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A lanthanum coordination polymer with 3,6-dichlorophthalate and 2,4-dichloro-6-(ethoxycarbonyl)benzoate as ligands

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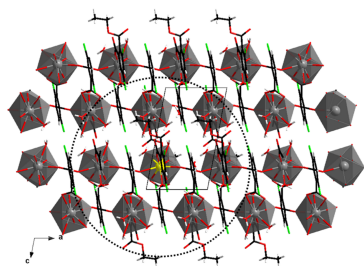
A one-dimensional lanthanum-based coordination polymer based on 3,6-dichlorophthalate has been prepared and structurally described, namely, poly[[tetraaqua[2,4-dichloro-6-(ethoxycarbonyl)benzoato](μ_3 -3,6-dichlorophthalato)lanthanum(III)] monohydrate], $\{[\text{La}(\text{C}_8\text{H}_2\text{Cl}_2\text{O}_4)(\text{C}_{10}\text{H}_7\text{Cl}_2\text{O}_4)(\text{H}_2\text{O})_4] \cdot \text{H}_2\text{O}\}_\infty$. Its crystal structure can be described based on molecular double chains in which lanthanum ions are linked to each other by ligands. There are several structural features that seem promising as far as luminescence properties are concerned, such as the presence of strong hydrogen bonds and of short halogen contacts, as well as quite long intermetallic distances. It is a pity that, to date, only a lanthanum-based compound has been obtained.

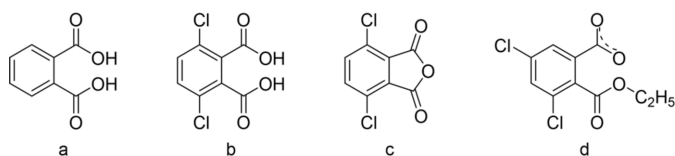
1. Chemical context

Materials traceability is an ongoing challenge. Indeed, the consumption of plastics is continuously growing worldwide, and their recycling is an environmental emergency. However, whatever the recycling process, homogeneous waste batches are required and marking plastics would enable rigorous waste sorting (Vollmer *et al.*, 2020). However, plastics must not only be marked according to the polymer matrix but also according to their complete formulation. Therefore, because of the wide variety of plastic formulations, marking them requires a large number of markers.

Our group was the first to design luminescent hetero-lanthanide coordination polymers (Kerbellec *et al.*, 2009) and to demonstrate that these compounds behave like true molecular alloys (Blais *et al.*, 2023; Ferlay & Hosseini, 2004; Haquin *et al.*, 2013). Luminescent markers based on lanthanide coordination polymers have proved their efficiency in the fight against counterfeiting (Guillou *et al.*, 2016). They could also be relevant for marking plastics to improve their recyclability (Daiguebonne *et al.*, 2025).

Recent studies strongly suggest that hetero-lanthanide coordination polymers with halogeno-derivatives of phthalic acid (Fig. 1) exhibit very promising luminescent properties and could be suitable for materials traceability (Blais *et al.*, 2025; Ngom *et al.*, 2024; Pointel, Suffren *et al.*, 2020; Pointel, Houard *et al.*, 2020; Hénaff *et al.*, 2026). There are several reasons that can explain such promising luminescent properties (Bünzli, 2010, 2015): (i) the adjacent positions of the two carboxylate functions enable the ligand to bridge several metal ions (Fig. 2), which can induce a fairly high rigidity of the molecular motif and therefore helps to limit non-radiative vibrational de-



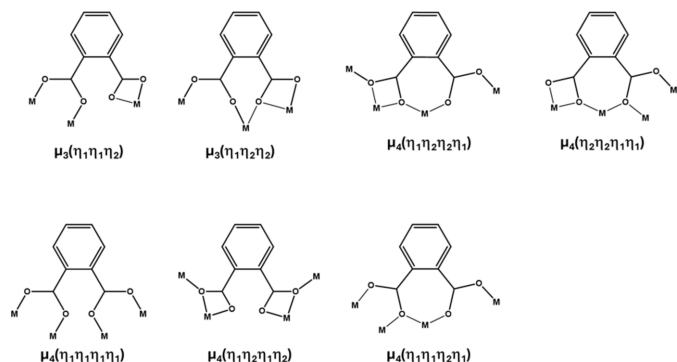
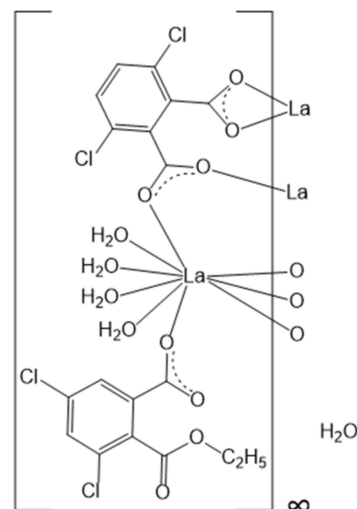
**Figure 1**

Schematic representations of benzene-1,2-dicarboxylic or phthalic acid (a), 3,6-dichlorophthalic acid (b), 4,7-dichlorobenzofuran-1,3-dione (c) and 2,4-dichloro-6-(ethoxycarbonyl)benzoate (d).

excitation; (ii) halogeno substituents can be involved in halogen-bond networks (Cavallo *et al.*, 2016; Fourmigué, 2009) that can keep molecular motifs away from each other and prevent π -stacking interactions, which is beneficial for reducing intermetallic energy transfers (Förster, 1960; Dexter, 1953; Blais *et al.*, 2022; Imbert *et al.*, 2003). The nature and the position of the halogeno substituents influence the energy of the first singlet and triplet excited states (Latva *et al.*, 1997; Steemers *et al.*, 1995), the photo-induced electron transfer (PET) mechanism (Freslon *et al.*, 2014) and the strength of the halogen interactions (Metrangolo *et al.*, 2008; Metrangolo & Resnati, 2001). However, contrary to halogenoterephthalate-based lanthanide coordination polymers (Smith *et al.*, 2024), halogenophthalate-based lanthanide coordination polymers have been little studied. So, for example, the only lanthanide coordination polymers based on dichlorophthalates described today are those involving 4,5-dichlorophthalate (Badiane *et al.*, 2018; Qiao *et al.*, 2018; He *et al.*, 2017) and, to the best of our knowledge, there is no example of lanthanide coordination polymers based on 3,6-dichlorophthalate (3,6-dcpa²⁻) in the literature.

We have thus undertaken a study of such compounds based on 3,6-dichlorophthalate. For reasons of commercial availability, and because anhydrides easily hydrolyse leading to the corresponding carboxylic acids, we have chosen to use 4,7-dichlorobenzofuran-1,3-dione as starting reactant. In the frame of this study, we have obtained a lanthanum coordination polymer with chemical formula $[\text{La}(\text{3,6-dcpa})(\text{C}_{10}\text{H}_7\text{Cl}_2\text{O}_4)(\text{H}_2\text{O})_4\cdot\text{H}_2\text{O}]_\infty$. In this compound, as expected, 3,6-dichloro-phthalate comes from 4,7-dichlorobenzofuran-1,3-dione. Unexpectedly, a second ligand is also produced: 2,4-

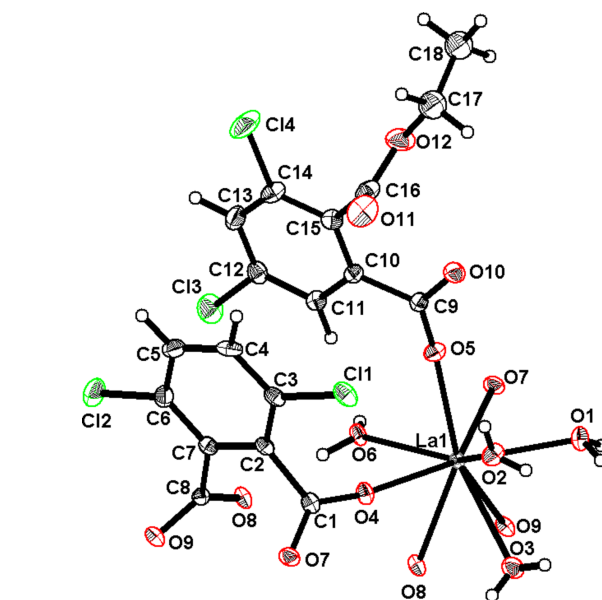
dichloro-6-(ethoxycarbonyl)benzoate. This kind of re-organization of the ligand is commonly observed (Feng *et al.*, 2016; Abdallah *et al.*, 2020). To the best of our knowledge, this compound constitutes the first example of a lanthanide coordination polymer based on the 3,6-dcpa²⁻ ligand. Despite great synthetic effort, to date we have not succeeded in synthesizing isomorphous compounds that involve luminescent lanthanide ions.

