Crystal structure and Hirshfeld surface analysis of the anionic tetrakis-complex of lanthanum(III) NMe₄La₄ with the CAPh-ligand dimethyl (2,2,2-trichloroacetyl)phosphoramidate

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The anionic tetrakis-complex of lanthanum(III) NMe₄La₄ with the CAPh-ligand dimethyl (2,2,2-trichloroacetyl)phosphoramidate (H₄L₄), namely, tetramethylammonium tetrakis[2,2,2-trichloro-1-[(dimethoxyphosphoryl)imino]-ethanolato]lanthanum(III), (C₄H₁₂N)[La(C₄H₆Cl₃NO₄P)₄], has been synthesized, crystallized and structurally characterized by X-ray diffraction. The lanthanide ion is surrounded by four anionic, bis-chelating CAPh ligands forming the complex anion with a coordination number of eight for La³⁺ and NMe₄⁺ as the counter-ion. The coordination polyhedron of the La³⁺ ion was interpreted as a triangular dodecahedron.

1. Chemical context

Considerable interest in the luminescence properties of lanthanide coordination compounds results from their potential applications in modern technologies and medicine (Eliseeva et al., 2010; Kido et al., 2002; Tsukube et al., 2002). In particular, use of P,N-substituted analogues of β-diketone such as carbacylamidophosphates (CAPh) (Amirkhanov et al., 2014) with the C(O)NHP(O) structural fragment as ligands is promising because of their powerful chelating properties (Skopenko et al., 2004; Amirkhanov et al., 2014) and ability to sensitize the luminescence of lanthanides (Kariaka et al., 2016; Pham et al., 2017; Kariaka et al., 2018). In this work, the synthesis and crystal structure of the anionic tetrakis-complex of lanthanum(III) containing the CAPh-ligand dimethyl (2,2,2-trichloroacetyl)phosphoramidate and a tetramethylammonium cation (formula NMe₄La₄) is reported.
2. Structural commentary

The title compound (C\textsubscript{4}H\textsubscript{12}N)[La(C\textsubscript{4}H\textsubscript{6}Cl\textsubscript{3}NO\textsubscript{4}P)\textsubscript{4}] crystallizes in the monoclinic crystal system with two molecules in the unit cell. Both the cation and the anion have crystallographically-imposed C\textsubscript{2} symmetry with atoms La1 and N3 located on the twofold axis. The molecular structure of the complex is shown in Fig. 1. In the complex, the La\textsuperscript{3+} ion has a triangular dodecahedral coordination environment formed by the eight O atoms of the bidentate CAPh ligands and the N(CH\textsubscript{3})\textsubscript{4}\textsuperscript{+} unit acts as the counter-ion (Fig. 1). The average La—O bond length is 2.494 Å while the La—O(C) bond lengths [2.534 (3)–2.566 (3) Å] are all longer than the La—O(P) bonds [2.432 (3)–2.445 (3) Å]. Deprotonation of the ligands leads to increasing /C\textsubscript{2}5/-conjugation in the chelating fragment and results in the bond-length changes. The C—O and P—O bond lengths are in the ranges 1.225 (5)–1.240 (6) Å and 1.475 (3)–1.476 (4) Å, respectively, with corresponding average values of 1.233 and 1.476 Å. The corresponding bond lengths in the neutral ligand H\textsubscript{L} are 1.202 (2) and 1.459 (2) Å (Amirkhanov et al., 2014). The C—O and P—O bonds of the ligand in the complex are longer than those in the neutral ligand (H\textsubscript{L}), indicating greater C—O and P—O double-bond character in H\textsubscript{L} than in NMe\textsubscript{4}La\textsubscript{L}\textsubscript{4}. The C—N and P—N bonds, with lengths in the ranges 1.291 (6)–1.292 (6) and 1.598 (4)–1.602 (5) Å, respectively, in NMe\textsubscript{4}La\textsubscript{L}\textsubscript{4} are shorter compared to those in the free ligand, in which the reported C—N bond length is 1.347 (2) Å and P—N is 1.676 (1) Å (Amirkhanov et al., 1995).

