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Synthesis and crystal structure of a new coordination polymer based on lanthanum and 1,4-phenylenediacetate ligands

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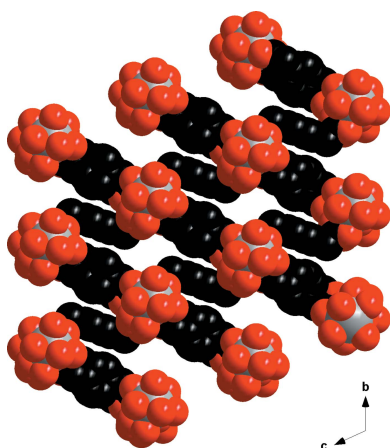
Reaction in gel between the sodium salt of 1,4-phenylenedi-acetic acid ($\text{Na}_2\text{C}_{10}\text{O}_4\text{H}_8\text{-Na}_2p\text{-pda}$) and lanthanum chloride yields single crystals of the three-dimensional coordination polymer poly[[tetraaquatris(μ -1,4-phenylenedi-acetato)dilanthanum(III)] octahydrate], $\{[\text{La}_2(\text{C}_{10}\text{H}_8\text{O}_4)_3(\text{H}_2\text{O})_4]\cdot 8\text{H}_2\text{O}\}_\infty$. The La^{III} coordination polyhedron can be described as a slightly distorted monocapped square antiprism. One of the two $p\text{-pda}^{2-}$ ligands is bound to four La^{III} ions and the other to two La^{III} ions. Each La^{III} atom is coordinated by five ligands, thereby generating a metal–organic framework with potential porosity properties.

1. Chemical context

In recent years, one of the most important fields of research in coordination chemistry and crystal engineering has been the design of metal–organic frameworks (MOFs), because of their intriguing network topologies and possible applications in gas storage (Eddaoudi *et al.*, 2002; Reneike *et al.*, 1999; Luo *et al.*, 2011*a,b*; Kustaryono *et al.*, 2010), catalysis (Lee *et al.*, 2009), separation (Hamon *et al.*, 2009), luminescence (Cui *et al.*, 2012; Daiguebonne *et al.*, 2008; Binnemans, 2009;) and molecular magnetism (Calvez *et al.*, 2008; Sessoli *et al.*, 2009). Our group has been involved in this field for more than a decade (Freslon *et al.*, 2014; Fan *et al.*, 2014; Luo *et al.*, 2011*a,b*; Badiane *et al.*, 2017*a,b*). The search for new ligands that can lead to new structural networks and/or new physical properties is a continuous concern (Qiu *et al.*, 2007; Fan *et al.*, 2015).

For the synthesis of MOFs, usually two complementary molecular precursors, a cation with vacant coordination sites and a bridging anion, are used to form the coordination polymer. This procedure offers the prospect of rationally designing extended solids with interesting properties. Most of the organic ligands used in MOF chemistry are rigid aromatic carboxylates (Luo *et al.*, 2007; Huang *et al.*, 2009). Compared to the rigid ligands, using flexible ligands such as 1,2- (Xin *et al.*, 2011), 1,3- (Wang *et al.*, 2012) or 1,4-phenylenedi-acetate (Fabelo *et al.*, 2009*a,b*) to construct coordination polymers seems to be more difficult, and developing synthetic methodologies is still a challenge. However, flexibility of the ligand can promote structural and functional diversity.

Numerous coordination polymers have been reported so far that involve d -block metal ions such as Cu^{II} (Singh & Barua, 2009; Fabelo *et al.*, 2009*a,b*; Chen *et al.*, 2010*a,b,c*), Zn^{II} (Singh



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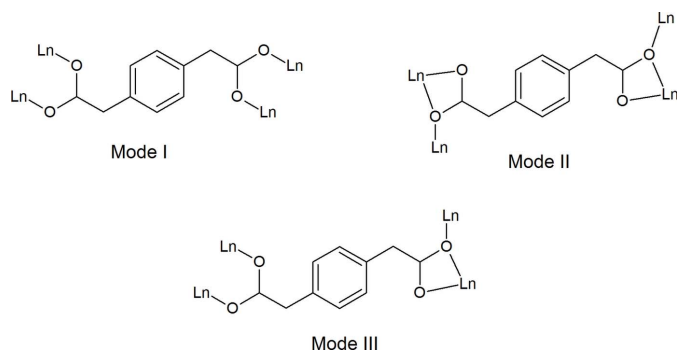


Figure 1
Bonding modes in lanthanide-containing coordination polymers with 1,4-phenylenediacetate ligands ($p\text{-pda}^{2-}$) reported in the literature to date.

& Barua, 2009), Cd^{II} (Chen *et al.*, 2010*a,b,c*; Singh & Barua, 2009; Li *et al.*, 2009), Mn^{II} (Singh & Barua, 2009; Chen *et al.*, 2010*a,b,c*), Co^{II} (Fabelo *et al.*, 2009*a,b*; Chen *et al.*, 2010*a,b,c*; Uebler & LaDuca, 2012; Li *et al.*, 2009) and Ni^{II} (Chen *et al.*, 2010*a,b,c*; Uebler & LaDuca, 2012; Li *et al.*, 2009). Lanthanide(III) ions have higher and variable coordination numbers (generally between 7 and 12) and incorporate in addition, apart from the main ligands, ancillary ligands such as water molecules into the lanthanide coordination sphere. A large number of studies have been reported on lanthanide coordination polymers based on 1,4-phenylenediacetic acid (Singh & Barua, 2009; Fabelo *et al.*, 2009*a,b*; Chen *et al.*, 2010*a,b,c*; Uebler & LaDuca, 2012; Li *et al.*, 2009; Rusinek *et al.*, 2013) as well as on other isomers of this acid such as 1,2- (Badiane *et al.*, 2017*a,b*; Xin *et al.*, 2011) and 1,3-phenylenediacetic acid (Wang *et al.*, 2012), and most of them tend to make porous materials through solvothermal synthesis.

Isomers of phenylenediacetic acid are flexible ligands and can therefore adopt different conformations in the crystal structure. 1,4-Phenylenediacetic acid is used as a readily available ligand that can coordinate two or more metal ions in bridging-mode, forming extended molecular networks (Pan *et al.*, 2003; Chen *et al.*, 2010*a,b,c*). The different coordination modes (Chen *et al.*, 2010*a,b,c*; Rusinek *et al.*, 2013; Ren *et al.*, 2011; Pan *et al.*, 2003; Singha *et al.*, 2014; Singha *et al.*, 2015) of the ligand with lanthanide ions that have been reported to date are shown in Fig. 1.

