metal-organic compounds

Acta Crystallographica Section E Structure Reports Online

ISSN 1600-5368

Poly[[tris(μ_2 -4,4'-bipyridine N,N'-dioxide)hexanitratodieuropium(III)] dichloromethane disolvate]

Adam J. Dillner, Cassandra P. Lilly and Jacqueline M. Knaust*

Allegheny College, 520 North Main St., Meadville, PA 16335, USA Correspondence e-mail: jknaust@allegheny.edu

Received 16 August 2010; accepted 18 August 2010

Key indicators: single-crystal X-ray study; T = 100 K; mean σ (C–C) = 0.002 Å; R factor = 0.020; wR factor = 0.050; data-to-parameter ratio = 21.0.

coordination The title one-dimensional network. $\{[Eu_2(NO_3)_6(C_{10}H_8N_2O_2)_3]\cdot 2CH_2Cl_2\}_n$, is isostructural with the previously reported Tb and Tl coordination networks and to its Gd analog. The Eu^{III} cation is coordinated in a distorted tricapped trigonal-prismatic fashion by nine O atoms from three bridging 4,4'-bipyridine N,N'-dioxide ligands and three chelating nitrate anions. None of the atoms lie on a special position, but there is an inversion center located between the rings of one of the ligands. The network topology is ladder-like, and each ladder interacts with six neighboring ladders through $C-H \cdots O$ hydrogen bonds. The packing motif of the ladders allows for the formation of channels that run parallel to the *a* axis; these channels are filled with CH_2Cl_2 solvent molecules that interact with the ladders through C- $H \cdots O$ hydrogen bonds.

Related literature

For the isostructural Tb and Tl coordination networks, see: Long *et al.* (2002); Moitsheki *et al.* (2006). For the isostructural Gd coordination network, see: Dillner *et al.* (2010). For additional discussions on Ln^{+3} (Ln = lanthanide) coordination networks with aromatic N,N° -dioxide ligands, see: Cardoso *et al.* (2001); Hill *et al.* (2005); Long *et al.* (2001); Sun *et al.* (2004). For background information on the applications of coordination networks, see: Roswell & Yaghi (2004); Rosi *et al.* (2003); Seo *et al.* (2000).



Experimental

Crystal data

$$\begin{split} & [\mathrm{Eu}_2(\mathrm{NO}_3)_6(\mathrm{C}_{10}\mathrm{H_8N_2O_2})_3]\cdot 2\mathrm{CH}_2\mathrm{Cl}_2 & \gamma = 78.392~(1)^\circ \\ & M_r = 1410.38 & V = 1163.45~(12)~\text{\AA}^3 \\ & \mathrm{Triclinic}, \ P\overline{1} & Z = 1 & \\ & a = 7.9841~(5)~\text{\AA} & & \mu = 3.00~\mathrm{mm}^{-1} \\ & c = 13.0522~(8)~\text{\AA} & & T = 100~\mathrm{K} \\ & \alpha = 86.013~(1)^\circ & & 0.44\times0.38\times0.32~\mathrm{mm} \\ & \beta = 80.255~(1)^\circ & \end{split}$$

Data collection

```
Bruker SMART APEX CCD
diffractometer
Absorption correction: multi-scan
(SADABS; Bruker, 2009)
T<sub>min</sub> = 0.278, T<sub>max</sub> = 0.383
```

Refinement

334 parameters
H-atom parameters constrained
$\Delta \rho_{\rm max} = 1.30 \text{ e} \text{ Å}^{-3}$
$\Delta \rho_{\rm min} = -0.90 \text{ e } \text{\AA}^{-3}$

Table 1

i jaiogen oona geometri (i i,	Hy	drogen-	bond	geometry	(A, '	°)
-------------------------------	----	---------	------	----------	-------	----

$D - H \cdots A$	D-H	$H \cdot \cdot \cdot A$	$D \cdots A$	$D - \mathbf{H} \cdot \cdot \cdot A$
C5-H5···O7 ⁱ	0.95	2.41	3.081 (2)	128
C9−H9···O9 ⁱⁱ	0.95	2.57	3.286 (2)	132
C12−H12···O2 ⁱⁱⁱ	0.95	2.44	3.309 (2)	152
$C16-H16B\cdots O12^{ii}$	0.99	2.42	3.242 (3)	140
C16-H16A···O8	0.99	2.55	3.307 (3)	133
C16−H16A···O9	0.99	2.50	3.086 (3)	118

Symmetry codes: (i) x + 1, y, z; (ii) -x + 1, -y + 2, -z + 2; (iii) -x + 2, -y + 2, -z + 1.