**Figure 2**

Coordination modes observed in lanthanide coordination polymers based on a phthalate ligand.

2. Structural commentary

Microwave-assisted reaction in water between lanthanum chloride and 4,7-dichlorobenzofuran-1,3-dione leads to a coordination polymer with chemical formula $[\text{La}(\text{3,6-dcpa})-$

**Figure 3**

Projection view of an extended asymmetric unit with the numbering scheme of $[\text{La}(\text{3,6-dcpa})(\text{C}_{10}\text{H}_7\text{Cl}_2\text{O}_4)(\text{H}_2\text{O})_4\cdot\text{H}_2\text{O}]_\infty$. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $-1 + x, y, z$; (ii) $1 - x, 1 - y, 2 - z$]. The crystallization water molecule is omitted.

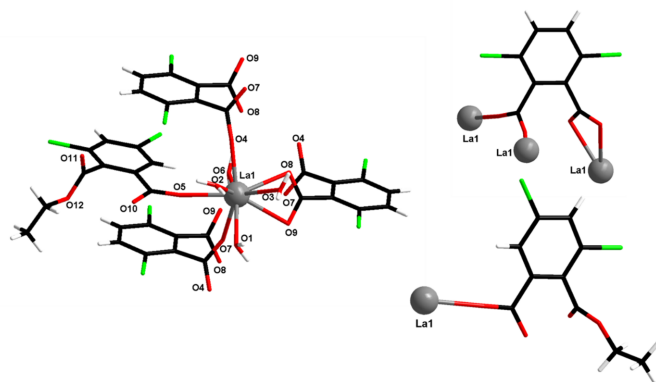


Figure 4
Schematic representation of the neighbourhood of the La^{3+} ion (left) and coordination modes of the 3,6-dcpa $^{2-}$ ligand (top right) and of the 2,4-dichloro-6-(ethoxycarbonyl)benzoate ligand (bottom right) of $[\text{La}(3,6\text{-dcpa})(\text{C}_{10}\text{H}_7\text{Cl}_2\text{O}_4)(\text{H}_2\text{O})_4\cdot\text{H}_2\text{O}]_\infty$.

$(\text{C}_{10}\text{H}_7\text{Cl}_2\text{O}_4)(\text{H}_2\text{O})_4\cdot\text{H}_2\text{O}]_\infty$ where 3,6-dcpa $^{2-}$ symbolizes 3,6-dichlorophthalate (CCDC-2430840) (Fig. 3).

There is one independent lanthanum ion in this crystal structure. It is ninefold coordinated by nine oxygen atoms. Four out of the nine are from four coordination water molecules (O1, O2, O3 and O6), four more (O4, O7ⁱ, O8ⁱⁱ and O9ⁱⁱⁱ) are from carboxylate functions that belong to three different 3,6-dcpa $^{2-}$ ligands and the remaining one (O5) is from a carboxylate function that belongs to the 2,4-dichloro-6-(ethoxycarbonyl)benzoate ligand. They form a spherical capped square antiprism (Table S1) (Casanova *et al.*, 2005; Alvarez *et al.*, 2005). There is also one independent 3,6-dcpa $^{2-}$ ligand and one independent 2,4-dichloro-6-(ethoxycarbonyl)benzoate ligand in the crystal structure. The former is $\mu_3(\eta_1\eta_1\eta_2)$ and the latter is $\mu_1(\eta_1)$ (Fig. 4) Finally, there is one crystallization water molecule (H13A–O13–H13B) in the crystal structure.

The crystal structure is mono-dimensional and can be described based on molecular double chains that spread parallel to the *a* axis (Fig. 5). Inside these molecular double

Table 1
Hydrogen-bond geometry ($\text{\AA}$, $^\circ$).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1—H1A...O13	0.84 (4)	2.00 (4)	2.787 (4)	155 (4)
O1—H1B...O10 ⁱⁱⁱ	0.80 (4)	1.89 (5)	2.663 (4)	164 (4)
O2—H2A...O10 ⁱⁱⁱ	0.77 (5)	2.28 (5)	2.972 (4)	150 (4)
O2—H2B...O1 ⁱⁱⁱ	0.80 (5)	2.11 (5)	2.868 (4)	159 (4)
O3—H3A...O10 ⁱⁱⁱ	0.82 (5)	2.10 (5)	2.850 (4)	152 (4)
O3—H3B...O13 ⁱ	0.76 (5)	2.13 (5)	2.883 (4)	174 (5)
O6—H6A...O9 ^{iv}	0.78 (4)	2.10 (4)	2.864 (3)	166 (4)
O6—H6B...O8	0.85 (4)	1.92 (4)	2.772 (3)	175 (4)
O13—H13A...O11 ⁱⁱⁱ	0.81 (5)	2.16 (5)	2.948 (4)	164 (5)
O13—H13B...O9 ^v	0.87 (5)	2.30 (5)	3.008 (4)	139 (4)

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

Table 2
Selected interatomic distances ($\text{\AA}$).

Cl2 ⁱ ...Cl3	3.4185 (16)	Cl3 ⁱⁱⁱ ...Cl4	3.4645 (15)
Cl2...Cl3	3.4287 (15)		

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

chains, lanthanum ions are linked to each other by 3,6-dcpa $^{2-}$ ligands while the ethyl groups of the 2,4-dichloro-6-(ethoxycarbonyl)benzoates point toward the intermolecular space. The shortest distances between lanthanide ions that belong to the same molecular motif are about 6 $\text{\AA}$ (Fig. 5).

It is noticeable that there is a dense network of strong intra- and inter-molecular hydrogen bonds (Fig. 5 and Table 1) in this crystal structure. Additionally, there are some weak π – π interactions (shortest centroid–centroid distances are 3.7 $\text{\AA}$).

3. Supramolecular features

The crystal structure can be described as a juxtaposition of molecular chains that spread along the *a*-axis direction. Beyond the network of strong hydrogen bonds, the cohesion of the crystal packing is reinforced by $\text{Cl}\cdots\text{Cl}$ interactions (Table 2). There are seven La^{3+} ions closer than 10 $\text{\AA}$ from a given La^{3+} ion (Table 3). All seven belong to two adjacent molecular motifs spreading parallel to the *ac* plane (Fig. 6).

