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Crystal structure and Hirshfeld surface analysis of the anionic tetrakis-complex of lanthanum(III) NMe_4LaL_4 with the CAPH-ligand dimethyl (2,2,2-trichloroacetyl)phosphoramidate

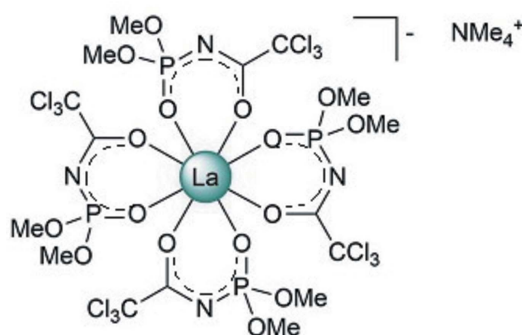
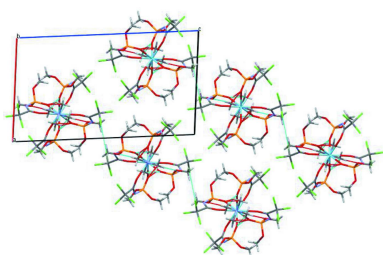
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The anionic tetrakis-complex of lanthanum(III) NMe_4LaL_4 with the CAPH-ligand dimethyl (2,2,2-trichloroacetyl)phosphoramidate (HL), namely, tetramethylammonium tetrakis{2,2,2-trichloro-1-[(dimethoxyphosphoryl)imino]ethanolato}lanthanum(III), $(\text{C}_4\text{H}_{12}\text{N})[\text{La}(\text{C}_4\text{H}_6\text{Cl}_3\text{NO}_4\text{P})_4]$, 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 La^{3+} and NMe_4^+ as the counter-ion. The coordination polyhedron of the La^{3+} 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 NMe_4LaL_4) is reported.



2. Structural commentary

The title compound $(C_4H_{12}N)[La(C_4H_6Cl_3NO_4P)_4]$ crystallizes in the monoclinic crystal system with two molecules in the unit cell. Both the cation and the anion have crystallographically-imposed C_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^{3+} ion has a triangular dodecahedral coordination environment formed by the eight O atoms of the bidentate CAPh ligands and the $N(CH_3)_4^+$ 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 π -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 HL 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 (HL), indicating greater C=O and P=O double-bond character in HL than in NMe_4LaL_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_4LaL_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 inter-

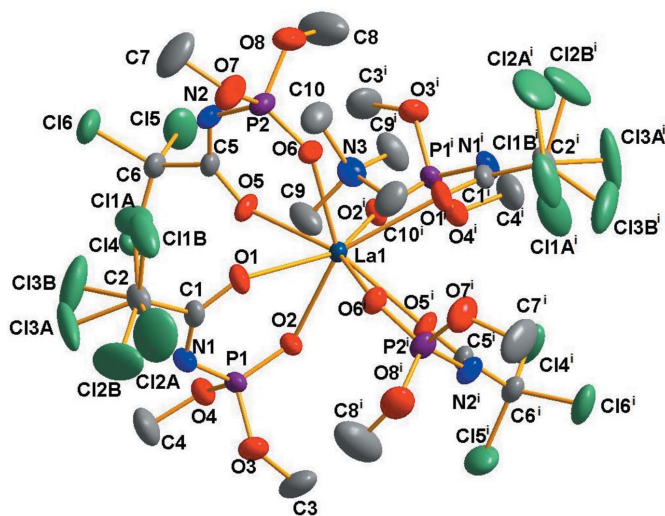


Figure 1
The molecular structure of the title compound with displacement ellipsoids drawn at the 25% probability level. Hydrogen atoms are omitted for clarity [Symmetry code: (i) $-x + \frac{1}{2}, y, -z + \frac{1}{2}$].

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C9–H9A...O6	0.96	2.35	3.184 (7)	145
C10–H10C...O2 ⁱ	0.96	2.33	3.218 (8)	154

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

actions (Table 1). In particular, the PO and OCH₃ 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...Cl12Aⁱⁱ [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_4^+ cation and the complex anion.