13873 measured reflections

 $R_{\rm int} = 0.015$

7017 independent reflections

6748 reflections with $I > 2\sigma(I)$

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *X-SEED*.

The authors are thankful to Allegheny College for providing funding in support of this research. The diffractometer was funded by the NSF (grant No. 0087210), the Ohio Board of Regents (grant No. CAP-491) and by Youngstown State University. The authors would like to acknowledge Youngstown State University and the STaRBURSTT Cyber-Instrumentation Consortium for assistance with the crystallography.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZL2302).

References

- Barbour, L. J. (2001). J. Supramol. Chem. 1, 189-191.
- Bruker (2009). APEX2, SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
- Cardoso, M. C. C., Zinner, L. B., Zukerman-Scheptor, J., Araújo Melo, D. M. & Vincentini, G. J. (2001). J. Alloys Compd, 323–324, 22–25.
- Dillner, A. J., Lilly, C. P. & Knaust, J. M. (2010). Acta Cryst. E66, m1158– m1159.
- Hill, R. J., Long, D. L., Champness, N. R., Hubberstry, P. & Schröder, M. (2005). Acc. Chem. Res. 38, 335–348.
- Long, D. L., Blake, A. J., Champness, N. R., Wilson, C. & Schröder, M. (2001). Angew. Chem. Int. Ed. 40, 2444–2447.
- Long, D. L., Blake, A. J., Champness, N. R., Wilson, C. & Schröder, M. (2002). *Chem. Eur. J.* 8, 2026–2033.
- Moitsheki, L. J., Bourne, S. A. & Nassimbeni, L. R. (2006). Acta Cryst. E62, m542-m544.
- Rosi, N. L., Eckert, J., Eddaoudi, M., Vodak, D. T., Kim, J., O'Keeffe, M. & Yaghi, O. M. (2003). *Science*, **300**, 1127–1129.
- Roswell, J. L. C. & Yaghi, O. M. (2004). Microporous Mesoporous Mater. 73, 3– 14.
- Seo, J. S., Whang, D., Lee, H., Jun, S. I., Oh, J., Jin Jeon, Y. J. & Kim, K. (2000). *Nature (London)*, **404**, 982–986.
- Sheldrick, G. M. (2008). Acta Cryst. A64, 112-122.
- Sun, H. L., Gao, S., Ma, B. Q., Chang, F. & Fu, W. F. (2004). Microporous Mesoporous Mater. 73, 89–95.

supporting information

Acta Cryst. (2010). E66, m1156-m1157 [https://doi.org/10.1107/S1600536810033246]

Poly[[tris(μ_2 -4,4'-bipyridine *N*,*N*'-dioxide)hexanitratodieuropium(III)] dichloromethane disolvate]

Adam J. Dillner, Cassandra P. Lilly and Jacqueline M. Knaust

S1. Comment

The synthesis of lanthanide coordination networks has been of recent interest due to the potential of the flexible coordination sphere of the Ln^{+3} metal ions to produce coordination networks with new, unusual, or high connectivity topologies (Hill *et al.*, 2005; Long *et al.*, 2001; and Sun *et al.*, 2004). Coordination networks with both a high connectivity topology and an open framework have potential for applications in areas such as absorption, ion exchange, or catalysis (Roswell *et al.*, 2004; Rosi *et al.*, 2003; and Seo *et al.* 2000). Aromatic *N*,*N*'-dioxide ligands have been attractive candidates for use with Ln^{+3} cations as the O-donor atoms of the ligand are complementary to the hard acid character of the lanthanide cations (Cardoso *et al.*, 2001; Hill *et al.*, 2005; Long *et al.*, 2001; Long *et al.*, 2002; and Sun *et al.*, 2004).