In this paper we report the synthesis and the crystal structure of a new coordination polymer with chemical formula $[\text{La}_2(p\text{-pda})_3(\text{H}_2\text{O})_4 \cdot 8\text{H}_2\text{O}]_\infty$.

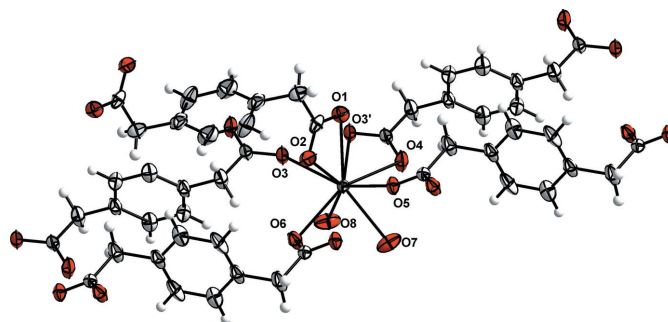
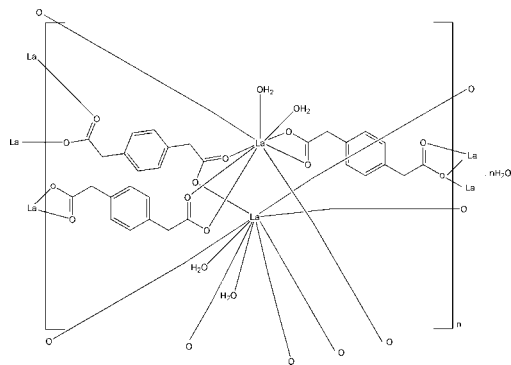


Figure 2
Coordination environment of La^{3+} in $[\text{La}_2(p\text{-pda})_3(\text{H}_2\text{O})_4 \cdot 8\text{H}_2\text{O}]_\infty$. Symmetry code: (') $2 - x, 1 - y, 1 - z$. Hydrogen atoms of the water molecules have been omitted for clarity.

2. Structural commentary

The crystallographically independent La^{3+} ion is nona-coordinated by seven oxygen atoms (O1, O2, O3, O4, O5, O6, O3') from five $p\text{-pda}^{2-}$ ligands and two oxygen atoms (O8 and O7) from the coordinating water molecules (Fig. 2). The coordination polyhedron can be described as a monocapped distorted square antiprism with atom O3' capping the polyhedron [symmetry code: (') $2 - x, 1 - y, 1 - z$]. The two square sides of the antiprism are formed by atoms O7, O6, O2, O5 and O8, O3, O1, O4, respectively. The dihedral angle between the two faces is $5.21(9)^\circ$. There are three independent ligands: **L1**, **L2** and **L3** (Fig. 3). The twisted ligand **L3** exhibits a coordination mode that has never previously been

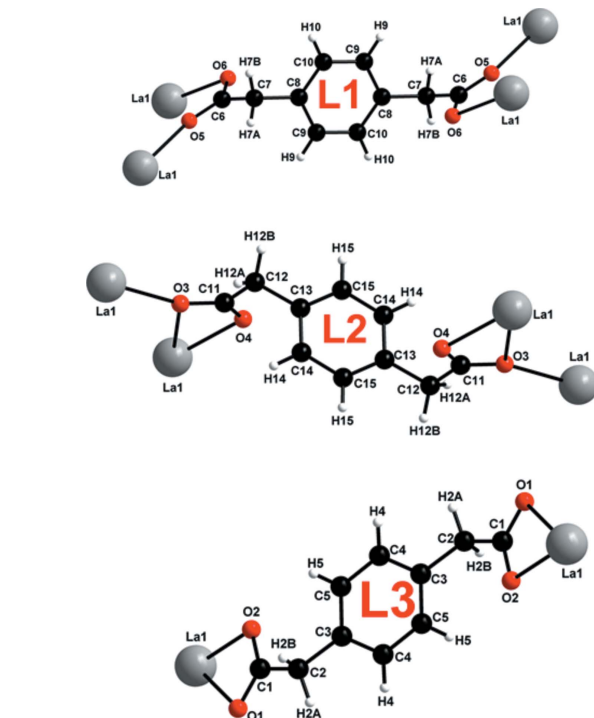


Figure 3
Coordination modes of ligand **L1** ($\mu\text{-4}$ bis-bidentate mode: $(\eta^1\text{-}\eta^1\text{-}\mu_2)$ - $(\eta^1\text{-}\eta^1\text{-}\mu_2)\text{-}\mu_4$), **L2** ($\mu\text{-4}$ bis-tridentate bridging and chelating mode: $(\eta^2\text{-}\eta^1\text{-}\mu_2)$ - $(\eta^2\text{-}\eta^1\text{-}\mu_2)\text{-}\mu_4$) and **L3** ($\mu\text{-2}$ bis-bidentate-chelating mode: $(\eta^1\text{-}\eta^1\text{-}\mu_1)$ - $(\eta^1\text{-}\eta^1\text{-}\mu_1)\text{-}\mu_2$).

Table 1
Hydrogen-bond geometry (Å, °).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|--------------------------------------|-----------|-------------|-------------|---------------|
| OW1—HW1A \cdots OW1 ⁱⁱⁱ | 0.87 (9) | 2.40 (11) | 3.067 (13) | 133 (9) |
| OW1—HW1B \cdots OW4 ^{iv} | 0.89 (9) | 2.54 (10) | 3.298 (11) | 145 (7) |
| OW2—HW2A \cdots O4 ⁱ | 0.82 (6) | 2.10 (6) | 2.895 (5) | 164 (6) |
| OW2—HW2B \cdots OW4 ^v | 0.82 (6) | 2.20 (5) | 2.855 (8) | 137 (5) |
| OW3—HW3A \cdots O6 ⁱ | 0.82 (8) | 2.02 (8) | 2.780 (8) | 154 (7) |
| OW3—HW3B \cdots OW1 ⁱⁱⁱ | 0.81 (7) | 2.40 (8) | 3.162 (11) | 156 (8) |
| OW4—HW4A \cdots OW2 ^{vi} | 0.81 (10) | 2.49 (9) | 2.855 (8) | 109 (9) |
| O7—H7A \cdots O2 ⁱ | 0.82 (4) | 1.95 (4) | 2.741 (5) | 161 (5) |
| O7—H7B \cdots OW4 | 0.81 (5) | 2.03 (5) | 2.800 (9) | 160 (5) |
| OW4—HW4B \cdots OW3 ^{vii} | 0.84 (9) | 2.11 (10) | 2.824 (11) | 143 (8) |
| O8—H8A \cdots OW3 ⁱ | 0.82 (4) | 2.38 (4) | 3.175 (8) | 165 (4) |
| O8—H8B \cdots O1 ⁱⁱⁱ | 0.83 (4) | 1.92 (4) | 2.725 (5) | 163 (5) |
| C7—H7D \cdots O4 ⁱ | 0.97 | 2.54 | 3.442 (6) | 154 |
| C12—H12B \cdots O6 ⁱⁱ | 0.97 | 2.51 | 3.406 (6) | 154 |

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x+2, -y+1, -z+1$; (iii) $-x+1, -y, -z+1$; (iv) $x, y-1, z$; (v) $x, y, z+1$; (vi) $x, y, z-1$; (vii) $x+1, y+1, z$.

observed in lanthanide-based coordination polymers involving the *p*-pda²⁻ ligand.

