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Trichlorido(*N*,*N*-dimethylformamide-κO)bis(1,10-phenanthroline-$\kappa^2 N,N'$)-lanthanum(III) *N*,*N*-dimethylformamide disolvate

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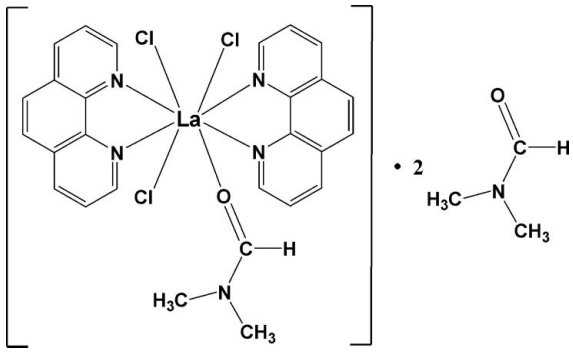
Key indicators: single-crystal X-ray study; T = 294 K; mean σ(C–C) = 0.005 Å; R factor = 0.033; wR factor = 0.082; data-to-parameter ratio = 15.7.

In the title compound, $[LaCl_3(C_{12}H_8N_2)_2(C_3H_7NO)]\cdot 2C_3H_7NO$, the La^{III} ion is eight-coordinated by four N donors from two 1,10-phenanthroline ligands, one O atom from one *N*,*N*-dimethylformamide molecule and three chloride anions. In the crystal structure, the La^{III} mononuclear units are linked to form a chain along the *a* axis by weak C—H···Cl hydrogen bonds. The chains are crosslinked to form a two-dimensional network parallel to the *ab* plane by π–π stacking interactions between the phen rings [centroid–centroid seperations range from 3.589 (2) to 3.708 (2) Å].

Related literature

For synthesis, see: Shi *et al.* (2004). For hydrogen-bond details, see: Desiraju & Steiner (1999). For related literature, see: Bünzli (2006); Edmonds *et al.* (2004); Molander & Romero (2002); Suárez *et al.* (2004); Wan *et al.* (2003); Ye *et al.* (2005).



Experimental

Crystal data

$[LaCl_3(C_{12}H_8N_2)_2(C_3H_7NO)]\cdot 2C_3H_7NO$
M_r = 824.96
Monoclinic, $P2_1/c$
a = 10.0344 (11) Å
b = 17.3861 (19) Å
c = 20.768 (2) Å
β = 91.521 (1)°
V = 3621.9 (7) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 1.44 mm^{-1}
T = 294 (2) K
0.28 × 0.18 × 0.16 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)
T_{min} = 0.691, T_{max} = 0.800
26591 measured reflections
6738 independent reflections
5246 reflections with $I > 2\sigma(I)$
R_{int} = 0.043

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.082
S = 1.01
6738 reflections
430 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.65 e Å^{-3}
$\Delta\rho_{min}$ = −0.35 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

La1—O1	2.572 (3)	La1—N2	2.758 (3)
La1—N3	2.694 (3)	La1—Cl2	2.7905 (10)
La1—N1	2.710 (3)	La1—Cl1	2.7999 (10)
La1—N4	2.721 (3)	La1—Cl3	2.8212 (10)
O1—La1—N3	72.27 (8)	N2—La1—Cl2	113.34 (7)
O1—La1—N1	68.04 (9)	O1—La1—Cl1	128.55 (6)
N3—La1—N1	139.37 (9)	N3—La1—Cl1	81.78 (7)
O1—La1—N4	123.48 (8)	N1—La1—Cl1	116.93 (7)
N3—La1—N4	60.79 (9)	N4—La1—Cl1	75.24 (7)
N1—La1—N4	154.78 (9)	N2—La1—Cl1	74.76 (7)
O1—La1—N2	64.66 (9)	Cl2—La1—Cl1	85.70 (3)
N3—La1—N2	95.27 (9)	O1—La1—Cl3	73.96 (6)
N1—La1—N2	60.07 (9)	N3—La1—Cl3	88.78 (7)
N4—La1—N2	143.87 (9)	N1—La1—Cl3	88.48 (7)
O1—La1—Cl2	138.37 (6)	N4—La1—Cl3	75.32 (7)
N3—La1—Cl2	144.41 (7)	N2—La1—Cl3	134.71 (7)
N1—La1—Cl2	75.66 (7)	Cl2—La1—Cl3	85.68 (4)
N4—La1—Cl2	83.83 (6)	Cl1—La1—Cl3	150.02 (3)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2···Cl3^{i}	0.93	2.80	3.662 (5)	155
C14—H14···O2	0.93	2.57	3.322 (6)	139
C22—H22···Cl2	0.93	2.78	3.524 (4)	138
C29—H29*A*···Cl3^{i}	0.96	2.81	3.766 (6)	176
C29—H29*C*···O3	0.96	2.42	3.319 (9)	157

Symmetry code: (i) $x+1, y, z$.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2003).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CI2472).