The description of the structure of the title compound is part of a set of consecutive papers on one-dimensional ladderlike coordination networks of the type $[Ln_2(NO_3)_6(C_{10}H_8N_2O_2)_3]_n$, with Ln = Eu (this publication) and Gd (Dillner *et al.*, 2010), respectively. Both compounds are also isostructural to the previously reported Tb and Tl coordination networks (Long *et al.*, 2002 and Moitsheki *et al.*, 2006).

The asymmetric unit of the title compound contains one Eu^{+3} cation, one and a half coordinated 4,4'-bipyridine-N,N'dioxide ligands, three coordinated nitrate anions, and one solvate CH₂Cl₂ molecule. None of the atoms lie on a special position, but there is an inversion center located between the rings of one of the ligands (O1, N1, C1-C5). The Eu^{+3} cation is coordinated in a distorted tricapped trigonal prismatic fashion by nine O atoms (Figure 1). Three bridging 4,4'-bipyridine-N,N'-dioxide ligands contribute three O donor atoms, and three nitrate anions contribute six O donor atoms. The network topology is ladder-like; however the sides and rungs of the ladder meet at angles of 70.09(<1)° (Eu^{i} —Eu— Eu^{iii}) and 108.91(<1)° (Eu^{i} —Eu— Eu^{ii}) forming a parallelogram rather than a square [Symmetry codes: (i) -x+3, -y+1, -z+1; (ii) x, y, z+1; (iii) x, y, z-1] (Figure 2). The ladders run parallel to the *c*-axis and lie in planes that are approximately parallel with the (1 2 0) plane.

Through C-H···O hydrogen bonding interactions the ladders are linked into a three-dimensional structure. Each ladder is linked to two similar ladders that lie in the same plane through four unique C-H···O hydrogen bonds per Eu⁺³ cation (Figure 3). There is one direct interaction between the ladders via a C-H···O hydrogen bond from a 4,4'-bipyridine-N,N'-dioxide ligand of one ladder to the nitrate anion of another ladder, C9—H9···O9^v [Symmetry code:(v) -x+1, -y+2, -z+2]. There is also an indirect interaction between the ladders through hydrogen bonding with the CH₂Cl₂ solvate molecules. Two O atoms of a nitrate ion hydrogen bond with one of the CH₂Cl₂ H atoms, C16—H16A···O8 and C16—H16A···O9; the other H atom of the CH₂Cl₂ molecule then hydrogen bonds with an O atoms of a nitrate ion of the neighboring ladder, C16—H16B···O12^v [Symmetry code:(v) -x+1, -y+2, -z+2]. The ladders are further linked to two neighboring ladders in the layer above and two in the layer below through hydrogen bonding interactions between 4,4'-bipyridine-N,N'-dioxide

ligands, C12—H12···O2^{vi}, and between a 4,4'-bipyridine-N,N'-dioxide ligand and a nitrate anion, C5—H5···O7^{iv} [Symmetry codes:(iv) x+1, y, z; (vi) -x+2, -y+2, -z+1] (Figure 4).

Though the Eu⁺³ cation is nine coordinate, the use of the coordinating nitrate counter ion limits the number of bridging 4,4'-bipyridine-N,N'-dioxide ligands resulting in a one-dimensional coordination network rather than a network with a high connectivity topology. However, the packing motif of the ladders allows for the formation of channels that run parallel to the *a*-axis; these channels are filled with the CH₂Cl₂ solvate molecules (Figure 5). The CH₂Cl₂ molecules interact with the ladders through C—H···O hydrogen bonding as described above.

S2. Experimental

 $Eu(NO_3)_3$ (0.051 g 0.15 mmol) was placed in the bottom of a test tube and covered with CH_2Cl_2 (5 ml). 4,4'-bipyridine-N,N'-dioxide H_2O (0.0376 g, 0.182 mmol) was dissolved in methanol (8 ml), and this solution was layered over the CH_2Cl_2 . The two solutions were allowed to slowly mix. Over a period of several weeks the $Eu(NO_3)_3$ dissolved, and colorless block-like crystals of the title compound formed.

S3. Refinement

All H atoms were positioned geometrically and refined using a riding model with C—H = 0.95 Å and with $U_{iso}(H) = 1.2$ times $U_{eq}(C)$.