3. Supramolecular features

There are no classical hydrogen bonds in the crystal structure of the title compound, although the complexes are linked via numerous weak C—H···O and Cl···Cl intermolecular interactions (Table 1). In particular, the PO and OCH\textsubscript{3} groups of the ligands are involved in the formation of interactions with the hydrogen atoms of the tetramethylammonium cation, linking the complex anion and the counter-ion in a chain along the b-axis direction. The Cl12A···Cl12A\textsuperscript{g} [symmetry code (ii): −x, −y + 1, −z + 1] interactions, at 3.475 (12) Å, are only 0.03 Å less than the sum of the van der Waals radii but definitely below the maximum separation (4.0 Å) considered to represent at least weak, attractive Cl···Cl interactions (Capdevila-Cortada et al., 2016). These serve to connect neighbouring chains. The crystal packing of the title compound is shown in Fig. 2.

4. Hirshfeld surface analysis and fingerprint plots

To visualize the intermolecular interactions in the title compound, the Hirshfeld surface and its corresponding two-dimensional fingerprint plots (Spackman et al., 2009) were calculated using CrystalExplorer17 (Turner et al., 2017). There are several light-red spots on the d_{norm} surface (Fig. 3), which correspond to O···H/H···O contacts. They are located near the oxygen atoms of the ligand PO groups and the hydrogen atoms of the tetramethylammonium cation. Thus, the strongest contacts in the crystal of the title compound exist between the NMe\textsubscript{4}\textsuperscript{+} cation and the complex anion.

The two-dimensional fingerprint plots show distances from the Hirshfeld surface to the nearest exterior atom (d\textsubscript{e} plots) and from an interior atom to the surface (d\textsubscript{i} plots), specify atom···atom contacts in a crystal and provide a quantitative idea of the types of intermolecular contacts experienced by molecules. An analysis of the fingerprint plots (Fig. 3) shows

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|-----|------|------|---------|
| C9—H9A···O6 | 0.96 | 2.35 | 3.184 (7) | 145 |
| C10—H10C···O2\textsuperscript{ii} | 0.96 | 2.33 | 3.218 (8) | 154 |

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

Figure 1
The molecular structure of the title compound with displacement ellipsoids drawn at the 25% probability level. Hydrogen atoms are omitted for clarity [Symmetry code: (i) −x + 1/2, y, −z + 1/2].

Figure 2
The crystal packing of the title compound viewed along the b-axis direction.
that the Cl···H/H···Cl contacts make the major contribution to the Hirshfeld surface at 50.7%. The closest Cl···H/H···Cl contact occurs at $d_i = d_c = 2.9$ Å. The next largest contributions come from H···H contacts (20.8%), O···H/H···O (13.6%) and Cl···Cl contacts (11.6%). The closest O···H/H···O contact occurs at $d_i = d_c = 1.35$ Å. The smallest percentage contributions to the Hirshfeld surface come from the N···H/H···N (3.1%), Cl···O/O···Cl (0.1%) and O···O (0.1%) interatomic contacts.

5. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.41, update of March 2020; Groom et al., 2016) for lanthanide complexes containing bidentate-coordinated CAPH ligands yielded 48 hits. Eight of them are tetrakis complexes Ca[Ln(CAPH)$_4$] of which five crystallize with two tetrakis complexes in the asymmetric unit. Using SHAPE analysis (SHAPE2.1; Llunell et al., 2013), the nine coordination polyhedra have been interpreted as square antiprismatic ($D4d$) and, for the other polyhedra, as trigonal dodecahedral ($D2d$).

No CAPH-based lanthanum tetrakis complexes have been reported to date. However, seven lanthanum complexes containing CAPHs coordinated in a bidentate manner are known. The average La—O(C) bond length is 2.411 Å while the average La—O(P) bond length is 2.351 Å. Only one tetrakis complex based on dimethyl(2,2,2-trichloroacetyl)phosphoramidate (NaErL$_4$) has been reported to date. The lengths of the CO, PO, PN and CN bonds in this complex are in the ranges 1.206–1.335, 1.422–1.489, 1.565–1.608 and 1.250–1.334 Å, respectively.

6. Synthesis and crystallization

The $^1$H NMR spectrum of a solution of the title compound in DMSO-$d_6$ was recorded on a Varian 400 NMR spectrometer at room temperature. The infrared (IR) spectrum was recorded on a Perkin–Elmer BX-II Bruker spectrometer using a KBr pellet.

