# A new lanthanum(III) complex containing acetyl-acetone and 1*H*-imidazole

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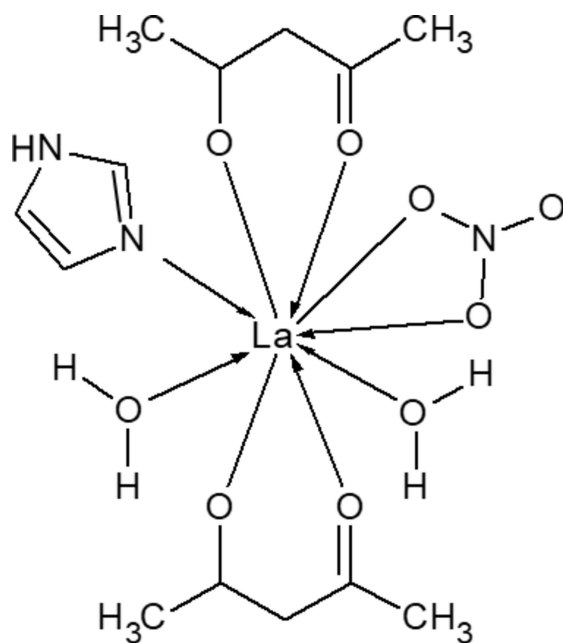
In the title complex, diaqua(1*H*-imidazole-κN^3)(nitrato-$\kappa^2 O,O'$)bis(4-oxopent-2-en-2-olato-$\kappa^2 O,O'$)lanthanum(III), [La(C$_5$H$_7$O$_2$)$_2$(NO$_3$)(C$_3$H$_4$N$_2$)(H$_2$O)$_2$], the La atom is coordinated by eight O atoms of two acetylacetonate (acac) anions acting as bidentate ligands, two water molecule as monodentate ligands, one nitrate anions as a bidentate ligand and one N atom of an imidazolate (ImH) molecule as a monodentate ligand. Thus, the coordination number of the La atom is nine in a monocapped square antiprismatic polyhedron. There are three types of intermolecular hydrogen bonds between ligands, the first involving nitrate–water O⋯H—O interactions running along the [001] direction, the second involving acac–water O⋯H—O interactions along the [010] direction and the third involving an Im–nitrate N—H⋯O interaction along the [100] direction (five interactions of this type). Thus, an overall one-dimensional network structure is generated. The molecular plane of an ImH molecule is almost parallel to that of a nitrate ligand, making an angle of only 6.04 (12)°. Interestingly, the ImH plane is nearly perpendicular to the planes of two neighbouring acac ligands.

1. Chemical context

Carboxylic acid-based linkers are often used in metal–organic complexes involving rare earth elements because they can easily build a framework structure due to the oxophilic nature of lanthanide ions. Recently, some imidazole-based metal organic complexes were reported to form such framework structures (Zurawski *et al.*, 2011). A remarkable feature of imidazole-based compounds is the ability to form porous networks, such as zeolitic imidazolate frameworks (ZIFs) (Zurawski *et al.*, 2012; Müller-Buschbaum *et al.*, 2015), which show a good performance for gas adsorption with feasible chemical and thermal stability. For example, ZIF-8 and ZIF-11 have a remarkable chemical resistance to boiling alkaline water and organic solvents, and high thermal stability up to 823 K (Park *et al.*, 2006; Zhong *et al.*, 2014). Another interesting feature of these complexes is that they exhibit luminescence based on *f–f* transitions of lanthanides assisted by the ligand antenna effect (Rybak *et al.*, 2012). The complexes of rare earth atoms with *β*-diketonates have been investigated widely because of their simple use as organic ligands