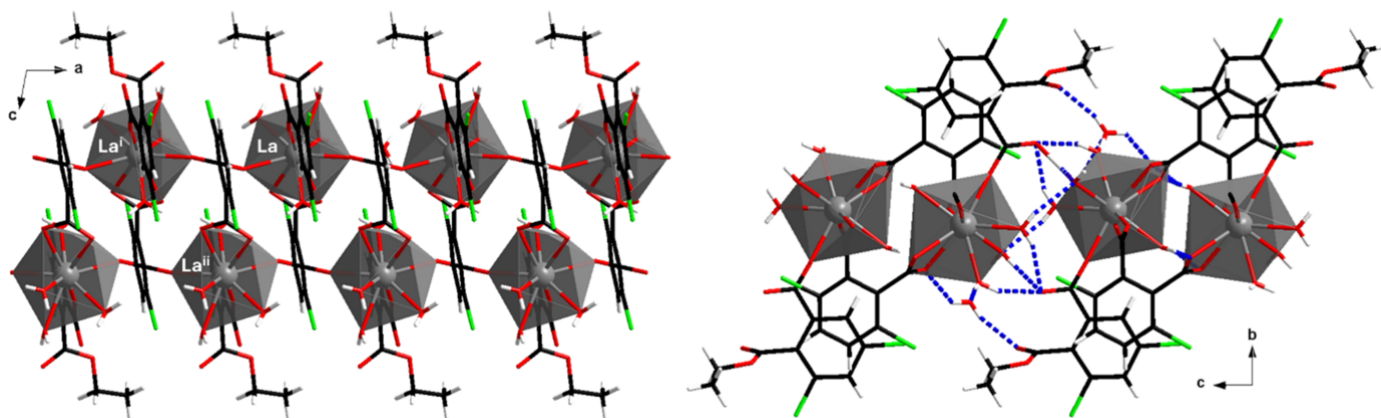


Figure 5
Left: Projection view along the *b* axis of a molecular double chain of $[\text{La}(3,6\text{-dcpa})(\text{C}_{10}\text{H}_7\text{Cl}_2\text{O}_4)(\text{H}_2\text{O})_4\cdot\text{H}_2\text{O}]_\infty$. Shortest intermetallic distances are $d(\text{La}^{\text{i}}-\text{La}^{\text{i}}) = 6.8045$ (8) $\text{\AA}$, $d(\text{La}^{\text{i}}-\text{La}^{\text{ii}}) = 6.0680$ (4) $\text{\AA}$ and $d(\text{La}^{\text{i}}-\text{La}^{\text{iii}}) = 6.3651$ (3) $\text{\AA}$ [Symmetry codes: (i) $-1+x, y, z$; (ii) $-x, 1-y, 2-z$]. Right: Projection view along the *a* axis of two adjacent molecular motifs. Dotted blue lines indicate hydrogen bonds.

Table 3

La $\cdots$ La distances ($\text{\AA}$) shorter than 10 $\text{\AA}$ in $[\text{La}(\text{3,6-dcpa})(\text{C}_{10}\text{H}_7\text{Cl}_2\text{O}_4)(\text{H}_2\text{O})_4\cdot\text{H}_2\text{O}]_{\infty}$.

Atom1	Atom2	Symmetry	Distance
La1	La1	$-x, 1 - y, 2 - z$	6.0682 (6)
La1	La1	$-x, 1 - y, 1 - z$	6.2554 (7)
La1	La1	$1 - x, 1 - y, 2 - z$	6.3650 (6)
La1	La1	$1 + x, y, z$	6.8044 (8)
La1	La1	$-1 + x, y, z$	6.8046 (8)
La1	La1	$1 - x, 1 - y, 1 - z$	8.5065 (8)
La1	La1	$-1 - x, 1 - y, 1 - z$	9.9248 (9)

In conclusion, this crystal structure presents interesting features as far as luminescent properties are concerned. Indeed, the lanthanide ions are quite far from each other and the dense network of hydrogen and halogen bonds is expected to limit non-radiative vibrational de-excitation. The reproducibility of the synthesis was checked by reproducing it several times. Unfortunately, to date, we have not succeeded in synthesizing any iso-structural coordination polymer based on a luminescent lanthanide ion.

4. Database survey

A search of the Cambridge Structural Database was performed using ConQuest (version 2024.2.0, CSD version 5.45, updated September 2024; Groom *et al.*, 2016). For lanthanide coordination polymers based on phthalate ligands, see: Li *et al.* (2009; CSD refcode KUGPUY); Meng *et al.* (2006; LEJPIA); Wan *et al.* (2002; WUJSID, WUJSOJ, WUJSUP, WUJTAW); Song *et al.* (2004, 2010; FIBWOD, YURGIC); Thirumurugan & Natarajan (2003; BEVPIC); Wang *et al.* (2008; FARJAL, KIWPOW) Pizon *et al.* (2010; IJEJOX); Luo *et al.* (2010; DUWRIX; Lush & Shen (2011; AZITOT); for 3,6-dichlorophthalate, see: Mattes & Dorau (1986; SAZQOZ); for lanthanide coordination polymers based on 4,5-dichloro-

Table 4

Experimental details.

Crystal data	
Chemical formula	$[\text{La}(\text{C}_8\text{H}_2\text{Cl}_2\text{O}_4)-(\text{C}_{10}\text{H}_7\text{Cl}_2\text{O}_4)(\text{H}_2\text{O})_4]\cdot\text{H}_2\text{O}$
M_r	724.04
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	150
a, b, c ($\text{\AA}$)	6.8045 (7), 32.376 (3), 11.5188 (12)
β ($^\circ$)	100.862 (4)
V ($\text{\AA}^3$)	2492.2 (4)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	2.21
Crystal size (mm)	$0.44 \times 0.07 \times 0.03$
Data collection	
Diffractometer	D8 VENTURE Bruker AXS
Absorption correction	Multi-scan (SADABS; Krause <i>et al.</i> , 2015)
$T_{\min}, T_{\max}$	0.777, 0.936
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	19761, 5674, 5503
R_{int} ($\sin \theta/\lambda$) $_{\text{max}}$ ($\text{\AA}^{-1}$)	0.028 0.650
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.033, 0.068, 1.27
No. of reflections	5674
No. of parameters	355
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ ($\text{e \AA}^{-3}$)	0.72, -1.05

Computer programs: APEX3 (Bruker, 2015), SAINT (Bruker, 2014), SHELXT (Sheldrick, 2015a), SHELXL2019/2 (Sheldrick, 2015b), SXRGRAPH (Farrugia, 1999), Mercury (Macrae *et al.*, 2020) and CRYSCALC (T. Roisnel, local program, 2024).

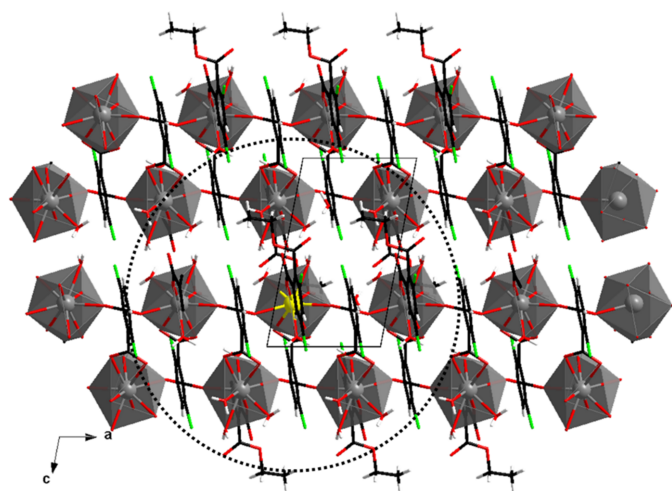
hthalates, see: Badiane *et al.* (2018; BETYOR); Qiao *et al.* (2018; GIQCIV, GIQCOB, GIQCUH, GIQDAO, MICCEJ); He *et al.* (2017; DEJGAD). For a structural comparison between these crystal structures, see: Hénaff *et al.* (2026).

