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## Influence of halogens on the crystal packing of 3,4,5,6-tetra-chloro-phthalate-based lanthanide coordination compounds†

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Crystal growth in water between lanthanide ions and tetra-chloro-benzene-1,2-di-carboxylate (tcpa<sup>2-</sup>) led to 6 new coordination compounds with respective chemical formulas [Y(tcpa)(OH)(H<sub>2</sub>O)<sub>3</sub>]<sub>∞</sub> (1), Nd<sub>4</sub>(tcpa)<sub>6</sub>(H<sub>2</sub>O)<sub>22</sub>·8H<sub>2</sub>O (2), [KLa(tcpa)<sub>2</sub>(H<sub>2</sub>O)<sub>10</sub>·H<sub>2</sub>O]<sub>∞</sub> (3), [KLa(tcpa)<sub>2</sub>(H<sub>2</sub>O)<sub>5</sub>·2H<sub>2</sub>O]<sub>∞</sub> (4), Y(tcpa)(Htcpa)(H<sub>2</sub>O)<sub>5</sub> (5) and [KTb(tcpa)<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>·H<sub>2</sub>O]<sub>∞</sub> (6). The crystal structures of these six compounds are described and compared with previously described crystal structures, focusing on the structural characteristics that are known for being key points for luminescence intensity. Trends induced by the presence of halogen atoms are identified.

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## Introduction

For more than two decades, luminescent lanthanide-based coordination polymers<sup>1</sup> are widely studied because of their potential interest in various technological fields<sup>2,3</sup> such as, sensing,<sup>4–7</sup> lighting and displays,<sup>8,9</sup> thermometry<sup>10,11</sup> or materials traceability,<sup>12–14</sup> for example. For most of these technological fields and particularly for materials traceability, highly luminescent compounds are required.<sup>15</sup> Optimization of luminescence properties can be achieved by playing with the metallic centers,<sup>16</sup> the shaping of the particles<sup>17</sup> or the choice of the ligand.<sup>18</sup> The latter leverage arm is the most crucial. Indeed, because of the shielded character of their 4f valence orbitals, lanthanide ions have a weak structuring effect, and the crystal packing is driven by the structuring characters of the ligands.

Benzene-poly-carboxylate ligands have been widely used<sup>19</sup> because they have several assets. First, their phenyl ring is well adapted for providing efficient antenna effect<sup>20</sup> and

ensures good luminescence properties of lanthanide ions. Structurally, it can also be involved in  $\pi$ -stacking interactions. Second, their carboxylate functions are suitable for the coordination of lanthanide ions that are typical hard Pearson's acids.<sup>21,22</sup> Structurally, they can also be involved in a hydrogen bond<sup>23</sup> network. However, recent studies have strongly suggested that  $\pi$ -stacking<sup>24</sup> interactions could constitute a pathway for long distance intermetallic energy transfers and thus could be detrimental to luminescence intensity.<sup>25,26</sup>

Therefore, on the one hand phenyl rings are beneficial because they provide efficient antenna effect, and on the other hand, they constitute a drawback for high luminescence properties. Recent studies have suggested that benzene-poly-carboxylate ligands substituted by halogen atoms could be a solution to this problem.<sup>27,28</sup> Indeed, in these studies, halogen bonds<sup>29,30</sup> impose the crystal packing and prevent  $\pi$ -stacking interactions leading to highly luminescent lanthanide coordination polymers.

To confirm this trend, the system Ln<sup>3+</sup>/tcpa<sup>2-</sup>/H<sub>2</sub>O where tcpa<sup>2-</sup> denotes 3,4,5,6-tetra-chloro-phthalate (Scheme 1) has been structurally studied.

Several crystal structures of lanthanide-containing coordination compounds based on this ligand have already been described. Their main structural features are gathered in Table 1.

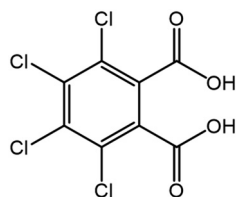
In this article, crystal structures obtained by our group in the frame of this systematic study are described, paying attention to intermolecular bonds. The work described below is a crystallo-chemical study, the aim of which is to provide information about the crystal packing trend. The

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† Electronic supplementary information (ESI) available: Asymmetric units with the numbering scheme, continuous shape measurements, Hirshfeld surface analysis, and selected Cl–Cl and O–O distances for compounds (1) to (6). CCDC 2117762, 2117764, 2118210, 2118211, 2384464 and 2384468. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d4ce00966e>



**Scheme 1** Schematic representation of 3,4,5,6-tetra-chloro-phthalic acid (3,4,5,6-tetra-chloro-benzene-1,2-di-carboxylic acid) hereafter denoted as  $H_2tcpa$ .

description of a new approach to synthesize new luminescent coordination compounds is outside the scope of this article.

## Experimental section

3,4,5,6-Tetra-chloro-phthalic acid (>98%) was purchased from TCI and used without further purification. Lanthanide oxides (4N) were purchased from Ampère. Lanthanide chlorides were prepared according to established procedures.<sup>38</sup>

### Synthesis of the di-sodium and di-potassium salts of 3,4,5,6-tetra-chloro-phthalic acid ( $H_2tcpa$ )

A stoichiometric amount of sodium hydroxide was added to an aqueous suspension of  $H_2tcpa$  under stirring. The obtained clear solution was evaporated to dryness. Then, the white microcrystalline powder was dissolved in ethanol. Addition of diethyl ether induced precipitation of the di-sodium salt ( $Na_2tcpa$ ) that was filtered and dried in air. It can be noticed that this compound can also be prepared from the anhydride acid by a similar process. The only difference is that the mixture anhydride acid/sodium hydroxide must be refluxed for 120 min.  $C_8Cl_4Na_2O_4$  (MW = 348 g mol<sup>-1</sup>) analysis: (calc.) found: C (27.6%) 27.5%; Cl (40.8%) 41.0%; O (18.4%) 18.2%; Na (13.2%) 13.3%. Thermogravimetric analysis confirms that this salt is anhydrous.

The di-potassium salt was prepared according to the same procedure, just replacing sodium hydroxide with potassium hydroxide.

### Crystal growth

$[Y(tcpa)(OH)(H_2O)_3]_\infty$  (1). 0.5 mmol of  $YCl_3(H_2O)_6$  (152 mg  $\equiv$  0.5 mmol) dissolved in 10 mL of deionized water was added to an aqueous solution of  $Na_2tcpa$  (0.75 mmol  $\equiv$  261 mg in 10 mL) under stirring at room temperature. Precipitation occurred. The white precipitate was filtered, and the filtrate was left for slow evaporation at room temperature. After a few days, colorless single crystals suitable for single crystal X-ray diffraction were collected.  $C_8H_7Cl_4O_8Y$  (MW = 461.9 g mol<sup>-1</sup>) analysis: (calc.) found: C (20.8%) 20.5%; H (1.5%) 1.6% Cl (30.7%) 31.0%; O (27.7%) 27.5%; Y (19.2%) 19.3%.

$Nd_4(tcpa)_6(H_2O)_{22}\cdot 8H_2O$  (2). 0.5 mmol of  $NdCl_3(H_2O)_6$  (179 mg  $\equiv$  0.5 mmol) dissolved in 10 mL of deionized water was added to an aqueous solution of  $Na_2tcpa$  (0.75 mmol  $\equiv$

261 mg in 10 mL) under stirring at room temperature. Precipitation occurred. The white precipitate was filtered, and the filtrate was left for slow evaporation at room temperature. After a few days, colorless single crystals suitable for single crystal X-ray diffraction were collected.  $C_{48}H_{60}O_{54}Nd_4Cl_{24}$  (MW = 2928.7 g mol<sup>-1</sup>) analysis: (calc.) found: C (19.7%) 19.5%; H (2.0%) 2.5% Cl (29.1%) 29.0%; O (29.5%) 29.5%; Nd (19.7%) 19.5%.

$[KLa(tcpa)_2(H_2O)_{10}\cdot H_2O]_\infty$  (3). 0.5 mmol of  $LaCl_3(H_2O)_7$  (186 mg  $\equiv$  0.5 mmol) dissolved in 10 mL of deionized water was added to an aqueous solution of  $K_2tcpa$  (0.75 mmol  $\equiv$  285 mg in 10 mL) under stirring at room temperature. Precipitation occurred. The white precipitate was filtered, and the filtrate was left for slow evaporation at room temperature. After a few days, colorless single crystals suitable for single crystal X-ray diffraction were collected.  $C_{16}H_{22}O_{19}Cl_8KLa$  (MW = 980.0 g mol<sup>-1</sup>) analysis: (calc.) found: C (19.6%) 20.0%; H (2.2%) 2.5% Cl (29.0%) 29.0%; O (31.0%) 30.4%; K (4.0%) 4.1%, La (14.2%) 14.0%.

$[KLa(tcpa)_2(H_2O)_5\cdot 2H_2O]_\infty$  (4). 2 mmol (743 mg  $\equiv$  2 mmol) of  $LaCl_3(H_2O)_7$ , 2 mmol (608 mg) of  $H_2tcpa$ , 4 mmol (224 mg) of KOH and 5 mL of deionized water were introduced in a closed 30 mL Teflon reactor. The mixture was heated to 180 °C for 7 days. Then it was cooled down at 2.5 °C min<sup>-1</sup> to room temperature. Colorless single-crystals suitable for single-crystal X-ray diffraction were collected.  $C_{16}H_{14}O_{15}Cl_8KLa$  (MW = 907.88 g mol<sup>-1</sup>) analysis: (calc.) found: C (21.1%) 21.0%; H (1.5%) 1.5% Cl (31.3%) 31.0%; O (26.4%) 26.5%; K (4.3%) 4.5%, La (15.3%) 15.5%.

$Y(tcpa)(Htcpa)(H_2O)_5$  (5). 1 mmol (303 mg  $\equiv$  1 mmol) of  $YCl_3(H_2O)_6$ , 1 mmol (304 mg) of  $H_2tcpa$  and 2 mmol (82 mg) of sodium hydroxide in 5 mL of de-ionized water were put in a sealed Pyrex test tube in a CEM Discover microwave oven and maintained for 1 hour under stirring ( $T = 130$  °C;  $P = 2.5$  bar). Colorless single crystals suitable for X-ray diffraction were collected.  $C_{16}H_{11}O_{13}Cl_8Y$  (MW = 783.9 g mol<sup>-1</sup>) analysis: (calc.) found: C (24.5%) 24.5%; H (1.4%) 1.5% Cl (36.2%) 36.0%; O (26.5%) 26.5%; Y (11.3%) 11.5%.

$[KTb(tcpa)_2(H_2O)_6\cdot H_2O]_\infty$  (6). 2 mmol (747 mg  $\equiv$  2 mmol) of  $TbCl_3(H_2O)_6$ , 2 mmol (612 mg) of  $H_2tcpa$  and 4 mmol (222 mg) of potassium hydroxide in 5 mL of de-ionized water were put in a sealed Pyrex test tube in a CEM Discover microwave oven and maintained for 1 hour under stirring ( $T = 130$  °C;  $P = 2.5$  bar). Colorless single crystals suitable for X-ray diffraction were collected.  $C_{16}H_{14}O_{15}Cl_8KTb$  (MW = 928.00 g mol<sup>-1</sup>) analysis: (calc.) found: C (20.7%) 21.0%; H (1.5%) 1.5% Cl (30.6%) 30.5%; O (25.9%) 26.0%; K (4.2%) 4.0%, Tb (17.1%) 17.0%.

