$, $b = 11.368(5)$, $c = 29.813(4)$ Å and $\beta = 95.851(3)°$. Block-diagonal least-squares refinement using automated diffractometer-collected data resulted in $R = 2.5$ and $R_w = 3.4$. The crystal structure consists of layers perpendicular to the *a* axis. Each layer is formed by an extended network of lanthanum ions coordinated with mellitate anions and water molecules, and linked through a complex three-dimensional hydrogen-bonding network. Among the six carboxylate groups of the mellitate anion, five form coordination bonds to six lanthanum atoms. The two independent lanthanum ions are both nine-coordinate and the configuration around lanthanum is a tricapped trigonal prism with the La-O bond distances ranging from 2.457 Å to 2.704 Å.

KEYWORDS: lanthanum, mellitic acid, hydrogen-bonding network, layer structure, three-dimensional

INTRODUCTION

Many aromatic complexes with rare earth elements exhibit a strong monochromatic fluorescence when exited with UV light and possess very important physical, chemical and biological properties which could be applied in several fields of science.[1] Mellitic acid (benzenehexacarboxylic acid) is one of 12 benzene carboxylic acids. The crystal structures of several mellitate anion complexes with both main group metal ions such as Ca[2] and Al[3], and transition metal ions such as Cu(II)[4], Ni(II)[5], Co(II)[6] and Y(III)[7], demonstrate that the multidentate complexing agent, mellitate anion, is capable of forming one-, two- or three-dimensional infinite connections with metal cations through carboxylate oxygen atoms. Among the six carboxyl groups of the mellitic acid, two to six can lose protons. This number varies with the nature of the cation and the reaction conditions employed. The polymeric chains obtained are held in the lattice in various ways, ranging from a

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1-dimensional ribbon-like structure[5] to 2-dimensional layered networks linked together by hydrogen bonds.[4]

In order to study the factors that determine the coordination mode of the mellitate anion it seemed appropriate to broaden our investigations by including other metals such as lanthanide. The considerable increase in size of lanthanide ions compared with first and second row transition-metal ions may cause a change in structure or in the coordination environment of the anion for homologous mellitate compounds of a lanthanide. To our knowledge, however, no X-ray investigation has been reported on such complexes. Our interests in two and three-dimensional polymers of metal ions interconnected by aromatic ligands with novel stereochemistry and unique physical properties led to the study of the preparation and structure determination of the lanthanum mellitate complex reported herein. The cerium(III)-mellitate complex has been prepared; the synthetic procedure and structure will be published elsewhere.

EXPERIMENTAL

Preparation

Crystals of $La_2C_{12}H_{18}O_{21}\cdot 2H_2O$ suitable for single crystal X-ray analysis were obtained by reaction of anhydrous $LaCl_3$(2.0 mM) and mellitic acid (0.2 mM) in an aqueous solution (5.0 mL); the pH of the solution was unadjusted. The mixture was stirred for 1 h and then filtered. The filtrate was sealed in a glass tube and after standing for two days in a water bath at 45 °C, colorless brick crystals were obtained. The crystals are only sparingly soluble in water. *Anal.* Calcd. %: C, 17.75; H, 2.71. Found %: C, 17.83; H, 2.35.

X-ray Structure Determination

Crystal data

$La_2C_{12}H_{22}O_{23}$, M = 811.8, monoclinic, space group *P*21/*n*, $a = 6.723(4)$, $b = 11.368(5)$, $c = 29.813(4)$ Å, $\beta = 95.851(3)°$, $V = 2267(1)$ Å^3, $Z = 4$, $D_c = 2.362$ g/cm^3, λ(Mo-Kα) = 0.71069 Å, $\mu = 38.38$ cm^{-1}, F(000) = 1544.

A single crystal of dimensions 0.08 × 0.08 × 0.15 mm was mounted with paraffin on a thin glass fiber. Intensity data were measured on a Rigaku AFC-5R four-circle diffractometer by an ω-2θ scan at 23°C and were corrected for Lorentz and polarization effects. Empirical absorption corrections were applied. A total of 5920 reflections for which $2\theta_{max} = 55.0°$ were collected. Of these data 5466 were unique.