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supplementary materials

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Trichlorido(*N*,*N*-dimethylformamide-κO)bis(1,10-phenanthroline-$\kappa^2 N,N'$)lanthanum(III) *N*,*N*-dimethylformamide disolvate

L.-M. Zhou, G.-H. Sun, L.-J. Gao, S.-M. Fang and W.-D. Yan

Comment

In recent years, much attention has been focused on the synthetic approach and structural control of rare-earth (RE) complexes with various ligands, such as 2,2'-bipyridine and 1,10-phenanthroline (phen), not only because of their fascinating structural diversities but also their potential applications as optical materials, electronic materials, catalytic materials, molecular based magnets and so on (Bünzli, 2006; Suárez *et al.*, 2004). Many novel functional complexes with 2,2'-bipyridine-like ligands have been reported (Edmonds *et al.*, 2004; Molander & Romero, 2002; Wan *et al.*, 2003; Ye *et al.*, 2005). We report here the crystal structure of a La^{III} complex with a chelating 1,10-phenanthroline ligand, $[La(phen)_2(DMF)Cl_3](DMF)_2$, the title compound, (I) (DMF is *N*,*N*-dimethylformamide).

Compound (I) consists of mononuclear $[La(phen)_2(DMF)Cl_3]$ units and free DMF molecules. The La^{III} ion is eight-coordinated and surrounded by four N donors from two phen ligands, one O atom from one DMF molecule, and three Cl^- anions (Fig. 1). The La—Cl distances range from 2.7905 (10) to 2.8212 (10) Å, and those of La—N range from 2.694 (3) to 2.758 (3) Å, which are in the normal range expected for such coordination complexes (Bünzli, 2006) (Table 1). The adjacent mononuclear $[La(phen)_2(DMF)Cl_3]$ units are linked into a chain along the *a* axis by weak C—H···Cl hydrogen bonding interactions (Table 2) between the phen ligands and coordinated Cl^- anions (Desiraju & Steiner,1999). The chains are cross-linked to generate a two-dimensional network parallel to the *ab* plane by intermolecular π-π stacking interactions between the phenanthroline ring systems, with centroid-centroid distances ranging from 3.589 (2) to 3.708 (2) Å (Fig. 2).

Experimental

Compound (I) was synthesized according to the literature method of Shi *et al.* (2004). The reaction of $LaCl_3·7H_2O$ (37 mg, 0.1 mmol) with 1,10-phenanthroline (20 mg, 0.1 mmol) in EtOH (25 ml) for a few minutes afforded a white powder solid, which was filtered, washed with acetone, and dried in air. Single crystals suitable for X-ray analysis were obtained by slow diffusion of Et_2O into the DMF solution of the solid mentioned above after several days (yield: ~30%). Analysis calculated for $C_{33}H_{37}Cl_3LaN_7O_3$: C 48.05, H 4.52, N 11.88%; found: C 48.26, H 4.48, N 11.96%.

Refinement

H atoms were included in calculated positions and treated in the subsequent refinement as riding atoms, with C—H = 0.93 (aromatic) or 0.96 Å (methyl) and U_{iso}(H) = 1.2–1.5 U_{eq}(C). A rotating group model was used for the methyl groups.

Figures

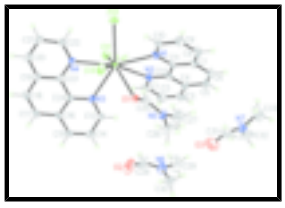

Fig. 1. The asymmetric unit of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

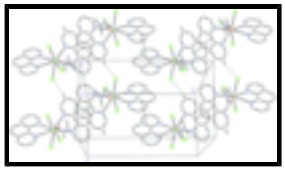

Fig. 2. View of a two-dimensional network generated by C—H···Cl (dashed lines) and π-π stacking (dashed-solid lines) interactions. Only H atoms involved in the interactions are shown for clarity.

Trichlorido(*N*,*N*-dimethylformamide-κ*O*)bis(1,10-phenanthroline-\ κ^2*N*,*N*')lanthanum(III) *N*,*N*-dimethylformamide disolvate

Crystal data

$[LaCl_3(C_{12}H_8N_2)_2(C_3H_7NO)]\cdot 2C_3H_7NO$	F_{000} = 1664
M_r = 824.96	D_x = 1.513 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: -P 2ybc	Cell parameters from 5052 reflections
a = 10.0344 (11) Å	θ = 2.3–22.9º
b = 17.3861 (19) Å	μ = 1.44 mm^{-1}
c = 20.768 (2) Å	T = 294 (2) K
β = 91.521 (1)º	Block, colourless
V = 3621.9 (7) Å^3	0.28 × 0.18 × 0.16 mm
Z = 4	

Data collection

Bruker SMART CCD area-detector diffractometer	6738 independent reflections
Radiation source: fine-focus sealed tube	5246 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.043
T = 293(2) K	θ_{max} = 25.5º
φ and ω scans	θ_{min} = 2.3º
Absorption correction: multi-scan (SADABS; Bruker, 1998)	h = −12→12
T_{min} = 0.691, T_{max} = 0.800	k = −21→21
26591 measured reflections	l = −25→25

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map

Least-squares matrix: full

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

$wR(F^2) = 0.082$

$S = 1.01$

6738 reflections

430 parameters

Primary atom site location: structure-invariant direct methods

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0362P)^2 + 2.0867P]$ where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{max} = 0.65$ e Å^{-3}