### Single crystal X-ray diffraction

Single-crystals were mounted on an APEXII Bruker-AXS diffractometer. Crystal data collection was performed at 150 K with Mo  $K_\alpha$  radiation ( $\lambda = 0.70713$  Å). Crystal structures were solved, using SIR 97,<sup>39</sup> by direct methods. They were refined, using SHELX97 (ref. 40) with the aid of the WINGX program.<sup>41,42</sup> All non-hydrogen atoms were refined anisotropically. Hydrogen

**Table 1** Selected information about previously reported lanthanide coordination compounds based on the  $\text{tcpa}^{2-}$  ligand coordination polymers

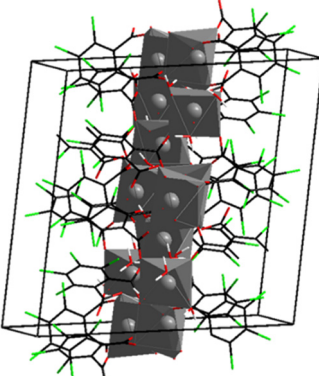
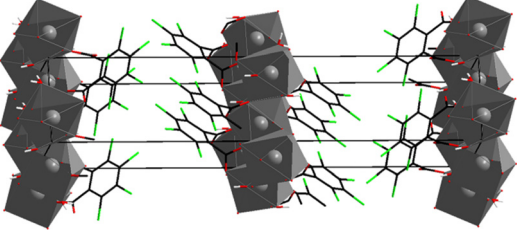
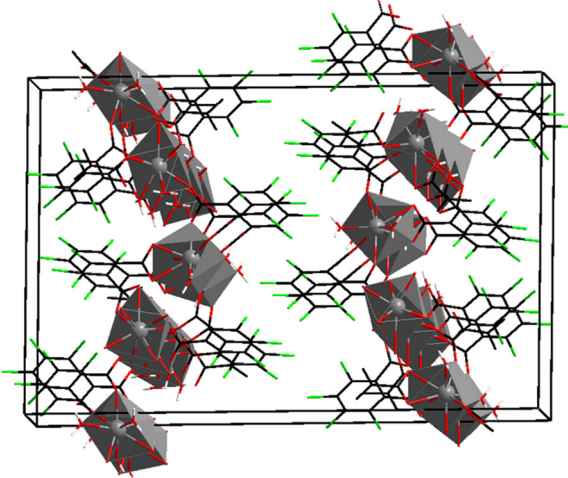
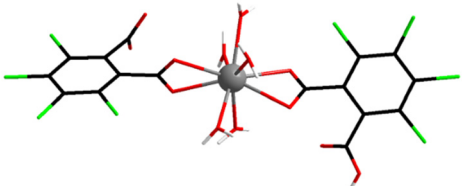
Chemical formula Ln Ref. CCDC No.	System Space group Cell parameters	Synthesis Dimensionality	Projection view of an extended unit cell
$[\text{Ln}_2(\text{tcpa})_3(\text{H}_2\text{O})_4 \cdot \text{H}_2\text{O}]_\infty$ Ln = La Ref. 31 CCDC-144448	Monoclinic $P2_1/c$ (No. 14) $a = 16.951(4) \text{ \AA}$ $b = 14.594(4) \text{ \AA}$ $c = 17.472(4) \text{ \AA}$ $\beta = 98.722(6)^\circ$ $V = 4272.3(2) \text{ \AA}^3$ $Z = 4$	Solvothermal 2D	
$[\text{Ln}(\text{tcpa})\text{OH}(\text{H}_2\text{O})]_\infty$ Ln = La Ref. 32 CCDC-1515750	Monoclinic $P2_1/n$ (No. 14) $a = 6.6874(10) \text{ \AA}$ $b = 6.0956(9) \text{ \AA}$ $c = 30.281(4) \text{ \AA}$ $\beta = 91.094(3)^\circ$ $V = 1234.1(3) \text{ \AA}^3$ $Z = 4$	Solvothermal 2D	
$[\text{Ln}(\text{tcpa})_3(\text{H}_2\text{O})_6]_\infty$ Ln = Eu, Gd, Tb, Dy, Ho, Er, Yb plus Y Ref. 33 CCDC-2300465	Monoclinic $P2_1/n$ (No. 14) $a = 6.2155(2) \text{ \AA}$ $b = 19.6652(7) \text{ \AA}$ $c = 30.3720(9) \text{ \AA}$ $\beta = 94.631(1)^\circ$ $V = 3700.22(20) \text{ \AA}^3$ $Z = 4$	Microwave assisted 2D	
<b>Complexes</b>			
$\text{Ln}(\text{tcpa})(\text{Htcpa})(\text{H}_2\text{O})_5$ Ln = Nd Ref. 34 CCDC-609797	Orthorhombic $Pca2(1)$ (No. 29) $a = 11.6518(6) \text{ \AA}$ $b = 18.7527(9) \text{ \AA}$ $c = 12.3626(6) \text{ \AA}$ $V = 2701.3(2) \text{ \AA}^3$ $Z = 4$	Slow evaporation 0D	

Table 1 (continued)

Complexes	Triclinic	Slow evaporation	
Ln(tcpa)(H <sub>2</sub> O) <sub>7</sub> -Htcpa-H <sub>2</sub> tcpa-H <sub>2</sub> O	<i>P</i> $\bar{1}$ (No. 2)	0D	
Ln = Pr, Er, Yb Ref. 35–37 CCDC-277252	<i>a</i> = 6.9395(5) Å <i>b</i> = 16.2519(13) Å <i>c</i> = 19.1287(15) Å $\alpha$ = 67.382(1)° $\beta$ = 86.524(1)° $\gamma$ = 81.535(1)° <i>V</i> = 1969.7(3) Å <sup>3</sup> <i>Z</i> = 2		

Lanthanide atoms, references and CCDC entries in bold rely on the reported cell parameters.

atoms were located at ideal positions. Absorption corrections were performed using the facilities of the WINGX program.<sup>43</sup> It must be noticed that single crystals of Nd<sub>4</sub>(tcpa)<sub>6</sub>(H<sub>2</sub>O)<sub>22</sub>·8H<sub>2</sub>O (2) were of poor quality. Consequently, there is some sizeable residual density in the vicinity of the Nd<sup>3+</sup> ions. Despite great synthetic efforts, it hasn't been possible to grow single crystals of better quality. Full details of the crystal structures have been deposited with the Cambridge Crystallographic Data Center under the depository numbers CCDC-2118210 for [Y(tcpa)(OH)(H<sub>2</sub>O)<sub>3</sub>]<sub>∞</sub> (1), CCDC-2117762 for Nd<sub>4</sub>(tcpa)<sub>6</sub>(H<sub>2</sub>O)<sub>22</sub>·8H<sub>2</sub>O (2), CCDC-2118211 for [KLa(tcpa)<sub>2</sub>(H<sub>2</sub>O)<sub>10</sub>·H<sub>2</sub>O]<sub>∞</sub> (3), CCDC-2117764 for [KLa(tcpa)<sub>2</sub>(H<sub>2</sub>O)<sub>5</sub>·2H<sub>2</sub>O]<sub>∞</sub> (4), CCDC-2384468 for Y(tcpa)(Htcpa)(H<sub>2</sub>O)<sub>5</sub> (5) and CCDC-2384464 for [KTb(tcpa)<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>·H<sub>2</sub>O]<sub>∞</sub> (6). Selected crystal and final structure refinement data are gathered in Table 2.

## Results and discussion

Reactions in water between lanthanide ions and tcpa<sup>2-</sup> ligands led to six different compounds with different crystal structures (Table 3 and Scheme 2).

### Description of the crystal structure of [Y(tcpa)(OH)(H<sub>2</sub>O)<sub>3</sub>]<sub>∞</sub> (1)

This compound crystallizes in the monoclinic system, space group *P*<sub>2</sub><sub>1</sub>/*m* (No. 11) with the following cell parameters: *a* = 8.7595(6) Å, *b* = 6.7789(5) Å, *c* = 11.8297(9) Å,  $\beta$  = 95.615(3)°, *V* = 699.07(9) Å<sup>3</sup> and *Z* = 2. There is one independent Y<sup>3+</sup> ion in the asymmetric unit (Fig. S1†). It is eight coordinated by eight oxygen atoms that form a C<sub>2v</sub>-bi-augmented trigonal prism (Table S1†).<sup>44,45</sup> Four out of the eight oxygen atoms are from three carboxylate groups of three different tcpa<sup>2-</sup> ligands (O1), one belongs to a hydroxy group (O3) and the remaining three are from coordination water molecules (O4 and O5). There is only one tcpa<sup>2-</sup> in the asymmetric unit. One of its carboxylate functions (O1–C7–O1) is  $\mu_3(\eta_1;\eta_2;\eta_1)$ , while the other one (O2–C8–O2) is non-binding (Fig. 1). There is no crystallization water molecule in this crystal structure.

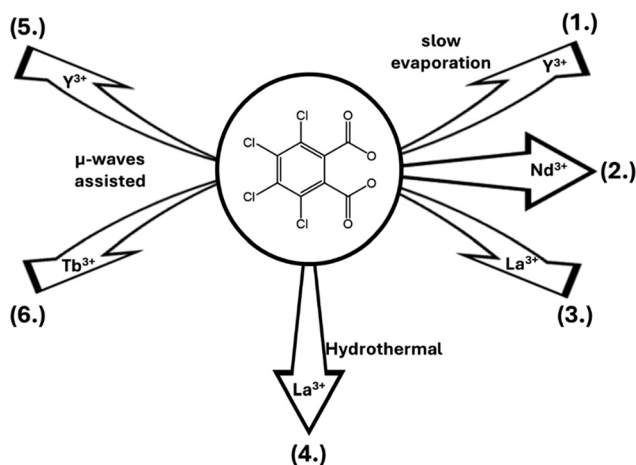
The crystal structure can be described based on molecular chain motifs that spread along the *b*-axis (Fig. 2). The inorganic sub-lattice is 1D. The molecular chains are decorated with tcpa<sup>2-</sup> ligands that point toward the inter-chain space. Phenyl rings are far from each other (the shortest centroid–centroid distances are about 6.8 Å). Therefore, the crystal packing relies on hydrogen and halogen bonds. In this crystal structure, there is only one