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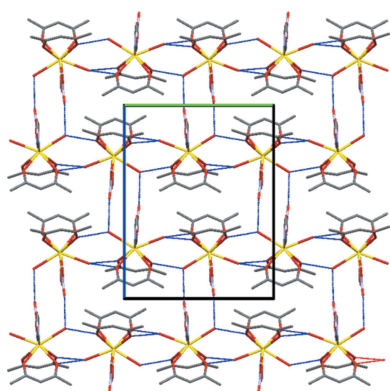
(Binnemans, 2005). These ligands can give an increase in luminescence efficiency and intensity, Eu(acac)$_3$ (acac is acetylacetonate) being one such complex (Kuz'mina & Eliseeva, 2006). In addition, Tb(acac)$_3$ is used as an active light-emitting layer in the first LED based on lanthanide complexes (Kido et al., 1990). From the viewpoint of high luminescence efficiency, the luminescence based on the f–d transition of Ce^{3+} is quite promising due to its allowed electronic transition. However, the emission of Ce^{3+} in metal–organic complexes have been reported only occasionally, for example, in [Ce(triRNTB)$_2$](CF$_3$SO$_3$)$_3$ [NTB = N-substituted tris(N-alkylbenzimidazol-2-ylmethyl)amine] and $^3_\infty$[Ce(Im)$_3$-(ImH)]·ImH (Zheng et al., 2007; Meyer et al., 2015). One of the reasons for this is the difficulty of retaining a certain distance between Ce^{3+} ions in order to avoid luminescence quenching caused by energy transfer between Ce^{3+} ions. [Ce(triRNTB)$_2$](CF$_3$SO$_3$)$_3$ shows a blue emission accompanied by neighbouring Ce···Ce distance of about 17~18 Å. NTB is a bulky ligand so that it can keep the neighbouring central ions far away. Also, it may be important for the emission of Ce^{3+} to construct a structure of isolated entities rather than a framework structure, which does not necessarily guarantee a sufficient long metal–metal distance. During the investigation of the synthesis of lanthanide complexes for Ce^{3+} emission using functional ligands, like imidazole with the antenna effect, as well as β-diketone derivatives, we have synthesized a novel lanthanum complex, although the cerium derivative has not been synthesized yet. This study reports structural data on a newly synthesized lanthanum complex comprising functional ligands of imidazole and acetylacetone.

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

D—H···A	D—H	H···A	D···A	D—H···A
N34—H34···O43^i	0.86	2.15	2.942 (2)	153
O11W—H11X···O24^{ii}	0.81 (3)	2.10 (3)	2.8353 (19)	152 (2)
O11W—H11Y···O12^{ii}	0.81 (3)	2.00 (3)	2.8014 (19)	168 (3)
O12W—H12Y···O44^{iii}	0.85 (3)	2.10 (3)	2.930 (2)	167 (3)
O12W—H12X···O22^{iv}	0.73 (3)	2.30 (3)	3.0025 (19)	161 (3)

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

(H$_2$O)$_2$]. Each molecule is isolated individually, i.e. the structure is not a framework structure. The central La atom is coordinated by eight O atoms from two acac anions, two water molecules, one nitrate anion and one N atom from one Im ligand (Fig. 1). Thus, the La atom has a monocapped square antiprismatic coordination. The La—O bond lengths can be classified into three categories; the first concerns interactions with a bidentate acac molecule, the second those with a nitrate ion behaving as a bidentate ligand and the third those with a water molecule. All the distances are quite comparable with the corresponding distances reported for acac complexes (Phillips et al., 1968; Antsyshkina et al., 1997; Fukuda et al., 2002) and for nitrate complexes (Al-Karaghouli & Wood, 1972; Frechette et al., 1992; Fukuda et al., 2002). An Im ligand coordinates to the central La atom as a monodentate ligand. The La—N distance is comparable with that of $^3_\infty$[Ce(Im)$_3$-(ImH)]·ImH (Meyer et al., 2015).

2. Structural commentary

The title complex crystallizes in the monoclinic space group P2$_1$/c, with one formula unit of [La(C$_5$H$_7$O$_2$)$_2$(NO$_3$)(C$_3$H$_4$N$_2$)-
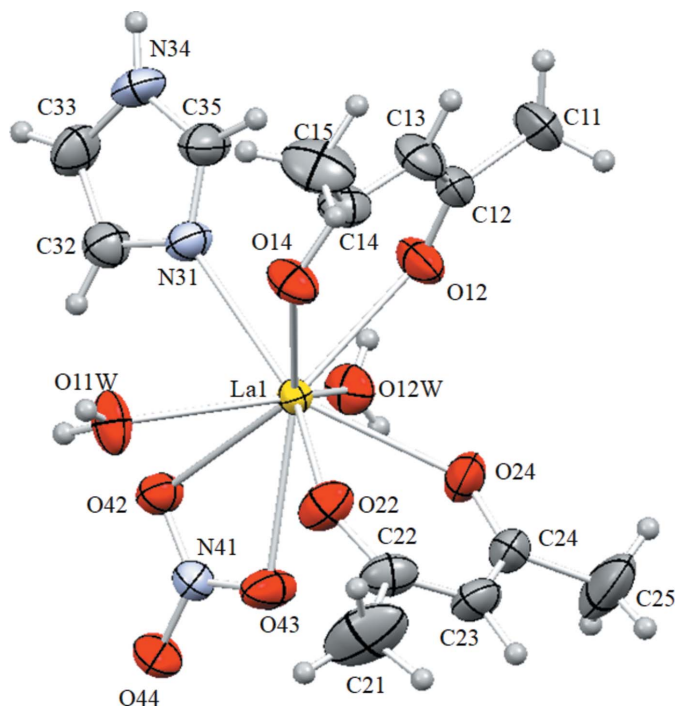