The monocapped square antiprisms are connected to each other by alternating **L1** bridging carboxylate oxygen atoms (O5 and O6) and edge-sharing polyhedra through **L2** oxygen atoms (O3), forming molecular chains along the *a*-axis direction (Fig. 4). These chains are connected to each other through

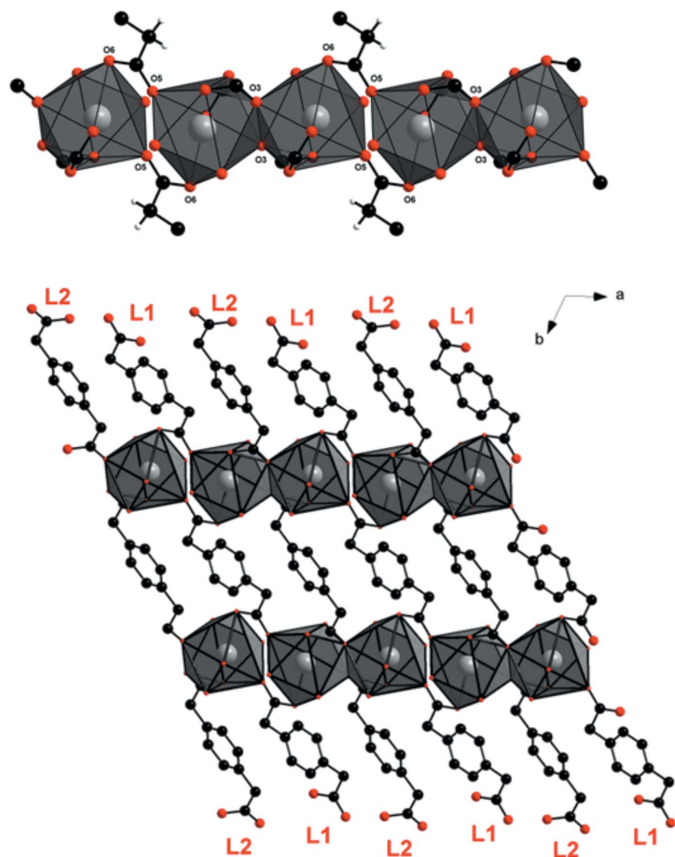


Figure 4
(Top) Projection view of a molecular chain extending parallel to the *a* axis. (Bottom) Projection view along the *c* axis of the two-dimensional molecular network of $[La_2(p\text{-pda})_3(H_2O)_4 \cdot 8H_2O]_\infty$. Hydrogen atoms have been omitted for clarity.

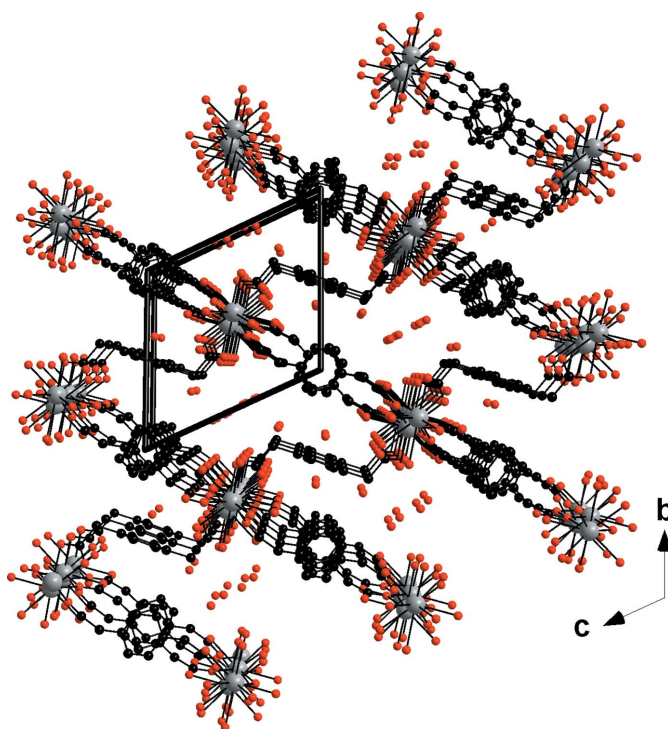


Figure 5
Perspective view along the *a* axis of $[La_2(p\text{-pda})_3(H_2O)_4 \cdot 8H_2O]_\infty$. Hydrogen atoms have been omitted for clarity.

ligands **L1** and **L2**, which play the role of spacers, forming molecular layers that extend parallel to the *ab* plane (Fig. 4).

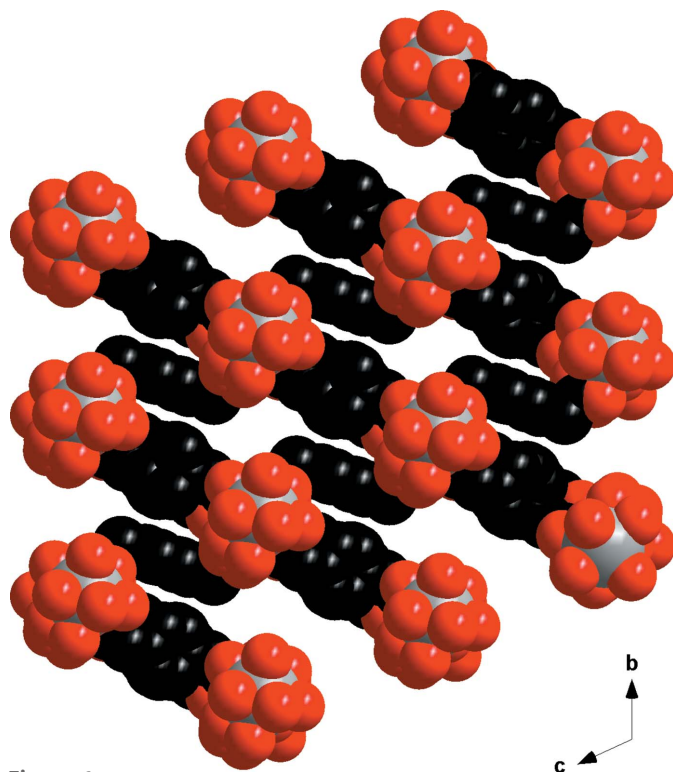


Figure 6
Projection view along the *a* axis of the molecular skeleton of $[La_2(p\text{-pda})_3(H_2O)_4 \cdot 8H_2O]_\infty$ in space-filling mode. Hydrogen atoms and crystallization water molecules have been omitted.