The structure was solved by the direct method[8] (MITHRIL) and refined anisotropically for non-hydrogen atoms by block-diagonal least-squares calculations. Reliability factors are defined as $R = \Sigma(|F_o| - |F_c|)|\Sigma|F_o|$ and $R_w = \{\Sigma w(|F_o| - |F_c|)^2|\Sigma w|F_o|^2\}^{1/2}$, where $w = 4|F_o^2|\sigma(F_o^2)$. Atomic scattering factors and anomalous dispersion terms were taken from the International Tables for X-ray Crystallography, Vol IV.[9] All calculations were performed on a micro VAX computer using the TEXSAN crystallographic software package.[10] The final R and R_w values are 0.025 and 0.034, respectively. The details of the X-ray data collection, structure solution and refinement, a full set of bond lengths and angles, thermal parameters, and complete F_c and F_o tables are available from M. Munakata.

RESULTS AND DISCUSSION

Preparation of single crystals of the present complex suitable for X-ray analysis depends partly on the reaction temperature. With the same concentrations the reaction gave a white crystalline precipitate in a water bath over 50°C in a few hours time, but did not deposit any solid product at room temperature for 1 week. The colorless brick crystals are stable in water but decompose gradually, due to loss of water once isolated and dried in the air.

The final atomic coordinates for non-hydrogen atoms and equivalent thermal parameters are given in Table 1, selected bond lengths and bond angles in Table 2 and Table 3, respectively. Fig. 1 shows the perspective view and atom labeling scheme of a segment of the structure. A projection of the structure on the *bc* plane; Fig. 2, allows us to visualize the chain structure of the mellitate anions as well as the polyhedron surrounding the lanthanum atoms. There are no discrete molecules in the lattice and the crystal structure consists of hexaanions $C_6(COO)_6^{6-}$ which lie in planes perpendicular to the unit cell *a* axis and are linked together by coordination to polyhedral lanthanum ions. This results in a novel lanthanum coordination polymer with a three-dimensional network structure, Fig. 3.

The coordination mode of the mellitate anion is of special interest. Among the six carboxylate groups of the mellitate anion, five form coordination bonds to six lanthanum atoms, Fig. 4, and the remaining group forms a hydrogen bond to the nearby water molecules. The five coordinated carboxylate groups can be classified into the following three types according to their coordination environment: (1) acting as a bidentate ligand to coordinate one lanthanum atom in the formation of

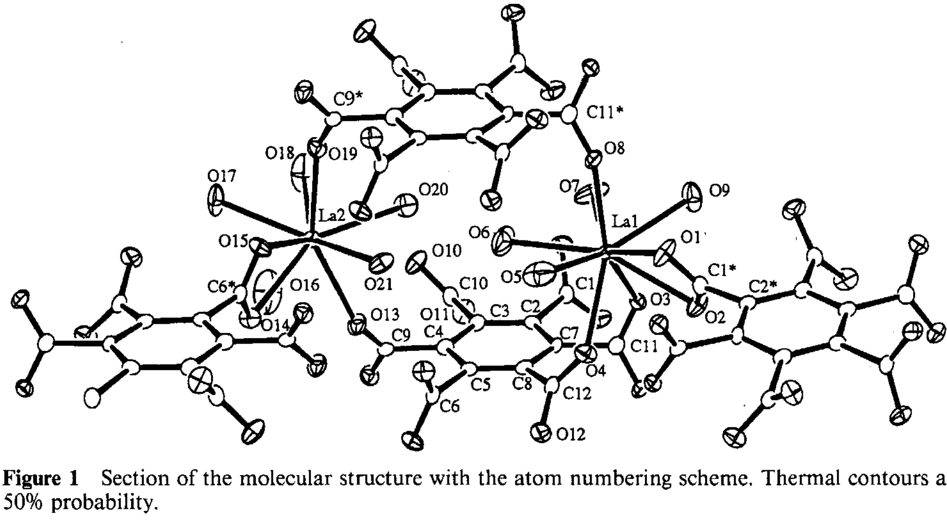

Figure 1 Section of the molecular structure with the atom numbering scheme. Thermal contours at 50% probability.