Preparation of NMe$_4$La$_4$. LaCl$_3$·7H$_2$O (0.0371 g, 0.1 mmol) in the presence of HOC(O)C$_2$H$_5$_3 (0.14 ml, 0.7 mmol) as dehydrating agent was dissolved in 2-propanol under heating. In a separate flask, NaL (0.1122 g, 0.4 mmol) was dissolved in acetone and NMe$_4$Cl (0.0121 g, 0.11 mmol) was added under stirring and heating. The two mixtures were combined and boiled for a minute, then cooled to room temperature. A white precipitate of NaCl was formed and was filtered off, washed with 2-propanol and dried in air.

Figure 3

The Hirshfeld surface mapped over $d_{norm}$ and two-dimensional fingerprint plots for the Cl···H/H···Cl (50.7%), H···H (20.8%), O···H/H···O (13.6%), Cl···Cl (11.6%) and N···H/H···N (3.1%) interactions in NMe$_4$[La$_4$].

Table 2

| Crystal data                                      |
|--------------------------------------------------|
| Chemical formula                                 |
| $\text{(C}_4\text{H}_{12}\text{N})[\text{La(C}_4\text{H}_6\text{Cl}_3\text{NO}_4\text{P}_4]\text{]}$ |
| $M_r$                                             |
| 1290.73                                          |
| Crystal system, space group                      |
| Monoclinic, $P2/n$                               |
| Temperature (K)                                  |
| 294                                             |
| $a$, $b$, $c$ (Å)                                |
| 12.1452 (4), 10.2003 (4), 21.2846 (7)             |
| $\beta$ (°)                                      |
| 94.521 (3)                                      |
| $V$ (Å$^3$)                                      |
| 2628.64 (15)                                    |
| $Z$                                              |
| 2                                               |
| Radiation type                                   |
| Mo $\Kappa$                                      |
| $\mu$ ($\text{mm}^{-1}$)                        |
| 1.60                                            |
| Crystal size (mm)                                |
| $0.6 \times 0.4 \times 0.2$                     |

Data collection

Diffractometer: Agilent Technologies Xcalibur, Saphire3
Absorption correction: Multi-scan (CrysAlis PRO; Agilent, 2014)
$T_{min}$, $T_{max}$: 0.694, 1.000
No. of measured, independent and observed $|F > 2\sigma(F)|$ reflections: 22447, 6050, 4597
$R_{int}$, $wR_{int}$: 0.058, 0.134, 1.01
No. of reflections: 6050
No. of parameters: 296
No. of restraints: 73
H-atom treatment: H-atom parameters constrained
$\Delta$,$\rho_{max}$, $\Delta$,$\rho_{min}$ (e Å$^{-3}$): 0.92, −0.91

Computer programs: CrysAlis PRO (Agilent, 2014), SHELXT (Sheldrick, 2015a), SHELXL2018/5 (Sheldrick, 2015b) and OLEX2 (Dolomanov et al., 2009).
IR (KBr pellet, cm\(^{-1}\)): 2954 [w, \(\nu(C-H)\)], 1614 [s, \(\nu(C=O)\)], 1487 (w), 1367 [s, \(\nu(C-N)\)], 1187 [m, \(\rho(CH_3)\)], 1158 [s, \(\nu(P=O)\)], 1042 [s, \(\delta(POC)\)], 1011 (m), 880 (s), 846 (m), 822 (m), 781 (w), 722 (m), 677 [m, \(\nu(CCl)\)], 548 [m, \(\nu(PNC)\)], 502 (m).

\(^1\)H NMR (400 MHz, DMSO-\(d_6\), 293 K): 3.61, 3.59 (d, 24H, \(\text{CH}_3\)), 3.18 (s, 12H, \(\text{CH}_3\)).

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The C-bound H atoms were placed in calculated positions and refined with a riding model: C—H = 0.96 Å with \(U_{iso}(H) = 1.5U_{eq}(C)\).

The structure exhibits disorder of the Cl atoms of one CCl\(_3\) substituent. All Cl—C bond distances were restrained to be similar to each other (within a standard deviation of 0.005 Å) with a target value of 1.745 Å. \(U^\theta\) values of the disordered chlorine atoms were restrained to be similar to each other (within a standard deviation of 0.02 Å\(^2\)). The disorder ratio is 50 to 50.