These layers are further connected through the twisted ligand **L3**, leading to a three-dimensional molecular framework (Fig. 5). Ligand **L3** acts as a spacer between the different polymeric layers because of its *anti-anti* conformation.

The framework has channels along the *a*-axis direction in which the water molecules of crystallization are located. They are bound to the molecular skeleton *via* a hydrogen-bonded network (Table 1). As can be seen from Fig. 6, the three-dimensional crystal structure could potentially present some porosity properties. Indeed, removal of the water molecules of crystallization could create empty channels, as has been reported previously (Kustaryono *et al.*, 2010; Kerbellec *et al.*, 2008). For the coordination polymer in this study, the potential porosity is calculated to be $750(20) \text{ m}^2 \text{ g}^{-1}$ for N_2 with a kinetic radius of 1.83 \AA . The calculation was performed using a method described elsewhere (Kustaryono *et al.*, 2010; Kerbellec *et al.*, 2008).

Other crystal structures of lanthanide coordination polymers with the *p*-pda²⁻ ligand have been reported previously. This series of compounds, first described by Pan *et al.* (2003) has been widely studied because of potential applications in various fields such as explosives detection (Singha *et al.*, 2014, 2015), gas sorption (Pan *et al.*, 2003) or catalysis (Ren *et al.*, 2011). These compounds, with general chemical formula $[\text{Ln}_2(\text{p-pda})_3(\text{H}_2\text{O})\cdot 2\text{H}_2\text{O}]_\infty$ with *Ln* = La–Ho have been obtained by hydrothermal synthesis and therefore present a lower hydration rate and a higher density than $[\text{La}_2(\text{p-pda})_3(\text{H}_2\text{O})_4\cdot 8\text{H}_2\text{O}]_\infty$ ($D_{\text{calc}} = 1871 \text{ g cm}^{-3}$ for $[\text{Ln}_2(\text{p-pda})_3(\text{H}_2\text{O})\cdot 2\text{H}_2\text{O}]_\infty$). Their three-dimensional crystal structures can be described on the basis of helicoidal molecular chains linked by *p*-pda²⁻ ligands.

The luminescent and porosity properties of these compounds are interesting, which suggests that the physical properties of compounds isostructural to $[\text{La}_2(\text{p-pda})_3(\text{H}_2\text{O})_4\cdot 8\text{H}_2\text{O}]_\infty$ and involving other lanthanide ions (lanthanum is a diamagnetic non-luminescent ion) would be worth studying. Unfortunately, despite great synthetic efforts, no such compound has been obtained to date.

The compound reported here was obtained by crystallization in a gel (see next section; Luo *et al.*, 2013), and as such is the first result from our group related to lanthanide-based coordination polymers with 1,4-phenylenediacetate ligands.

3. Synthesis and crystallization

Lanthanum oxide (La_2O_3) was suspended in a small quantity of water. The suspension was then brought to about 323 K and concentrated hydrochloric acid was added dropwise under magnetic stirring, until a clear solution was obtained. The solution was then evaporated to dryness and the resulting solid was dissolved in absolute ethanol for removal of the residual hydrochloric acid. Crystallization of the salt was then obtained by adding diethyl ether (Et_2O). The obtained microcrystalline solid was filtered and dried in the open air. The product $\text{LaCl}_3\cdot 7\text{H}_2\text{O}$ was obtained in close to 100% yield.

1,4-Phenylenediacetic acid, $\text{H}_2(\text{p-pda})$, was purchased from Sigma–Aldrich and used without further purification. Its

Table 2
Experimental details.

| | |
|--|---|
| Crystal data | |
| Chemical formula | $[\text{La}_2(\text{C}_{10}\text{H}_8\text{O}_4)_3(\text{H}_2\text{O})_4]\cdot 8\text{H}_2\text{O}$ |
| M_r | 1070.05 |
| Crystal system, space group | Triclinic, $P\bar{1}$ |
| Temperature (K) | 293 |
| <i>a</i> , <i>b</i> , <i>c</i> (Å) | 9.1197 (2), 11.1231 (2), 11.9434 (2) |
| α , β , γ (°) | 107.049 (1), 107.729 (1), 106.622 (1) |
| <i>V</i> (Å ³) | 1005.21 (3) |
| <i>Z</i> | 1 |
| Radiation type | Mo <i>K</i> α |
| μ (mm ⁻¹) | 2.18 |
| Crystal size (mm) | 0.08 × 0.06 × 0.05 |
| Data collection | |
| Diffractometer | Nonius KappaCCD |
| No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections | 4588, 4588, 3751 |
| R_{int} | 0.045 |
| ($\sin \theta/\lambda$) _{max} (Å ⁻¹) | 0.649 |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, <i>S</i> | 0.030, 0.068, 1.03 |
| No. of reflections | 4588 |
| No. of parameters | 283 |
| No. of restraints | 18 |
| H-atom treatment | H atoms treated by a mixture of independent and constrained refinement |
| $\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³) | 1.76, −0.65 |

Computer programs: *COLLECT* (Bruker, 2004), *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997), *SHELXT* (Sheldrick, 2015a), *SHELXL* (Sheldrick, 2015b), *DIAMOND* (Brandenburg, 2001), *WinGX* (Farrugia, 2012).

disodium salt was prepared by addition of two equivalents of sodium hydroxide to a suspension of the acid in de-ionized water. The obtained clear solution was evaporated to dryness and then refluxed in ethanol for one h. Addition of diethyl ether provoked precipitation of $\text{Na}_2(\text{p-pda})$ in 90% yield. UV–vis absorption spectrum of a $4.3 \times 10^{-4} \text{ mol L}^{-1}$ aqueous solution of the disodium salt of $\text{H}_2(\text{p-pda})$ was measured with a Perkin–Elmer Lambda 650 spectrometer equipped with a 60 mm integrating sphere. It showed a maximum absorption at 225 nm. This short absorption wavelength, compared to other ligands in the literature (Badiane *et al.*, 2017a,b; Freslon *et al.*, 2016; Fan *et al.*, 2015; Badiane *et al.*, 2018), can be related to the $-\text{CH}_2-$ groups that cut conjugation.