Table 1 Final atomic coordinates and equivalent thermal parameters

Atom	*x/a*	*y/b*	*z/c*	B_{eq}(Å^2)
La(1)	0.50091(3)	0.03294(2)	0.265525(7)	1.137(9)
La(2)	0.72352(3)	0.23664(2)	0.502594(7)	1.166(9)
O(1)	0.6083(5)	-0.1449(3)	0.2202(1)	2.5(1)
O(2)	0.2987(4)	-0.0918(3)	0.2017(1)	2.2(1)
O(3)	0.3392(4)	-0.3757(3)	0.25317(9)	1.5(1)
O(4)	0.2561(5)	-0.5950(3)	0.1998(1)	1.9(1)
O(5)	0.6520(6)	-0.1175(4)	0.3240(1)	4.1(2)
O(6)	0.5866(6)	0.1200(4)	0.3470(1)	3.9(2)
O(7)	0.5296(5)	0.2529(3)	0.2659(2)	3.4(2)
O(8)	0.6392(4)	-0.4413(3)	0.2396(1)	1.8(1)
O(9)	0.5326(6)	0.1095(3)	0.1858(1)	3.1(2)
O(10)	0.1985(5)	-0.0776(3)	0.0776(1)	2.3(1)
O(11)	0.5070(5)	-0.0400(3)	0.1081(1)	2.3(1)
O(12)	0.4445(5)	-0.6690(3)	0.1496(1)	2.0(1)
O(13)	0.1254(4)	-0.3236(3)	0.0184(1)	2.1(1)
O(14)	0.1285(4)	-0.5910(3)	0.0657(1)	1.9(1)
O(15)	0.4275(4)	-0.5652(3)	0.0438(1)	1.9(1)
O(16)	-0.0456(8)	-0.8450(4)	0.0500(2)	5.8(2)
O(17)	0.9235(6)	0.3137(3)	0.5738(1)	3.3(2)
O(18)	0.7754(8)	0.4620(3)	0.4995(1)	4.7(2)
O(19)	0.4319(4)	-0.2507(3)	0.0184(1)	1.9(1)
O(20)	0.1561(5)	-0.8143(3)	-0.0799(1)	2.8(1)
O(21)	0.2202(4)	-0.5544(3)	-0.0502(1)	2.2(1)
O(22)	1.010(1)	0.1721(7)	0.1470(2)	10.3(5)
O(23)	0.073(1)	0.035(1)	0.8383(3)	16.8(8)
C(1)	0.4437(6)	-0.1573(3)	0.1968(1)	1.4(1)
C(2)	0.4171(6)	-0.2559(3)	0.1631(1)	1.1(1)
C(3)	0.3732(6)	-0.2312(3)	0.1172(1)	1.3(1)
C(4)	0.3364(6)	-0.3243(3)	0.0867(1)	1.3(1)
C(5)	0.3374(5)	-0.4403(3)	0.1023(1)	1.1(1)
C(6)	0.2936(6)	-0.5385(3)	0.0685(1)	1.2(1)
C(7)	0.4212(6)	-0.3720(3)	0.1782(1)	1.1(1)
C(8)	0.3753(6)	-0.4638(3)	0.1478(1)	1.2(1)
C(9)	0.2954(6)	-0.2975(3)	0.0371(1)	1.3(1)
C(10)	0.3583(6)	-0.1055(3)	0.0999(1)	1.4(1)
C(11)	0.4722(6)	-0.3983(3)	0.2277(1)	1.2(1)
C(12)	0.3565(6)	-0.5861(3)	0.1668(1)	1.2(1)

four-membered chelate rings, as two *para*-related carboxylate groups bonded to C(2) and C(5), respectively; (2) acting as a bidentate ligand to bridge two lanthanum atoms, as two carboxylate groups bonded to C(4) and C(7) in a *para* position; (3) acting in a monodentate fashion as the one bonded to C(8). The type (1) and type (2) bindings between the carboxylate groups and the lanthanum ions are primarily responsible for the formation of the three-dimensional frameworks, Fig. 2 and Fig. 3. This is the first example in which the mellitate anion exhibits such a unique coordination mode compared with the published data[4-7] on analogous complexes of copper(II), nickel(II), cobalt(II) and yttrium(III).