The two-dimensional fingerprint plots show distances from the Hirshfeld surface to the nearest exterior atom (d_e plots) and from an interior atom to the surface (d_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

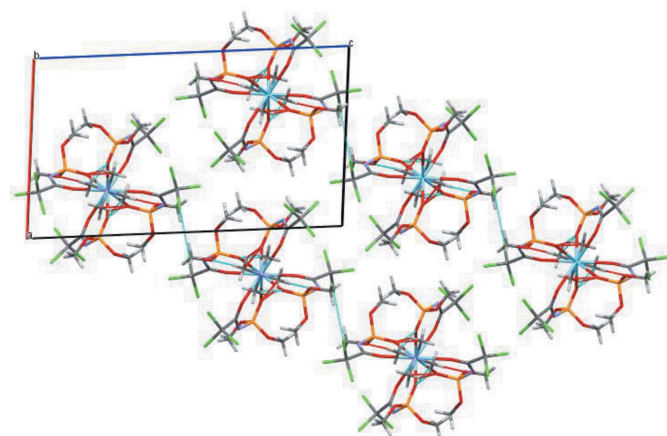
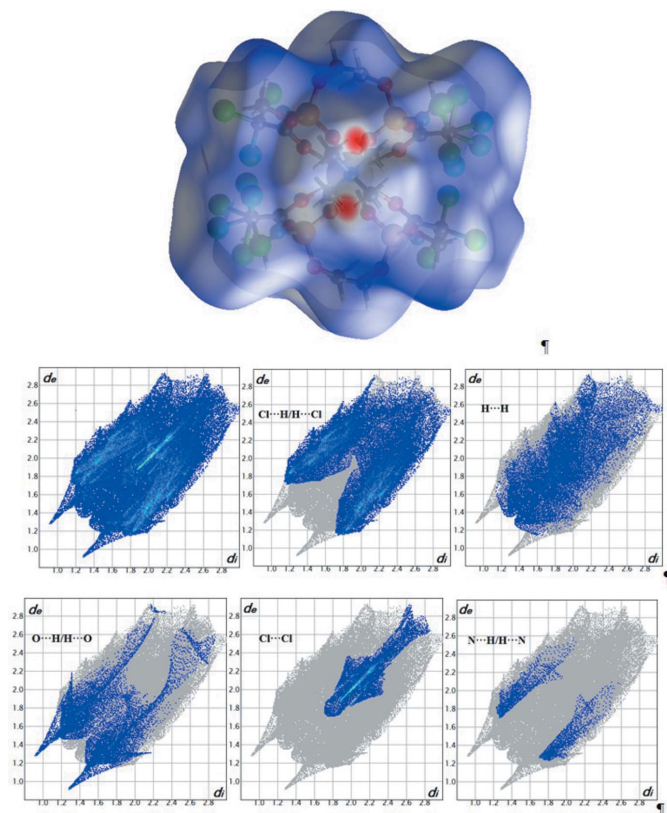


Figure 2
The crystal packing of the title compound viewed along the *b*-axis direction.


Figure 3

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

that the Cl \cdots H/H \cdots Cl contacts make the major contribution to the Hirshfeld surface at 50.7%. The closest Cl \cdots H/H \cdots Cl contact occurs at $d_i = d_e = 2.9$ Å. The next largest contributions come from H \cdots H contacts (20.8%), O \cdots H/H \cdots O contacts (13.6%) and Cl \cdots Cl contacts (11.6%). The closest O \cdots H/H \cdots O contact occurs at $d_i = d_e = 1.35$ Å. The smallest percentage contributions to the Hirshfeld surface come from the N \cdots H/H \cdots N (3.1%), Cl \cdots O/O \cdots Cl (0.1%) and O \cdots 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 Cat[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 triangular 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

Table 2

Experimental details.