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Computing details

Data collection: CrysAlis PRO (Agilent, 2014); cell refinement: CrysAlis PRO (Agilent, 2014); data reduction: CrysAlis PRO (Agilent, 2014); program(s) used to solve structure: ShelXT (Sheldrick, 2015a); program(s) used to refine structure: SHELXL2018/3 (Sheldrick, 2015b); molecular graphics: OLEX2 (Dolomanov et al., 2009); software used to prepare material for publication: OLEX2 (Dolomanov et al., 2009).

Tetramethylammonium tetrakis[2,2,2-trichloro-1-[(dimethoxyphosphoryl)imino]ethanolato]lanthanum(III)

Crystal data

\[(\text{C}_4\text{H}_{12}\text{N}|\text{La(C}_4\text{H}_6\text{Cl}_3\text{NO}_4\text{P})_4]\]  
\[M_r = 1290.73\]

Monoclinic, \(P2_1/n\)  
\(a = 12.1452 (4)\) Å  
\(b = 10.2003 (4)\) Å  
\(c = 21.2846 (7)\) Å  
\(\beta = 94.521 (3)\)°  
\(V = 2628.64 (15)\) Å³  
\(Z = 2\)

Data collection

Agilent Technologies Xcalibur, Sapphire3 diffractometer  
Radiation source: Enhance (Mo) X-ray Source  
Graphite monochromator  
Detector resolution: 16.1827 pixels mm⁻¹  
\(\omega\) scans  
Absorption correction: multi-scan  
(CrysAlisPro; Agilent, 2014)

\(T_{	ext{min}} = 0.694, T_{	ext{max}} = 1.000\)

Refinement

Refinement on \(F^2\)  
Least-squares matrix: full  
\[R(F^2 > 2\sigma(F^2)) = 0.058\]  
\(wR(F^2) = 0.134\)  
\(S = 1.01\)  
6050 reflections  
296 parameters  
73 restraints  
Primary atom site location: structure-invariant direct methods

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Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.057P)^2 + 0.0726P]$$
$$P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\text{max}} < 0.001$$
$$\Delta \rho_{\text{max}} = 0.92 \text{ e Å}^{-3}$$
$$\Delta \rho_{\text{min}} = -0.91 \text{ e Å}^{-3}$$