Single crystals of the coordination polymer were obtained by slow diffusion of dilute aqueous solutions of lanthanum chloride (0.25 mmol in 10 mL) and of the sodium salt of *para*-phenylenediacetate (0.25 mmol in 10 mL) through an agar-agar gel in a U-shaped tube. The gel was purchased from Acros Organics and jellified according to established procedures (Henisch, 1988; Daiguebonne *et al.*, 2003). After several weeks, prismatic single crystals were obtained.

4. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Hydrogen atoms bound to the organic ligands were placed at idealized positions ($\text{C}-\text{H} = 0.93\text{--}0.97 \text{ \AA}$) and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

The water hydrogen atoms were localized and constrained. The thermal agitation of the two water molecules of crystallization was constrained. In order to stabilize the refinement several restraints (DANG, DFIX) were used for the hydrogen atoms bound to water oxygens.

Acknowledgements

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supporting information

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Synthesis and crystal structure of a new coordination polymer based on lanthanum and 1,4-phenylenediacetate ligands

Magatte Camara, Insa Badiane, Mamoudou Diallo, Carole Daguebonne and Olivier Guillou

Computing details

Data collection: *COLLECT* (Bruker, 2004); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015b); molecular graphics: *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *WinGX* (Farrugia, 2012).

Poly[[tetraaquatris(μ -1,4-phenylenediacetato)dilanthanum(III)] octahydrate]

Crystal data

$[\text{La}_2(\text{C}_{10}\text{H}_8\text{O}_4)_3(\text{H}_2\text{O})_4] \cdot 8\text{H}_2\text{O}$

$M_r = 1070.05$

Triclinic, $P\bar{1}$

Hall symbol: -P 1

$a = 9.1197$ (2) Å

$b = 11.1231$ (2) Å

$c = 11.9434$ (2) Å

$\alpha = 107.049$ (1)°

$\beta = 107.729$ (1)°

$\gamma = 106.622$ (1)°

$V = 1005.21$ (3) Å³

$Z = 1$

$F(000) = 534$

$D_x = 1.768$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 15558 reflections

$\theta = 2.9\text{--}27.5^\circ$

$\mu = 2.18$ mm⁻¹

$T = 293$ K

Prism, colorless

$0.08 \times 0.06 \times 0.05$ mm

Data collection

Nonius KappaCCD
diffractometer

Radiation source: Enraf Nonius FR590

Horizontally mounted graphite crystal
monochromator

Detector resolution: 9 pixels mm⁻¹

CCD rotation images, thick slices scans

4588 measured reflections

4588 independent reflections

3751 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.045$

$\theta_{\text{max}} = 27.5^\circ$, $\theta_{\text{min}} = 3.6^\circ$

$h = -10 \rightarrow 11$

$k = -14 \rightarrow 14$

$l = -15 \rightarrow 15$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.030$

$wR(F^2) = 0.068$

$S = 1.03$

4588 reflections

283 parameters

18 restraints

0 constraints

Primary atom site location: dual

Secondary atom site location: dual

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0308P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$$(\Delta/\sigma)_{\max} = 0.001$$

$$\Delta\rho_{\max} = 1.76 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.65 \text{ e } \text{\AA}^{-3}$$

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|-------------|-------------|-------------|----------------------------------|
| La1 | 0.75090 (2) | 0.52031 (2) | 0.47969 (2) | 0.02048 (7) |
| O5 | 0.4472 (3) | 0.3677 (2) | 0.4069 (2) | 0.0332 (6) |
| O3 | 1.0575 (3) | 0.5881 (3) | 0.6253 (2) | 0.0323 (6) |
| O1 | 0.7627 (3) | 0.3041 (3) | 0.5311 (2) | 0.0336 (6) |
| O6 | 0.8146 (3) | 0.7579 (3) | 0.6435 (3) | 0.0362 (6) |
| O2 | 0.7422 (3) | 0.4674 (3) | 0.6736 (2) | 0.0351 (6) |
| O4 | 0.6840 (3) | 0.3616 (3) | 0.2490 (2) | 0.0415 (7) |
| O7 | 0.5690 (4) | 0.5882 (4) | 0.3233 (3) | 0.0486 (8) |
| H7A | 0.468 (3) | 0.558 (4) | 0.307 (5) | 0.058* |
| H7B | 0.591 (5) | 0.651 (4) | 0.302 (5) | 0.058* |
| O8 | 0.9316 (4) | 0.7051 (3) | 0.4326 (4) | 0.0503 (8) |
| H8A | 0.947 (6) | 0.785 (3) | 0.470 (4) | 0.060* |
| H8B | 1.026 (4) | 0.712 (4) | 0.435 (5) | 0.060* |
| C6 | 0.6834 (4) | 0.7426 (3) | 0.6621 (3) | 0.0260 (7) |
| C11 | 0.8165 (4) | 0.3436 (3) | 0.2659 (3) | 0.0261 (7) |
| C1 | 0.7640 (4) | 0.3589 (4) | 0.6405 (4) | 0.0315 (8) |
| C13 | 0.6579 (5) | 0.1147 (4) | 0.0739 (4) | 0.0340 (9) |
| C12 | 0.8247 (5) | 0.2382 (4) | 0.1565 (4) | 0.0390 (9) |
| H12A | 0.857342 | 0.281262 | 0.102898 | 0.058* |
| H12B | 0.910563 | 0.207990 | 0.192279 | 0.058* |
| C14 | 0.6017 (5) | 0.0190 (4) | 0.1196 (4) | 0.0427 (10) |
| H14 | 0.669560 | 0.030195 | 0.201149 | 0.051* |
| C8 | 0.8472 (5) | 0.9325 (4) | 0.8881 (4) | 0.0340 (9) |
| C10 | 0.9564 (5) | 1.0646 (4) | 0.9217 (4) | 0.0433 (10) |
| H10 | 0.928413 | 1.109955 | 0.869797 | 0.052* |
| C15 | 0.5547 (5) | 0.0946 (4) | -0.0469 (4) | 0.0412 (10) |
| H15 | 0.589046 | 0.157191 | -0.080797 | 0.049* |
| C7 | 0.6832 (5) | 0.8578 (4) | 0.7675 (4) | 0.0445 (11) |
| H7C | 0.660724 | 0.923722 | 0.734480 | 0.067* |
| H7D | 0.592152 | 0.819798 | 0.789973 | 0.067* |
| C9 | 0.8927 (6) | 0.8687 (4) | 0.9685 (4) | 0.0461 (11) |
| H9 | 0.820475 | 0.779508 | 0.948162 | 0.055* |
| C3 | 0.8997 (5) | 0.3972 (4) | 0.8732 (4) | 0.0392 (9) |
| C4 | 1.0738 (6) | 0.4427 (5) | 0.9267 (4) | 0.0514 (11) |
| H4 | 1.125405 | 0.405378 | 0.878263 | 0.062* |
| C5 | 0.8281 (6) | 0.4561 (5) | 0.9477 (4) | 0.0501 (11) |
| H5 | 0.711419 | 0.427472 | 0.913133 | 0.060* |