Table 2 Crystals and final refinement data

	(1)	(2)	(3)	(4)	(5)	(6)
Molecular formula	C <sub>8</sub> H <sub>10</sub> Cl <sub>4</sub> O <sub>8</sub> Y	C <sub>48</sub> H <sub>60</sub> O <sub>54</sub> Nd <sub>4</sub> Cl <sub>24</sub>	C <sub>16</sub> H <sub>22</sub> Cl <sub>8</sub> O <sub>19</sub> KLa	C <sub>16</sub> H <sub>14</sub> Cl <sub>8</sub> O <sub>15</sub> KLa	C <sub>16</sub> H <sub>11</sub> Cl <sub>8</sub> O <sub>13</sub> Y	C <sub>16</sub> H <sub>14</sub> Cl <sub>8</sub> O <sub>15</sub> KTb
Formula weight (g mol <sup>-1</sup> )	464.87	2928.72	979.94	907.88	783.76	927.89
System	Monoclinic	Triclinic	Triclinic	Triclinic	Orthorhombic	Triclinic
Space group (No.)	<i>P</i> <sub>2</sub> <sub>1</sub> / <i>m</i> (No. 11)	<i>P</i> $\bar{1}$ (No. 2)	<i>P</i> $\bar{1}$ (No. 2)	<i>P</i> $\bar{1}$ (No. 2)	<i>Pca</i> 2 <sub>1</sub> (No. 29)	<i>P</i> $\bar{1}$ (No. 2)
<i>a</i> (Å)	8.7595(6)	10.8914(15)	8.2758(3)	8.1777(11)	11.5640(6)	8.7604(5)
<i>b</i> (Å)	6.7789(5)	13.7161(17)	13.9934(7)	12.7369(19)	18.5537(9)	11.5722(6)
<i>c</i> (Å)	11.8297(9)	16.245(2)	14.3376(6)	13.969(2)	12.1650(6)	13.8453(7)
$\alpha$ (°)	90	74.024(6)	85.9932(14)	85.230(6)	90	90.302(2)
$\beta$ (°)	95.615(3)	86.691(6)	77.9272(12)	77.920(6)	90	97.300(2)
$\gamma$ (°)	90	72.279(5)	75.6109(13)	87.757(6)	90	102.131(2)
<i>V</i> (Å <sup>3</sup> )	699.07(9)	2221.5(5)	1572.45(12)	1417.5(4)	2610.1(2)	1360.39(13)
<i>Z</i>	2	1	2	2	4	2
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	2.208	2.189	2.070	2.127	1.995	2.265
<i>R</i> (%)	4.86	4.64	4.15	2.98	2.65	1.33
<i>R</i> <sub>w</sub> (%)	12.08	10.27	12.32	7.39	5.29	3.13
GoF	1.071	1.298	1.057	1.074	0.998	1.077
CCDC entry	2118210	2117762	2118211	2117764	2384468	2384464

Table 3 Summary of the compounds studied

Reactants	Crystal growth	Formula	Code
$\text{YCl}_3(\text{H}_2\text{O})_6; \text{Na}_2\text{tcpa}$	Slow evaporation	$[\text{Y}(\text{tcpa})(\text{OH})(\text{H}_2\text{O})_3]_\infty$	(1)
$\text{NdCl}_3(\text{H}_2\text{O})_6; \text{Na}_2\text{tcpa}$	Slow evaporation	$\text{Nd}_4(\text{tcpa})_6(\text{H}_2\text{O})_{22} \cdot 8\text{H}_2\text{O}$	(2)
$\text{LaCl}_3(\text{H}_2\text{O})_7; \text{K}_2\text{tcpa}$	Slow evaporation	$[\text{KLa}(\text{tcpa})_2(\text{H}_2\text{O})_{10} \cdot \text{H}_2\text{O}]_\infty$	(3)
$\text{LaCl}_3(\text{H}_2\text{O})_7; \text{K}_2\text{tcpa}$	Hydrothermal synthesis	$[\text{KLa}(\text{tcpa})_2(\text{H}_2\text{O})_5 \cdot 2\text{H}_2\text{O}]_\infty$	(4)
$\text{YCl}_3(\text{H}_2\text{O})_6; \text{Na}_2\text{tcpa}$	$\mu$ -Wave assisted	$\text{Y}(\text{tcpa})(\text{Htcpa})(\text{H}_2\text{O})_5$	(5)
$\text{TbCl}_3(\text{H}_2\text{O})_6; \text{K}_2\text{tcpa}$	$\mu$ -Wave assisted	$[\text{KTb}(\text{tcpa})_2(\text{H}_2\text{O})_6 \cdot \text{H}_2\text{O}]_\infty$	(6)



Scheme 2 Synthesis scheme.

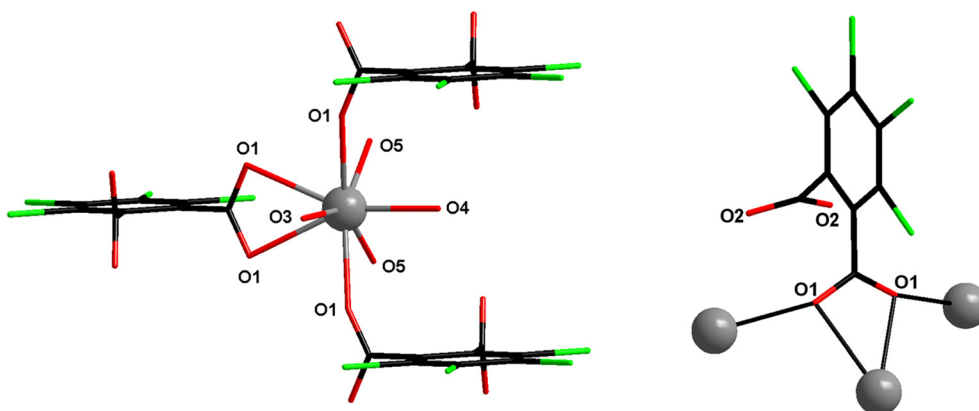
Cl–Cl distance shorter than 3.5 Å (the distance below which halogen bonds are expected to be efficient) between Cl atoms that belong to different phenyl rings (Cl1–Cl4) (Table S2†). On the other hand, there is an important network of strong hydrogen bonds (Table S3†). Hirshfeld surface analysis<sup>46,47</sup> has been performed with CrystalExplorer software<sup>48</sup> (Fig. S2†).

#### Description of the crystal structure of $\text{Nd}_4(\text{tcpa})_6(\text{H}_2\text{O})_{22} \cdot 8\text{H}_2\text{O}$ (2)

This compound crystallizes in the triclinic system, space group  $P\bar{1}$  (No. 2) with the following cell parameters:  $a =$

10.8914(15) Å,  $b = 13.7161(17)$  Å,  $c = 16.245(2)$  Å,  $\alpha = 74.024(6)^\circ$ ,  $\beta = 86.691(6)^\circ$ ,  $\gamma = 72.279(5)^\circ$ ,  $V = 2221.5(5)$  Å<sup>3</sup> and  $Z = 2$ . There are two independent  $\text{Nd}^{3+}$  ions in this crystal structure. Both are nine coordinated by nine oxygen atoms (Fig. 3). Nd1 is surrounded by three oxygen atoms (O1, O2 and O6) from two carboxylate functions that belong to two different  $\text{tcpa}^{2-}$  ligands and six oxygen atoms (O13, O14, O15, O16, O17 and O18) from coordination water molecules that form a slightly distorted  $C_s$ -muffin (Table S4†). Nd2 is bound to three oxygen atoms (O8, O9 and O10) from three carboxylate functions that belong to three different  $\text{tcpa}^{2-}$  ligands and to six oxygen atoms (O19, O20, O21, O22 and O23) from coordination water molecules that form a slightly distorted  $C_{4v}$ -spherical capped square antiprism (Table S4†). There are three independent ligands (hereafter referred to as **A**, **B** and **C**) in the crystal structure. Ligand **A** is  $\mu_1(\eta_2)$ . It is bound to only one Nd1 ion. Ligand **B** is  $\mu_2(\eta_1\eta_1)$ . It connects a Nd1 ion and a Nd2 ion. Ligand **C** is  $\mu_2(\eta_1\eta_1)$  and links two Nd2 ions. It can be noticed that, in ligand **B**, the two carboxylate functions are engaged, while in ligand **C** only one is involved, with the remaining one being non-binding. There are eight crystallization water molecules (OW1, OW2, OW3 and OW4) per molecular motif in this crystal structure.

The crystal structure is 0D and can be described based on isolated tetra-nuclear molecular motifs (Fig. 4). In this molecular motif, the two Nd2 ions are linked to each other (Nd2–Nd2 distance is about 4 Å) by two bridging ligands **C** and two  $\mu_2(\eta_1\eta_1)$  coordination water molecules (O19). This di-nuclear unit is bound to Nd1 ions by a bridging ligand **B**

Fig. 1  $\text{Y}^{3+}$  surrounding (left) and coordination mode of the  $\text{tcpa}^{2-}$  ligand (right) in  $[\text{Y}(\text{tcpa})(\text{OH})(\text{H}_2\text{O})_3]_\infty$ . Hydrogen atoms are omitted for clarity.



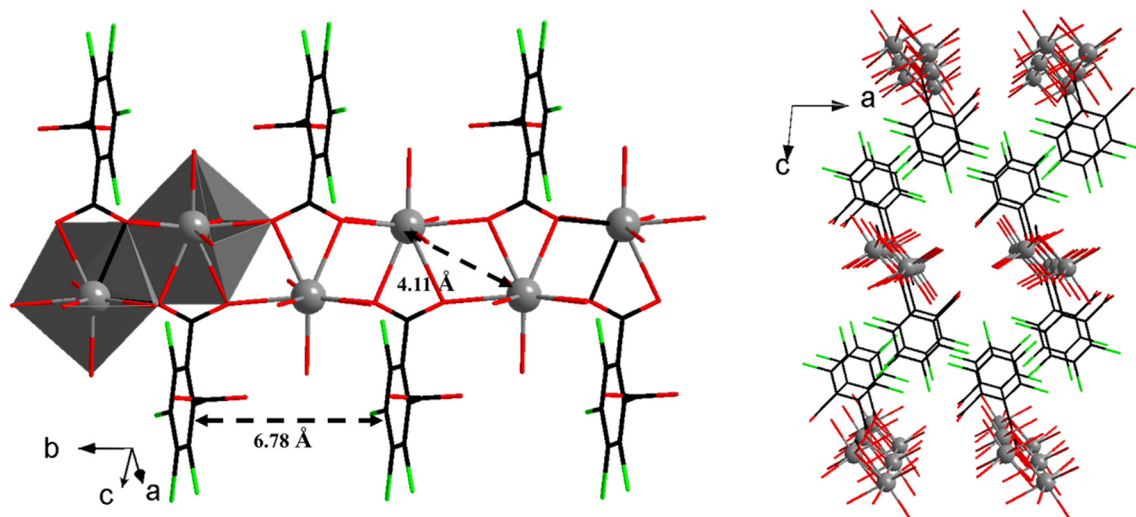


Fig. 2 Left: Projection view of a chain-like molecular motif of  $[Y(tcpa)(OH)(H_2O)_3]_\infty$ . The two polyhedra on the left have been drawn to highlight the 1D character of the inorganic sub-lattice. Right: Perspective view of an extended unit cell of  $[Y(tcpa)(OH)(H_2O)_3]_\infty$ .

(Nd1–Nd2 distances are about 7 Å). There is no  $\pi$ -stacking interaction in this crystal structure (the shortest centroid–centroid distance is greater than 6 Å).