**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 (Å²) |
|------------------|------------------|------------------|------------------|------------------|
| x                | y                | z                | $U_{iso}$/$U_{eq}$ | Occ. (<1) |
| La1             | 0.250000         | 0.21428 (4)      | 0.750000         | 0.03981 (13)     | 0.5             |
| Cl1A            | 0.3621 (6)       | 0.4311 (8)       | 0.5516 (5)       | 0.161 (4)        | 0.5             |
| Cl1B            | 0.3145 (7)       | 0.4844 (6)       | 0.5495 (4)       | 0.144 (3)        | 0.5             |
| Cl2A            | 0.1378 (7)       | 0.4598 (8)       | 0.5184 (4)       | 0.192 (4)        | 0.5             |
| Cl2B            | 0.1311 (6)       | 0.3878 (10)      | 0.4787 (4)       | 0.198 (4)        | 0.5             |
| Cl3A            | 0.2545 (8)       | 0.2694 (7)       | 0.4592 (2)       | 0.173 (4)        | 0.5             |
| Cl3B            | 0.3288 (8)       | 0.2511 (8)       | 0.4835 (4)       | 0.189 (4)        | 0.5             |
| Cl4             | 0.45286 (16)     | -0.0370 (2)      | 0.58761 (10)     | 0.1269 (9)       |                 |
| Cl5             | 0.63096 (17)     | 0.0478 (2)       | 0.68243 (11)     | 0.1275 (8)       |                 |
| Cl6             | 0.63761 (15)     | 0.1310 (2)       | 0.57995 (9)      | 0.1166 (7)       |                 |
| P1              | 0.12224 (10)     | 0.04178 (13)     | 0.61305 (6)      | 0.0523 (3)       |                 |
| P2              | 0.51080 (11)     | 0.38211 (15)     | 0.72817 (7)      | 0.0647 (4)       |                 |
| O1              | 0.2329 (3)       | 0.3040 (3)       | 0.63703 (15)     | 0.0652 (10)      |                 |
| O2              | 0.1564 (3)       | 0.0524 (3)       | 0.68093 (14)     | 0.0552 (8)       |                 |
| O3              | -0.0061 (3)      | 0.0420 (4)       | 0.60037 (19)     | 0.0790 (11)      |                 |
| O4              | 0.1617 (3)       | -0.0966 (3)      | 0.59196 (15)     | 0.0657 (9)       |                 |
| O5              | 0.4069 (3)       | 0.1198 (3)       | 0.69257 (18)     | 0.0656 (10)      |                 |
| O6              | 0.4008 (3)       | 0.3734 (3)       | 0.75292 (16)     | 0.0596 (9)       |                 |
| O7              | 0.5136 (4)       | 0.5137 (4)       | 0.6907 (2)       | 0.0980 (14)      |                 |
| O8              | 0.6052 (4)       | 0.4070 (6)       | 0.7800 (2)       | 0.1051 (15)      |                 |
| N1              | 0.1613 (4)       | 0.1495 (4)       | 0.56501 (18)     | 0.0629 (11)      |                 |
| N2              | 0.5497 (3)       | 0.2658 (5)       | 0.6845 (2)       | 0.0689 (13)      |                 |
| C1              | 0.2094 (4)       | 0.2568 (5)       | 0.5840 (2)       | 0.0564 (13)      |                 |
| C2              | 0.2429 (3)       | 0.3432 (4)       | 0.52989 (18)     | 0.0770 (17)      |                 |
| C3              | -0.0712 (5)      | -0.0440 (9)      | 0.6346 (4)       | 0.134 (3)        |                 |
| H3A             | -0.056390        | -0.133010        | 0.623339         | 0.201*           |                 |
| H3B             | -0.148061        | -0.025051        | 0.624583         | 0.201*           |                 |
| H3C             | -0.053309        | -0.031932        | 0.678933         | 0.201*           |                 |
| C4              | 0.1430 (7)       | -0.1401 (7)      | 0.5277 (3)       | 0.106 (2)        |                 |
| H4A             | 0.176063         | -0.079196        | 0.500412         | 0.159*           |                 |