Figure 1
View of the molecular structure of the title complex, with displacement ellipsoids for non-H atoms drawn at the 50% probability level.

ular to the molecular planes of the two neighbouring acac anions, making angles of 84.68 (11) and 85.27 (11)°, respectively.

4. Database survey

The crystal structures of other related acac complexes including lanthanide ions have been reported (Berg & Acosta, 1968; Binnemans, 2005; Filotti *et al.*, 1996; Fujinaga *et al.*, 1981; Lim *et al.*, 1996; Phillips *et al.*, 1968; Richardson *et al.*, 1968; Stites *et al.*, 1948). The crystal structures of other related ImH complexes including lanthanide ions have also been reported (Dan *et al.*, 2004; Dechnik *et al.*, 2016; Meyer *et al.*, 2015; Pan *et al.*, 2016; Zhou *et al.*, 2008; Zurawski *et al.*, 2013).

5. Synthesis and crystallization

Colourless plate-like crystals were obtained by slow evaporation from a methanol solution of $La(NO_3)_3 \cdot 6H_2O$, acetylacetone and 1*H*-imidazole (1:5:5 molar ratio). The products were filtered off and dried at room temperature.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. H atoms bonded to C atoms were positioned geometrically after each cycle in idealized locations and refined as riding on their parent C atoms, with C—H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. H atoms bonded to water O atoms were located in a difference Fourier map, and isotro-
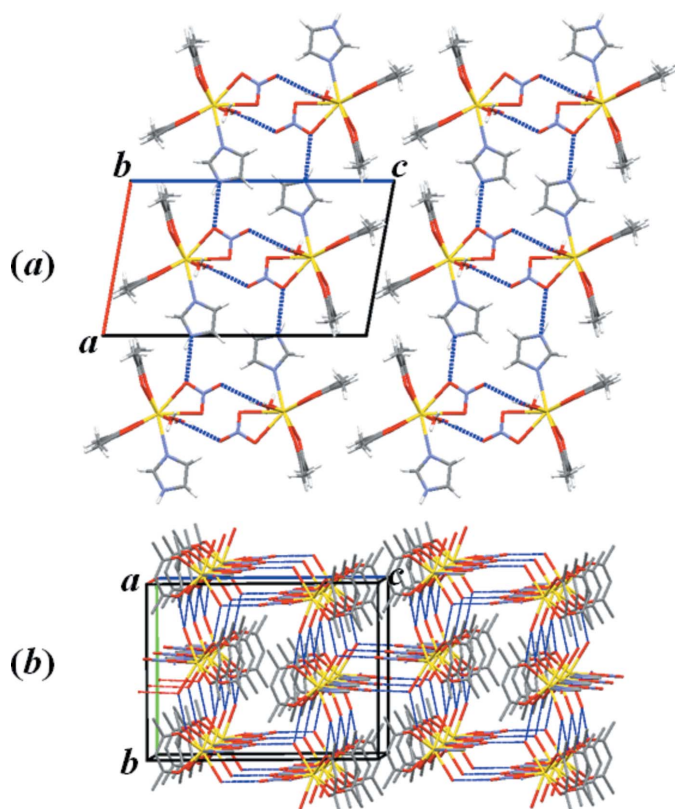

Figure 2
Connection of discrete complexes by intermolecular hydrogen-bonding (blue dashed lines) chains in the *ac* plane projected (*a*) along the *b* axis and (*b*) along the *a* axis. Colour code: La yellow, C grey, N purple and O red. H atoms have been omitted.