In contrast, there is a dense framework of hydrogen bonds (Table S5 and Fig. S3†) that involve oxygen atoms from the carboxylate functions and the coordination and the crystallization water molecules. Additionally, in this crystal structure, the chloride atoms point to the outside of the molecular motifs and are engaged in a framework of halogen bonds between chloride atoms that belong to different molecular motifs (Table S6 and Fig. S3†). Hirshfeld surface analysis<sup>46,47</sup> has been performed with CrystalExplorer software<sup>48</sup> (Fig. S4†).

### Description of the crystal structure of $[KLa(tcpa)_2(H_2O)_{10} \cdot H_2O]_\infty$ (3)

This compound crystallizes in the triclinic system, space group  $P\bar{1}$  (No. 2) with the following cell parameters:  $a = 8.2758(3)$  Å,  $b = 13.9934(7)$  Å,  $c = 14.3376(6)$  Å,  $\alpha = 85.9932(14)^\circ$ ,  $\beta = 77.9272(12)^\circ$ ,  $\gamma = 75.6109(13)^\circ$ ,  $V = 1572.45(12)$  Å<sup>3</sup> and  $Z = 2$ . There is only one independent  $K^+$  ion in this crystal structure. It is bound to six oxygen atoms that form a distorted octahedron. Five out of the six (OW1, OW2, OW3 and OW5) are from coordination water molecules, while the sixth (O4) belongs to a  $tcpa^{2-}$  carboxylate function. It can be noticed that OW2 oxygen atoms bind two  $K^+$  ions in a  $\mu_2(\eta_1\eta_1)$  way and that the

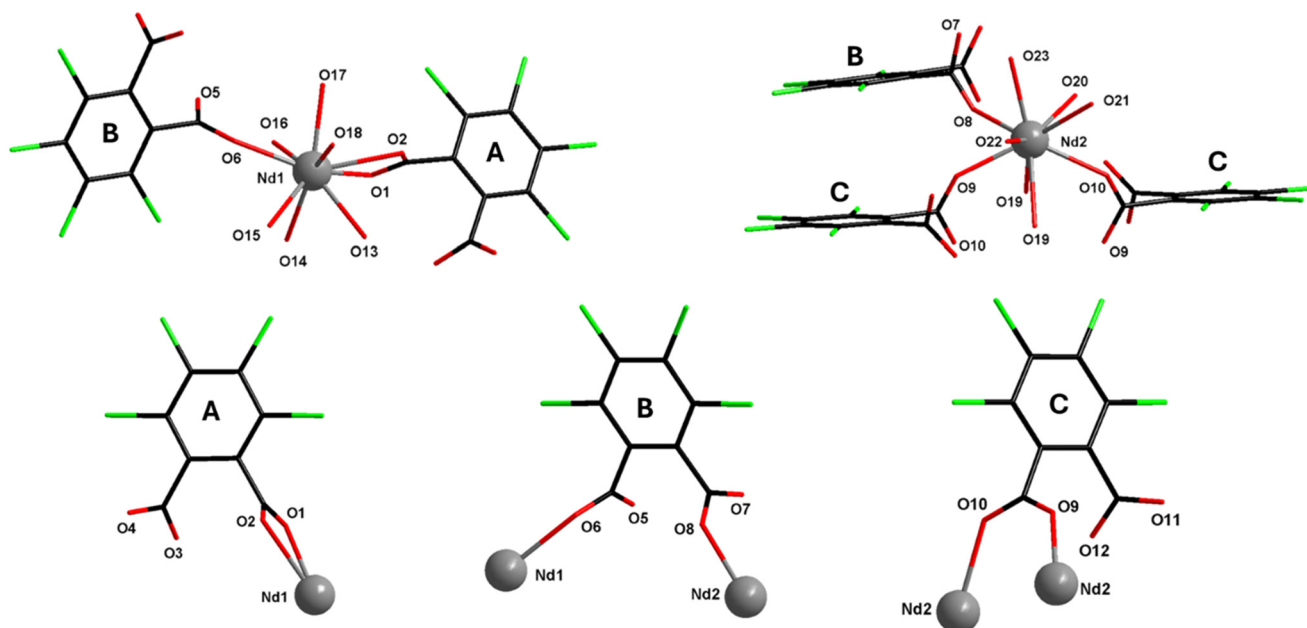


Fig. 3 Neighborhoods of Nd1 and Nd2 (top) and coordination modes of the ligands A, B and C (bottom) in  $Nd_4(tcpa)_6(H_2O)_{22} \cdot 8H_2O$ .

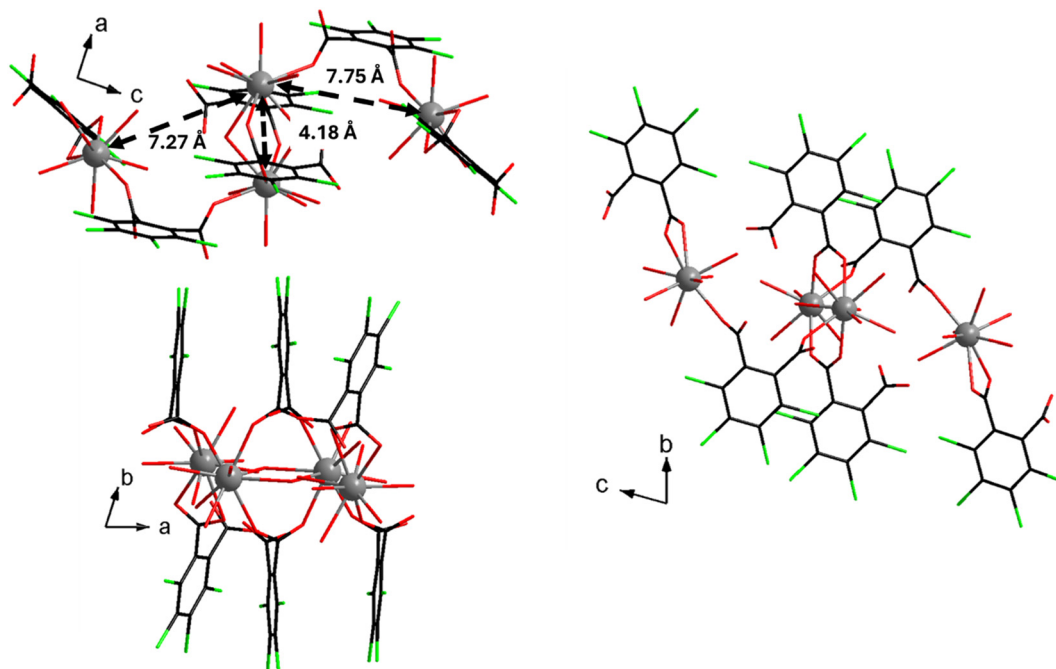


Fig. 4 Projection views along the *b*- (top left), the *c*- (bottom left) and the *a*-axis (right) of the molecular motif in  $\text{Nd}_4(\text{tcpa})_6(\text{H}_2\text{O})_{22}\cdot 8\text{H}_2\text{O}$ .

carboxylate function binds a  $\text{K}^+$  ion and a  $\text{La}^{3+}$  ion in a  $\mu_2(\eta_1\eta_1)$  way. There is also only one independent  $\text{La}^{3+}$  ion in the crystal structure. It is linked to nine oxygen atoms that form a distorted  $C_{4v}$ -spherical capped square antiprism (Table S7<sup>†</sup>). Six out of the nine (O9, O10, O11, O12, O13 and O14) are from coordination water molecules and the remaining three (O3, O7 and O8) belong to three

carboxylate functions from three different  $\text{tcpa}^{2-}$  ligands (Fig. 5).

There are two independent  $\text{tcpa}^{2-}$  ligands in the crystal structure hereafter referred to as **A** and **B**. Ligand **A** binds a  $\text{K}^+$  ion and a  $\text{La}^{3+}$  ion in a  $\mu_2(\eta_1;\eta_1)$  fashion by one of its carboxylate functions. The other carboxylate function is non-binding. Similarly, ligand **B** binds two  $\text{La}^{3+}$  ions in a  $\mu_2(\eta_1;\eta_1)$

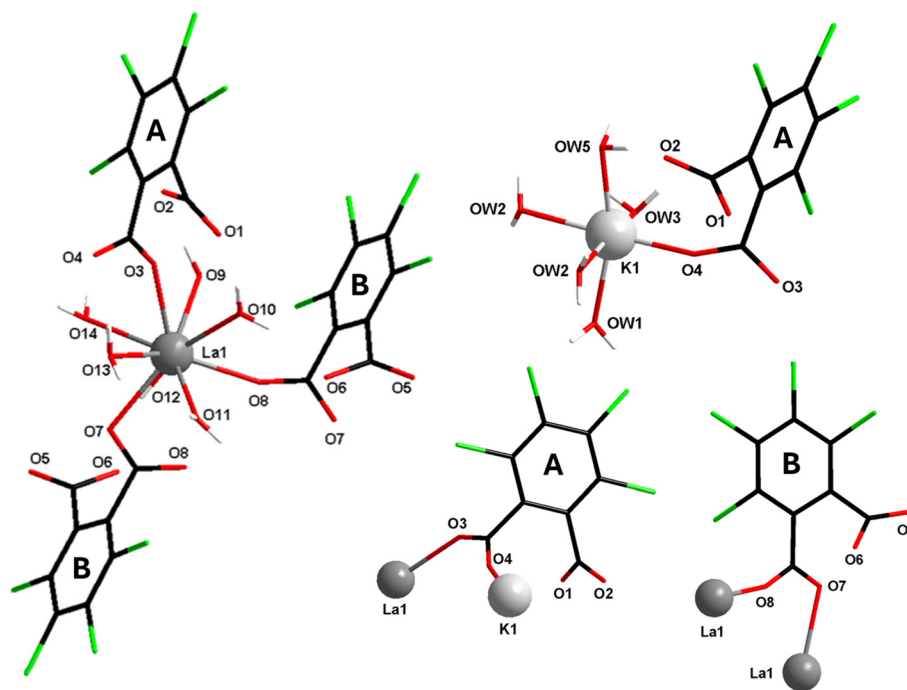


Fig. 5  $\text{La}^{3+}$  surrounding (left),  $\text{K}^+$  surrounding (top right) and ligand coordination modes (bottom right) in  $[\text{KLa}(\text{tcpa})_2(\text{H}_2\text{O})_{10}\cdot\text{H}_2\text{O}]_\infty$  ( $\text{La}^{3+}$  and  $\text{K}^+$  ions are in dark grey and light grey, respectively).