$\Delta\rho_{min} = -0.35$ e Å^{-3}

Extinction correction: none

Special details

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

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

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

	x	*y*	*z*	U_{iso}*/U_{eq}
La1	0.26566 (2)	0.257762 (11)	0.006982 (10)	0.03058 (8)
Cl1	0.42502 (11)	0.22137 (6)	−0.09739 (5)	0.0509 (3)
Cl2	0.09143 (12)	0.32315 (6)	−0.08456 (5)	0.0587 (3)
Cl3	0.03624 (10)	0.23105 (6)	0.07937 (5)	0.0520 (3)
O1	0.3370 (3)	0.27886 (15)	0.12551 (12)	0.0440 (6)
O2	0.6722 (5)	0.1430 (3)	0.2457 (2)	0.1301 (19)
O3	0.7636 (5)	0.4546 (3)	0.2676 (3)	0.144 (2)
N1	0.2527 (3)	0.40798 (16)	0.04116 (15)	0.0373 (7)
N2	0.4970 (3)	0.34111 (17)	0.02658 (15)	0.0400 (8)
N3	0.3672 (3)	0.12430 (16)	0.05227 (14)	0.0356 (7)
N4	0.1654 (3)	0.12260 (16)	−0.03921 (14)	0.0352 (7)
N5	0.3434 (4)	0.35285 (19)	0.21560 (15)	0.0496 (9)
N6	0.8099 (4)	0.2435 (2)	0.2642 (2)	0.0698 (11)
N7	0.7912 (6)	0.5802 (3)	0.24929 (19)	0.0836 (14)
C1	0.6158 (4)	0.3090 (3)	0.0201 (2)	0.0585 (12)
H1	0.6203	0.2614	0.0000	0.070*
C2	0.7353 (4)	0.3434 (3)	0.0421 (3)	0.0701 (14)
H2	0.8166	0.3187	0.0373	0.084*
C3	0.7290 (4)	0.4140 (3)	0.0707 (2)	0.0641 (13)
H3	0.8067	0.4377	0.0859	0.077*
C4	0.6068 (4)	0.4505 (2)	0.07696 (19)	0.0468 (10)
C5	0.5942 (5)	0.5259 (3)	0.1058 (2)	0.0581 (12)

H5	0.6703	0.5528	0.1188	0.070*
C6	0.4740 (5)	0.5572 (2)	0.1138 (2)	0.0598 (12)
H6	0.4683	0.6055	0.1328	0.072*
C7	0.3546 (4)	0.5186 (2)	0.09412 (19)	0.0462 (10)
C8	0.2273 (5)	0.5492 (2)	0.1026 (2)	0.0632 (13)
H8	0.2175	0.5962	0.1233	0.076*
C9	0.1166 (5)	0.5098 (2)	0.0802 (2)	0.0602 (12)
H9	0.0315	0.5296	0.0854	0.072*
C10	0.1348 (4)	0.4399 (2)	0.04980 (19)	0.0453 (10)
H10	0.0595	0.4137	0.0345	0.054*
C11	0.3634 (4)	0.44669 (19)	0.06299 (17)	0.0357 (8)
C12	0.4919 (4)	0.4117 (2)	0.05481 (17)	0.0375 (9)
C13	0.4663 (4)	0.1231 (2)	0.09572 (19)	0.0428 (10)
H13	0.4993	0.1700	0.1107	0.051*
C14	0.5246 (4)	0.0559 (2)	0.1206 (2)	0.0484 (10)
H14	0.5949	0.0584	0.1506	0.058*
C15	0.4764 (4)	−0.0129 (2)	0.10010 (18)	0.0433 (10)
H15	0.5136	−0.0583	0.1160	0.052*
C16	0.3702 (4)	−0.0157 (2)	0.05486 (17)	0.0377 (9)
C17	0.3136 (4)	−0.0860 (2)	0.0320 (2)	0.0489 (10)
H17	0.3460	−0.1323	0.0485	0.059*
C18	0.2146 (4)	−0.0872 (2)	−0.01270 (19)	0.0474 (10)
H18	0.1801	−0.1340	−0.0269	0.057*
C19	0.1617 (4)	−0.0170 (2)	−0.03869 (18)	0.0380 (9)
C20	0.0596 (4)	−0.0155 (2)	−0.08625 (19)	0.0494 (11)
H20	0.0237	−0.0613	−0.1021	0.059*
C21	0.0136 (4)	0.0529 (2)	−0.1090 (2)	0.0509 (11)
H21	−0.0535	0.0545	−0.1407	0.061*
C22	0.0683 (4)	0.1209 (2)	−0.08395 (18)	0.0437 (10)
H22	0.0350	0.1675	−0.0995	0.052*
C23	0.2118 (3)	0.0541 (2)	−0.01683 (17)	0.0330 (8)
C24	0.3191 (3)	0.05489 (19)	0.03160 (17)	0.0325 (8)
C25	0.2831 (4)	0.3200 (2)	0.16585 (19)	0.0435 (9)
H25	0.1920	0.3285	0.1605	0.052*
C26	0.4842 (5)	0.3404 (3)	0.2277 (2)	0.0818 (17)
H26A	0.5181	0.3064	0.1957	0.123*
H26B	0.4978	0.3179	0.2696	0.123*
H26C	0.5304	0.3887	0.2260	0.123*
C27	0.2728 (6)	0.4020 (3)	0.2598 (2)	0.0888 (19)
H27A	0.1803	0.4043	0.2470	0.133*
H27B	0.3103	0.4528	0.2591	0.133*
H27C	0.2812	0.3814	0.3026	0.133*
C28	0.7594 (6)	0.1871 (4)	0.2296 (3)	0.0913 (18)
H28	0.7935	0.1800	0.1888	0.110*
C29	0.9215 (7)	0.2898 (4)	0.2434 (3)	0.125 (3)
H29A	0.9457	0.2742	0.2009	0.187*
H29B	0.9961	0.2826	0.2727	0.187*
H29C	0.8964	0.3430	0.2428	0.187*
C30	0.7630 (5)	0.2612 (3)	0.3266 (2)	0.0706 (14)