| | | | | |
|------|-------------|------------|------------|-------------|
| C2 | 0.7931 (6) | 0.2928 (4) | 0.7347 (4) | 0.0460 (10) |
| H2A | 0.684726 | 0.235879 | 0.727251 | 0.069* |
| H2B | 0.848359 | 0.233001 | 0.711571 | 0.069* |
| OW1 | 0.6313 (10) | 0.0072 (5) | 0.4440 (6) | 0.1327 (17) |
| HW1A | 0.589 (11) | -0.025 (9) | 0.491 (8) | 0.159* |
| HW1B | 0.639 (13) | -0.072 (6) | 0.411 (8) | 0.159* |
| OW2 | 0.5351 (5) | 0.6185 (4) | 0.9718 (4) | 0.0741 (11) |
| HW2A | 0.476 (7) | 0.639 (6) | 0.920 (5) | 0.111* |
| HW2B | 0.622 (6) | 0.678 (5) | 1.033 (5) | 0.111* |
| OW3 | 0.0357 (9) | 0.0056 (6) | 0.3870 (6) | 0.1327 (17) |
| HW3A | 0.059 (10) | 0.059 (7) | 0.354 (7) | 0.159* |
| HW3B | 0.122 (7) | 0.023 (10) | 0.447 (6) | 0.159* |
| OW4 | 0.7105 (10) | 0.7873 (7) | 0.2433 (6) | 0.154 (3) |
| HW4A | 0.649 (10) | 0.805 (11) | 0.192 (8) | 0.185* |
| HW4B | 0.810 (5) | 0.831 (11) | 0.255 (10) | 0.185* |

Atomic displacement parameters (Å²)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|--------------|--------------|--------------|--------------|-------------|--------------|
| La1 | 0.01729 (10) | 0.02001 (10) | 0.01850 (10) | 0.00633 (7) | 0.00482 (7) | 0.00498 (7) |
| O5 | 0.0242 (13) | 0.0258 (13) | 0.0312 (13) | 0.0032 (10) | 0.0034 (11) | 0.0040 (11) |
| O3 | 0.0227 (13) | 0.0340 (14) | 0.0229 (12) | 0.0074 (11) | 0.0027 (10) | 0.0011 (11) |
| O1 | 0.0352 (14) | 0.0353 (14) | 0.0339 (14) | 0.0161 (12) | 0.0168 (12) | 0.0155 (12) |
| O6 | 0.0247 (13) | 0.0283 (13) | 0.0415 (15) | 0.0089 (10) | 0.0129 (12) | -0.0005 (11) |
| O2 | 0.0403 (15) | 0.0427 (15) | 0.0332 (14) | 0.0254 (13) | 0.0173 (12) | 0.0200 (12) |
| O4 | 0.0267 (14) | 0.0515 (17) | 0.0253 (13) | 0.0175 (12) | 0.0040 (11) | -0.0052 (12) |
| O7 | 0.0425 (17) | 0.075 (2) | 0.067 (2) | 0.0390 (17) | 0.0345 (17) | 0.0532 (18) |
| O8 | 0.0456 (18) | 0.0523 (18) | 0.088 (2) | 0.0315 (16) | 0.0434 (18) | 0.0469 (19) |
| C6 | 0.0228 (17) | 0.0219 (17) | 0.0260 (17) | 0.0100 (14) | 0.0051 (14) | 0.0052 (14) |
| C11 | 0.0187 (16) | 0.0250 (17) | 0.0236 (16) | 0.0060 (13) | 0.0062 (14) | 0.0018 (14) |
| C1 | 0.0184 (17) | 0.041 (2) | 0.0332 (19) | 0.0099 (15) | 0.0083 (15) | 0.0177 (17) |
| C13 | 0.0261 (19) | 0.030 (2) | 0.0297 (19) | 0.0117 (16) | 0.0070 (16) | -0.0041 (16) |
| C12 | 0.0233 (18) | 0.040 (2) | 0.0318 (19) | 0.0098 (16) | 0.0074 (16) | -0.0057 (17) |
| C14 | 0.039 (2) | 0.044 (2) | 0.028 (2) | 0.0198 (19) | 0.0002 (18) | 0.0047 (18) |
| C8 | 0.031 (2) | 0.0293 (19) | 0.0290 (19) | 0.0102 (16) | 0.0138 (16) | -0.0032 (16) |
| C10 | 0.042 (2) | 0.033 (2) | 0.037 (2) | 0.0058 (18) | 0.0114 (19) | 0.0059 (18) |
| C15 | 0.043 (2) | 0.037 (2) | 0.031 (2) | 0.0133 (19) | 0.0076 (18) | 0.0078 (17) |
| C7 | 0.026 (2) | 0.040 (2) | 0.043 (2) | 0.0127 (17) | 0.0102 (18) | -0.0078 (19) |
| C9 | 0.042 (2) | 0.0225 (19) | 0.048 (2) | -0.0033 (17) | 0.016 (2) | 0.0006 (18) |
| C3 | 0.043 (2) | 0.044 (2) | 0.035 (2) | 0.0206 (19) | 0.0123 (18) | 0.0260 (18) |
| C4 | 0.051 (3) | 0.073 (3) | 0.041 (2) | 0.037 (2) | 0.022 (2) | 0.023 (2) |
| C5 | 0.032 (2) | 0.077 (3) | 0.042 (2) | 0.024 (2) | 0.0112 (19) | 0.027 (2) |
| C2 | 0.055 (3) | 0.040 (2) | 0.039 (2) | 0.017 (2) | 0.012 (2) | 0.0233 (19) |
| OW1 | 0.192 (4) | 0.069 (2) | 0.109 (3) | 0.009 (3) | 0.079 (3) | 0.028 (2) |
| OW2 | 0.063 (3) | 0.086 (3) | 0.074 (3) | 0.032 (2) | 0.020 (2) | 0.043 (2) |
| OW3 | 0.192 (4) | 0.069 (2) | 0.109 (3) | 0.009 (3) | 0.079 (3) | 0.028 (2) |
| OW4 | 0.158 (6) | 0.115 (4) | 0.103 (4) | -0.017 (4) | -0.019 (4) | 0.084 (4) |