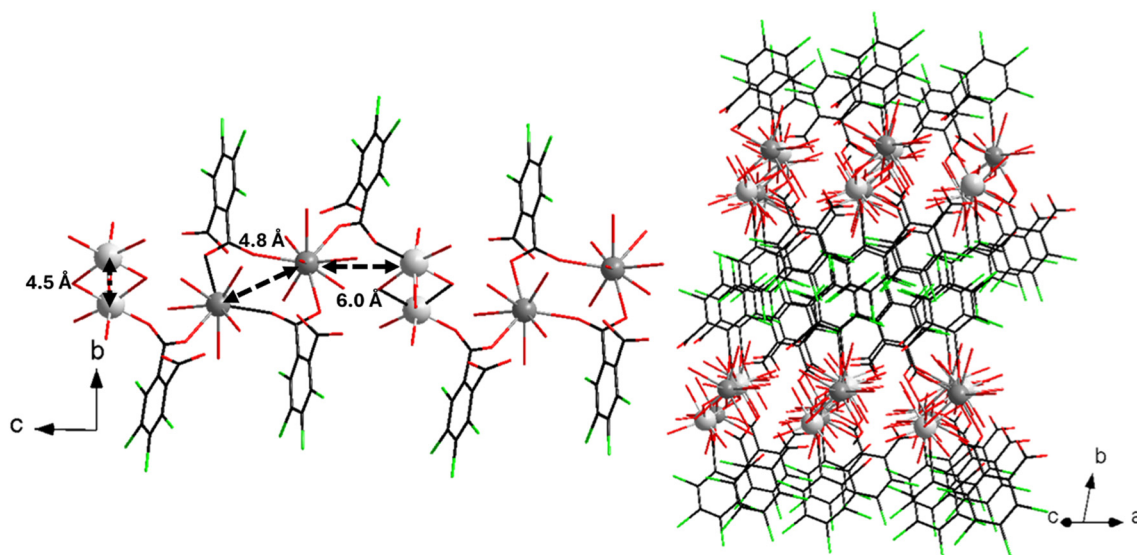


Fig. 6 Projection view along the *a*-axis of a chain-like molecular motif (left) and perspective view along the *a* + *c* direction (right) of  $[\text{KLa}(\text{tcpa})_2(\text{H}_2\text{O})_{10}\cdot\text{H}_2\text{O}]_n$ .

fashion by one of its carboxylate functions while the other one is non-binding (Fig. 5). Additionally, there is one crystallization water molecule per asymmetric unit in this crystal structure.

The crystal structure can be described based on chain-like molecular motifs, spreading parallel to the *a* + *c* direction, in which dimers of potassium alternate with dimers of lanthanum (Fig. 6). There is no  $\pi$ -stacking interaction in this crystal structure (adjacent phenyl rings are far from each

other). Ligands  $\text{tcpa}^{2-}$  are located at the outskirts of the molecular motifs and ligands that belong to adjacent molecular motifs point to each other giving rise to halogen bonds between neighboring molecular motifs (Table S8 and Fig. S5†). On the other hand, there is an intense framework of strong hydrogen bonds inside a given molecular motif and between adjacent molecular motifs (Table S9 and Fig. S5†). Hirshfeld surface analysis<sup>46,47</sup> has been performed with CrystalExplorer software<sup>48</sup> (Fig. S6†).

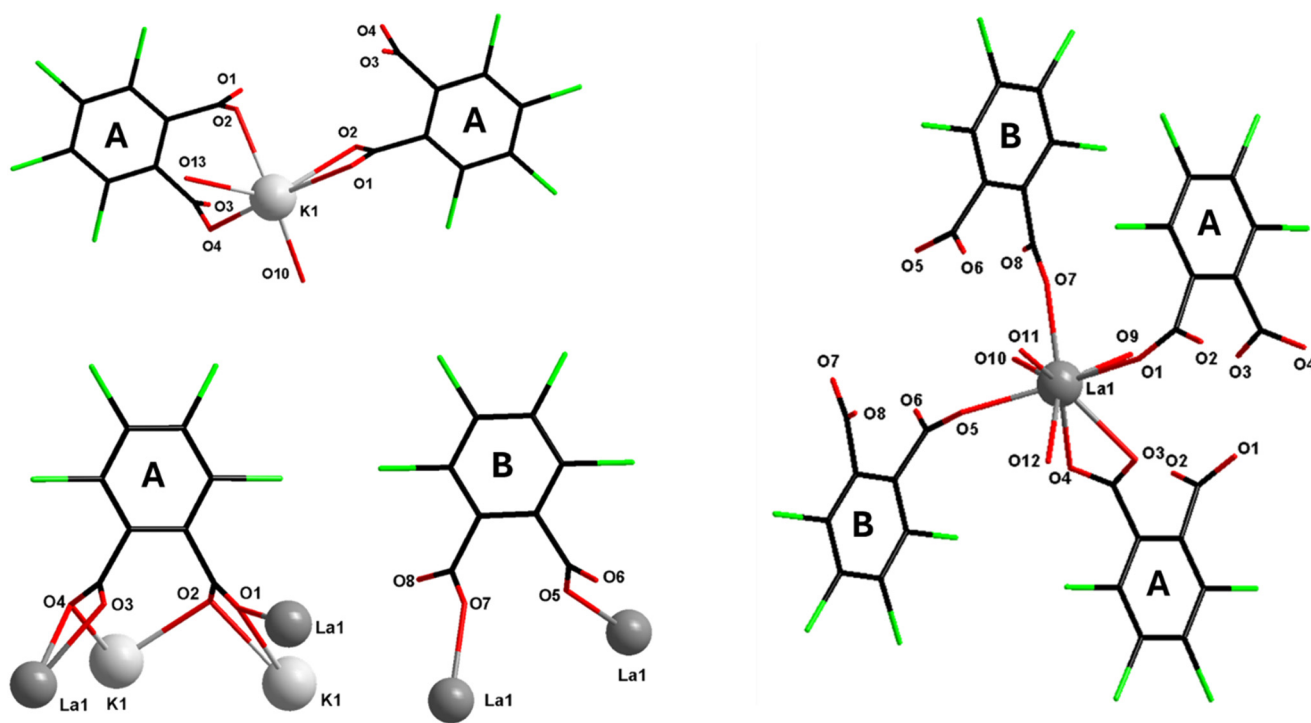


Fig. 7  $\text{K}^+$  and  $\text{La}^{3+}$  surroundings (top left and right, respectively) and ligand coordination modes (bottom left) in  $[\text{KLa}(\text{tcpa})_2(\text{H}_2\text{O})_5\cdot 2\text{H}_2\text{O}]_n$ . Hydrogen atoms have been omitted for clarity.



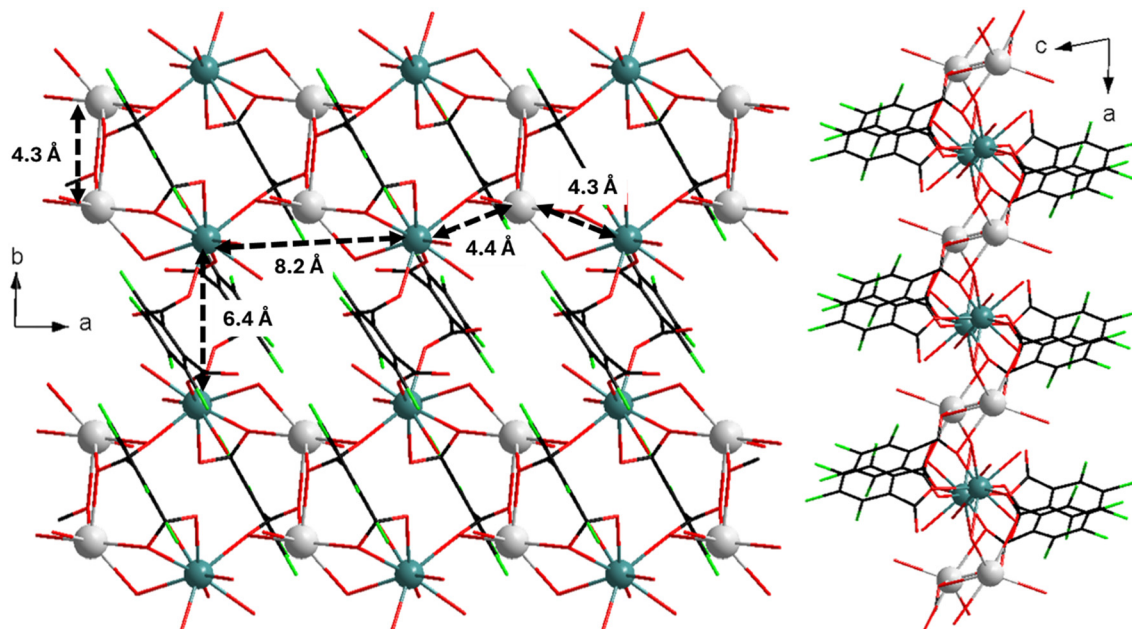


Fig. 8 Projection views along the *c*-axis (left) and the *b*-axis (right) of the molecular motif in  $[\text{KLa}(\text{tcpa})_2(\text{H}_2\text{O})_5 \cdot 2\text{H}_2\text{O}]_\infty$ . Hydrogen atoms have been omitted for clarity.

#### Description of the crystal structure of $[\text{KLa}(\text{tcpa})_2(\text{H}_2\text{O})_5 \cdot 2\text{H}_2\text{O}]_\infty$ (4)

This compound crystallizes in the triclinic system, space group  $P\bar{1}$  (No. 2) with the following cell parameters:  $a = 8.1777(11)$  Å,  $b = 12.7369(19)$  Å,  $c = 13.969(2)$  Å,  $\alpha = 85.230(6)^\circ$ ,  $\beta = 77.920(6)^\circ$ ,  $\gamma = 87.757(6)^\circ$ ,  $V = 1417.5(4)$  Å<sup>3</sup> and  $Z = 2$ . There is one independent  $\text{K}^+$  ion in the crystal

structure. It is surrounded by six oxygen atoms (O1, O2, O4, O10 and O13) that form a distorted octahedron. Four out of the six belong to three carboxylate functions from two different  $\text{tcpa}^{2-}$  ligands and the remaining two are from coordination water molecules (Fig. 7). There is one independent  $\text{La}^{3+}$  ion in this crystal structure. It is nine coordinated by nine oxygen atoms that form a slightly