H30A	0.6812	0.2341	0.3334	0.106*
H30B	0.7477	0.3155	0.3298	0.106*
H30C	0.8285	0.2458	0.3586	0.106*
C31	0.7195 (7)	0.5191 (4)	0.2607 (3)	0.0947 (19)
H31	0.6279	0.5257	0.2638	0.114*
C32	0.9289 (7)	0.5736 (6)	0.2425 (4)	0.176 (5)
H32A	0.9736	0.5875	0.2822	0.265*
H32B	0.9570	0.6072	0.2088	0.265*
H32C	0.9506	0.5214	0.2318	0.265*
C33	0.7247 (9)	0.6535 (4)	0.2441 (3)	0.163 (4)
H33A	0.7305	0.6725	0.2009	0.245*
H33B	0.7666	0.6894	0.2734	0.245*
H33C	0.6327	0.6476	0.2547	0.245*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
La1	0.03234 (12)	0.02500 (11)	0.03420 (12)	0.00314 (9)	−0.00294 (8)	−0.00165 (9)
Cl1	0.0566 (6)	0.0495 (6)	0.0471 (6)	0.0077 (5)	0.0107 (5)	−0.0044 (5)
Cl2	0.0715 (8)	0.0464 (6)	0.0568 (7)	0.0191 (5)	−0.0240 (6)	−0.0020 (5)
Cl3	0.0413 (5)	0.0584 (7)	0.0565 (6)	−0.0077 (5)	0.0072 (5)	−0.0122 (5)
O1	0.0524 (17)	0.0405 (15)	0.0387 (15)	0.0028 (12)	−0.0036 (13)	−0.0026 (12)
O2	0.125 (4)	0.137 (4)	0.128 (4)	−0.054 (3)	−0.008 (3)	−0.042 (3)
O3	0.154 (5)	0.095 (4)	0.182 (5)	−0.011 (3)	−0.047 (4)	0.037 (3)
N1	0.0376 (18)	0.0280 (16)	0.0460 (19)	0.0024 (13)	−0.0009 (15)	0.0007 (14)
N2	0.0380 (18)	0.0356 (18)	0.046 (2)	0.0034 (14)	−0.0009 (15)	−0.0005 (14)
N3	0.0353 (17)	0.0339 (17)	0.0373 (18)	0.0038 (13)	−0.0059 (14)	−0.0009 (13)
N4	0.0363 (17)	0.0318 (17)	0.0372 (17)	0.0019 (13)	−0.0058 (14)	−0.0023 (13)
N5	0.061 (2)	0.051 (2)	0.036 (2)	−0.0058 (17)	−0.0053 (17)	−0.0072 (16)
N6	0.069 (3)	0.064 (3)	0.077 (3)	−0.002 (2)	0.013 (2)	−0.014 (2)
N7	0.139 (5)	0.056 (3)	0.055 (3)	−0.011 (3)	−0.005 (3)	0.005 (2)
C1	0.040 (2)	0.051 (3)	0.085 (3)	0.013 (2)	0.001 (2)	−0.005 (2)
C2	0.033 (3)	0.079 (4)	0.099 (4)	0.007 (2)	0.001 (3)	0.004 (3)
C3	0.039 (3)	0.078 (4)	0.075 (3)	−0.011 (2)	−0.010 (2)	0.007 (3)
C4	0.049 (3)	0.051 (3)	0.040 (2)	−0.013 (2)	−0.0027 (19)	0.0043 (19)
C5	0.066 (3)	0.058 (3)	0.050 (3)	−0.027 (2)	−0.010 (2)	−0.002 (2)
C6	0.079 (4)	0.039 (2)	0.061 (3)	−0.016 (2)	−0.004 (3)	−0.009 (2)
C7	0.063 (3)	0.031 (2)	0.044 (2)	−0.0052 (19)	−0.001 (2)	−0.0037 (17)
C8	0.083 (4)	0.035 (2)	0.072 (3)	0.007 (2)	0.005 (3)	−0.014 (2)
C9	0.060 (3)	0.046 (3)	0.075 (3)	0.020 (2)	−0.002 (3)	−0.009 (2)
C10	0.042 (2)	0.037 (2)	0.057 (3)	0.0067 (18)	−0.004 (2)	−0.0037 (19)
C11	0.046 (2)	0.0257 (18)	0.035 (2)	−0.0021 (16)	−0.0010 (18)	0.0037 (15)
C12	0.041 (2)	0.036 (2)	0.036 (2)	−0.0059 (17)	−0.0014 (17)	0.0055 (16)
C13	0.046 (2)	0.033 (2)	0.049 (2)	0.0002 (17)	−0.010 (2)	−0.0032 (17)
C14	0.046 (2)	0.049 (3)	0.050 (3)	0.0069 (19)	−0.011 (2)	0.002 (2)
C15	0.050 (2)	0.036 (2)	0.044 (2)	0.0122 (18)	−0.003 (2)	0.0074 (17)
C16	0.046 (2)	0.031 (2)	0.036 (2)	0.0074 (17)	0.0035 (18)	0.0010 (16)
C17	0.068 (3)	0.026 (2)	0.053 (3)	0.0053 (19)	0.005 (2)	0.0012 (18)