3. Supramolecular features

The discrete complexes are linked by five kinds of hydrogen bonds (Table 1). There are two types of hydrogen bond chains that lie nearly within the *ac* plane; the first type are the chains parallel to [100] by centrosymmetric pairs of intermolecular O···H—N hydrogen bonds between the O atom of a nitrate anion and the H atom of an ImH ligand, and the other type are the chains parallel to [001], formed also by centrosymmetric pairs of intermolecular O···H—O hydrogen bonds between the O atom of a nitrate anion and the H atom of a water molecule (O12*W*) (Fig. 2*a*). It is notable, as shown in Fig. 2(*b*), that these hydrogen bonds are both almost parallel to the *ac* plane. This arises from the fact that the angle difference between the molecular planes of the nitrate and ImH molecules is only 6.04 (12)°. Along the [010] direction, there are three types of hydrogen-bond chains, all of which are the hydrogen bond between the O atom of the acac anion and the H atom of water molecule (Fig. 3). All the ligands coordinating to the central La atom are involved in hydrogen bonding with neighbouring complexes. In this way, all molecules are connected by hydrogen bonds running in every axis direction, leading to a three-dimensional supramolecular network structure. Furthermore, it should be mentionned that the molecular plane of each ImH ligand is almost perpendic-
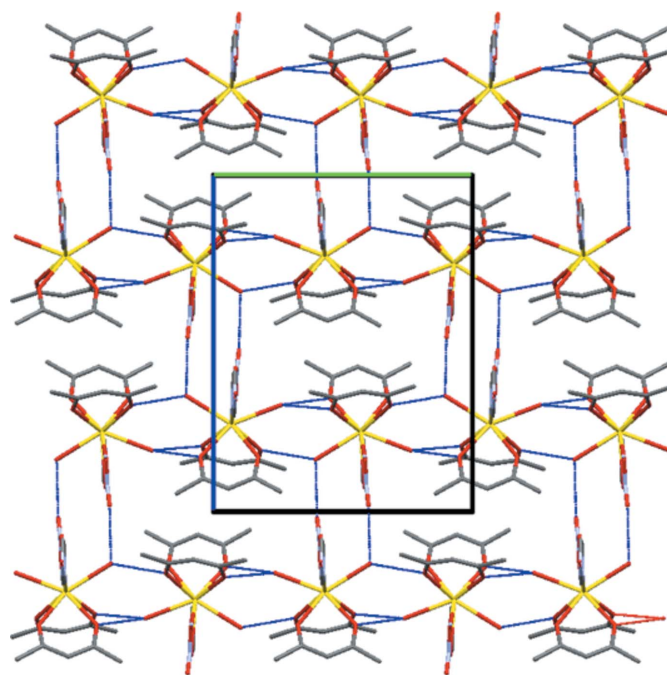

Figure 3
Connection of discrete complexes by intermolecular hydrogen-bonding (blue dashed lines) chains in the *bc* plane. Colour code: La yellow, C grey, N purple and O red. H atoms have been omitted.

research communications

Crystal data	
Chemical formula	$[La(C_5H_7O_2)_2(NO_3)(C_3H_4N_2)-(H_2O)_2]$
M_r	503.24
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	293
a, b, c (Å)	9.8233 (9), 12.4719 (12), 16.4432 (16)
β (°)	100.184 (7)
V (Å^3)	1982.8 (3)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	2.20
Crystal size (mm)	$0.42 \times 0.39 \times 0.12$
Data collection	
Diffractometer	XTALAB-MINI
Absorption correction	Multi-scan (*REQAB*; Rigaku, 1998)
T_{min}, T_{max}	0.456, 0.772
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	19723, 4543, 4317
R_{int}	0.019
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.649
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.016, 0.040, 1.07
No. of reflections	4543
No. of parameters	251
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.51, −0.54

Computer programs: *CrystalClear* (Rigaku/MSC, 2006), *SORTAV* (Blessing, 1995), *SHELXS2013* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015) and *ORTEP-3 for Windows* and *WinGX* (Farrugia, 2012).

pically refined without any distance restraint and with restraints of $U_{iso}(H) = 1.5U_{eq}(O)$.

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A new lanthanum(III) complex containing acetylacetone and 1*H*-imidazole

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Computing details

Data collection: *CrystalClear* (Rigaku/MSC, 2006); cell refinement: *CrystalClear* (Rigaku/MSC, 2006); data reduction: *CrystalClear* (Rigaku/MSC, 2006) and *SORTAV* (Blessing, 1995); program(s) used to solve structure: *SHELXS2013* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *WinGX* (Farrugia, 2012).