Interatomic distances and angles of the mellitate anion are within the range of values previously reported for mellitic acid.[11] The benzene ring is planar with the maximum deviation of 0.0207 Å. The carboxyl carbon atoms deviate from the least-squares plane of the benzene ring in the range of +0.0997 Å to -0.1485 Å. Each plane of the carboxylate group is twisted out of the plane of the benzene ring

Table 2 Selected bond lengths (Å) for the complex

La(1)-O(1)	2.576(3)	O(4)-C(12)	1.253(5)
La(1)-O(2)	2.638(3)	O(8)-C(11)	1.244(5)
La(1)-O(3)^{i}	2.522(3)	O(10)-C(10)	1.246(5)
La(1)-O(4)^{i}	2.556(3)	O(11)-C(10)	1.251(5)
La(1)-O(5)	2.576(4)	O(12)-C(12)	1.250(5)
La(1)-O(6)	2.631(4)	O(13)-C(9)	1.255(5)
La(1)-O(7)	2.507(4)	O(14)-C(6)	1.256(5)
La(1)-O(8)	2.457(3)	O(15)-C(6)	1.258(5)
La(1)-O(9)	2.561(3)	O(19)-C(9)	1.241(5)
La(2)-O(13)^{i}	2.463(3)	C(1)-C(2)	1.503(5)
La(2)-O(14)^{iii}	2.633(3)	C(2)-C(3)	1.400(5)
La(2)-O(15)^{iii}	2.616(3)	C(2)-C(7)	1.394(5)
La(2)-O(16)^{iii}	2.704(5)	C(3)-C(4)	1.401(5)
La(2)-O(17)	2.550(3)	C(3)-C(10)	1.519(5)
La(2)-O(18)	2.589(4)	C(4)-C(5)	1.398(5)
La(2)-O(19)^{ii}	2.465(3)	C(4)-C(9)	1.507(5)
La(2)-O(20)^{iii}	2.608(3)	C(5)-C(6)	1.511(5)
La(2)-O(21)^{iii}	2.601(3)	C(5)-C(8)	1.381(5)
O(1)-C(1)	1.255(5)	C(7)-C(8)	1.396(5)
O(2)-C(1)	1.247(5)	C(7)-C(11)	1.511(5)
O(3)-C(11)	1.257(5)	C(8)-C(12)	1.511(5)

Equivalent positions: (i) 1/2 − x, 1/2 + y, 1/2 − z; (ii) − x, − y, − z;
(ii) 1/2 + x, 1/2 − y, 1/2 + z.