C18	0.058 (3)	0.029 (2)	0.055 (3)	−0.0016 (18)	0.001 (2)	−0.0068 (18)
C19	0.041 (2)	0.033 (2)	0.040 (2)	−0.0037 (16)	0.0047 (18)	−0.0050 (16)
C20	0.053 (3)	0.046 (3)	0.050 (3)	−0.010 (2)	−0.005 (2)	−0.012 (2)
C21	0.048 (3)	0.053 (3)	0.051 (3)	−0.005 (2)	−0.015 (2)	−0.008 (2)
C22	0.046 (2)	0.038 (2)	0.046 (2)	0.0038 (18)	−0.013 (2)	−0.0015 (18)
C23	0.0292 (19)	0.035 (2)	0.035 (2)	0.0036 (15)	0.0055 (16)	−0.0026 (16)
C24	0.036 (2)	0.0276 (18)	0.034 (2)	0.0024 (15)	0.0035 (17)	−0.0016 (15)
C25	0.045 (2)	0.044 (2)	0.041 (2)	0.0005 (19)	−0.0059 (19)	0.0025 (19)
C26	0.063 (3)	0.124 (5)	0.057 (3)	−0.015 (3)	−0.015 (3)	−0.008 (3)
C27	0.112 (5)	0.093 (4)	0.062 (4)	0.009 (3)	−0.003 (3)	−0.030 (3)
C28	0.090 (5)	0.102 (5)	0.082 (4)	0.007 (4)	−0.007 (4)	−0.018 (4)
C29	0.132 (6)	0.112 (5)	0.134 (6)	−0.038 (5)	0.071 (5)	−0.032 (5)
C30	0.070 (3)	0.070 (3)	0.072 (3)	0.000 (3)	−0.004 (3)	−0.002 (3)
C31	0.110 (5)	0.089 (5)	0.085 (4)	0.009 (4)	−0.006 (4)	0.023 (4)
C32	0.092 (6)	0.277 (12)	0.158 (8)	−0.051 (6)	−0.041 (5)	0.131 (8)
C33	0.309 (12)	0.073 (5)	0.110 (6)	0.048 (6)	0.048 (7)	−0.017 (4)

Geometric parameters (Å, °)

La1—O1	2.572 (3)	C9—H9	0.93
La1—N3	2.694 (3)	C10—H10	0.93
La1—N1	2.710 (3)	C11—C12	1.440 (5)
La1—N4	2.721 (3)	C13—C14	1.400 (5)
La1—N2	2.758 (3)	C13—H13	0.93
La1—Cl2	2.7905 (10)	C14—C15	1.355 (5)
La1—Cl1	2.7999 (10)	C14—H14	0.93
La1—Cl3	2.8212 (10)	C15—C16	1.402 (5)
O1—C25	1.237 (4)	C15—H15	0.93
O2—C28	1.217 (7)	C16—C24	1.411 (5)
O3—C31	1.213 (7)	C16—C17	1.424 (5)
N1—C10	1.323 (4)	C17—C18	1.342 (6)
N1—C11	1.366 (4)	C17—H17	0.93
N2—C1	1.326 (5)	C18—C19	1.430 (5)
N2—C12	1.361 (4)	C18—H18	0.93
N3—C13	1.325 (4)	C19—C20	1.404 (5)
N3—C24	1.365 (4)	C19—C23	1.406 (5)
N4—C22	1.329 (4)	C20—C21	1.355 (6)
N4—C23	1.356 (4)	C20—H20	0.93
N5—C25	1.314 (5)	C21—C22	1.399 (5)
N5—C26	1.445 (5)	C21—H21	0.93
N5—C27	1.453 (6)	C22—H22	0.93
N6—C28	1.310 (7)	C23—C24	1.454 (5)
N6—C30	1.424 (6)	C25—H25	0.93
N6—C29	1.455 (7)	C26—H26A	0.96
N7—C31	1.308 (7)	C26—H26B	0.96
N7—C32	1.397 (8)	C26—H26C	0.96
N7—C33	1.441 (8)	C27—H27A	0.96
C1—C2	1.405 (6)	C27—H27B	0.96
C1—H1	0.93	C27—H27C	0.96