5. Synthesis and crystallization

Lanthanum oxide (4N) was purchased from Ampère. Hydrated lanthanum chloride $[\text{LaCl}_3(\text{H}_2\text{O})_6]$ was prepared according to established procedures (Desreux, 1989). 4,7-Dichlorobenzofuran-1,3-dione ($\text{C}_8\text{H}_2\text{Cl}_2\text{O}_3$, 98%) was purchased from BDLpharm and used without further purification. 0.5 mmol (185.6 mg) of $\text{LaCl}_3(\text{H}_2\text{O})_6$, 0.75 mmol (162.7 mg) of $\text{C}_8\text{H}_2\text{Cl}_2\text{O}_3$, 1.5 mL of a solution of sodium hydroxide (1 mol L^{-1}) and 3.5 mL of deionized water were put in a 10 mL sealed Pyrex test tube in a CEM Discover microwave oven and maintained for 10 min under stirring ($T = 403 \text{ K}$; $P = 2.5 \text{ bar}$). Single crystals suitable for X-ray diffraction were obtained after slow evaporation of the supernatant solution extracted after the synthesis.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. Except for O-bound H atoms that were introduced in the structural model through

**Figure 6**

Projection view along the b axis of two adjacent molecular motifs. The dotted circle centred on the given La^{3+} ion (in yellow) has a 10 $\text{\AA}$ radius.

Fourier difference map analysis, H atoms were finally included in their calculated positions ($C-H = 0.95-0.98 \text{ \AA}$) and treated as riding on their parent atom with $U_{iso}(H) = 1.2-1.5U_{eq}(C)$.

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References

- Abdallah, A., Puget, M., Daiguebonne, C., Suffren, Y., Calvez, G., Bernot, K. & Guillou, O. (2020). *CrystEngComm* **22**, 2020–2030.
- Alvarez, S., Alemany, P., Casanova, D., Cirera, J., Llunell, M. & Avnir, D. (2005). *Coord. Chem. Rev.* **249**, 1693–1708.
- Badiane, A. M., Freslon, S., Daiguebonne, C., Suffren, Y., Bernot, K., Calvez, G., Costuas, K., Camara, M. & Guillou, O. (2018). *Inorg. Chem.* **57**, 3399–3410.
- Blais, C., Chang, A., Ngom, F., Daiguebonne, C., Suffren, Y., Yao, A., Gautier, R., Camara, M., Calvez, G., Bernot, K. & Guillou, O. (2025). *Inorg. Chem.* **64**, 10194–10207.
- Blais, C., Daiguebonne, C., Suffren, Y., Bernot, K., Calvez, G., Le Pollès, L., Roiland, C., Freslon, S. & Guillou, O. (2022). *Inorg. Chem.* **61**, 11897–11915.
- Blais, C., Morvan, T., Daiguebonne, C., Suffren, Y., Calvez, G., Bernot, K. & Guillou, O. (2023). *Inorg. Chem.* **61**, 19588–19596.
- Bruker (2014). *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (2015). *APEX3*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bünzli, J. G. (2010). *Chem. Rev.* **110**, 2729–2755.
- Bünzli, J. G. (2015). *Coord. Chem. Rev.* **293–294**, 19–47.
- Casanova, D., Llunell, M., Alemany, P. & Alvarez, S. (2005). *Chem. A Eur. J.* **11**, 1479–1494.
- Cavallo, G., Metrangolo, P., Milani, R., Pilati, T., Priimagi, A., Resnati, G. & Terraneo, G. (2016). *Chem. Rev.* **116**, 2478–2601.
- Daiguebonne, C., Blais, C., Bernot, K. & Guillou, O. (2025). *Acc. Chem. Res.* in press.
- Desreux, J. F. (1989). *Lanthanide Probes in Life, Chemical and Earth Sciences* edited by G. R. Choppin & J. C. G. Bünzli, p. 43. Amsterdam: Elsevier.
- Dexter, D. L. (1953). *J. Chem. Phys.* **21**, 836–850.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Feng, X., Li, R. F., Wang, Y. & Tian, P. H. (2016). *Z. Kristallogr. New Cryst. Struct.* **231**, 1139–1141.
- Ferlay, S. & Hosseini, W. (2004). *Chem. Commun.* pp. 788–789.
- Förster, T. (1960). *Comparative effects of radiation*. New York: John Wiley & Sons.
- Fournigüé, M. (2009). *Curr. Opin. Solid State Mater. Sci.* **13**, 36–45.
- Freslon, S., Luo, Y., Calvez, G., Daiguebonne, C., Guillou, O., Bernot, K., Michel, V. & Fan, X. (2014). *Inorg. Chem.* **53**, 1217–1228.
- Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.
- Guillou, O., Daiguebonne, C., Calvez, G. & Bernot, K. (2016). *Acc. Chem. Res.* **49**, 844–856.
- Haquin, V., Etienne, M., Daiguebonne, C., Freslon, S., Calvez, G., Bernot, K., Le Pollès, L., Ashbrook, S. E., Mitchell, M. R., Bünzli, J. C. G., Eliseeva, S. V. & Guillou, O. (2013). *Eur. J. Inorg. Chem.* pp. 3464–3476.
- He, H., Chen, S.-H., Zhang, D.-Y., Hao, R., Zhang, C., Yang, E.-C. & Zhao, X.-J. (2017). *Dalton Trans.* **46**, 13502–13509.
- Hénaff, C., Blais, C., Chang, A., Bernot, K., Daiguebonne, C. & Guillou, O. (2026). *J. Mol. Struct.* **1349**, 143600.
- Imbert, D., Cantuel, M., Bünzli, J. G., Bernardinelli, G. & Piguet, C. (2003). *J. Am. Chem. Soc.* **125**, 15698–15699.
- Kerbellec, N., Kustaryono, D., Haquin, V., Etienne, M., Daiguebonne, C. & Guillou, O. (2009). *Inorg. Chem.* **48**, 2837–2843.
- Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). *J. Appl. Cryst.* **48**, 3–10.
- Latva, M., Takalo, H., Mikkala, V.-M., Matachescu, C., Rodríguez-Ubis, J. C. & Kankare, J. (1997). *J. Lumin.* **75**, 149–169.
- Li, X., Zha, M. Q., Wang, X.-W. & Cao, R. (2009). *Inorg. Chim. Acta* **362**, 3357–3363.
- Luo, F., Luo, M.-B. & Tong, X.-L. (2010). *J. Coord. Chem.* **63**, 1147–1156.
- Lush, S. F. & Shen, F. M. (2011). *Acta Cryst.* **E67**, m1370–m1371.
- Mattes, R. & Dorau, A. (1986). *Chem. Sci.* **41**, 808–814.
- Macrae, C. F., Sovago, I., Cottrell, S. J., Galek, P. T. A., McCabe, P., Pidcock, E., Platings, M., Shields, G. P., Stevens, J. S., Towler, M. & Wood, P. A. (2020). *J. Appl. Cryst.* **53**, 226–235.
- Meng, Z.-R., Zhang, Q.-Z., Wu, X.-Y., Chen, L.-J. & Lu, C.-Z. (2006). *Acta Cryst.* **E62**, m1033–m1035.
- Metrangolo, P. & Resnati, G. (2001). *Chem. Eur. J.* **7**, 2511–2519.
- Metrangolo, P., Resnati, G., Pilati, T. & Biella, S. (2008). *Struct. Bond* pp. 105–136. Berlin, Heidelberg: Springer-Verlag.
- Ngom, F., Chang, A., Blais, C., Daiguebonne, C., Suffren, Y., Camara, M., Calvez, G., Bernot, K. & Guillou, O. (2024). *Inorg. Chem.* **63**, 13048–13058.
- Pizon, D., Henry, N., Loiseau, T., Roussel, P. & Abraham, F. (2010). *J. Solid State Chem.* **183**, 1943–1948.
- Pointel, Y., Houard, F., Suffren, Y., Daiguebonne, C., Le Natur, F., Freslon, S., Calvez, G., Bernot, K. & Guillou, O. (2020). *Inorg. Chem.* **59**, 11028–11040.
- Pointel, Y., Suffren, Y., Daiguebonne, C., Le Natur, F., Freslon, S., Calvez, G., Bernot, K. & Guillou, O. (2020). *Inorg. Chem.* **59**, 10673–10687.
- Qiao, Y.-H., Chen, S.-H., Xu, S., Yang, E. C. & Zhao, X.-J. (2018). *Z. Anorg. Allg. Chem.* **644**, 1108–1114.
- Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
- Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
- Smith, J. A., Singh-Wilmot, M. A., Hossack, C. H., Cahill, C. L. & Ford, R. A. C. (2024). *Cryst. Growth Des.* **24**, 7822–7836.
- Song, W.-D., Yan, J.-B., Wang, H., Ji, L.-L., Ma, D.-Y. & Ng, S. W. (2010). *J. Coord. Chem.* **63**, 625–633.
- Song, Y.-S., Yan, B. & Chen, Z.-X. (2004). *Can. J. Chem.* **82**, 1745–1751.
- Stemers, F. J., Verboom, W., Reinhoudt, D. N., van der Tol, E. B. & Verhoeven, J. W. (1995). *J. Am. Chem. Soc.* **117**, 9408–9414.
- Thirumurugan, A. & Natarajan, S. (2003). *J. Chem. Sci.* **115**, 573–586.
- Vollmer, I., Jenks, M. J. F., Roelands, M. C. P., White, R. J., van Harmelen, T., de Wild, P., van der Laan, G. P., Meirer, F., Keurentjes, J. T. F. & Weckhuysen, B. M. (2020). *Angew. Chem. Int. Ed.* **59**, 15402–15423.
- Wan, Y., Jin, L., Wang, K., Zhang, L., Zheng, X. J. & Lu, S. (2002). *New J. Chem.* **26**, 1590–1596.
- Wang, G.-M., Duan, C.-S., Liu, H.-L. & Li, H. (2008). *Acta Cryst.* **E64**, m468–m469.