| H4B             | 0.064984         | -0.144940        | 0.516385         | 0.159*           |                 |
| H4C             | 0.175366         | -0.225158        | 0.523438         | 0.159*           |                 |
| C5              | 0.4942 (4)       | 0.1588 (5)       | 0.6742 (2)       | 0.0566 (12)      |                 |
| C6              | 0.5510 (4)       | 0.0575 (6)       | 0.6321 (3)       | 0.0686 (15)      |                 |
|   | $U_{11}$  | $U_{22}$  | $U_{33}$  | $U_{12}$  | $U_{13}$  | $U_{23}$  |
|---|-----------|-----------|-----------|-----------|-----------|-----------|
| La1 | 0.0393 (2) | 0.0445 (2) | 0.0364 (2) | 0.000 | 0.00772 (15) | 0.000 |
| Cl1A | 0.155 (5) | 0.215 (8) | 0.110 (4) | −0.118 (6) | −0.006 (4) | 0.053 (6) |
| Cl1B | 0.275 (9) | 0.089 (3) | 0.070 (3) | −0.080 (5) | 0.027 (5) | 0.002 (3) |
| Cl1C | 0.251 (8) | 0.159 (6) | 0.163 (6) | 0.071 (6) | 0.005 (5) | 0.103 (5) |
| Cl2A | 0.185 (6) | 0.237 (9) | 0.158 (6) | −0.055 (6) | −0.075 (5) | 0.138 (6) |
| Cl2B | 0.343 (11) | 0.137 (5) | 0.049 (2) | −0.122 (6) | 0.069 (4) | −0.026 (3) |
| Cl3A | 0.271 (9) | 0.138 (5) | 0.183 (7) | 0.040 (6) | 0.173 (7) | 0.041 (5) |
| Cl3B | 0.0931 (12) | 0.178 (2) | 0.1139 (15) | −0.0351 (13) | 0.0339 (12) | −0.0808 (15) |
| Cl5 | 0.1168 (15) | 0.1399 (18) | 0.1283 (17) | 0.0669 (14) | 0.0249 (13) | 0.0000 (14) |
| Cl6 | 0.1028 (13) | 0.1584 (19) | 0.0973 (13) | −0.0220 (12) | 0.0623 (11) | −0.0242 (13) |
| P1 | 0.0515 (7) | 0.0621 (8) | 0.0423 (7) | −0.0098 (6) | −0.0031 (6) | 0.0026 (6) |
| P2 | 0.0508 (7) | 0.0657 (9) | 0.0790 (10) | −0.0134 (6) | 0.0141 (7) | −0.0072 (8) |
| O1 | 0.099 (3) | 0.061 (2) | 0.0360 (18) | −0.0053 (19) | 0.0088 (19) | −0.0010 (16) |
| O2 | 0.067 (2) | 0.058 (2) | 0.0399 (17) | −0.0198 (16) | −0.0003 (16) | 0.0034 (15) |
| O3 | 0.052 (2) | 0.099 (3) | 0.084 (3) | −0.005 (2) | −0.007 (2) | 0.010 (2) |
| O4 | 0.081 (2) | 0.067 (2) | 0.0484 (19) | 0.0014 (19) | 0.0001 (18) | −0.0004 (17) |
| O5 | 0.059 (2) | 0.062 (2) | 0.082 (3) | −0.0047 (17) | 0.0393 (19) | −0.0126 (19) |
| O6 | 0.0552 (19) | 0.056 (2) | 0.069 (2) | −0.0110 (16) | 0.0149 (17) | −0.0134 (17) |
| O7 | 0.105 (3) | 0.070 (3) | 0.126 (4) | −0.009 (2) | 0.050 (3) | 0.010 (3) |
| O8 | 0.072 (3) | 0.131 (4) | 0.111 (4) | −0.033 (3) | −0.003 (3) | −0.023 (3) |
| N1 | 0.077 (3) | 0.069 (3) | 0.042 (2) | −0.019 (2) | −0.005 (2) | 0.007 (2) |
| N2 | 0.049 (2) | 0.078 (3) | 0.082 (3) | −0.010 (2) | 0.022 (2) | −0.014 (3) |
| C1 | 0.064 (3) | 0.062 (3) | 0.043 (3) | 0.007 (3) | 0.010 (2) | 0.013 (2) |
| C2 | 0.109 (5) | 0.073 (4) | 0.048 (3) | −0.009 (4) | 0.004 (3) | 0.012 (3) |
| C3 | 0.063 (4) | 0.194 (9) | 0.143 (7) | −0.033 (5) | 0.006 (5) | 0.043 (7) |
| C4 | 0.154 (7) | 0.105 (6) | 0.057 (4) | 0.012 (5) | 0.005 (4) | −0.018 (4) |
| C5 | 0.049 (3) | 0.076 (4) | 0.047 (3) | 0.003 (3) | 0.016 (2) | −0.004 (3) |
|       | x (Å)            | y (Å)            | z (Å)            | x (°) | y (°) | z (°) |
|-------|-----------------|-----------------|-----------------|-------|-------|-------|
| C6    | 0.053 (3)       | 0.094 (4)       | 0.062 (3)       | 0.000 (3) | 0.019 (3) | −0.012 (3) |
| C7    | 0.148 (8)       | 0.114 (7)       | 0.212 (11)      | −0.012 (6) | 0.101 (8) | 0.048 (7)   |
| C8    | 0.168 (9)       | 0.215 (11)      | 0.183 (10)      | −0.071 (8) | −0.057 (8) | 0.081 (9)   |
| N3    | 0.095 (5)       | 0.044 (3)       | 0.078 (4)       | 0.000  | 0.004 (4) | 0.000   |
| C9    | 0.162 (7)       | 0.071 (4)       | 0.071 (4)       | 0.034 (5) | −0.016 (4) | −0.008 (3) |
| C10   | 0.100 (5)       | 0.073 (4)       | 0.127 (6)       | −0.009 (4) | 0.035 (5) | −0.027 (3) |