C2—C3	1.365 (6)	C28—H28	0.93
C2—H2	0.93	C29—H29A	0.96
C3—C4	1.389 (6)	C29—H29B	0.96
C3—H3	0.93	C29—H29C	0.96
C4—C12	1.403 (5)	C30—H30A	0.96
C4—C5	1.448 (6)	C30—H30B	0.96
C5—C6	1.337 (6)	C30—H30C	0.96
C5—H5	0.93	C31—H31	0.93
C6—C7	1.424 (6)	C32—H32A	0.96
C6—H6	0.93	C32—H32B	0.96
C7—C8	1.398 (6)	C32—H32C	0.96
C7—C11	1.412 (5)	C33—H33A	0.96
C8—C9	1.375 (6)	C33—H33B	0.96
C8—H8	0.93	C33—H33C	0.96
C9—C10	1.384 (5)		
O1—La1—N3	72.27 (8)	N2—C12—C11	118.4 (3)
O1—La1—N1	68.04 (9)	C4—C12—C11	119.3 (3)
N3—La1—N1	139.37 (9)	N3—C13—C14	124.3 (3)
O1—La1—N4	123.48 (8)	N3—C13—H13	117.9
N3—La1—N4	60.79 (9)	C14—C13—H13	117.9
N1—La1—N4	154.78 (9)	C15—C14—C13	118.6 (4)
O1—La1—N2	64.66 (9)	C15—C14—H14	120.7
N3—La1—N2	95.27 (9)	C13—C14—H14	120.7
N1—La1—N2	60.07 (9)	C14—C15—C16	120.0 (3)
N4—La1—N2	143.87 (9)	C14—C15—H15	120.0
O1—La1—Cl2	138.37 (6)	C16—C15—H15	120.0
N3—La1—Cl2	144.41 (7)	C15—C16—C24	117.5 (3)
N1—La1—Cl2	75.66 (7)	C15—C16—C17	122.8 (3)
N4—La1—Cl2	83.83 (6)	C24—C16—C17	119.7 (3)
N2—La1—Cl2	113.34 (7)	C18—C17—C16	121.6 (4)
O1—La1—Cl1	128.55 (6)	C18—C17—H17	119.2
N3—La1—Cl1	81.78 (7)	C16—C17—H17	119.2
N1—La1—Cl1	116.93 (7)	C17—C18—C19	120.6 (3)
N4—La1—Cl1	75.24 (7)	C17—C18—H18	119.7
N2—La1—Cl1	74.76 (7)	C19—C18—H18	119.7
Cl2—La1—Cl1	85.70 (3)	C20—C19—C23	117.3 (3)
O1—La1—Cl3	73.96 (6)	C20—C19—C18	122.6 (3)
N3—La1—Cl3	88.78 (7)	C23—C19—C18	120.1 (3)
N1—La1—Cl3	88.48 (7)	C21—C20—C19	119.8 (4)
N4—La1—Cl3	75.32 (7)	C21—C20—H20	120.1
N2—La1—Cl3	134.71 (7)	C19—C20—H20	120.1
Cl2—La1—Cl3	85.68 (4)	C20—C21—C22	119.1 (4)
Cl1—La1—Cl3	150.02 (3)	C20—C21—H21	120.5
C25—O1—La1	128.0 (2)	C22—C21—H21	120.5
C10—N1—C11	118.1 (3)	N4—C22—C21	123.5 (4)
C10—N1—La1	119.3 (2)	N4—C22—H22	118.3
C11—N1—La1	121.1 (2)	C21—C22—H22	118.3
C1—N2—C12	117.8 (3)	N4—C23—C19	123.1 (3)
C1—N2—La1	121.3 (3)	N4—C23—C24	118.0 (3)

C12—N2—La1	119.8 (2)	C19—C23—C24	118.9 (3)
C13—N3—C24	117.0 (3)	N3—C24—C16	122.6 (3)
C13—N3—La1	121.4 (2)	N3—C24—C23	118.4 (3)
C24—N3—La1	121.6 (2)	C16—C24—C23	119.0 (3)
C22—N4—C23	117.3 (3)	O1—C25—N5	125.7 (4)
C22—N4—La1	121.5 (2)	O1—C25—H25	117.2
C23—N4—La1	121.2 (2)	N5—C25—H25	117.2
C25—N5—C26	120.0 (4)	N5—C26—H26A	109.5
C25—N5—C27	122.0 (4)	N5—C26—H26B	109.5
C26—N5—C27	118.0 (4)	H26A—C26—H26B	109.5
C28—N6—C30	122.0 (5)	N5—C26—H26C	109.5
C28—N6—C29	122.7 (5)	H26A—C26—H26C	109.5
C30—N6—C29	115.3 (4)	H26B—C26—H26C	109.5
C31—N7—C32	120.1 (6)	N5—C27—H27A	109.5
C31—N7—C33	118.4 (7)	N5—C27—H27B	109.5
C32—N7—C33	121.5 (6)	H27A—C27—H27B	109.5
N2—C1—C2	123.4 (4)	N5—C27—H27C	109.5
N2—C1—H1	118.3	H27A—C27—H27C	109.5
C2—C1—H1	118.3	H27B—C27—H27C	109.5
C3—C2—C1	118.4 (4)	O2—C28—N6	126.1 (6)
C3—C2—H2	120.8	O2—C28—H28	116.9
C1—C2—H2	120.8	N6—C28—H28	116.9
C2—C3—C4	120.2 (4)	N6—C29—H29A	109.5
C2—C3—H3	119.9	N6—C29—H29B	109.5
C4—C3—H3	119.9	H29A—C29—H29B	109.5
C3—C4—C12	118.0 (4)	N6—C29—H29C	109.5
C3—C4—C5	122.7 (4)	H29A—C29—H29C	109.5
C12—C4—C5	119.4 (4)	H29B—C29—H29C	109.5
C6—C5—C4	120.6 (4)	N6—C30—H30A	109.5
C6—C5—H5	119.7	N6—C30—H30B	109.5
C4—C5—H5	119.7	H30A—C30—H30B	109.5
C5—C6—C7	121.8 (4)	N6—C30—H30C	109.5
C5—C6—H6	119.1	H30A—C30—H30C	109.5
C7—C6—H6	119.1	H30B—C30—H30C	109.5
C8—C7—C11	117.6 (4)	O3—C31—N7	124.9 (7)
C8—C7—C6	123.4 (4)	O3—C31—H31	117.5
C11—C7—C6	119.1 (4)	N7—C31—H31	117.5
C9—C8—C7	120.1 (4)	N7—C32—H32A	109.5
C9—C8—H8	120.0	N7—C32—H32B	109.5
C7—C8—H8	120.0	H32A—C32—H32B	109.5
C8—C9—C10	118.4 (4)	N7—C32—H32C	109.5
C8—C9—H9	120.8	H32A—C32—H32C	109.5
C10—C9—H9	120.8	H32B—C32—H32C	109.5
N1—C10—C9	124.0 (4)	N7—C33—H33A	109.5
N1—C10—H10	118.0	N7—C33—H33B	109.5
C9—C10—H10	118.0	H33A—C33—H33B	109.5
N1—C11—C7	121.8 (3)	N7—C33—H33C	109.5
N1—C11—C12	118.4 (3)	H33A—C33—H33C	109.5
C7—C11—C12	119.7 (3)	H33B—C33—H33C	109.5