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A lanthanum coordination polymer with 3,6-dichlorophthalate and 2,4-dichloro-6-(ethoxycarbonyl)benzoate as ligands

Christine Hénaff, Thierry Roisnel, Chloé Blais, Olivier Guillou and Carole Daiguebonne

Computing details

Poly[[tetraqua[2,4-dichloro-6-(ethoxycarbonyl)benzoato](μ_3 -3,6-dichlorophthalato)lanthanum(III)] monohydrate]

Crystal data

[La(C₈H₂Cl₂O₄)(C₁₀H₇Cl₂O₄)(H₂O)₄].H₂O

$M_r = 724.04$

Monoclinic, $P2_1/c$

$a = 6.8045$ (7) Å

$b = 32.376$ (3) Å

$c = 11.5188$ (12) Å

$\beta = 100.862$ (4)°

$V = 2492.2$ (4) Å³

$Z = 4$

$F(000) = 1424$

$D_x = 1.930$ Mg m⁻³

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

Cell parameters from 9930 reflections

$\theta = 2.6$ – 27.5°

$\mu = 2.21$ mm⁻¹

$T = 150$ K

Stick, colourless

$0.44 \times 0.07 \times 0.03$ mm

Data collection

D8 VENTURE Bruker AXS

diffractometer

Radiation source: Incoatec microfocus sealed tube

Multilayer monochromator

Detector resolution: 7.39 pixels mm⁻¹

rotation images scans

Absorption correction: multi-scan
(SADABS; Krause *et al.*, 2015)

$T_{\min} = 0.777$, $T_{\max} = 0.936$

19761 measured reflections

5674 independent reflections

5503 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.028$

$\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 1.9^\circ$

$h = -8 \rightarrow 8$

$k = -41 \rightarrow 41$

$l = -14 \rightarrow 14$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.033$

$wR(F^2) = 0.068$

$S = 1.27$

5674 reflections

355 parameters

0 restraints

Primary atom site location: dual

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + 7.126P]$

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

$(\Delta/\sigma)_{\max} = 0.002$

$\Delta\rho_{\max} = 0.72$ e Å⁻³

$\Delta\rho_{\min} = -1.05$ e Å⁻³

Special details

Experimental. A suitable crystal for X-ray diffraction single crystal experiment (colourless stick, dimensions = 0.030 x 0.070 x 0.440 mm) was selected and mounted with a cryoloop on the goniometer head of a D8 Venture (Bruker-AXS) diffractometer equipped with a CMOS-PHOTON70 detector, using Mo-K α radiation (λ = 0.71073 Å, multilayer monochromator) at T = 150 (2) K. Crystal structure has been described in monoclinic symmetry and *P* 2₁/c (I.T.#14) centric space group (R_{int} =0.0280; R_{sigma} =0.0262). Cell parameters have been refined as follows: a = 6.8045 (7) Å, b = 32.376 (3) Å, c =11.5188 (12) Å, β = 100.862 (4) °, V = 2492.2 (4) Å³. Number of formula unit Z is equal to 4 and calculated density d and absorption coefficient μ values are 1.930 g.cm⁻³ and 2.207mm⁻¹ respectively. Crystal structure was solved by dual-space algorithm using *SHELXT* program and then refined with full-matrix least-squares methods based on F^2 (*SHELXL* program). All non-Hydrogen atoms were refined with anisotropic atomic displacement parameters. Except Hydrogen atoms linked to Oxygen atoms that were introduced in the structural model through Fourier difference maps analysis, H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters. A final refinement on F^2 with 5674 unique intensities and 355 parameters converged at $\omega R(F^2)$ =0.0678 (R_F = 0.0325) for 5503 observed reflections with $I > 2\sigma$.

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.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2 , conventional R-factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F , and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
La1	0.15728 (3)	0.49053 (2)	0.77186 (2)	0.01071 (6)
Cl1	0.52632 (12)	0.57653 (3)	0.57191 (7)	0.02214 (17)
Cl2	0.86113 (15)	0.66386 (3)	1.04825 (9)	0.0310 (2)
Cl3	0.35058 (15)	0.65895 (3)	1.01756 (8)	0.0320 (2)
Cl4	0.1852 (2)	0.74928 (3)	0.62045 (10)	0.0402 (3)
O1	−0.1375 (4)	0.45586 (8)	0.6315 (2)	0.0190 (5)
H1A	−0.216 (7)	0.4425 (13)	0.666 (4)	0.023*
H1B	−0.111 (6)	0.4389 (13)	0.586 (4)	0.023*
O2	0.2230 (4)	0.48617 (8)	0.5597 (2)	0.0201 (5)
H2A	0.195 (7)	0.4665 (14)	0.522 (4)	0.024*
H2B	0.227 (6)	0.5050 (14)	0.515 (4)	0.024*
O3	0.2806 (4)	0.41711 (8)	0.7131 (2)	0.0214 (5)
H3A	0.234 (7)	0.4074 (13)	0.648 (4)	0.026*
H3B	0.390 (7)	0.4112 (14)	0.728 (4)	0.026*
O4	0.5011 (3)	0.51206 (7)	0.7824 (2)	0.0185 (5)
O5	0.0711 (4)	0.55684 (7)	0.6732 (2)	0.0187 (5)
O6	0.2443 (4)	0.53789 (8)	0.9496 (2)	0.0162 (5)
H6A	0.172 (6)	0.5421 (13)	0.994 (4)	0.019*
H6B	0.365 (7)	0.5414 (13)	0.985 (4)	0.019*
O7	0.8332 (3)	0.51060 (7)	0.8259 (2)	0.0175 (5)
O8	0.6424 (3)	0.55065 (7)	1.05147 (19)	0.0160 (5)
O9	0.9632 (3)	0.56660 (7)	1.08782 (19)	0.0163 (5)
O10	−0.0218 (4)	0.59396 (8)	0.5099 (2)	0.0203 (5)