Table 3 Selected bond angles (°) for the complex

O(1)-La(1)-O(2)	49.51(9)	O(15)-La(2)-O(16)	116.1(1)
O(1)-La(1)-O(3)	120.25(9)	O(15)-La(2)-O(17)	70.0(1)
O(1)-La(1)-O(6)	137.1(1)	O(16)-La(2)-O(19)	143.4(1)
O(2)-La(1)-O(4)	70.5(1)	O(17)-La(2)-O(18)	68.2(1)
O(2)-La(1)-O(6)	156.5(1)	La(1)-O(1)-C(1)	95.8(2)
O(2)-La(1)-O(7)	124.9(1)	La(1)-O(2)-C(1)	93.1(2)
O(2)-La(1)-O(8)	117.2(1)	O(1)-C(1)-O(2)	121.5(4)
O(3)-La(1)-O(4)	71.9(1)	La(1)-O(3)-C(11)	117.8(2)
O(3)-La(1)-O(5)	135.2(1)	La(2)-O(14)-C(6)	94.0(2)
O(4)-La(1)-O(6)	86.2(1)	La(2)-O(15)-C(6)	94.8(2)
O(4)-La(1)-O(8)	143.5(1)	C(1)-C(2)-C(3)	120.2(3)
O(4)-La(1)-O(9)	133.8(1)	C(1)-C(2)-C(7)	119.6(3)
O(5)-La(1)-O(6)	65.9(1)	C(3)-C(2)-C(7)	120.0(3)
O(5)-La(1)-O(9)	142.1(1)	C(2)-C(7)-C(11)	119.8(3)
O(6)-La(1)-O(7)	67.1(1)	C(2)-C(3)-C(10)	121.4(3)
O(6)-La(1)-O(8)	83.6(1)	C(4)-C(3)-C(10)	119.3(3)
O(7)-La(1)-O(8)	78.8(1)	C(3)-C(4)-C(5)	120.2(4)
O(13)-La(2)-O(14)	73.3(1)	C(3)-C(4)-C(9)	119.1(3)
O(13)-La(2)-O(18)	113.2(1)	C(5)-C(4)-C(9)	120.8(3)
O(13)-La(2)-O(21)	71.1(1)	O(14)-C(6)-O(15)	121.7(4)
O(14)-La(2)-O(15)	49.46(9)	O(10)-C(10)-O(11)	125.5(4)
O(14)-La(2)-O(19)	121.4(1)	O(4)-C(12)-O(12)	125.2(4)

in the range of 48.23° to 74.39°. These twists and deviations might be due to the repulsion of the oxygen atoms of the adjacent carboxylate groups, and also to the formation of the hydrogen-bonding network, as will be discussed later. The mean C–O bond length, 1.251 Å, is comparable with those in Cu(II) (1.249 Å) and Y(III) (1.251 Å) complexes. Nevertheless, the C–O distances in the present compound, ranging from 1.241 Å to 1.258 Å, are not significantly different compared with

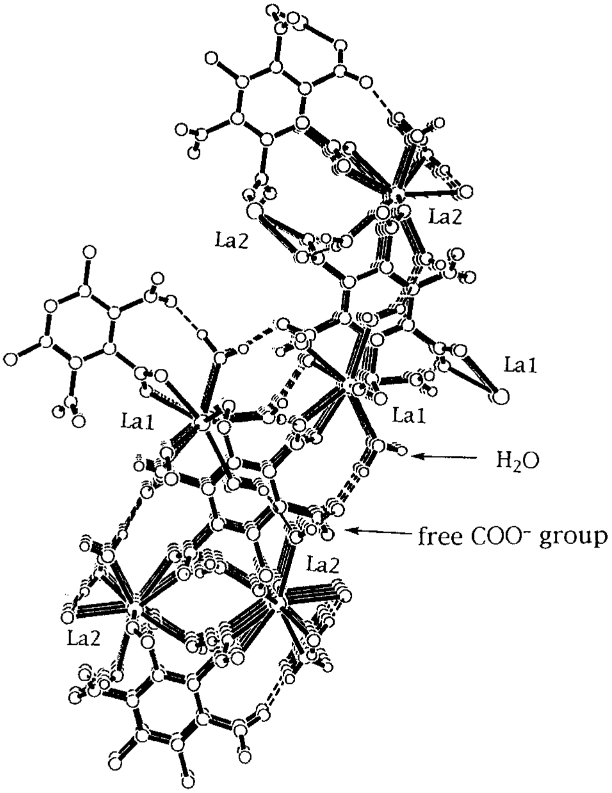

Figure 2 Projection of the structure on the *bc* plane. The hydrogen bonding is indicated by dashed lines.

those in the analogus β-type Cu mellitate compound which vary from 1.19 Å to 1.31 Å.

The two independent lanthanum ions are both nine coordinate in an essentially tricapped trigonal prism configuration, Fig. 5. This mode of bonding is commonly found in lanthanide coordination compounds.[12] La(1) is coordinated with four water molecules and five mellitate oxygen atoms while La(2) is bonded to five water molecules and four mellitate oxygen atoms. The two lanthanum ions are connected by a mellitate anion in an infinite -La(2)-La(2)-La(1)-La(1)- chain arrangement, Fig. 5(c). The La(1)-O distances range from 2.457 Å to 2.638 Å while the La(2)-O bond lengths are in the range of 2.463 Å to 2.704 Å.