Geometric parameters (Å, °)

| | | | |
|---------------------------------------|------------|---------------------------|------------|
| La1—O5 | 2.507 (2) | C12—H12B | 0.9700 |
| La1—O5 ⁱ | 2.905 (3) | C14—H14 | 0.9300 |
| La1—O3 ⁱⁱ | 2.781 (2) | C14—C15 ⁱⁱⁱ | 1.399 (6) |
| La1—O3 | 2.545 (2) | C8—C10 | 1.373 (6) |
| La1—O1 | 2.673 (2) | C8—C7 | 1.509 (5) |
| La1—O6 | 2.559 (2) | C8—C9 | 1.388 (6) |
| La1—O2 | 2.569 (2) | C10—H10 | 0.9300 |
| La1—O4 | 2.566 (2) | C10—C9 ^{iv} | 1.382 (6) |
| La1—O7 | 2.543 (3) | C15—H15 | 0.9300 |
| La1—O8 | 2.562 (3) | C7—H7C | 0.9700 |
| La1—C11 | 3.066 (3) | C7—H7D | 0.9700 |
| La1—C1 | 2.988 (4) | C9—H9 | 0.9300 |
| O5—C6 ⁱ | 1.255 (4) | C3—C4 | 1.385 (6) |
| O3—C11 ⁱⁱ | 1.264 (4) | C3—C5 | 1.381 (6) |
| O1—C1 | 1.264 (4) | C3—C2 | 1.509 (6) |
| O6—C6 | 1.256 (4) | C4—H4 | 0.9300 |
| O2—C1 | 1.248 (4) | C4—C5 ^v | 1.391 (6) |
| O4—C11 | 1.246 (4) | C5—H5 | 0.9300 |
| O7—H7A | 0.824 (19) | C2—H2A | 0.9700 |
| O7—H7B | 0.806 (18) | C2—H2B | 0.9700 |
| O8—H8A | 0.815 (19) | OW1—HW1A | 0.87 (2) |
| O8—H8B | 0.833 (19) | OW1—HW1B | 0.88 (2) |
| C6—C7 | 1.512 (5) | OW2—HW2A | 0.821 (19) |
| C11—C12 | 1.516 (5) | OW2—HW2B | 0.81 (2) |
| C1—C2 | 1.514 (5) | OW3—HW3A | 0.82 (2) |
| C13—C12 | 1.507 (5) | OW3—HW3B | 0.81 (2) |
| C13—C14 | 1.376 (6) | OW4—HW4A | 0.81 (2) |
| C13—C15 | 1.371 (5) | OW4—HW4B | 0.84 (2) |
| C12—H12A | 0.9700 | | |
| O5—La1—O5 ⁱ | 61.48 (9) | C11—O4—La1 | 101.3 (2) |
| O5—La1—O3 | 146.45 (9) | La1—O7—H7A | 116 (3) |
| O5—La1—O3 ⁱⁱ | 118.58 (7) | La1—O7—H7B | 133 (3) |
| O5—La1—O1 | 75.87 (8) | H7A—O7—H7B | 109 (3) |
| O5—La1—O6 | 107.86 (8) | La1—O8—H8A | 118 (3) |
| O5—La1—O2 | 75.29 (8) | La1—O8—H8B | 122 (3) |
| O5—La1—O4 | 80.33 (8) | H8A—O8—H8B | 104 (3) |
| O5—La1—O7 | 71.93 (9) | O5 ⁱ —C6—La1 | 68.28 (18) |
| O5—La1—O8 | 140.13 (9) | O5 ⁱ —C6—O6 | 120.2 (3) |
| O5 ⁱ —La1—C11 | 156.28 (8) | O5 ⁱ —C6—C7 | 120.1 (3) |
| O5—La1—C11 | 98.48 (8) | O6—C6—La1 | 52.33 (16) |
| O5—La1—C1 | 75.84 (9) | O6—C6—C7 | 119.7 (3) |
| O5 ⁱ —La1—C1 | 88.69 (9) | C7—C6—La1 | 169.6 (2) |
| O3—La1—O5 ⁱ | 118.22 (7) | O3 ⁱⁱ —C11—La1 | 65.08 (17) |
| O3 ⁱⁱ —La1—O5 ⁱ | 179.00 (7) | O3 ⁱⁱ —C11—C12 | 120.3 (3) |
| O3—La1—O3 ⁱⁱ | 61.11 (8) | O4—C11—La1 | 55.16 (17) |