Diaqua(1*H*-imidazole-κN^3)(nitrato-$\kappa^2 O,O'$)bis(4-oxopent-2-en-2-olato-$\kappa^2 O,O'$)lanthanum(III)

Crystal data

[La(C$_5$H$_7$O$_2$)$_2$(NO$_3$)(C$_3$H$_4$N$_2$)(H$_2$O)$_2$]	$F(000) = 1000$
$M_r = 503.24$	$D_x = 1.686$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 19036 reflections
$a = 9.8233$ (9) Å	$\theta = 3$–27.5°
$b = 12.4719$ (12) Å	$\mu = 2.20$ mm^{-1}
$c = 16.4432$ (16) Å	$T = 293$ K
$\beta = 100.184$ (7)°	Prism, colorless
$V = 1982.8$ (3) Å^3	$0.42 \times 0.39 \times 0.12$ mm
$Z = 4$	

Data collection

XTALAB-MINI diffractometer	19723 measured reflections
Radiation source: sealed x-ray tube	4543 independent reflections
Graphite monochromator	4317 reflections with $I > 2\sigma(I)$
Detector resolution: 10 pixels mm^{-1}	$R_{int} = 0.019$
phi or ω oscillation scans	$\theta_{max} = 27.5°$, $\theta_{min} = 3.0°$
Absorption correction: multi-scan (*REQAB*; Rigaku, 1998)	$h = -12 \rightarrow 12$
	$k = -16 \rightarrow 16$
$T_{min} = 0.456$, $T_{max} = 0.772$	$l = -21 \rightarrow 21$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: mixed
$R[F^2 > 2\sigma(F^2)] = 0.016$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.040$	
$S = 1.07$	$w = 1/[\sigma^2(F_o^2) + (0.0179P)^2 + 0.8453P]$ where $P = (F_o^2 + 2F_c^2)/3$
4543 reflections	
251 parameters	$(\Delta/\sigma)_{max} < 0.001$
0 restraints	$\Delta\rho_{max} = 0.51$ e Å^{-3}
0 constraints	$\Delta\rho_{min} = -0.54$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	

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}
La1	0.49302 (2)	0.06987 (2)	0.73872 (2)	0.02341 (4)
C11	0.3206 (3)	−0.1406 (2)	0.94575 (16)	0.0675 (7)
H11A	0.2657	−0.1885	0.9076	0.101*
H11B	0.272	−0.1238	0.9899	0.101*
H11C	0.4071	−0.1742	0.9679	0.101*
C12	0.3473 (2)	−0.03887 (17)	0.90146 (12)	0.0416 (4)
O12	0.40186 (14)	−0.05003 (10)	0.83749 (8)	0.0404 (3)
C13	0.3101 (2)	0.05849 (17)	0.93181 (13)	0.0489 (5)
H13	0.2668	0.0566	0.9777	0.059*
C14	0.33217 (18)	0.15900 (16)	0.89926 (11)	0.0395 (4)
O14	0.38770 (15)	0.17374 (10)	0.83705 (8)	0.0454 (3)
C15	0.2866 (2)	0.2580 (2)	0.93995 (16)	0.0622 (6)
H15A	0.2468	0.3083	0.8983	0.093*
H15B	0.3651	0.29	0.9745	0.093*
H15C	0.2191	0.2386	0.973	0.093*
C21	0.8806 (3)	0.2748 (2)	0.8716 (2)	0.0910 (11)
H21A	0.8263	0.3193	0.9011	0.136*
H21B	0.8983	0.3122	0.8235	0.136*
H21C	0.9668	0.2578	0.9067	0.136*
C22	0.80297 (19)	0.17260 (16)	0.84555 (12)	0.0424 (4)
O22	0.67656 (13)	0.18282 (10)	0.81634 (9)	0.0448 (3)
C23	0.8740 (2)	0.07563 (17)	0.85616 (14)	0.0456 (5)
H23	0.9679	0.0784	0.878	0.055*
C24	0.81648 (19)	−0.02525 (16)	0.83686 (12)	0.0425 (4)
O24	0.69227 (13)	−0.04257 (11)	0.80450 (9)	0.0446 (3)
C25	0.9079 (3)	−0.1227 (2)	0.8548 (2)	0.0856 (10)
H25A	0.8662	−0.1726	0.8875	0.128*
H25B	0.9968	−0.1014	0.8847	0.128*
H25C	0.919	−0.1561	0.8038	0.128*
N31	0.22279 (15)	0.07647 (12)	0.67424 (10)	0.0367 (3)
C32	0.1625 (2)	0.07834 (15)	0.59247 (12)	0.0411 (4)
H32	0.2101	0.0768	0.5484	0.049*
C33	0.0238 (2)	0.08279 (17)	0.58553 (14)	0.0481 (5)
H33	−0.0409	0.0853	0.5369	0.058*
N34	−0.00239 (16)	0.08292 (14)	0.66351 (12)	0.0496 (4)
H34	−0.0826	0.0852	0.6776	0.06*
C35	0.1190 (2)	0.07876 (18)	0.71465 (13)	0.0483 (5)
H35	0.1289	0.0776	0.7719	0.058*
N41	0.62511 (15)	0.09036 (12)	0.57886 (9)	0.0329 (3)