The most interesting feature of the structure is the intricate arrangement of hydrogen-bonding. Water molecules are distributed about the crystal structure and nine of the eleven independent water molecules complete the coordination polyhedra around the lanthanum ions. The two oxygen atoms, O(22) and O(23), bonded to two crystallization water molecules are not associated directly with lanthanum cations, which explains their very large thermal parameters. The structue contains a three-dimensional hydrogen-bonded network linking polyhedral lanthanum cations with benzenehexacarboxylate anions, Fig. 2 and Fig. 3. Table 4 lists

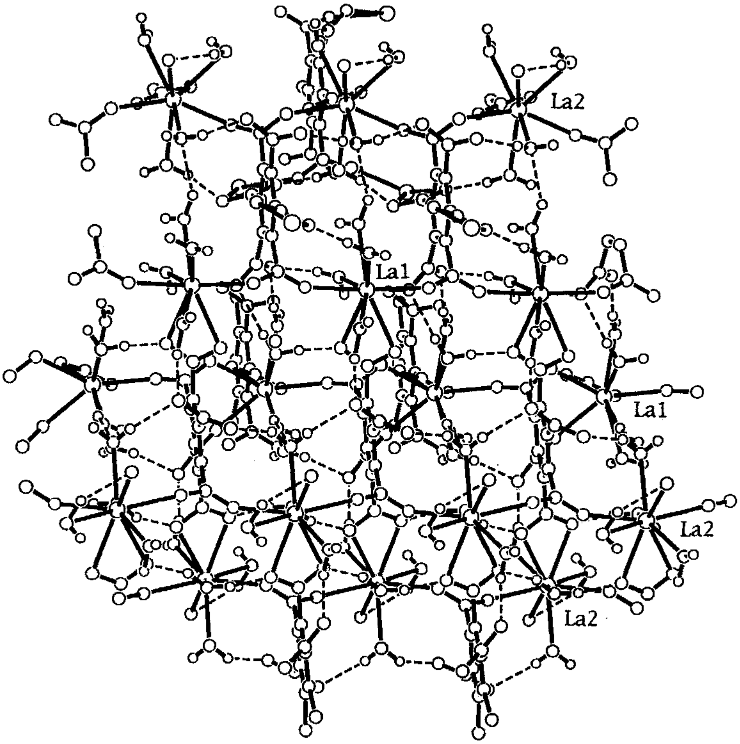

Figure 3 Projection of the structure on the *ac* plane. The hydrogen bonding is indicated by dashed lines.

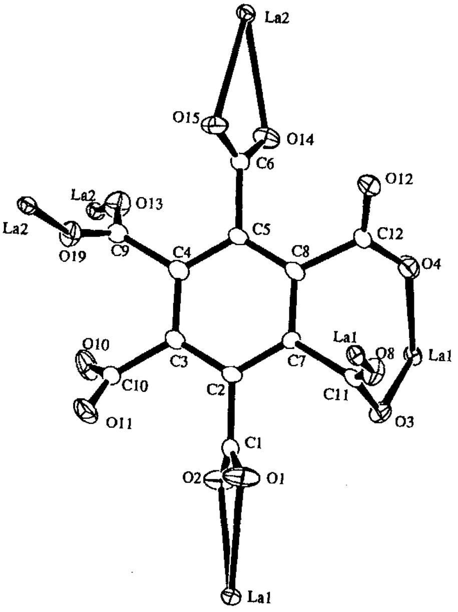

Figure 4 The coordination environment of the $C_6(COO)_6^{6-}$ anion.