Crystal data	
Chemical formula	(C $_4$ H $_{12}$ N)[La(C $_4$ H $_6$ Cl $_3$ NO $_4$ P) $_4$]
M_r	1290.73
Crystal system, space group	Monoclinic, <i>P2$_1$/n</i>
Temperature (K)	294
a , b , c (Å)	12.1452 (4), 10.2003 (4), 21.2846 (7)
β ($^\circ$)	94.521 (3)
V (Å 3)	2628.64 (15)
Z	2
Radiation type	Mo $K\alpha$
μ (mm $^{-1}$)	1.60
Crystal size (mm)	0.6 \times 0.4 \times 0.2
Data collection	
Diffractometer	Agilent Technologies Xcalibur, Sapphire3
Absorption correction	Multi-scan (<i>CrysAlis PRO</i> ; Agilent, 2014)
T_{min} , T_{max}	0.694, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	22447, 6050, 4597
R_{int}	0.070
$(\sin \theta/\lambda)_{\text{max}}$ (Å $^{-1}$)	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	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
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å $^{-3}$)	0.92, -0.91

Computer programs: *CrysAlis PRO* (Agilent, 2014), *SHELXT* (Sheldrick, 2015a), *SHELXL2018/3* (Sheldrick, 2015b) and *OLEX2* (Dolomanov *et al.*, 2009).

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 ^1H 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 $_4$ LaL $_4$. LaCl $_3$ ·7H $_2$ O (0.0371 g, 0.1 mmol) in the presence of HC(OC $_2$ 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 and the filtrate left in a flask in a desiccator over CaCl $_2$. After two days, colourless crystals suitable for X-ray diffraction studies were obtained. The crystals were filtered off, washed with 2-propanol and dried in air.

IR (KBr pellet, cm^{-1}): 2954 [*w*, $\nu(\text{C}-\text{H}_{\text{aliph}}$)], 1614 [*s*, $\nu(\text{C}=\text{O})$], 1487 (*w*), 1367 [*s*, $\nu(\text{C}-\text{N})$], 1187 [*m*, $\rho(\text{CH}_3)$], 1158 [*s*, $\nu(\text{P}=\text{O})$], 1042 [*s*, $\delta(\text{POC})$], 1011 (*m*), 880 (*s*), 846 (*m*), 822 (*m*), 781 (*w*), 722 (*m*), 677 [*m*, $\nu(\text{CCl})$], 548 [*m*, $\delta(\text{PNC})$], 502 (*m*).

^1H NMR (400 MHz, $\text{DMSO}-d_6$, 293 K): 3.61, 3.59 (*d*, 24H, CH_3 [*L*] $^-$), 3.18 (*s*, 12H, CH_3 [NMe_4] $^+$).

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 $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$.

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^{ij} 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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Crystal structure and Hirshfeld surface analysis of the anionic tetrakis-complex of lanthanum(III) NMe_4LaL_4 with the CPh-ligand dimethyl (2,2,2-trichloroacetyl)phosphoramidate

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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

$(\text{C}_4\text{H}_{12}\text{N})[\text{La}(\text{C}_4\text{H}_6\text{Cl}_3\text{NO}_4\text{P})_4]$
 $M_r = 1290.73$
 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
 $Z = 2$

$F(000) = 1280$
 $D_x = 1.631$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 3067 reflections
 $\theta = 3.2\text{--}23.6^\circ$
 $\mu = 1.60$ mm⁻¹
 $T = 294$ K
 Block, colourless
 $0.6 \times 0.4 \times 0.2$ mm

Data collection

Agilent Technologies Xcalibur, Sapphire3
 diffractometer
 Radiation source: Enhance (Mo) X-ray Source
 Graphite monochromator
 Detector resolution: 16.1827 pixels mm⁻¹
 ω scans
 Absorption correction: multi-scan
 (CrysAlisPro; Agilent, 2014)
 $T_{\min} = 0.694$, $T_{\max} = 1.000$

22447 measured reflections
 6050 independent reflections
 4597 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.070$
 $\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 3.2^\circ$
 $h = -15 \rightarrow 15$
 $k = -13 \rightarrow 12$
 $l = -25 \rightarrow 27$

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

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

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

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

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

$$\Delta\rho_{\max} = 0.92 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.91 \text{ e } \text{\AA}^{-3}$$