O42	0.49735 (12)	0.08624 (10)	0.57207 (8)	0.0374 (3)
O43	0.69523 (14)	0.08635 (14)	0.65120 (8)	0.0545 (4)
O44	0.68294 (15)	0.09930 (13)	0.51860 (8)	0.0491 (3)
O11W	0.45059 (16)	0.26240 (10)	0.68241 (9)	0.0411 (3)
H11X	0.389 (3)	0.303 (2)	0.6897 (16)	0.062*
H11Y	0.499 (3)	0.311 (2)	0.6723 (16)	0.062*
O12W	0.45109 (17)	−0.10477 (11)	0.65529 (9)	0.0453 (3)
H12Y	0.425 (3)	−0.100 (2)	0.6035 (17)	0.068*
H12X	0.438 (3)	−0.160 (2)	0.6658 (17)	0.068*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
La1	0.02352 (5)	0.02229 (5)	0.02468 (6)	−0.00018 (3)	0.00500 (3)	−0.00149 (3)
C11	0.0832 (18)	0.0650 (15)	0.0637 (15)	0.0058 (13)	0.0387 (14)	0.0254 (12)
C12	0.0416 (10)	0.0513 (11)	0.0344 (9)	0.0007 (8)	0.0134 (8)	0.0079 (8)
O12	0.0528 (8)	0.0354 (7)	0.0377 (7)	0.0031 (6)	0.0208 (6)	0.0043 (5)
C13	0.0549 (12)	0.0635 (14)	0.0332 (10)	0.0012 (10)	0.0214 (9)	−0.0042 (9)
C14	0.0319 (9)	0.0516 (11)	0.0362 (9)	−0.0029 (8)	0.0087 (7)	−0.0183 (8)
O14	0.0577 (9)	0.0372 (7)	0.0476 (7)	−0.0012 (6)	0.0263 (7)	−0.0107 (6)
C15	0.0545 (13)	0.0666 (15)	0.0713 (15)	−0.0042 (11)	0.0267 (12)	−0.0364 (12)
C21	0.0437 (13)	0.0679 (18)	0.153 (3)	−0.0129 (12)	−0.0071 (16)	−0.0437 (19)
C22	0.0306 (9)	0.0505 (11)	0.0451 (10)	−0.0057 (8)	0.0042 (8)	−0.0153 (8)
O22	0.0336 (7)	0.0409 (7)	0.0553 (8)	−0.0023 (5)	−0.0043 (6)	−0.0132 (6)
C23	0.0250 (8)	0.0615 (13)	0.0485 (12)	−0.0006 (8)	0.0016 (8)	−0.0030 (9)
C24	0.0326 (9)	0.0486 (11)	0.0463 (11)	0.0071 (8)	0.0069 (8)	0.0125 (9)
O24	0.0350 (7)	0.0363 (7)	0.0592 (9)	0.0022 (5)	−0.0008 (6)	0.0087 (6)
C25	0.0454 (13)	0.0614 (16)	0.143 (3)	0.0176 (12)	−0.0008 (16)	0.0247 (17)
N31	0.0256 (7)	0.0463 (9)	0.0378 (8)	−0.0009 (6)	0.0046 (6)	0.0008 (6)
C32	0.0393 (10)	0.0477 (11)	0.0365 (10)	−0.0002 (8)	0.0074 (8)	0.0017 (8)
C33	0.0360 (10)	0.0576 (13)	0.0457 (12)	0.0011 (9)	−0.0067 (9)	−0.0005 (9)
N34	0.0239 (7)	0.0671 (12)	0.0586 (11)	−0.0023 (7)	0.0093 (7)	−0.0053 (8)
C35	0.0340 (10)	0.0740 (15)	0.0381 (10)	−0.0028 (9)	0.0096 (8)	−0.0022 (9)
N41	0.0332 (7)	0.0373 (8)	0.0294 (7)	−0.0018 (6)	0.0085 (6)	−0.0029 (6)
O42	0.0294 (6)	0.0460 (7)	0.0364 (7)	0.0021 (5)	0.0048 (5)	0.0011 (5)
O43	0.0291 (7)	0.1049 (13)	0.0294 (7)	−0.0024 (7)	0.0049 (5)	0.0017 (7)
O44	0.0501 (8)	0.0691 (9)	0.0326 (7)	−0.0106 (7)	0.0198 (6)	−0.0067 (6)
O11W	0.0485 (8)	0.0256 (6)	0.0502 (8)	0.0026 (5)	0.0113 (6)	0.0023 (5)
O12W	0.0726 (10)	0.0261 (6)	0.0336 (7)	−0.0018 (6)	−0.0002 (7)	−0.0023 (5)