| | | | |
|---------------------------|-------------|-----------------------------|------------|
| O3—La1—O1 | 73.20 (8) | O4—C11—O3 ⁱⁱ | 119.9 (3) |
| O3—La1—O6 | 80.93 (8) | O4—C11—C12 | 119.8 (3) |
| O3—La1—O2 | 74.87 (8) | C12—C11—La1 | 171.2 (2) |
| O3—La1—O4 | 108.82 (8) | O1—C1—La1 | 63.39 (19) |
| O3—La1—O8 | 73.39 (9) | O1—C1—C2 | 119.8 (3) |
| O3 ⁱⁱ —La1—C11 | 24.36 (8) | O2—C1—La1 | 58.58 (18) |
| O3—La1—C11 | 85.47 (8) | O2—C1—O1 | 121.5 (3) |
| O3—La1—C1 | 70.64 (9) | O2—C1—C2 | 118.7 (3) |
| O3 ⁱⁱ —La1—C1 | 90.37 (9) | C2—C1—La1 | 172.4 (3) |
| O1—La1—O5 ⁱ | 109.68 (7) | C14—C13—C12 | 120.5 (4) |
| O1—La1—O3 ⁱⁱ | 69.49 (8) | C15—C13—C12 | 122.1 (4) |
| O1—La1—C11 | 74.29 (9) | C15—C13—C14 | 117.4 (4) |
| O1—La1—C1 | 25.01 (9) | C11—C12—H12A | 109.2 |
| O6—La1—O5 ⁱ | 46.41 (7) | C11—C12—H12B | 109.2 |
| O6—La1—O3 ⁱⁱ | 133.56 (8) | C13—C12—C11 | 112.0 (3) |
| O6—La1—O1 | 126.21 (9) | C13—C12—H12A | 109.2 |
| O6—La1—O2 | 78.86 (9) | C13—C12—H12B | 109.2 |
| O6—La1—O4 | 149.49 (10) | H12A—C12—H12B | 107.9 |
| O6—La1—O8 | 71.55 (10) | C13—C14—H14 | 119.1 |
| O6—La1—C11 | 149.62 (9) | C13—C14—C15 ⁱⁱⁱ | 121.8 (4) |
| O6—La1—C1 | 101.90 (10) | C15 ⁱⁱⁱ —C14—H14 | 119.1 |
| O2—La1—O5 ⁱ | 66.57 (8) | C10—C8—C7 | 121.6 (4) |
| O2—La1—O3 ⁱⁱ | 112.44 (8) | C10—C8—C9 | 117.8 (4) |
| O2—La1—O1 | 49.39 (8) | C9—C8—C7 | 120.6 (4) |
| O2—La1—C11 | 123.42 (9) | C8—C10—H10 | 119.5 |
| O2—La1—C1 | 24.50 (9) | C8—C10—C9 ^{iv} | 121.1 (4) |
| O4—La1—O5 ⁱ | 132.95 (7) | C9 ^{iv} —C10—H10 | 119.5 |
| O4—La1—O3 ⁱⁱ | 47.75 (7) | C13—C15—C14 ⁱⁱⁱ | 120.7 (4) |
| O4—La1—O1 | 84.13 (9) | C13—C15—H15 | 119.6 |
| O4—La1—O2 | 131.27 (9) | C14 ⁱⁱⁱ —C15—H15 | 119.6 |
| O4—La1—C11 | 23.49 (8) | C6—C7—H7C | 108.9 |
| O4—La1—C1 | 108.61 (10) | C6—C7—H7D | 108.9 |
| O7—La1—O5 ⁱ | 70.81 (9) | C8—C7—C6 | 113.4 (3) |
| O7—La1—O3 | 141.53 (10) | C8—C7—H7C | 108.9 |
| O7—La1—O3 ⁱⁱ | 110.19 (9) | C8—C7—H7D | 108.9 |
| O7—La1—O1 | 142.43 (10) | H7C—C7—H7D | 107.7 |
| O7—La1—O6 | 82.59 (10) | C8—C9—H9 | 119.4 |
| O7—La1—O2 | 134.87 (9) | C10 ^{iv} —C9—C8 | 121.1 (4) |
| O7—La1—O4 | 71.95 (10) | C10 ^{iv} —C9—H9 | 119.4 |
| O7—La1—O8 | 68.46 (10) | C4—C3—C2 | 120.7 (4) |
| O7—La1—C11 | 91.69 (10) | C5—C3—C4 | 118.0 (4) |
| O7—La1—C1 | 147.21 (10) | C5—C3—C2 | 121.2 (4) |
| O8—La1—O5 ⁱ | 108.04 (8) | C3—C4—H4 | 119.8 |
| O8—La1—O3 ⁱⁱ | 72.59 (9) | C3—C4—C5 ^v | 120.4 (4) |
| O8—La1—O1 | 138.11 (8) | C5 ^v —C4—H4 | 119.8 |
| O8—La1—O2 | 139.28 (10) | C3—C5—C4 ^v | 121.6 (4) |
| O8—La1—O4 | 83.41 (11) | C3—C5—H5 | 119.2 |
| O8—La1—C11 | 78.57 (10) | C4 ^v —C5—H5 | 119.2 |

| | | | |
|---|-------------|---------------|-----------|
| O8—La1—C1 | 144.03 (10) | C1—C2—H2A | 109.0 |
| C1—La1—C11 | 98.95 (10) | C1—C2—H2B | 109.0 |
| La1—O5—La1 ⁱ | 118.52 (9) | C3—C2—C1 | 112.8 (3) |
| C6 ⁱ —O5—La1 ⁱ | 88.1 (2) | C3—C2—H2A | 109.0 |
| C6 ⁱ —O5—La1 | 153.4 (2) | C3—C2—H2B | 109.0 |
| La1—O3—La1 ⁱⁱ | 118.89 (8) | H2A—C2—H2B | 107.8 |
| C11 ⁱⁱ —O3—La1 | 150.5 (2) | HW1A—OW1—HW1B | 88 (7) |
| C11 ⁱⁱ —O3—La1 ⁱⁱ | 90.56 (19) | HW2A—OW2—HW2B | 121 (5) |
| C1—O1—La1 | 91.6 (2) | HW3A—OW3—HW3B | 108 (4) |
| C6—O6—La1 | 104.8 (2) | HW4A—OW4—HW4B | 107 (4) |
| C1—O2—La1 | 96.9 (2) | | |

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x+2, -y+1, -z+1$; (iii) $-x+1, -y, -z$; (iv) $-x+2, -y+2, -z+2$; (v) $-x+2, -y+1, -z+2$.

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|---------------------------------------|-----------|-------------|-------------|---------------|
| OW1—HW1A \cdots OW1 ^{vi} | 0.87 (9) | 2.40 (11) | 3.067 (13) | 133 (9) |
| OW1—HW1B \cdots OW4 ^{vii} | 0.89 (9) | 2.54 (10) | 3.298 (11) | 145 (7) |
| OW2—HW2A \cdots O4 ⁱ | 0.82 (6) | 2.10 (6) | 2.895 (5) | 164 (6) |
| OW2—HW2B \cdots OW4 ^{viii} | 0.82 (6) | 2.20 (5) | 2.855 (8) | 137 (5) |
| OW3—HW3A \cdots O6 ⁱ | 0.82 (8) | 2.02 (8) | 2.780 (8) | 154 (7) |
| OW3—HW3B \cdots OW1 ^{vi} | 0.81 (7) | 2.40 (8) | 3.162 (11) | 156 (8) |
| OW4—HW4A \cdots OW2 ^{ix} | 0.81 (10) | 2.49 (9) | 2.855 (8) | 109 (9) |
| O7—H7A \cdots O2 ⁱ | 0.82 (4) | 1.95 (4) | 2.741 (5) | 161 (5) |
| O7—H7B \cdots OW4 | 0.81 (5) | 2.03 (5) | 2.800 (9) | 160 (5) |
| OW4—HW4B \cdots OW3 ^x | 0.84 (9) | 2.11 (10) | 2.824 (11) | 143 (8) |
| O8—H8A \cdots OW3 ⁱ | 0.82 (4) | 2.38 (4) | 3.175 (8) | 165 (4) |
| O8—H8B \cdots O1 ⁱⁱ | 0.83 (4) | 1.92 (4) | 2.725 (5) | 163 (5) |
| C7—H7D \cdots O4 ⁱ | 0.97 | 2.54 | 3.442 (6) | 154 |
| C12—H12B \cdots O6 ⁱⁱ | 0.97 | 2.51 | 3.406 (6) | 154 |

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x+2, -y+1, -z+1$; (vi) $-x+1, -y, -z+1$; (vii) $x, y-1, z$; (viii) $x, y, z+1$; (ix) $x, y, z-1$; (x) $x+1, y+1, z$.