Figure 1

The coordination environment of the Eu^{+3} cation in the title compound with atom labels and 50% probability displacement ellipsoids. Hydrogen atoms have been omitted for clarity. Color scheme: Nd: green, C: grey, N: blue, O: red, Cl: yellow. Symmetry codes: (i) -x+3, -y+1, -z+1; (ii) x, y, z+1; (iii) x, y, z-1; (vii) -x+2, -y+1, z+2.

supporting information



Figure 2

Ladder-like network topology seen in the title compound viewed perpendicular to the (1 2 0) plane. The sides and rungs of the ladder meet at angles of $70.09(<1)^{\circ}$ (Euⁱ—Eu—Euⁱⁱⁱ) and $108.91(<1)^{\circ}$ (Euⁱ—Eu—Euⁱⁱ). Hydrogen atoms and solvate molecules have been omitted for clarity. Color scheme: Nd: green, C: grey, N: blue, O: red. Symmetry codes: (i) - x+3, -y+1, -z+1; (ii) x, y, z+1; (iii) x, y, z-1.



Figure 3

C—H···O hydrogen bonding interactions between 4,4'-bipyridine-N,N'-dioxide ligands and between CH₂Cl₂ solvate molecules and nitrate anions. These interactions are responsible for linking together ladders that lie in the same plane. Hydrogen bonds are shown as dashed red lines. Color scheme: Nd: green, C: grey, H: white, N: blue, O: red, Cl: yellow. Symmetry code: (v) -x+1, -y+2, -z+2.



Figure 4

C—H···O hydrogen bonding interactions between 4,4'-bipyridine-N,N'-dioxide ligands, C12—H12···O2^{vi}, and between a 4,4'-bipyridine-N,N'-dioxide ligand and a nitrate anion, C5—H5···O7^{iv}. These interactions link the ladder shown in aqua to the four ladders above and below it that are shown in blue and yellow. Hydrogen bonds are shown as dashed red lines. Symmetry codes: (iv) x+1, y, z; (vi) -x+2, -y+2, -z+1.



Figure 5

Packing of the title compound viewed along the *a*-axis with CH_2Cl_2 solvate molecules represented by van der Waals radii. Color scheme: Nd: green, C: grey, H: white, N: blue, O: red, Cl: yellow.

poly[[tris(μ_2 -4,4'-bipyridine N,N'-dioxide)hexanitratodieuropium(III)] dichloromethane disolvate]

Crystal data	
$[Eu_{2}(NO_{3})_{6}(C_{10}H_{8}N_{2}O_{2})_{3}]\cdot 2CH_{2}Cl_{2}$ $M_{r} = 1410.38$ Trialinia R_{1}	Z = 1 F(000) = 690 $D_{1} = 2.012 \text{ Mg m}^{-3}$
Hall symbol: -P 1 a = 7.9841 (5) Å	$D_x = 2.015$ Mg m ² Mo K α radiation, $\lambda = 0.71073$ Å Cell parameters from 9986 reflections
b = 11.5723 (7) Å c = 13.0522 (8) Å	$\theta = 2.4 - 31.4^{\circ}$ $\mu = 3.00 \text{ mm}^{-1}$
$\begin{aligned} \alpha &= 86.013 (1)^{\circ} \\ \beta &= 80.255 (1)^{\circ} \\ \nu &= 78.392 (1)^{\circ} \end{aligned}$	T = 100 K Block, colourless $0.44 \times 0.38 \times 0.32$ mm
$V = 1163.45 (12) Å^3$	