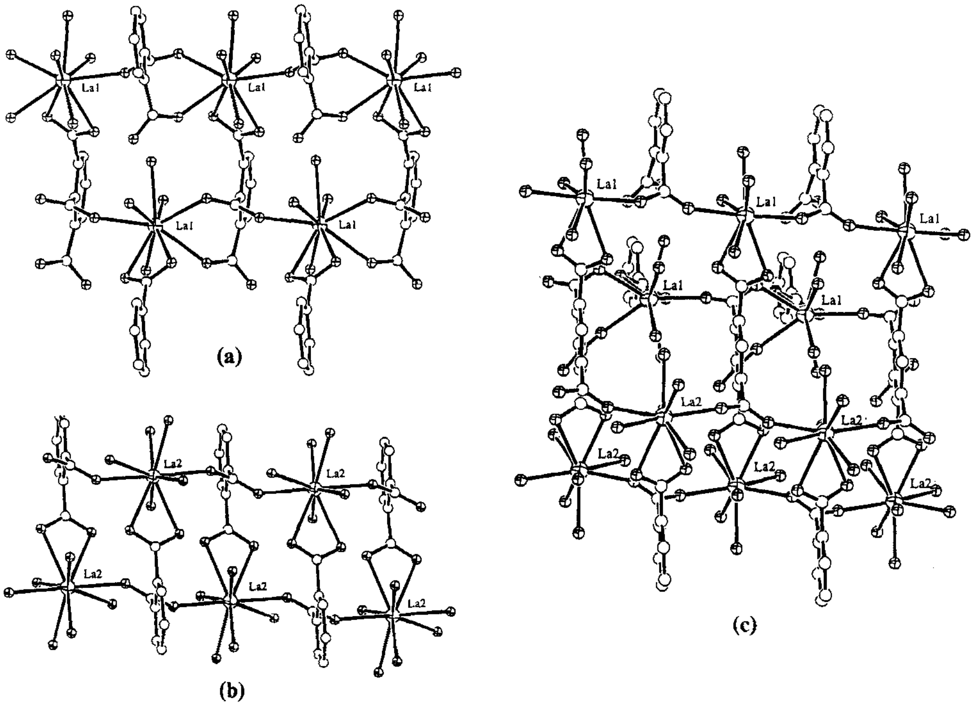

Figure 5 Stereoscopic view of a chain of the lanthanum ions connected by mellitate anion where non-bonded carboxylate groups are ommited for clarity, (a) for La(1); (b) for La(2) and (c) for La(2)-La(2)-La(1)-La(1) network arrangement.

Table 4 Hydrogen bond distances Å

O(2)...O(23)^{ii}	2.735(9)	O(3)...O(7)^{i}	2.884(5)
O(4)...O(5)^{i}	2.775(5)	O(5)...O(22)^{i}	2.801(9)
O(10)...O(18)^{iii}	2.767(5)	O(11)...O(17)^{iii}	2.803(5)
O(12)...O(9)	2.780(5)	O(12)...O(17)^{iii}	2.788(5)
O(12)...O(5)^{i}	2.808(5)	O(13)...O(16)^{ii}	2.811(6)
O(16)...O(22)	2.885(9)	O(18)...O(16)^{ii}	2.986(6)
O(20)...O(10)^{ii}	2.690(5)	O(20)...O(11)^{ii}	2.995(5)
O(1)...O(7)^{i}	2.692(5)	O(15)...O(21)^{ii}	2.721(4)
O(20)...O(18)^{iii}	2.945(5)	O(20)...O(23)	2.991(1)
O(21)...O(13)^{ii}	2.945(5)	O(21)...O(14)^{ii}	2.867(4)

Symmetry code: (i) 1/2 − x, 1/2 + y, 1/2 − z; (ii) −x, −y, −z;
(iii) 1/2 + x, 1/2 − y, 1/2 + z.

hydrogen bond distances within 3.0 Å. Short intermolecular hydrogen bonds have also been observed in copper(II) and yttrium(III) mellitate complexes, but the O(20)···O(10) distance of 2.690 Å in the present structure is among the shortest reported to date. The extremely short intermolecular hydrogen bond distances in Table 4 also suggest that in addition to the presence of hydrogen bonds between atoms of adjacent layers, there is the possibility of hydrogen-bonding through an intermediate molecule such as a water molecule situated between the layers. This complex three-dimensional hydrogen-bonding network, as well as the three-dimensional coordination network, obviously increases the crystal cohesion.

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