O11	0.1928 (5)	0.66501 (9)	0.4265 (2)	0.0350 (7)
O12	−0.1099 (4)	0.68329 (9)	0.4598 (2)	0.0321 (6)
O13	−0.3045 (4)	0.39310 (9)	0.7472 (3)	0.0286 (6)
H13A	−0.272 (7)	0.3738 (15)	0.711 (4)	0.034*
H13B	−0.220 (7)	0.3931 (15)	0.814 (4)	0.034*
C1	0.6686 (5)	0.52900 (10)	0.8040 (3)	0.0139 (6)
C2	0.6774 (4)	0.57584 (10)	0.8076 (3)	0.0135 (6)
C3	0.6275 (5)	0.59966 (11)	0.7059 (3)	0.0158 (6)
C4	0.6544 (5)	0.64206 (11)	0.7079 (3)	0.0208 (7)
H4	0.622165	0.657699	0.637085	0.025*
C5	0.7287 (5)	0.66131 (11)	0.8138 (3)	0.0215 (7)
H5	0.747350	0.690401	0.816744	0.026*
C6	0.7758 (5)	0.63795 (11)	0.9160 (3)	0.0192 (7)
C7	0.7527 (5)	0.59551 (10)	0.9149 (3)	0.0138 (6)
C8	0.7894 (5)	0.56959 (9)	1.0260 (3)	0.0128 (6)
C9	0.0562 (5)	0.59016 (10)	0.6172 (3)	0.0140 (6)
C10	0.1326 (5)	0.62886 (10)	0.6833 (3)	0.0153 (6)
C11	0.1994 (5)	0.62682 (10)	0.8049 (3)	0.0163 (6)
H11	0.203366	0.601080	0.844882	0.020*
C12	0.2599 (5)	0.66250 (11)	0.8673 (3)	0.0192 (7)
C13	0.2529 (6)	0.70049 (11)	0.8124 (3)	0.0235 (7)
H13	0.290133	0.724962	0.856623	0.028*
C14	0.1899 (6)	0.70185 (11)	0.6906 (3)	0.0227 (7)
C15	0.1311 (5)	0.66659 (11)	0.6241 (3)	0.0184 (7)
C16	0.0752 (6)	0.67031 (11)	0.4919 (3)	0.0235 (7)
C17	−0.1740 (9)	0.69157 (16)	0.3343 (4)	0.0497 (13)
H17A	−0.180144	0.665521	0.288787	0.060*
H17B	−0.078142	0.710400	0.306355	0.060*
C18	−0.3711 (10)	0.7106 (2)	0.3177 (6)	0.076 (2)
H18A	−0.418000	0.716488	0.233614	0.114*
H18B	−0.464813	0.691644	0.345401	0.114*
H18C	−0.363204	0.736350	0.362901	0.114*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
La1	0.00833 (9)	0.01307 (9)	0.01034 (8)	−0.00037 (7)	0.00073 (6)	−0.00107 (7)
Cl1	0.0187 (4)	0.0346 (5)	0.0126 (3)	0.0022 (3)	0.0016 (3)	0.0008 (3)
Cl2	0.0370 (5)	0.0243 (4)	0.0304 (5)	−0.0050 (4)	0.0029 (4)	−0.0104 (4)
Cl3	0.0349 (5)	0.0384 (5)	0.0217 (4)	−0.0004 (4)	0.0030 (4)	−0.0065 (4)
Cl4	0.0657 (8)	0.0160 (4)	0.0377 (5)	−0.0049 (5)	0.0063 (5)	0.0054 (4)
O1	0.0181 (12)	0.0223 (13)	0.0159 (11)	−0.0045 (10)	0.0018 (9)	−0.0044 (10)
O2	0.0268 (13)	0.0183 (13)	0.0158 (12)	−0.0007 (11)	0.0057 (10)	−0.0012 (10)
O3	0.0206 (13)	0.0244 (13)	0.0177 (12)	0.0044 (11)	−0.0003 (10)	−0.0039 (10)
O4	0.0123 (11)	0.0225 (12)	0.0204 (11)	−0.0030 (10)	0.0023 (9)	−0.0013 (10)
O5	0.0223 (12)	0.0144 (11)	0.0197 (11)	0.0004 (10)	0.0046 (10)	0.0012 (9)
O6	0.0098 (11)	0.0244 (13)	0.0144 (11)	0.0002 (10)	0.0024 (9)	−0.0049 (9)
O7	0.0120 (11)	0.0191 (12)	0.0216 (11)	0.0032 (9)	0.0039 (9)	0.0006 (10)

O8	0.0115 (11)	0.0222 (12)	0.0133 (10)	−0.0031 (9)	−0.0001 (8)	0.0017 (9)
O9	0.0108 (10)	0.0227 (12)	0.0148 (11)	0.0010 (9)	0.0009 (9)	0.0008 (9)
O10	0.0220 (12)	0.0208 (12)	0.0163 (11)	0.0026 (10)	−0.0007 (9)	−0.0006 (9)
O11	0.0485 (18)	0.0363 (16)	0.0247 (14)	−0.0026 (14)	0.0189 (13)	0.0013 (12)
O12	0.0415 (17)	0.0302 (15)	0.0211 (13)	0.0112 (13)	−0.0028 (12)	0.0021 (11)
O13	0.0266 (15)	0.0311 (15)	0.0281 (15)	−0.0008 (12)	0.0054 (12)	−0.0013 (12)
C1	0.0136 (15)	0.0200 (16)	0.0089 (13)	−0.0008 (12)	0.0040 (11)	−0.0007 (12)
C2	0.0081 (13)	0.0184 (15)	0.0148 (14)	0.0017 (12)	0.0039 (11)	0.0001 (12)
C3	0.0109 (14)	0.0231 (17)	0.0138 (14)	0.0035 (13)	0.0034 (12)	0.0009 (12)
C4	0.0173 (16)	0.0215 (17)	0.0248 (17)	0.0072 (14)	0.0073 (14)	0.0098 (14)
C5	0.0194 (17)	0.0165 (16)	0.0293 (18)	0.0016 (14)	0.0065 (14)	0.0035 (14)
C6	0.0167 (16)	0.0195 (17)	0.0213 (16)	−0.0018 (13)	0.0034 (13)	−0.0037 (13)
C7	0.0105 (14)	0.0173 (15)	0.0142 (14)	0.0004 (12)	0.0041 (11)	0.0019 (12)
C8	0.0153 (15)	0.0129 (14)	0.0100 (13)	0.0010 (12)	0.0022 (11)	−0.0010 (11)
C9	0.0112 (14)	0.0148 (15)	0.0172 (15)	−0.0007 (12)	0.0058 (12)	−0.0017 (12)
C10	0.0152 (15)	0.0146 (15)	0.0177 (15)	0.0006 (12)	0.0069 (12)	−0.0011 (12)
C11	0.0159 (15)	0.0167 (15)	0.0172 (15)	−0.0009 (13)	0.0058 (12)	0.0012 (12)
C12	0.0174 (16)	0.0247 (18)	0.0151 (15)	0.0001 (14)	0.0024 (12)	−0.0034 (13)
C13	0.0258 (18)	0.0191 (17)	0.0254 (18)	−0.0032 (15)	0.0039 (15)	−0.0057 (14)
C14	0.0292 (19)	0.0148 (16)	0.0252 (18)	0.0003 (14)	0.0078 (15)	0.0024 (14)
C15	0.0190 (16)	0.0192 (16)	0.0175 (16)	0.0013 (13)	0.0050 (13)	0.0019 (13)
C16	0.035 (2)	0.0151 (16)	0.0211 (17)	0.0008 (15)	0.0069 (15)	0.0030 (13)
C17	0.071 (4)	0.046 (3)	0.023 (2)	0.011 (3)	−0.013 (2)	0.0057 (19)
C18	0.065 (4)	0.086 (5)	0.063 (4)	0.016 (4)	−0.022 (3)	0.019 (4)