Special details

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

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
La1	0.250000	0.21428 (4)	0.750000	0.03981 (13)	
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)	

C7	0.6023 (7)	0.5480 (8)	0.6526 (5)	0.153 (4)
H7A	0.611203	0.480202	0.622176	0.230*
H7B	0.669571	0.557443	0.679135	0.230*
H7C	0.585323	0.629264	0.631261	0.230*
C8	0.6282 (9)	0.3183 (11)	0.8254 (6)	0.193 (5)
H8A	0.607447	0.232728	0.809925	0.289*
H8B	0.587835	0.338915	0.861107	0.289*
H8C	0.705986	0.319673	0.837739	0.289*
N3	0.250000	0.7094 (6)	0.750000	0.0726 (18)
C9	0.2854 (6)	0.6266 (6)	0.8055 (3)	0.103 (2)
H9A	0.346838	0.573073	0.795873	0.154*
H9B	0.225194	0.571408	0.815623	0.154*
H9C	0.306877	0.681805	0.840903	0.154*
C10	0.3433 (5)	0.7929 (6)	0.7331 (4)	0.098 (2)
H10A	0.322433	0.839259	0.694795	0.148*
H10B	0.406334	0.738757	0.727330	0.148*
H10C	0.361400	0.854619	0.766399	0.148*

Atomic displacement parameters (Å²)

	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)
Cl2A	0.251 (8)	0.159 (6)	0.163 (6)	0.071 (6)	0.005 (5)	0.103 (5)
Cl2B	0.185 (6)	0.237 (9)	0.158 (6)	-0.055 (6)	-0.075 (5)	0.138 (6)
Cl3A	0.343 (11)	0.137 (5)	0.049 (2)	-0.122 (6)	0.069 (4)	-0.026 (3)
Cl3B	0.271 (9)	0.138 (5)	0.183 (7)	0.040 (6)	0.173 (7)	0.041 (5)
Cl4	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)

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 (4)

Geometric parameters (Å, °)

La1—O1	2.566 (3)	O7—C7	1.442 (7)
La1—O1 ⁱ	2.566 (3)	O8—C8	1.337 (9)
La1—O2	2.432 (3)	N1—C1	1.291 (6)
La1—O2 ⁱ	2.432 (3)	N2—C5	1.292 (6)
La1—O5 ⁱ	2.534 (3)	C1—C2	1.531 (6)
La1—O5	2.534 (3)	C3—H3A	0.9600
La1—O6	2.445 (3)	C3—H3B	0.9600
La1—O6 ⁱ	2.445 (3)	C3—H3C	0.9600
Cl1A—C2	1.735 (5)	C4—H4A	0.9600
Cl1B—C2	1.716 (5)	C4—H4B	0.9600
Cl2A—C2	1.747 (4)	C4—H4C	0.9600
Cl2B—C2	1.733 (4)	C5—C6	1.564 (7)
Cl3A—C2	1.698 (4)	C7—H7A	0.9600
Cl3B—C2	1.764 (4)	C7—H7B	0.9600
Cl4—C6	1.751 (6)	C7—H7C	0.9600
Cl5—C6	1.756 (6)	C8—H8A	0.9600
Cl6—C6	1.756 (5)	C8—H8B	0.9600
P1—O2	1.475 (3)	C8—H8C	0.9600
P1—O3	1.561 (4)	N3—C9	1.488 (6)
P1—O4	1.568 (4)	N3—C9 ⁱ	1.488 (6)
P1—N1	1.598 (4)	N3—C10 ⁱ	1.484 (6)
P2—O6	1.476 (3)	N3—C10	1.484 (7)
P2—O7	1.563 (4)	C9—H9A	0.9600
P2—O8	1.548 (5)	C9—H9B	0.9600
P2—N2	1.602 (5)	C9—H9C	0.9600
O1—C1	1.240 (6)	C10—H10A	0.9600
O3—C3	1.419 (7)	C10—H10B	0.9600
O4—C4	1.439 (6)	C10—H10C	0.9600
O5—C5	1.225 (5)		
O1 ⁱ —La1—O1	138.20 (15)	Cl3A—C2—Cl2A	106.8 (5)
O2 ⁱ —La1—O1 ⁱ	71.11 (10)	C1—C2—Cl1A	111.3 (4)
O2 ⁱ —La1—O1	143.90 (11)	C1—C2—Cl1B	117.3 (4)
O2—La1—O1 ⁱ	143.90 (11)	C1—C2—Cl2A	105.2 (4)
O2—La1—O1	71.11 (10)	C1—C2—Cl2B	112.5 (4)
O2 ⁱ —La1—O2	94.48 (15)	C1—C2—Cl3A	117.2 (4)
O2 ⁱ —La1—O5	72.55 (11)	C1—C2—Cl3B	108.6 (4)
O2 ⁱ —La1—O5 ⁱ	77.50 (11)	O3—C3—H3A	109.5
O2—La1—O5 ⁱ	72.55 (11)	O3—C3—H3B	109.5