N2—C12—C4	122.3 (4)		
N3—La1—O1—C25	−145.3 (3)	C5—C6—C7—C8	179.1 (4)
N1—La1—O1—C25	43.6 (3)	C5—C6—C7—C11	−2.5 (7)
N4—La1—O1—C25	−110.9 (3)	C11—C7—C8—C9	−0.7 (6)
N2—La1—O1—C25	109.8 (3)	C6—C7—C8—C9	177.7 (4)
Cl2—La1—O1—C25	12.5 (4)	C7—C8—C9—C10	0.3 (7)
Cl1—La1—O1—C25	151.2 (3)	C11—N1—C10—C9	−0.7 (6)
Cl3—La1—O1—C25	−51.4 (3)	La1—N1—C10—C9	165.5 (3)
O1—La1—N1—C10	−105.8 (3)	C8—C9—C10—N1	0.5 (7)
N3—La1—N1—C10	−118.8 (3)	C10—N1—C11—C7	0.1 (5)
N4—La1—N1—C10	16.9 (4)	La1—N1—C11—C7	−165.8 (3)
N2—La1—N1—C10	−178.3 (3)	C10—N1—C11—C12	178.9 (3)
Cl2—La1—N1—C10	53.4 (3)	La1—N1—C11—C12	13.0 (4)
Cl1—La1—N1—C10	130.9 (3)	C8—C7—C11—N1	0.6 (6)
Cl3—La1—N1—C10	−32.5 (3)	C6—C7—C11—N1	−177.9 (4)
O1—La1—N1—C11	59.9 (3)	C8—C7—C11—C12	−178.2 (4)
N3—La1—N1—C11	46.9 (3)	C6—C7—C11—C12	3.3 (6)
N4—La1—N1—C11	−177.4 (2)	C1—N2—C12—C4	−0.2 (6)
N2—La1—N1—C11	−12.6 (2)	La1—N2—C12—C4	167.8 (3)
Cl2—La1—N1—C11	−140.8 (3)	C1—N2—C12—C11	−179.1 (4)
Cl1—La1—N1—C11	−63.4 (3)	La1—N2—C12—C11	−11.1 (4)
Cl3—La1—N1—C11	133.2 (3)	C3—C4—C12—N2	−1.4 (6)
O1—La1—N2—C1	101.3 (3)	C5—C4—C12—N2	179.2 (3)
N3—La1—N2—C1	33.7 (3)	C3—C4—C12—C11	177.5 (4)
N1—La1—N2—C1	179.5 (3)	C5—C4—C12—C11	−1.9 (5)
N4—La1—N2—C1	−11.4 (4)	N1—C11—C12—N2	−1.0 (5)
Cl2—La1—N2—C1	−124.6 (3)	C7—C11—C12—N2	177.8 (3)
Cl1—La1—N2—C1	−46.2 (3)	N1—C11—C12—C4	−179.9 (3)
Cl3—La1—N2—C1	127.3 (3)	C7—C11—C12—C4	−1.2 (5)
O1—La1—N2—C12	−66.3 (3)	C24—N3—C13—C14	0.8 (6)
N3—La1—N2—C12	−133.8 (3)	La1—N3—C13—C14	−179.2 (3)
N1—La1—N2—C12	11.9 (2)	N3—C13—C14—C15	−1.0 (6)
N4—La1—N2—C12	−179.0 (2)	C13—C14—C15—C16	0.0 (6)
Cl2—La1—N2—C12	67.9 (3)	C14—C15—C16—C24	1.0 (6)
Cl1—La1—N2—C12	146.2 (3)	C14—C15—C16—C17	−179.0 (4)
Cl3—La1—N2—C12	−40.3 (3)	C15—C16—C17—C18	−178.0 (4)
O1—La1—N3—C13	−33.8 (3)	C24—C16—C17—C18	1.9 (6)
N1—La1—N3—C13	−21.1 (3)	C16—C17—C18—C19	−0.5 (6)
N4—La1—N3—C13	178.9 (3)	C17—C18—C19—C20	179.0 (4)
N2—La1—N3—C13	27.5 (3)	C17—C18—C19—C23	−0.9 (6)
Cl2—La1—N3—C13	171.8 (2)	C23—C19—C20—C21	−0.1 (6)
Cl1—La1—N3—C13	101.2 (3)	C18—C19—C20—C21	180.0 (4)
Cl3—La1—N3—C13	−107.3 (3)	C19—C20—C21—C22	−0.5 (6)
O1—La1—N3—C24	146.2 (3)	C23—N4—C22—C21	−0.6 (6)
N1—La1—N3—C24	158.9 (2)	La1—N4—C22—C21	−179.8 (3)
N4—La1—N3—C24	−1.2 (2)	C20—C21—C22—N4	0.9 (6)
N2—La1—N3—C24	−152.5 (3)	C22—N4—C23—C19	−0.1 (5)
Cl2—La1—N3—C24	−8.2 (3)	La1—N4—C23—C19	179.1 (3)
Cl1—La1—N3—C24	−78.8 (3)	C22—N4—C23—C24	179.3 (3)