Data collection

Bruker SMART APEX CCD	13873 measured reflections
Radiation source: fine-focus sealed tube	6748 reflections with $I > 2\sigma(I)$
Graphite monochromator	$R_{\rm int} = 0.015$
ωscans	$\theta_{\text{max}} = 31.5^{\circ}, \ \theta_{\text{min}} = 1.6^{\circ}$
Absorption correction: multi-scan	$h = -11 \rightarrow 11$
(SADABS; Bruker, 2009)	$k = -16 \rightarrow 16$
$T_{\min} = 0.278, T_{\max} = 0.383$	$l = -18 \rightarrow 18$
Refinement	
Refinement on F^2	Secondary atom site location: difference Fourier
Least-squares matrix: full	map
$R[F^2 > 2\sigma(F^2)] = 0.020$	Hydrogen site location: inferred from
$wR(F^2) = 0.050$	neighbouring sites
S = 1.06	H-atom parameters constrained
7017 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0274P)^2 + 0.6833P]$
334 parameters	where $P = (F_o^2 + 2F_c^2)/3$
0 restraints	$(\Delta/\sigma)_{\rm max} = 0.004$
Primary atom site location: structure-invariant	$\Delta \rho_{\rm max} = 1.30 \text{ e} \text{ Å}^{-3}$
direct methods	$\Delta \rho_{\rm min} = -0.90 \text{ e } \text{\AA}^{-3}$

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.

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 $F^2 > 2sigma(F^2)$ 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	у	Ζ	$U_{ m iso}$ */ $U_{ m eq}$	
Eu1	0.777642 (10)	0.833489 (7)	0.717497 (6)	0.01106 (3)	
01	1.02598 (16)	0.82745 (11)	0.59308 (10)	0.0154 (2)	
O2	0.95680 (16)	0.87385 (12)	0.83140 (9)	0.0161 (2)	
03	0.62858 (17)	0.87321 (12)	0.57648 (9)	0.0171 (2)	
04	0.80290 (19)	0.63688 (12)	0.64041 (12)	0.0232 (3)	
05	0.95209 (19)	0.63704 (12)	0.76308 (11)	0.0220 (3)	
06	0.9737 (2)	0.47449 (13)	0.68284 (15)	0.0332 (4)	
O7	0.48093 (17)	0.79129 (13)	0.77651 (10)	0.0201 (3)	
08	0.64275 (17)	0.77354 (13)	0.89511 (10)	0.0202 (3)	
09	0.37320 (17)	0.75544 (13)	0.93758 (11)	0.0227 (3)	
O10	0.80793 (18)	1.04165 (12)	0.66196 (10)	0.0194 (3)	
011	0.59940 (17)	1.02059 (12)	0.78740 (11)	0.0195 (3)	
O12	0.6447 (3)	1.19617 (15)	0.73702 (16)	0.0456 (5)	
N1	1.15666 (18)	0.73751 (13)	0.56743 (11)	0.0133 (3)	
N2	0.92011 (18)	0.86855 (13)	0.93519 (11)	0.0132 (3)	
N3	0.69461 (19)	0.86783 (13)	0.47577 (11)	0.0137 (3)	

N4	0.9118 (2)	0.57887 (14)	0.69524 (14)	0.0197 (3)
N5	0.49525 (19)	0.77188 (13)	0.87204 (12)	0.0150 (3)
N6	0.6829 (2)	1.08969 (14)	0.72861 (13)	0.0205 (3)
C1	1.1740 (3)	0.68713 (17)	0.47511 (14)	0.0203 (4)
H1	1.0935	0.7159	0.4290	0.024*
C2	1.3082 (3)	0.59415 (17)	0.44756 (14)	0.0206 (4)
H2	1.3193	0.5593	0.3824	0.025*
C3	1.4281 (2)	0.55034 (15)	0.51380 (13)	0.0136 (3)
C4	1.4069 (2)	0.60727 (17)	0.60769 (14)	0.0183 (3)
H4	1.4871	0.5816	0.6545	0.022*
C5	1.2711 (2)	0.69995 (17)	0.63285 (14)	0.0188 (3)
Н5	1.2582	0.7376	0.6969	0.023*
C6	0.9832 (2)	0.76980 (16)	0.98827 (14)	0.0158 (3)
H6	1.0515	0.7039	0.9517	0.019*
C7	0.9489 (2)	0.76417 (16)	1.09564 (14)	0.0162 (3)
H7	0.9927	0.6941	1.1327	0.019*
C8	0.8500(2)	0.86102 (15)	1.14977 (13)	0.0130 (3)
C9	0.7874 (2)	0.96184 (15)	1.09182 (13)	0.0147 (3)
H9	0.7201	1.0294	1.1265	0.018*
C10	0.8226 (2)	0.96384 (15)	0.98487 (13)	0.0151 (3)
H10	0.7784	1.0323	0.9459	0.018*
C11	0.7453 (2)	0.96291 (16)	0.42433 (13)	0.0166 (3)
H11	0.7435	1.0314	0.4610	0.020*
C12	0.7997 (2)	0.96088 (16)	0.31839 (13)	0.0161 (3)
H12	0.8336	1.0286	0.2821	0.019*
C13	0.8053 (2)	0.86034 (15)	0.26417 (13)	0.0126 (3)
C14	0.7613 (3)	0.76130 (16)	0.32116 (14)	0.0184 (3)
H14	0.7700	0.6898	0.2872	0.022*
C15	0.7053 (3)	0.76727 (17)	0.42647 (14)	0.0198 (3)
H15	0.6739	0.7000	0.4649	0.024*
C16	0.5593 (3)	0.60128 (19)	1.10281 (18)	0.0274 (4)
H16A	0.5804	0.6067	1.0258	0.033*
H16B	0.5400	0.6821	1.1285	0.033*
Cl1	0.74307 (7)	0.51437 (4)	1.14770 (4)	0.02594 (10)
Cl2	0.37189 (7)	0.54009 (6)	1.14595 (5)	0.03328 (12)
	× /			× /