O2—La1—O5	77.50 (11)	O3—C3—H3C	109.5
O2—La1—O6	141.22 (11)	H3A—C3—H3B	109.5
O2—La1—O6 ⁱ	97.00 (12)	H3A—C3—H3C	109.5
O2 ⁱ —La1—O6	97.00 (12)	H3B—C3—H3C	109.5
O2 ⁱ —La1—O6 ⁱ	141.22 (11)	O4—C4—H4A	109.5
O5—La1—O1 ⁱ	125.40 (12)	O4—C4—H4B	109.5
O5—La1—O1	72.06 (12)	O4—C4—H4C	109.5
O5 ⁱ —La1—O1 ⁱ	72.06 (12)	H4A—C4—H4B	109.5
O5 ⁱ —La1—O1	125.40 (12)	H4A—C4—H4C	109.5
O5 ⁱ —La1—O5	135.31 (15)	H4B—C4—H4C	109.5
O6 ⁱ —La1—O1 ⁱ	78.01 (12)	O5—C5—N2	132.3 (5)
O6—La1—O1 ⁱ	74.58 (12)	O5—C5—C6	113.6 (5)
O6 ⁱ —La1—O1	74.58 (12)	N2—C5—C6	114.0 (4)
O6—La1—O1	78.01 (12)	Cl4—C6—Cl5	108.3 (3)
O6—La1—O5 ⁱ	146.17 (12)	Cl4—C6—Cl6	108.0 (3)
O6 ⁱ —La1—O5	146.17 (12)	Cl5—C6—Cl6	108.5 (3)
O6—La1—O5	70.98 (11)	C5—C6—Cl4	111.2 (3)
O6 ⁱ —La1—O5 ⁱ	70.98 (11)	C5—C6—Cl5	107.6 (4)
O6—La1—O6 ⁱ	96.81 (16)	C5—C6—Cl6	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 ⁱ —N3—C9	110.8 (6)
P1—O2—La1	136.36 (18)	C10—N3—C9 ⁱ	108.2 (4)
C3—O3—P1	120.0 (4)	C10—N3—C9	109.9 (4)
C4—O4—P1	121.4 (4)	C10 ⁱ —N3—C9 ⁱ	109.9 (4)
C5—O5—La1	137.2 (3)	C10 ⁱ —N3—C9	108.2 (4)
P2—O6—La1	136.72 (19)	C10 ⁱ —N3—C10	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

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—C3	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—C1—C2—Cl1A	-148.0 (5)
O2—P1—O3—C3	-50.1 (6)	N1—C1—C2—Cl1B	-176.4 (5)
O2—P1—O4—C4	-179.4 (5)	N1—C1—C2—Cl2A	98.0 (6)
O2—P1—N1—C1	-10.0 (6)	N1—C1—C2—Cl2B	59.0 (7)
O3—P1—O2—La1	-112.9 (3)	N1—C1—C2—Cl3A	-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—Cl5	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 (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C9—H9A \cdots O6	0.96	2.35	3.184 (7)	145
C10—H10C \cdots O2 ⁱⁱ	0.96	2.33	3.218 (8)	154

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