Cl3—La1—N3—C24	72.7 (3)	La1—N4—C23—C24	−1.5 (4)
O1—La1—N4—C22	142.5 (3)	C20—C19—C23—N4	0.5 (5)
N3—La1—N4—C22	−179.5 (3)	C18—C19—C23—N4	−179.6 (3)
N1—La1—N4—C22	31.9 (4)	C20—C19—C23—C24	−179.0 (3)
N2—La1—N4—C22	−125.4 (3)	C18—C19—C23—C24	1.0 (5)
Cl2—La1—N4—C22	−3.6 (3)	C13—N3—C24—C16	0.3 (5)
Cl1—La1—N4—C22	−90.7 (3)	La1—N3—C24—C16	−179.7 (3)
Cl3—La1—N4—C22	83.6 (3)	C13—N3—C24—C23	−179.0 (3)
O1—La1—N4—C23	−36.7 (3)	La1—N3—C24—C23	1.0 (4)
N3—La1—N4—C23	1.3 (2)	C15—C16—C24—N3	−1.2 (5)
N1—La1—N4—C23	−147.3 (2)	C17—C16—C24—N3	178.9 (3)
N2—La1—N4—C23	55.4 (3)	C15—C16—C24—C23	178.1 (3)
Cl2—La1—N4—C23	177.2 (3)	C17—C16—C24—C23	−1.8 (5)
Cl1—La1—N4—C23	90.1 (2)	N4—C23—C24—N3	0.3 (5)
Cl3—La1—N4—C23	−95.6 (3)	C19—C23—C24—N3	179.8 (3)
C12—N2—C1—C2	1.4 (7)	N4—C23—C24—C16	−179.0 (3)
La1—N2—C1—C2	−166.4 (4)	C19—C23—C24—C16	0.4 (5)
N2—C1—C2—C3	−1.1 (8)	La1—O1—C25—N5	−152.2 (3)
C1—C2—C3—C4	−0.6 (8)	C26—N5—C25—O1	−1.7 (6)
C2—C3—C4—C12	1.7 (7)	C27—N5—C25—O1	178.4 (4)
C2—C3—C4—C5	−178.9 (4)	C30—N6—C28—O2	−1.9 (10)
C3—C4—C5—C6	−176.6 (4)	C29—N6—C28—O2	175.0 (7)
C12—C4—C5—C6	2.8 (6)	C32—N7—C31—O3	1.7 (10)
C4—C5—C6—C7	−0.6 (7)	C33—N7—C31—O3	−178.2 (6)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···Cl3^{i}	0.93	2.80	3.662 (5)	155
C14—H14···O2	0.93	2.57	3.322 (6)	139
C22—H22···Cl2	0.93	2.78	3.524 (4)	138
C29—H29A···Cl3^{i}	0.96	2.81	3.766 (6)	176
C29—H29C···O3	0.96	2.42	3.319 (9)	157

Symmetry codes: (i) *x*+1, *y*, *z*.

Fig. 1

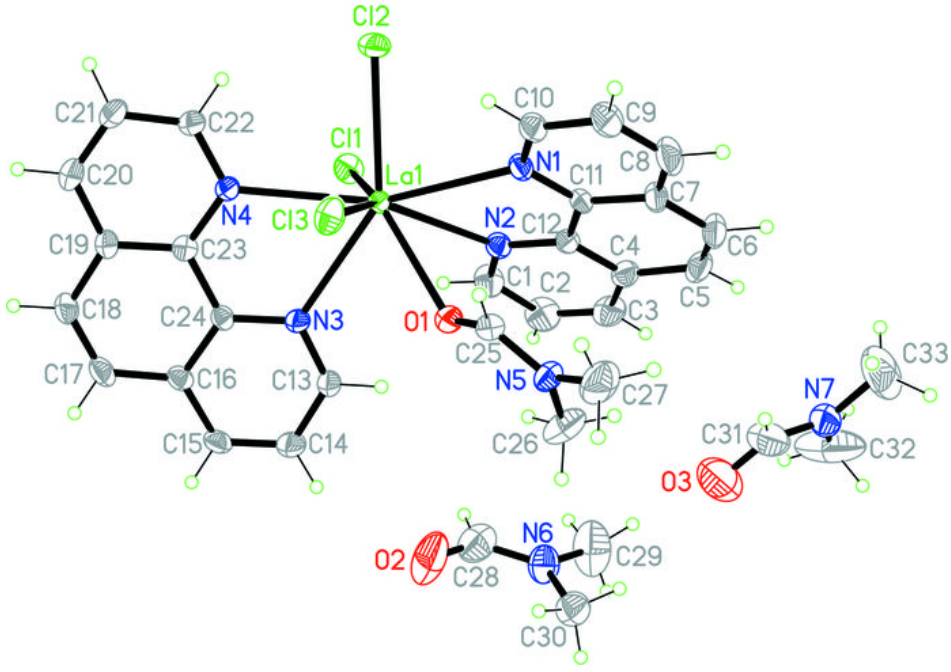
Cl2
C21
C22
Cl1
La1
C10
C9
N1
C8
C11
C7
C20
N4
Cl3
N2
C12
C4
C6
C19
C23
C1
C2
C5
C18
C24
N3
O1
C3
C25
C33
C17
C16
C13
N5
C27
N7
C26
C31
C32
C15
C14
O3
N6
O2
C28
C29
C30

Fig. 2