**Geometric parameters (Å, °)**

| Bond          | Length (Å) | Angle (°) |
|---------------|------------|-----------|
| La1—O1        | 2.566 (3)  |           |
| La1—O1i       | 2.566 (3)  |           |
| La1—O2        | 2.432 (3)  |           |
| La1—O2i       | 2.432 (3)  |           |
| La1—O2i       | 2.432 (3)  |           |
| La1—O5        | 2.534 (3)  |           |
| La1—O5i       | 2.534 (3)  |           |
| La1—O5i       | 2.534 (3)  |           |
| Cl1A—C2       | 1.735 (5)  |           |
| Cl1B—C2       | 1.716 (5)  |           |
| Cl2A—C2       | 1.747 (4)  |           |
| Cl2B—C2       | 1.733 (4)  |           |
| Cl3A—C2       | 1.698 (4)  |           |
| Cl3B—C2       | 1.764 (4)  |           |
| Cl4—C6        | 1.751 (6)  |           |
| Cl5—C6        | 1.756 (6)  |           |
| Cl6—C6        | 1.756 (5)  |           |
| P1—O2         | 1.475 (3)  |           |
| P1—O3         | 1.561 (4)  |           |
| P1—O4         | 1.568 (4)  |           |
| P1—N1         | 1.598 (4)  |           |
| P2—O6         | 1.476 (3)  |           |
| P2—O7         | 1.563 (4)  |           |
| P2—O8         | 1.548 (5)  |           |
| P2—N2         | 1.602 (5)  |           |
| O1—C1         | 1.240 (6)  |           |
| O3—C3         | 1.419 (7)  |           |
| O4—C4         | 1.439 (6)  |           |
| O5—C5         | 1.225 (5)  |           |
| O1—La1—O1     | 138.20 (15)|           |
| O2—La1—O1     | 71.11 (10) |           |
| O2—La1—O1i    | 143.90 (11)|           |
| O2—La1—O1i    | 143.90 (11)|           |
| O2—La1—O1     | 71.11 (10) |           |
| O2—La1—O2     | 94.48 (15) |           |
| O2—La1—O5     | 72.55 (11) |           |
| O2—La1—O5i    | 77.50 (11) |           |
| O2—La1—O5i    | 72.55 (11) |           |

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O2—La1—O5  77.50 (11)  O3—C3—H3C  109.5
O2—La1—O6  141.22 (11)  H3A—C3—H3B  109.5
O2—La1—O6i  97.00 (12)  H3A—C3—H3C  109.5
O2i—La1—O6  97.00 (12)  H3B—C3—H3C  109.5
O2i—La1—O6i  141.22 (11)  O4—C4—H4A  109.5
O5—La1—O1i  125.40 (12)  O4—C4—H4B  109.5
O5—La1—O1  72.06 (12)  O4—C4—H4C  109.5
O5i—La1—O1i  125.40 (12)  H4A—C4—H4B  109.5
O5i—La1—O1  135.31 (15)  H4A—C4—H4C  109.5
O5i—La1—O5  70.98 (11)  O5—C5—N2  132.3 (5)
O6i—La1—O1i  135.31 (15)  O5—C5—C6  113.6 (5)
O6i—La1—O1  70.98 (11)  N2—C5—C6  114.0 (4)
O6—La1—O1  78.01 (12)  O5—C5—C6  113.6 (5)
O6—La1—O5  96.81 (16)  O5—C5—C6  113.2 (4)
O6—La1—O6i  96.81 (16)  O5—C5—C6  113.2 (4)
O2—P1—O3  111.7 (2)  O7—C7—H7A  109.5
O2—P1—O4  106.12 (19)  O7—C7—H7B  109.5
O2—P1—N1  120.1 (2)  O7—C7—H7C  109.5
O3—P1—O4  106.0 (2)  H7A—C7—H7B  109.5
O3—P1—N1  103.4 (2)  H7A—C7—H7C  109.5
O4—P1—N1  108.8 (2)  H7B—C7—H7C  109.5
O6—P2—O7  106.9 (2)  O8—C8—H8A  109.5
O6—P2—O8  113.3 (2)  O8—C8—H8B  109.5
O6—P2—N2  118.6 (2)  O8—C8—H8C  109.5
O7—P2—N2  108.7 (3)  H8A—C8—H8B  109.5
O8—P2—O7  100.2 (3)  H8A—C8—H8C  109.5
O8—P2—N2  107.4 (3)  H8B—C8—H8C  109.5
C1—O1—La1  135.3 (3)  C9—N3—C9i  110.8 (6)
P1—O2—La1  136.36 (18)  C10—N3—C9i  108.2 (4)
C3—O3—P1  120.0 (4)  C10—N3—C9i  109.9 (4)
C4—O4—P1  121.4 (4)  C10—N3—C9i  109.9 (4)
C5—O5—La1  137.2 (3)  C10—N3—C9i  108.2 (4)
P2—O6—La1  136.72 (19)  C10—N3—C9i  110.0 (6)
C7—O7—P2  122.8 (4)  N3—C9—H9A  109.5
C8—O8—P2  120.3 (6)  N3—C9—H9B  109.5
C1—N1—P1  122.2 (3)  N3—C9—H9C  109.5
C5—N2—P2  123.4 (4)  H9A—C9—H9B  109.5
O1—C1—N1  132.9 (5)  H9A—C9—H9C  109.5
O1—C1—C2  113.9 (4)  H9B—C9—H9C  109.5
N1—C1—C2  113.2 (4)  N3—C10—H10A  109.5
Cl1A—C2—Cl2A  105.7 (5)  N3—C10—H10B  109.5
Cl1B—C2—Cl2B  106.9 (5)  N3—C10—H10C  109.5
Cl1B—C2—Cl3B  105.8 (5)  H10A—C10—H10B  109.5
Cl2B—C2—Cl3B  104.9 (5)  H10A—C10—H10C  109.5
### Supporting Information