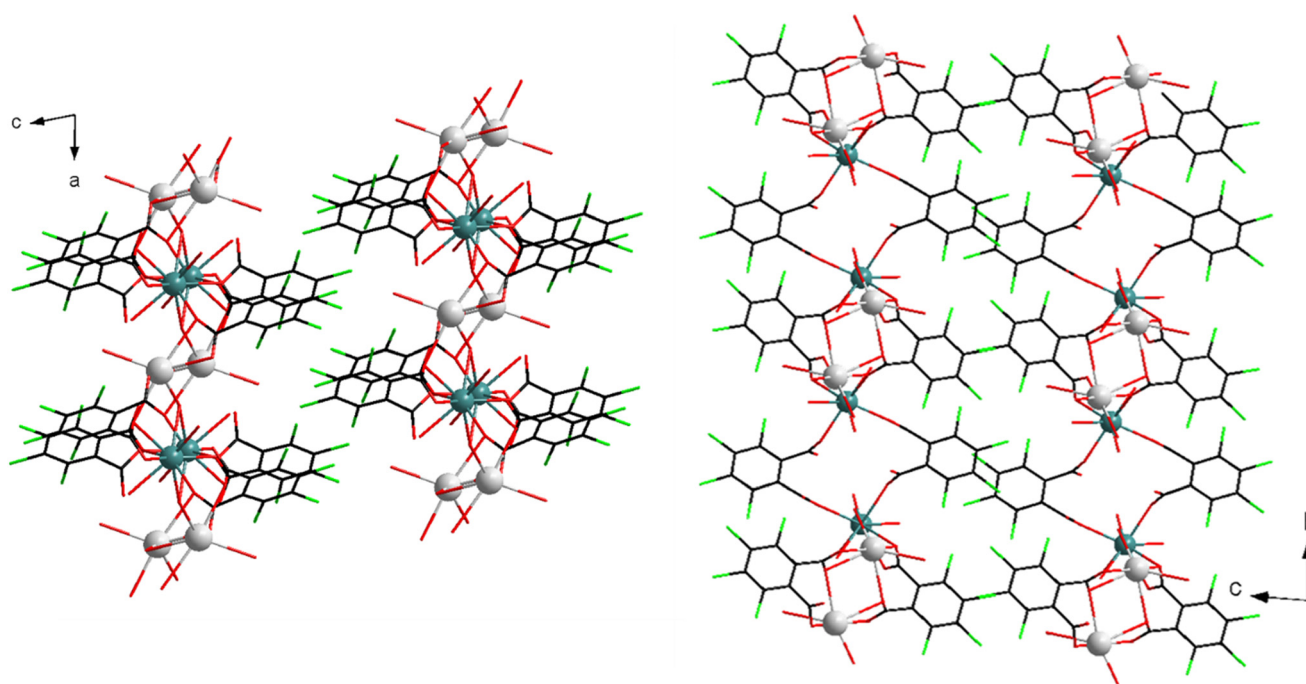


Fig. 9 Projection views along the *b*-axis (left) and the *a*-axis (right) of two adjacent molecular motifs of  $[\text{KLa}(\text{tcpa})_2(\text{H}_2\text{O})_5 \cdot 2\text{H}_2\text{O}]_\infty$ . Hydrogen atoms and crystallization water molecules have been omitted for clarity.

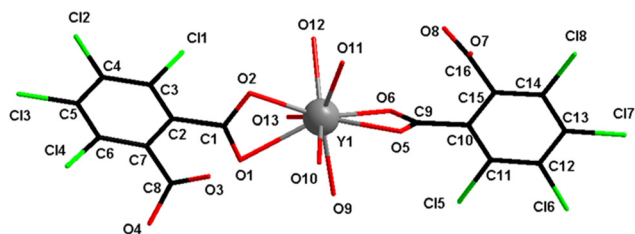


Fig. 10 Projection view of the asymmetric unit with the numbering scheme of  $\text{Y}(\text{tcpa})(\text{Htcpa})(\text{H}_2\text{O})_5$ . Hydrogen atoms have been omitted for clarity.

distorted  $C_{4v}$ -spherical capped square antiprism (Table S10†). Four out of the nine are from coordination water molecules (O9, O10, O11 and O12), while the five others (O1, O3, O4, O5 and O7) belong to four carboxylate functions from four different  $\text{tcpa}^{2-}$  ligands (Fig. 7).

There are two independent ligands in this crystal structure hereafter referred to as **A** and **B**. Ligand **A** binds two  $\text{La}^{3+}$  and two  $\text{K}^+$  ions. Its two carboxylate functions are respectively  $\mu_2(\eta_2\eta_1)$  and  $\mu_3(\eta_1\eta_2\eta_1)$  (Fig. 7). In contrast, ligand **B** links only two  $\text{La}^{3+}$  ions by its two carboxylate functions that are both  $\mu_1(\eta_1)$ .

Lastly, there are two crystallization water molecules (OW1 and OW2) per asymmetric unit in this crystal structure.

The crystal structure can be described based on molecular bi-dimensional motifs that spread parallel to the ( $ab$ ) plane (Fig. 8). Inside these molecular motifs,  $\text{La}^{3+}$  ions are quite far from each other (the smallest  $\text{La}^{3+}$ - $\text{La}^{3+}$  distances are about 6.4 Å). On the opposite,  $\text{K}^+$  ions are quite close from each other (the smallest distances between  $\text{K}^+$  ions are 4.3 Å).

$\text{tcpa}^{2-}$  ligands are located at the periphery of the molecular motif and chloride atoms point toward the intermolecular space (Fig. 9). There is no  $\pi$ -stacking in this crystal structure (phenyl rings are far from each other). In

contrast, there is a dense framework of strong hydrogen bonds in this crystal structure (Fig. S7 and Table S11†). There are also numerous halogen bonds that reinforce the crystal packing (Fig. S7 and Table S12†). Hirshfeld surface analysis<sup>46,47</sup> has been performed with CrystalExplorer software<sup>48</sup> (Fig. S8†).

### Description of the crystal structure of $\text{Y}(\text{tcpa})(\text{Htcpa})(\text{H}_2\text{O})_5$ (5)

This compound crystallizes in the orthorhombic system, space group  $Pca2_1$  (No. 29) with the following cell parameters:  $a = 11.5640(6)$  Å,  $b = 18.5537(9)$  Å,  $c = 12.1650(6)$  Å,  $V = 2610.06(23)$  Å<sup>3</sup> and  $Z = 4$ . There is only one independent  $\text{Y}^{3+}$  ion in the crystal structure. It is bound to nine oxygen atoms that form a slightly distorted  $C_s$ -muffin (Table S13†). Five out of the nine oxygen atoms (O9, O10, O11, O12 and O14) are from coordination water molecules and the remaining four (O1, O2, O5 and O6) belong to two carboxylate functions from two different ligands (Fig. 10). One of the carboxylate functions is protonated (O4). Both binding carboxylate functions are  $\mu_1(\eta_2)$ . There is no crystallization water molecule in this crystal structure.

The crystal structure can be described based on mono-lanthanide complexes with the chemical formula  $\text{Y}(\text{tcpa})(\text{Htcpa})(\text{H}_2\text{O})_5$ . Lanthanide ions that belong to adjacent molecular motifs are between 6 and 7 Å far from each other (Fig. 11). There is no  $\pi$ -stacking in this crystal structure (phenyl rings are far from each other) and the crystal packing is ensured by both halogen bond (Table S14†) and hydrogen bond (Table S15†) networks. Hirshfeld surface analysis<sup>46,47</sup> has been performed with CrystalExplorer software<sup>48</sup> (Fig. S9†).

It can be noticed that this crystal structure has been previously described based on a Nd-derivative.<sup>34</sup>

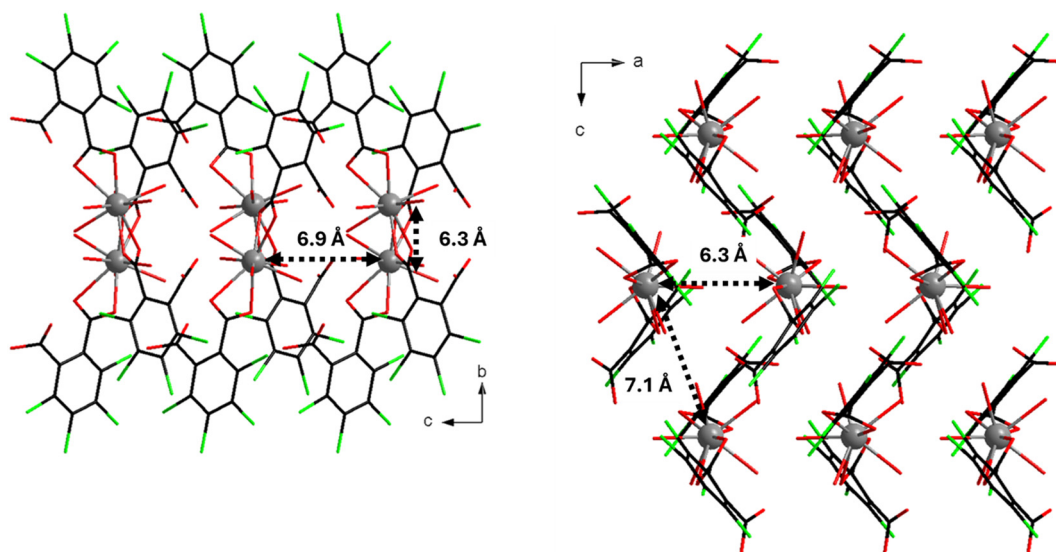


Fig. 11 Projection views along the  $a$ -axis (left) and the  $b$ -axis (right) of an extended unit cell of  $\text{Y}(\text{tcpa})(\text{Htcpa})(\text{H}_2\text{O})_5$ .

### Description of the crystal structure of $[\text{KTb}(\text{tcpa})_2(\text{H}_2\text{O})_6 \cdot \text{H}_2\text{O}]_\infty$ (6)

This compound crystallizes in the triclinic system, space group  $P\bar{1}$  (No. 2) with the following cell parameters:  $a = 8.7604(5)$  Å,  $b = 11.5722(6)$  Å,  $c = 13.8453(7)$  Å,  $\alpha = 90.302(2)^\circ$ ,  $\beta = 97.300(2)^\circ$ ,  $\gamma = 102.131(2)^\circ$ ,  $V = 1360.39(13)$  Å<sup>3</sup> and  $Z = 2$ . There is one independent  $\text{K}^+$  ion in this crystal structure. It is bound to five oxygen atoms that form a distorted square-based pyramid. Three out of the five oxygen atoms (O2, O4 and O7) are from three  $\eta_1$  carboxylate functions that belong to three different  $\text{tcpa}^{2-}$  ligands. The remaining two (O14 and O15) are from coordination water molecules (Fig. 12). There is one independent  $\text{Tb}^{3+}$  ion that is eight coordinated by eight oxygen atoms that form a distorted  $D_{4d}$ -square antiprism (Table S16<sup>†</sup>). Four out of them (O1, O5, O7 and O8) are from three carboxylate functions ( $\eta_1$ ,  $\eta_1$  and  $\eta_2$ ) that belong to three different  $\text{tcpa}^{2-}$  ligands (Fig. 12). The four others (O9, O10, O11 and O12) are from coordination water molecules. There is only one crystallization water molecule (O13) in the crystal structure.

There are two independent  $\text{tcpa}^{2-}$  ligands in the crystal structure hereafter referred to as ligand A and ligand B. Ligand A is  $\mu_3(\eta_1, \eta_1, \eta_1)$  and binds two  $\text{K}^+$  ions and one  $\text{Tb}^{3+}$  ion. Ligand B is  $\mu_3(\eta_2, \eta_1, \eta_1)$  and binds two  $\text{Tb}^{3+}$  ions and one

$\text{K}^+$  ion (Fig. 12). There is only one crystallization water molecule in the crystal structure.

The crystal structure can be described based on chain-like molecular motifs that spread parallel to the  $a + c$  direction (Fig. 13). In these molecular motifs,  $\text{Tb}^{3+}/\text{K}^+$  dimers are linked to each other by  $\text{tcpa}^{2-}$  ligands and the shortest Tb–Tb distance inside the molecular motifs is 6.4383(3) Å. The inorganic sublattice is 0D. The  $\text{tcpa}^{2-}$  ligands point toward the intermolecular space which causes quite large intermetallic distances ( $>10$  Å) between metal ions that belong to adjacent molecular motifs. There is no  $\pi$ -stacking interaction in this crystal structure (phenyl rings are far from each other). The stability of the crystal packing is ensured by strong hydrogen-bond (Fig. S10 and Table S17<sup>†</sup>) and halogen-bond (Table S18<sup>†</sup>) networks. Hirshfeld surface analysis<sup>46,47</sup> has been performed with CrystalExplorer software<sup>48</sup> (Fig. S11<sup>†</sup>).