Geometric parameters (Å, °)

La1—O4	2.422 (2)	O12—C17	1.454 (5)
La1—O5	2.448 (2)	O13—H13A	0.81 (5)
La1—O7 ⁱ	2.488 (2)	O13—H13B	0.87 (5)
La1—O6	2.537 (2)	C1—C2	1.518 (5)
La1—O2	2.570 (2)	C2—C3	1.390 (4)
La1—O1	2.584 (2)	C2—C7	1.398 (4)
La1—O8 ⁱⁱ	2.595 (2)	C3—C4	1.385 (5)
La1—O3	2.651 (3)	C4—C5	1.379 (5)
La1—O9 ⁱⁱ	2.684 (2)	C4—H4	0.9500
La1—C8 ⁱⁱ	3.004 (3)	C5—C6	1.385 (5)
Cl1—C3	1.737 (3)	C5—H5	0.9500
Cl2—C6	1.740 (4)	C6—C7	1.383 (5)
Cl3—C12	1.729 (3)	C7—C8	1.511 (4)
Cl4—C14	1.733 (4)	C9—C10	1.507 (4)
O1—H1A	0.84 (4)	C10—C11	1.390 (5)
O1—H1B	0.80 (4)	C10—C15	1.398 (5)
O2—H2A	0.77 (5)	C11—C12	1.381 (5)
O2—H2B	0.80 (5)	C11—H11	0.9500
O3—H3A	0.82 (5)	C12—C13	1.379 (5)
O3—H3B	0.76 (5)	C13—C14	1.388 (5)
O4—C1	1.247 (4)	C13—H13	0.9500

O5—C9	1.251 (4)	C14—C15	1.391 (5)
O6—H6A	0.78 (4)	C15—C16	1.504 (5)
O6—H6B	0.85 (4)	C17—C18	1.455 (8)
O7—C1	1.252 (4)	C17—H17A	0.9900
O8—C8	1.255 (4)	C17—H17B	0.9900
O9—C8	1.263 (4)	C18—H18A	0.9800
O10—C9	1.257 (4)	C18—H18B	0.9800
O11—C16	1.210 (5)	C18—H18C	0.9800
O12—C16	1.313 (5)		
C12 ⁱⁱⁱ ...C13	3.4185 (16)	C13 ^{iv} ...C14	3.4645 (15)
C12...C13	3.4287 (15)		
O4—La1—O5	85.14 (8)	O4—C1—O7	125.5 (3)
O4—La1—O7 ⁱ	143.67 (8)	O4—C1—C2	118.4 (3)
O5—La1—O7 ⁱ	75.00 (8)	O7—C1—C2	116.1 (3)
O4—La1—O6	73.11 (8)	C3—C2—C7	118.9 (3)
O5—La1—O6	81.00 (8)	C3—C2—C1	121.9 (3)
O7 ⁱ —La1—O6	73.93 (8)	C7—C2—C1	119.0 (3)
O4—La1—O2	73.96 (8)	C4—C3—C2	121.7 (3)
O5—La1—O2	71.11 (8)	C4—C3—Cl1	118.1 (3)
O7 ⁱ —La1—O2	125.01 (8)	C2—C3—Cl1	120.2 (3)
O6—La1—O2	138.13 (8)	C5—C4—C3	119.2 (3)
O4—La1—O1	141.71 (8)	C5—C4—H4	120.4
O5—La1—O1	90.05 (8)	C3—C4—H4	120.4
O7 ⁱ —La1—O1	69.51 (8)	C4—C5—C6	119.5 (3)
O6—La1—O1	143.43 (8)	C4—C5—H5	120.2
O2—La1—O1	68.58 (8)	C6—C5—H5	120.2
O4—La1—O8 ⁱⁱ	75.46 (7)	C7—C6—C5	121.8 (3)
O5—La1—O8 ⁱⁱ	149.22 (8)	C7—C6—Cl2	120.4 (3)
O7 ⁱ —La1—O8 ⁱⁱ	107.29 (7)	C5—C6—Cl2	117.8 (3)
O6—La1—O8 ⁱⁱ	70.69 (8)	C6—C7—C2	118.9 (3)
O2—La1—O8 ⁱⁱ	123.90 (8)	C6—C7—C8	122.9 (3)
O1—La1—O8 ⁱⁱ	119.92 (8)	C2—C7—C8	118.0 (3)
O4—La1—O3	85.50 (8)	O8—C8—O9	122.2 (3)
O5—La1—O3	136.70 (8)	O8—C8—C7	117.2 (3)
O7 ⁱ —La1—O3	129.51 (8)	O9—C8—C7	120.5 (3)
O6—La1—O3	135.31 (8)	O8—C8—La1 ⁱⁱ	59.15 (16)
O2—La1—O3	65.67 (8)	O9—C8—La1 ⁱⁱ	63.26 (16)
O1—La1—O3	72.34 (8)	C7—C8—La1 ⁱⁱ	173.1 (2)
O8 ⁱⁱ —La1—O3	66.07 (8)	O5—C9—O10	124.8 (3)
O4—La1—O9 ⁱⁱ	124.74 (7)	O5—C9—C10	118.0 (3)
O5—La1—O9 ⁱⁱ	144.12 (7)	O10—C9—C10	117.2 (3)
O7 ⁱ —La1—O9 ⁱⁱ	69.12 (7)	C11—C10—C15	120.2 (3)
O6—La1—O9 ⁱⁱ	88.95 (7)	C11—C10—C9	119.1 (3)
O2—La1—O9 ⁱⁱ	131.49 (8)	C15—C10—C9	120.7 (3)
O1—La1—O9 ⁱⁱ	77.78 (7)	C12—C11—C10	119.5 (3)
O8 ⁱⁱ —La1—O9 ⁱⁱ	49.35 (7)	C12—C11—H11	120.2