| Cl3A—C2—Cl1A | 109.8 (5) | H10B—C10—H10C | 109.5 |
|---------------|-----------|-----------------|-------|
| La1—O1—C1—N1 | 17.5 (10)  | O5—C5—C6—Cl6   | 154.3 (4) |
| La1—O1—C1—C2 | −163.2 (3) | O6—P2—O7—C7    | −171.5 (6) |
| La1—O5—C5—N2 | 10.5 (10)  | O6—P2—O8—C8    | 63.4 (8)  |
| La1—O5—C5—C6 | −171.8 (3) | O6—P2—N2—C5    | −6.4 (6)  |
| P1—N1—C1—O1  | −2.6 (9)   | O7—P2—O6—La1   | 126.7 (3) |
| P1—N1—C1—C2  | 178.1 (3)  | O7—P2—O8—C8    | 176.9 (8) |
| P2—N2—C5—O5  | −0.1 (9)   | O7—P2—N2—C5    | −128.7 (5) |
| P2—N2—C5—C6  | −177.8 (4) | O8—P2—O6—La1   | −123.8 (3) |
| O1—C1—C2—Cl1A | 32.5 (6)  | O8—P2—O7—C7    | 70.2 (7)  |
| O1—C1—C2—Cl1B | 4.1 (7)   | O8—P2—N2—C5    | 123.6 (5) |
| O1—C1—C2—Cl2A | −81.5 (6) | N1—P1—O2—La1   | 8.3 (4)   |
| O1—C1—C2—Cl2B | −120.5 (6) | N1—P1—O3—Cl3   | 179.4 (5) |
| O1—C1—C2—Cl3A | 160.0 (5) | N1—P1—O4—C4    | −48.8 (5) |
| O1—C1—C2—Cl3B | 123.9 (6) | N1—P1—O4—C4    | −148.0 (5) |
| O2—P1—O3—C3  | −50.1 (6)  | N1—P1—O4—C4    | −176.4 (5) |
| O2—P1—O4—C4  | −179.4 (5) | N1—P1—O4—C4    | 98.0 (6)  |
| O2—P1—N1—C1  | −10.0 (6)  | N1—P1—Cl2—Cl3A | 59.0 (7)  |
| O3—P1—O2—La1 | −112.9 (3) | N1—C1—C2—Cl3B  | −20.5 (7) |
| O3—P1—O4—C4  | 61.8 (5)   | N1—C1—C2—Cl3B  | −56.6 (6) |
| O3—P1—N1—C1  | 115.2 (5)  | N2—P2—O6—La1   | 3.5 (4)   |
| O4—P1—O2—La1 | 132.1 (3)  | N2—P2—O7—C7    | −42.3 (7) |
| O4—P1—O3—C3  | 65.0 (6)   | N2—P2—O8—C8    | −69.6 (8) |
| O4—P1—N1—C1  | −132.4 (4) | N2—C5—C6—Cl4   | −149.4 (4) |
| O5—C5—C6—Cl4 | 32.5 (6)   | N2—C5—C6—Cl4   | 92.3 (5)  |
| O5—C5—C6—Cl5 | −85.9 (5)  | N2—C5—C6—Cl6   | −27.5 (6) |

Symmetry code: (i) −x+1/2, y, −z+3/2.

**Hydrogen-bond geometry (Å, °)**

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|-----|------|-------|---------|
| C9—H9.4···O6 | 0.96 | 2.35 | 3.184 (7) | 145 |
| C10—H10C···O28* | 0.96 | 2.33 | 3.218 (8) | 154 |

Symmetry code: (ii) −x+1/2, y+1, −z+3/2.