Geometric parameters (Å, º)

La1—O14	2.4402 (12)	C22—O22	1.256 (2)
La1—O22	2.4597 (12)	C22—C23	1.392 (3)
La1—O12	2.4880 (12)	C23—C24	1.393 (3)
La1—O24	2.4939 (13)	C23—H23	0.93
La1—O12W	2.5682 (13)	C24—O24	1.261 (2)
La1—O11W	2.5808 (13)	C24—C25	1.510 (3)

La1—O43	2.6589 (14)	C25—H25A	0.96
La1—N31	2.6800 (15)	C25—H25B	0.96
La1—O42	2.7556 (13)	C25—H25C	0.96
C11—C12	1.509 (3)	N31—C35	1.312 (2)
C11—H11A	0.96	N31—C32	1.370 (3)
C11—H11B	0.96	C32—C33	1.348 (3)
C11—H11C	0.96	C32—H32	0.93
C12—O12	1.270 (2)	C33—N34	1.352 (3)
C12—C13	1.386 (3)	C33—H33	0.93
C13—C14	1.395 (3)	N34—C35	1.333 (3)
C13—H13	0.93	N34—H34	0.86
C14—O14	1.255 (2)	C35—H35	0.93
C14—C15	1.509 (3)	N41—O44	1.2311 (19)
C15—H15A	0.96	N41—O42	1.2413 (18)
C15—H15B	0.96	N41—O43	1.266 (2)
C15—H15C	0.96	O11W—H11X	0.81 (3)
C21—C22	1.508 (3)	O11W—H11Y	0.81 (3)
C21—H21A	0.96	O12W—H12Y	0.85 (3)
C21—H21B	0.96	O12W—H12X	0.73 (3)
C21—H21C	0.96		
O14—La1—O22	73.14 (5)	C14—C15—H15B	109.5
O14—La1—O12	69.07 (4)	H15A—C15—H15B	109.5
O22—La1—O12	108.72 (5)	C14—C15—H15C	109.5
O14—La1—O24	113.79 (5)	H15A—C15—H15C	109.5
O22—La1—O24	69.51 (5)	H15B—C15—H15C	109.5
O12—La1—O24	74.00 (5)	C22—C21—H21A	109.5
O14—La1—O12W	139.24 (5)	C22—C21—H21B	109.5
O22—La1—O12W	142.79 (5)	H21A—C21—H21B	109.5
O12—La1—O12W	78.27 (5)	C22—C21—H21C	109.5
O24—La1—O12W	78.12 (5)	H21A—C21—H21C	109.5
O14—La1—O11W	71.54 (5)	H21B—C21—H21C	109.5
O22—La1—O11W	73.17 (5)	O22—C22—C23	125.16 (17)
O12—La1—O11W	137.69 (5)	O22—C22—C21	116.06 (19)
O24—La1—O11W	138.02 (5)	C23—C22—C21	118.78 (19)
O12W—La1—O11W	126.65 (5)	C22—O22—La1	136.44 (12)
O14—La1—O43	139.68 (5)	C22—C23—C24	125.62 (18)
O22—La1—O43	71.78 (5)	C22—C23—H23	117.2
O12—La1—O43	142.12 (5)	C24—C23—H23	117.2
O24—La1—O43	70.97 (5)	O24—C24—C23	125.06 (18)
O12W—La1—O43	80.85 (5)	O24—C24—C25	116.3 (2)
O11W—La1—O43	79.79 (5)	C23—C24—C25	118.66 (19)
O14—La1—N31	74.90 (5)	C24—O24—La1	135.53 (12)
O22—La1—N31	140.50 (4)	C24—C25—H25A	109.5
O12—La1—N31	80.27 (5)	C24—C25—H25B	109.5
O24—La1—N31	146.66 (4)	H25A—C25—H25B	109.5
O12W—La1—N31	76.15 (5)	C24—C25—H25C	109.5
O11W—La1—N31	75.15 (5)	H25A—C25—H25C	109.5