### Common features

Based on these six crystal structures, some common points can be identified. First, the great versatility of the  $\text{tcpa}^{2-}$  ligands can be noticed. Indeed, to date, not less than eleven different crystal structures (six in this work and five in

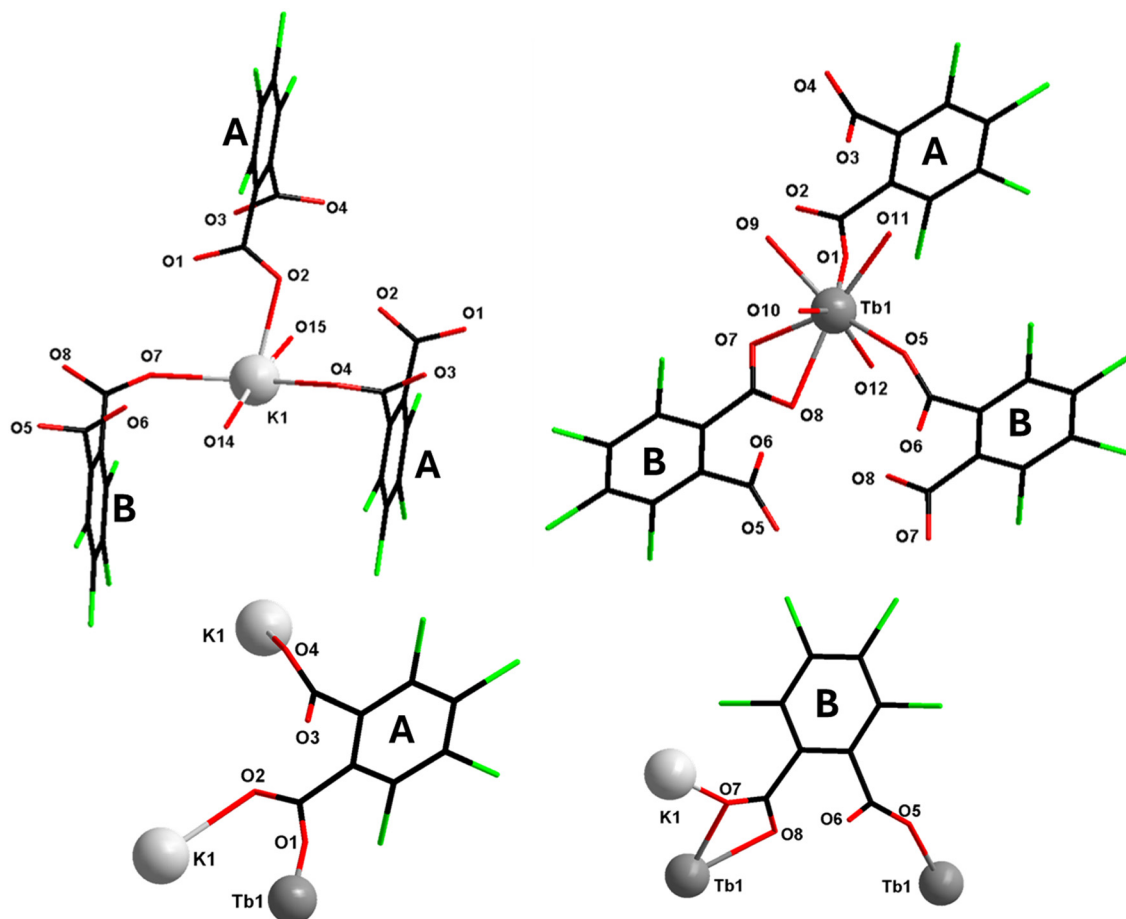


Fig. 12  $\text{K}^+$  and  $\text{Tb}^{3+}$  ion surroundings (top) and  $\text{tcpa}^{2-}$  ligand coordination modes (bottom) in  $[\text{KTb}(\text{tcpa})_2(\text{H}_2\text{O})_6 \cdot \text{H}_2\text{O}]_\infty$ .

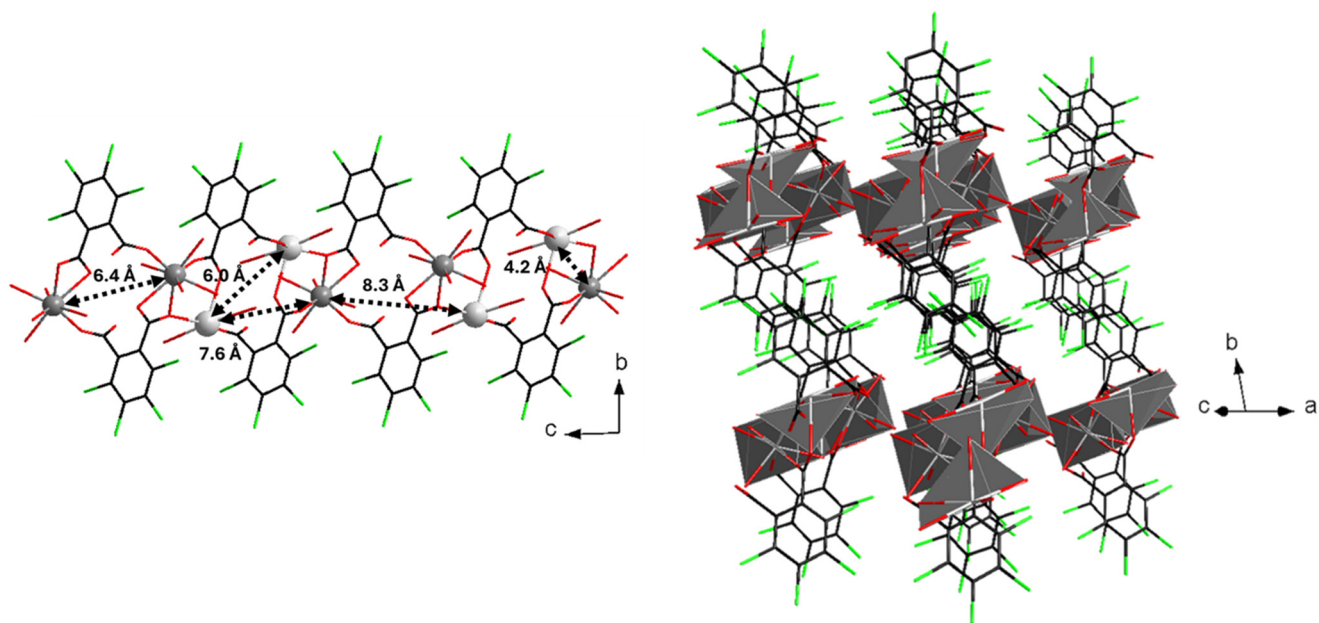


Fig. 13 Left: Projection view along the *a*-axis of a chain-like molecular motif of  $[\text{KTb}(\text{tcpa})_2(\text{H}_2\text{O})_6 \cdot \text{H}_2\text{O}]_\infty$ . Right: Perspective view along the *a* + *c* direction of  $[\text{KTb}(\text{tcpa})_2(\text{H}_2\text{O})_6 \cdot \text{H}_2\text{O}]_\infty$ .  $\text{Tb}^{3+}$  and  $\text{K}^+$  coordination polyhedra are drawn.

previous studies) can be obtained by reaction in water between lanthanide ions and  $\text{tcpa}^{2-}$  ligands, depending on the lanthanide ion and/or the crystal growth conditions. This great versatility, which has already been observed for other systems involving

non-halogenated ligands,<sup>49</sup> mainly relies on the shielded nature of the 4f valence orbitals, which does not promote a preferential coordination direction. This results in a wide variety of coordination modes for the  $\text{tcpa}^{2-}$  ligand (Fig. 14).

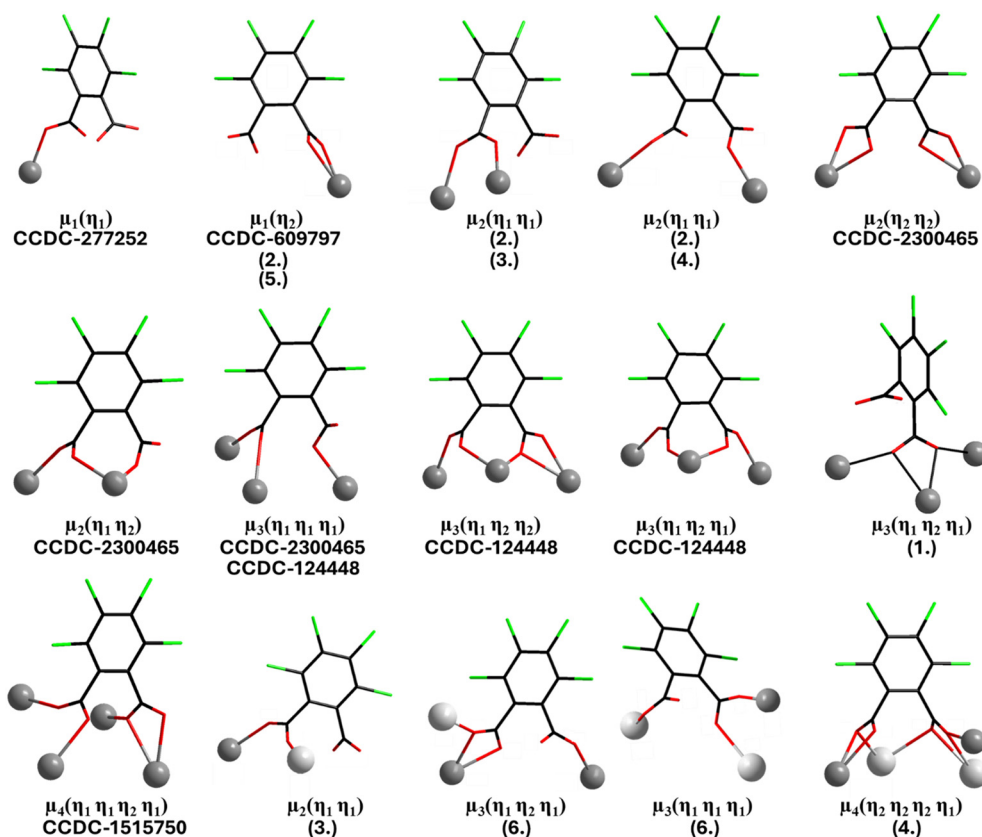
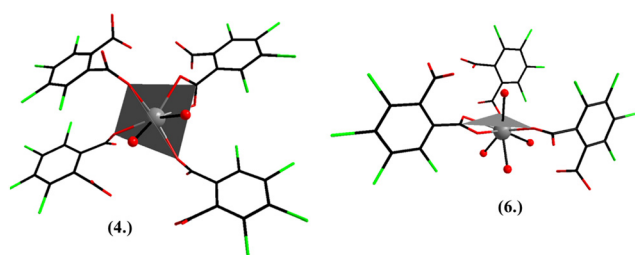


Fig. 14 Coordination modes of the  $\text{tcpa}^{2-}$  ligand in reported crystal structures.