O3—La1—O9 ⁱⁱ	71.52 (7)	C10—C11—H11	120.2
O4—La1—C8 ⁱⁱ	99.99 (8)	C13—C12—C11	121.8 (3)
O5—La1—C8 ⁱⁱ	155.69 (8)	C13—C12—C13	119.5 (3)
O7 ⁱ —La1—C8 ⁱⁱ	87.61 (8)	C11—C12—C13	118.7 (3)
O6—La1—C8 ⁱⁱ	77.89 (8)	C12—C13—C14	117.9 (3)
O2—La1—C8 ⁱⁱ	133.19 (8)	C12—C13—H13	121.0
O1—La1—C8 ⁱⁱ	99.77 (8)	C14—C13—H13	121.0
O8 ⁱⁱ —La1—C8 ⁱⁱ	24.53 (8)	C13—C14—C15	122.2 (3)
O3—La1—C8 ⁱⁱ	67.60 (8)	C13—C14—C14	118.3 (3)
O9 ⁱⁱ —La1—C8 ⁱⁱ	24.86 (8)	C15—C14—C14	119.5 (3)
La1—O1—H1A	114 (3)	C14—C15—C10	118.3 (3)
La1—O1—H1B	118 (3)	C14—C15—C16	118.9 (3)
H1A—O1—H1B	101 (4)	C10—C15—C16	122.7 (3)
La1—O2—H2A	120 (3)	O11—C16—O12	125.6 (4)
La1—O2—H2B	127 (3)	O11—C16—C15	123.2 (4)
H2A—O2—H2B	108 (4)	O12—C16—C15	110.9 (3)
La1—O3—H3A	120 (3)	O12—C17—C18	107.8 (5)
La1—O3—H3B	121 (3)	O12—C17—H17A	110.2
H3A—O3—H3B	107 (4)	C18—C17—H17A	110.2
C1—O4—La1	167.0 (2)	O12—C17—H17B	110.2
C9—O5—La1	169.9 (2)	C18—C17—H17B	110.2
La1—O6—H6A	123 (3)	H17A—C17—H17B	108.5
La1—O6—H6B	122 (3)	C17—C18—H18A	109.5
H6A—O6—H6B	109 (4)	C17—C18—H18B	109.5
C1—O7—La1 ⁱⁱⁱ	151.1 (2)	H18A—C18—H18B	109.5
C8—O8—La1 ⁱⁱ	96.32 (18)	C17—C18—H18C	109.5
C8—O9—La1 ⁱⁱ	91.88 (18)	H18A—C18—H18C	109.5
C16—O12—C17	115.5 (3)	H18B—C18—H18C	109.5
H13A—O13—H13B	105 (5)		
La1—O4—C1—O7	133.7 (9)	C6—C7—C8—O9	−65.7 (4)
La1—O4—C1—C2	−44.7 (11)	C2—C7—C8—O9	119.3 (3)
La1 ⁱⁱⁱ —O7—C1—O4	111.9 (4)	La1—O5—C9—O10	90.4 (13)
La1 ⁱⁱⁱ —O7—C1—C2	−69.7 (5)	La1—O5—C9—C10	−91.1 (13)
O4—C1—C2—C3	−70.8 (4)	O5—C9—C10—C11	−5.8 (4)
O7—C1—C2—C3	110.6 (3)	O10—C9—C10—C11	172.9 (3)
O4—C1—C2—C7	114.2 (3)	O5—C9—C10—C15	176.1 (3)
O7—C1—C2—C7	−64.3 (4)	O10—C9—C10—C15	−5.2 (4)
C7—C2—C3—C4	1.4 (5)	C15—C10—C11—C12	1.5 (5)
C1—C2—C3—C4	−173.6 (3)	C9—C10—C11—C12	−176.6 (3)
C7—C2—C3—C11	−178.0 (2)	C10—C11—C12—C13	1.1 (5)
C1—C2—C3—C11	7.0 (4)	C10—C11—C12—C13	−177.7 (2)
C2—C3—C4—C5	−1.4 (5)	C11—C12—C13—C14	−2.4 (5)
C11—C3—C4—C5	178.0 (3)	C13—C12—C13—C14	176.4 (3)
C3—C4—C5—C6	0.3 (5)	C12—C13—C14—C15	1.2 (6)
C4—C5—C6—C7	0.8 (5)	C12—C13—C14—C14	−178.8 (3)
C4—C5—C6—C12	−177.9 (3)	C13—C14—C15—C10	1.2 (5)
C5—C6—C7—C2	−0.8 (5)	C14—C14—C15—C10	−178.7 (3)

C12—C6—C7—C2	177.9 (2)	C13—C14—C15—C16	−176.8 (3)
C5—C6—C7—C8	−175.7 (3)	C14—C14—C15—C16	3.2 (5)
C12—C6—C7—C8	3.0 (4)	C11—C10—C15—C14	−2.6 (5)
C3—C2—C7—C6	−0.3 (4)	C9—C10—C15—C14	175.5 (3)
C1—C2—C7—C6	174.8 (3)	C11—C10—C15—C16	175.4 (3)
C3—C2—C7—C8	174.9 (3)	C9—C10—C15—C16	−6.5 (5)
C1—C2—C7—C8	−10.0 (4)	C17—O12—C16—O11	0.2 (6)
La1 ⁱⁱ —O8—C8—O9	−4.8 (3)	C17—O12—C16—C15	174.7 (3)
La1 ⁱⁱ —O8—C8—C7	173.3 (2)	C14—C15—C16—O11	93.0 (5)
La1 ⁱⁱ —O9—C8—O8	4.7 (3)	C10—C15—C16—O11	−85.0 (5)
La1 ⁱⁱ —O9—C8—C7	−173.4 (2)	C14—C15—C16—O12	−81.6 (4)
C6—C7—C8—O8	116.1 (3)	C10—C15—C16—O12	100.4 (4)
C2—C7—C8—O8	−58.8 (4)	C16—O12—C17—C18	−172.7 (4)

Symmetry codes: (i) $x-1, y, z$; (ii) $-x+1, -y+1, -z+2$; (iii) $x+1, y, z$; (iv) $x, -y+3/2, z+1/2$.

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1A $\cdots$ O13	0.84 (4)	2.00 (4)	2.787 (4)	155 (4)
O1—H1B $\cdots$ O10 ^v	0.80 (4)	1.89 (5)	2.663 (4)	164 (4)
O2—H2A $\cdots$ O10 ^v	0.77 (5)	2.28 (5)	2.972 (4)	150 (4)
O2—H2B $\cdots$ O1 ^v	0.80 (5)	2.11 (5)	2.868 (4)	159 (4)
O3—H3A $\cdots$ O10 ^v	0.82 (5)	2.10 (5)	2.850 (4)	152 (4)
O3—H3B $\cdots$ O13 ⁱⁱⁱ	0.76 (5)	2.13 (5)	2.883 (4)	174 (5)
O6—H6A $\cdots$ O9 ⁱ	0.78 (4)	2.10 (4)	2.864 (3)	166 (4)
O6—H6B $\cdots$ O8	0.85 (4)	1.92 (4)	2.772 (3)	175 (4)
O13—H13A $\cdots$ O11 ^v	0.81 (5)	2.16 (5)	2.948 (4)	164 (5)
O13—H13B $\cdots$ O9 ⁱⁱ	0.87 (5)	2.30 (5)	3.008 (4)	139 (4)

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

Continuous Shape Measurements (CShM) for $[\text{La}(3,6\text{-dcpa})(\text{C}_{10}\text{H}_7\text{Cl}_2\text{O}_4)(\text{H}_2\text{O})_4\cdot\text{H}_2\text{O}]_\infty$. The lower is the CShM value, the better is the agreement with the given coordination polyhedron.

[ML9]	EP-9	OPY-9	HBPY-9	JTC-9	JCCU-9	CCU-9	JCSAPR-9	CSAPR-9	JTCTPR-9	TCTPR-9	JTDIC-9	HH-9	MFF-9
La	35.863	21.416	20.115	15.640	11.075	9.311	2.176	1.059	2.715	1.073	13.106	10.786	1.588

EP-9 $\equiv D_{9h}$ -Enneagon; OPY-9 $\equiv C_{8v}$ -Octagonal pyramid; HBPY-9 $\equiv D_{7h}$ -Heptagonal bipyramid; JTC-9 $\equiv C_{3v}$ -Johnson triangular cupola J3; JCCU-9 $\equiv C_{4v}$ -Capped cube J8; CCU-9 $\equiv C_{4v}$ -Spherical-relaxed capped cube; JCSAPR-9 C_{4v} -Capped square antiprism J10; **CSAPR-9** $\equiv C_{4v}$ -**Spherical capped square antiprism**; JTCTPR-9 $\equiv D_{3h}$ -Tricapped trigonal prism J51; TCTPR-9 $\equiv D_{3h}$ -Spherical tricapped trigonal prism; JTDIC-9 $\equiv C_{3v}$ -Tridiminished icosahedron J63; HH-9 $\equiv C_{2v}$ -Hula-hoop; MFF-9 $\equiv C_s$ -Muffin.