O43—La1—N31	124.47 (5)	H25B—C25—H25C	109.5
O14—La1—O42	134.63 (4)	C35—N31—C32	104.87 (16)
O22—La1—O42	109.56 (4)	C35—N31—La1	127.18 (13)
O12—La1—O42	139.84 (4)	C32—N31—La1	127.95 (12)
O24—La1—O42	108.91 (4)	C33—C32—N31	109.82 (18)
O12W—La1—O42	63.95 (4)	C33—C32—H32	125.1
O11W—La1—O42	66.69 (4)	N31—C32—H32	125.1
O43—La1—O42	46.51 (4)	C32—C33—N34	106.18 (18)
N31—La1—O42	78.03 (4)	C32—C33—H33	126.9
C12—C11—H11A	109.5	N34—C33—H33	126.9
C12—C11—H11B	109.5	C35—N34—C33	107.42 (17)
H11A—C11—H11B	109.5	C35—N34—H34	126.3
C12—C11—H11C	109.5	C33—N34—H34	126.3
H11A—C11—H11C	109.5	N31—C35—N34	111.71 (19)
H11B—C11—H11C	109.5	N31—C35—H35	124.1
O12—C12—C13	124.82 (18)	N34—C35—H35	124.1
O12—C12—C11	116.26 (19)	O44—N41—O42	122.31 (15)
C13—C12—C11	118.91 (18)	O44—N41—O43	120.53 (15)
C12—O12—La1	136.74 (12)	O42—N41—O43	117.15 (14)
C12—C13—C14	125.47 (18)	N41—O42—La1	96.13 (10)
C12—C13—H13	117.3	N41—O43—La1	100.21 (10)
C14—C13—H13	117.3	La1—O11W—H11X	127.1 (18)
O14—C14—C13	124.32 (17)	La1—O11W—H11Y	135.3 (18)
O14—C14—C15	116.57 (19)	H11X—O11W—H11Y	92 (2)
C13—C14—C15	119.11 (18)	La1—O12W—H12Y	117.7 (18)
C14—O14—La1	139.35 (12)	La1—O12W—H12X	134 (2)
C14—C15—H15A	109.5	H12Y—O12W—H12X	106 (3)
C13—C12—O12—La1	6.4 (3)	C23—C24—O24—La1	10.7 (3)
C11—C12—O12—La1	−174.35 (15)	C25—C24—O24—La1	−168.80 (18)
O12—C12—C13—C14	−3.0 (4)	C35—N31—C32—C33	0.6 (2)
C11—C12—C13—C14	177.8 (2)	La1—N31—C32—C33	−179.32 (13)
C12—C13—C14—O14	0.9 (4)	N31—C32—C33—N34	−0.4 (2)
C12—C13—C14—C15	−179.5 (2)	C32—C33—N34—C35	0.1 (2)
C13—C14—O14—La1	−2.3 (3)	C32—N31—C35—N34	−0.6 (2)
C15—C14—O14—La1	178.08 (15)	La1—N31—C35—N34	179.36 (12)
C23—C22—O22—La1	−14.8 (3)	C33—N34—C35—N31	0.3 (3)
C21—C22—O22—La1	166.00 (19)	O44—N41—O42—La1	−179.37 (15)
O22—C22—C23—C24	−0.6 (4)	O43—N41—O42—La1	−0.25 (16)
C21—C22—C23—C24	178.6 (2)	O44—N41—O43—La1	179.40 (14)
C22—C23—C24—O24	2.3 (4)	O42—N41—O43—La1	0.26 (17)
C22—C23—C24—C25	−178.2 (2)		

Hydrogen-bond geometry (Å, º)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N34—H34⋯O43[i]	0.86	2.15	2.942 (2)	153
O11W—H11X⋯O24[ii]	0.81 (3)	2.10 (3)	2.8353 (19)	152 (2)

O11*W*—H11*Y*···O12[ii]	0.81 (3)	2.00 (3)	2.8014 (19)	168 (3)
O12*W*—H12*Y*···O44[iii]	0.85 (3)	2.10 (3)	2.930 (2)	167 (3)
O12*W*—H12*X*···O22[iv]	0.73 (3)	2.30 (3)	3.0025 (19)	161 (3)

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