**Table 4** The shortest intermetallic ( $\text{Ln}^{3+}-\text{Ln}^{3+}$ ) distances and the number of coordination water molecules per lanthanide ion in lanthanide-based coordination polymers with phthalate ( $\text{pa}^{2-}$ ) or tetra-chloro-phthalate ligands

Chemical formula	Ref.	Shortest intermetallic distance (Å)	Number of coordination water molecules per lanthanide ion
$[\text{Er}_2(\text{pa})_3(\text{H}_2\text{O})]_\infty$	52	11.9763(5)	1
$[\text{Eu}_2(\text{pa})_3(\text{H}_2\text{O})]_\infty$	50	11.7241(36)	1
$[\text{Nd}_2(\text{pa})_3(\text{H}_2\text{O})_2]_\infty$	51	11.271(1)	1
$[\text{Y}(\text{tcpa})(\text{OH})(\text{H}_2\text{O})_3]_\infty$	(1)	7.5446(9)	3
$[\text{KLa}(\text{tcpa})_2(\text{H}_2\text{O})_{10}\cdot\text{H}_2\text{O}]_\infty$	(3)	13.3585(7)	6
$[\text{KLa}(\text{tcpa})_2(\text{H}_2\text{O})_5\cdot 2\text{H}_2\text{O}]_\infty$	(4)	13.969(2)	4
$[\text{KTb}(\text{tcpa})_2(\text{H}_2\text{O})_6\cdot\text{H}_2\text{O}]_\infty$	(6)	11.5772(4)	4
$[\text{La}_2(\text{tcpa})_3(\text{H}_2\text{O})_4\cdot\text{H}_2\text{O}]_\infty$	31	16.951(4)	4 and 0
$[\text{La}(\text{tcpa})\text{OH}(\text{H}_2\text{O})]_\infty$	32	15.4490(21)	1 (plus -OH)
$[\text{Y}_2(\text{tcpa})_3(\text{H}_2\text{O})_6]_\infty$	33	10.9887(9)	3



**Scheme 3** Schematic representation of the surroundings of lanthanide ions in  $[\text{KLa}(\text{tcpa})_2(\text{H}_2\text{O})_5\cdot 2\text{H}_2\text{O}]_\infty$  (4) and  $[\text{KTb}(\text{tcpa})_2(\text{H}_2\text{O})_6\cdot\text{H}_2\text{O}]_\infty$  (6). Coordination water molecules are symbolized by red balls. Distribution of the ligands is symbolized by grey areas.

Fig. 14 shows that the  $\text{tcpa}^{2-}$  ligand can bind several metals. This relies on the two carboxylate functions that are linked to adjacent C atoms of the phenyl ring. Indeed, such coordination modes that linked as many as four metal ions have previously been observed for lanthanide-based coordination polymers with benzene-1,2-di-carboxylate (or phthalate) ligands.<sup>50–52</sup>

If we focus our attention on rare-earth-based coordination polymers, we notice that, in all cases (CCDC-144448, CCDC-1515750, CCDC-2300465, (1), (3), (4) and (6)), metal ions constitute the core of the molecular motif and  $\text{tcpa}^{2-}$  ligands

are localized at its periphery. This trend also relies on the relative positions of the carboxylate functions and has previously been observed for lanthanide-based coordination polymers with phthalate ligands.<sup>50–52</sup>

In all the crystal structures of lanthanide-based coordination polymers, the halogen atoms face each other and point to the intermolecular space. In all cases, they are involved in a network of halogen bonds that contribute to the stability of the crystal packing and tend to keep molecular motifs away from each other. Consequently, the intermetallic distances between lanthanide ions that belong to adjacent molecular motifs tend to be longer in coordination polymers with tetra-chloro phthalate than in those with phthalate (Table 4). Of course, this is not systematic, and in some crystal structures, some short intermetallic distances are observed.

The number of coordination water molecules per lanthanide ion also tends to be greater in the crystal structures of the lanthanide-based coordination polymers with tetra-chloro-phthalate ligands than in those with phthalate ligands (Table 4). This probably relies on the arrangement of the ligands in both sides of the lanthanide ions that leaves space for coordinated water molecules in the apical position.

Finally, in contrast with what is commonly observed in lanthanide-based coordination polymers with non-halogenated benzene-poly-carboxylate ligands, there is no  $\pi$ -stacking interaction (phenyl rings are far from each other) in any of the crystal structures described above. Stability of the crystal packings is thus essentially ensured by dense networks of strong hydrogen bonds that involve coordination and crystallization water molecules and O atoms from the carboxylate functions. It is reinforced by networks of halogen bonds.

### Comparison of the crystal structures of

#### $[\text{KLa}(\text{tcpa})_2(\text{H}_2\text{O})_5\cdot 2\text{H}_2\text{O}]_\infty$ (4) and $[\text{KTb}(\text{tcpa})_2(\text{H}_2\text{O})_6\cdot\text{H}_2\text{O}]_\infty$ (6)

Two out of the six crystal structures described above deserve to be compared. Indeed, both contain a lanthanide ion and a potassium ion, two  $\text{tcpa}^{2-}$  ligands and seven water molecules. Because of the commonly admitted chemical similarity of lanthanide ions,<sup>53</sup> examples of two lanthanide-based

**Table 5** Summary of some structural characteristics of compounds  $[\text{KLa}(\text{tcpa})_2(\text{H}_2\text{O})_5\cdot 2\text{H}_2\text{O}]_\infty$  (4) and  $[\text{KTb}(\text{tcpa})_2(\text{H}_2\text{O})_6\cdot\text{H}_2\text{O}]_\infty$  (6)

Compound	(4)	(6)
$\text{Ln}^{3+}$		
Coordination number	9	8
Coordination polyhedron	Spherical capped square antiprism	Square antiprism
Number of coordination water molecules	4	2
Number of coordinated ligands	4	3
$\text{K}^+$		
Coordination number	6	5
Coordination polyhedron	Octahedron	Square-based pyramid
Number of coordination water molecules	5	2
Number of coordinated ligands	1	3
$\text{tcpa}^{2-}$		
Number of independent ligands	2	2
Coordination modes	$\mu_4(\eta_2\eta_2\eta_2\eta_1)$ and $\mu_2(\eta_1\eta_1)$	$\mu_3(\eta_1\eta_1\eta_1)$ and $\mu_3(\eta_1\eta_2\eta_1)$
Dimensionality	2D	1D



coordination polymers with identical ligands and hydration rates and different crystal structures are quite scarce. Some structural characteristics of both compounds are summarized in Table 5.

The crystal structure of (4) is 2D while that of (6) is 1D. In both cases, the metal ions are located at the heart of the molecular motifs and the  $\text{tcpa}^{2-}$  ligands at their periphery (Fig. 8 and 13). Inside the molecular motifs, lanthanide ions and potassium ions alternate. Because of the coordination modes of the ligands ( $\mu_4$  and  $\mu_2$  in (4);  $\mu_3$  and  $\mu_3$  in (6)), metal ions are quite close to each other in these two crystal structures (the shortest  $\text{Ln}^{3+}$ - $\text{Ln}^{3+}$  distances inside the two molecular motifs are 6.4 Å).

The neighborhoods of the lanthanide ions are noticeably different between the two crystal structures. Indeed,  $\text{La}^{3+}$  ions are nine coordinated in (4) and  $\text{Tb}^{3+}$  ions are eight coordinated in (6). In both cases, the organization of ligands around lanthanide ions is governed by the minimization of steric repulsions between them and coordination water molecules complete the coordination sphere (Scheme 3).

Scheme 3 shows that the lanthanide coordination polyhedra formed by atoms that have been considered as representative of the  $\text{Ln}^{3+}$ -ligand binding directions (O1, O5, O7 and C8 for (4); O1, O5 and C16 for (6)) are a distorted square plane and triangle for (4) and (6), respectively. This agrees with what have been previously reported<sup>54</sup> and confirms the weak covalency contribution in  $\text{Ln}^{3+}$ -ligand bonds.<sup>55</sup>

## Conclusions and outlook

This crystallo-chemical systematic study strongly suggests that halogenated phthalates are good candidates for the design of efficient lanthanide-based luminescent coordination polymers. Although, despite great efforts, it has not been possible to perform luminescence measurements (these compounds have been obtained as single-crystals only), this systematic study allows us to identify structural trends:

- First, the adjacent positions of the two carboxylate functions in phthalate ligands are an important feature. It makes possible the linkage of numerous metal ions per ligand, which is an asset as far as extended and rigid inorganic sublattices are targeted. On the other hand, it seems that it favors high hydration rates and therefore promotes the presence of high energy O-H vibrators in the vicinity of lanthanide ions, which is a drawback for intense luminescence.

- Halogen atoms, by facing each other, tend to enlarge intermolecular distances, which favors large intermetallic distances and weak intermetallic energy transfers. This is beneficial for luminescence properties.

- The crystal packings are ensured by networks of hydrogen bonds and, to a lesser extent, of halogen bonds. However, halogenated ligands seem to prevent  $\pi$ -stacking. This is very interesting as far as highly luminescent coordination polymers are targeted.

From a global point of view, this study suggests that halogenated ligands, especially halogenated phthalates, are promising candidates for the design of highly luminescent lanthanide-based coordination polymers. This agrees with previous studies. Indeed, to the best of our knowledge, there are only a few studies that consider luminescence properties of lanthanide-based coordination polymers with halogenated phthalates as ligands, and all of them describe compounds that exhibit quite intense luminescence.<sup>14,27,28,33,56</sup> To date, this crystallo-chemical study, which is well upstream of the application, strongly suggests that the nature of halogen atoms, their number and their position are worth studying.

## Data availability

The data supporting this article have been included as part of the ESI.† Crystallographic data have been deposited at the CCDC under the depository numbers CCDC-2118210 for  $[\text{Y}(\text{tcpa})(\text{OH})(\text{H}_2\text{O})_3]_\infty$  (1), CCDC-2117762 for  $\text{Nd}_4(\text{tcpa})_6(\text{H}_2\text{O})_{22}\cdot 8\text{H}_2\text{O}$  (2), CCDC-2118211 for  $[\text{KLa}(\text{tcpa})_2(\text{H}_2\text{O})_{10}\cdot\text{H}_2\text{O}]_\infty$  (3), CCDC-2117764 for  $[\text{KLa}(\text{tcpa})_2(\text{H}_2\text{O})_5\cdot 2\text{H}_2\text{O}]_\infty$  (4), CCDC-2384468 for  $\text{Y}(\text{tcpa})(\text{Htcpa})(\text{H}_2\text{O})_5$  (5) and CCDC-2384464 for  $[\text{KTb}(\text{tcpa})_2(\text{H}_2\text{O})_6\cdot\text{H}_2\text{O}]_\infty$  (6).

## Author contributions

F. Ngom: investigation; C. Blais: project administration; I. Badiane: project administration; C. Hénaff: investigation; M. Camara: resources, writing – review and editing; C. Daiguebonne: formal analysis, writing – review and editing; O. Guillou: conceptualization, writing – review and editing.

## Conflicts of interest

There are no conflicts to declare.

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