Atomic displacement parameters $(Å^2)$

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Eu1	0.01154 (4)	0.01311 (4)	0.00801 (4)	-0.00167 (3)	-0.00067 (3)	-0.00117 (3)
01	0.0136 (5)	0.0141 (5)	0.0158 (6)	0.0005 (4)	0.0027 (4)	-0.0023 (4)
02	0.0181 (6)	0.0241 (6)	0.0067 (5)	-0.0068 (5)	0.0001 (4)	-0.0016 (4)
03	0.0172 (6)	0.0261 (7)	0.0070 (5)	-0.0033 (5)	0.0003 (4)	-0.0003 (5)
O4	0.0248 (7)	0.0175 (6)	0.0291 (7)	-0.0008(5)	-0.0117 (6)	-0.0038 (5)
05	0.0253 (7)	0.0188 (6)	0.0216 (7)	0.0000 (5)	-0.0075 (5)	-0.0028 (5)
06	0.0305 (8)	0.0156 (6)	0.0535 (11)	0.0042 (6)	-0.0140 (8)	-0.0097 (7)
O7	0.0183 (6)	0.0307 (7)	0.0133 (6)	-0.0089(5)	-0.0042 (5)	0.0008 (5)
08	0.0147 (6)	0.0315 (7)	0.0159 (6)	-0.0088 (5)	-0.0042 (5)	0.0060 (5)

09	0.0154 (6)	0.0277 (7)	0.0220 (7)	-0.0046 (5)	0.0030 (5)	0.0063 (5)
O10	0.0206 (6)	0.0181 (6)	0.0168 (6)	-0.0015 (5)	0.0019 (5)	-0.0005 (5)
011	0.0192 (6)	0.0187 (6)	0.0179 (6)	-0.0011 (5)	0.0024 (5)	-0.0014 (5)
O12	0.0585 (12)	0.0154 (7)	0.0507 (12)	0.0006 (7)	0.0168 (9)	-0.0023 (7)
N1	0.0121 (6)	0.0134 (6)	0.0132 (6)	-0.0018 (5)	0.0015 (5)	-0.0024 (5)
N2	0.0126 (6)	0.0196 (7)	0.0086 (6)	-0.0060(5)	-0.0007(5)	-0.0018 (5)
N3	0.0141 (6)	0.0183 (7)	0.0085 (6)	-0.0026 (5)	-0.0019 (5)	0.0000 (5)
N4	0.0167 (7)	0.0158 (7)	0.0260 (8)	-0.0026 (6)	-0.0020 (6)	-0.0020 (6)
N5	0.0141 (6)	0.0145 (6)	0.0155 (7)	-0.0026 (5)	-0.0010 (5)	0.0013 (5)
N6	0.0234 (8)	0.0168 (7)	0.0187 (7)	0.0001 (6)	-0.0008 (6)	-0.0004 (6)
C1	0.0230 (9)	0.0223 (9)	0.0137 (8)	0.0040 (7)	-0.0053 (7)	-0.0051 (7)
C2	0.0232 (9)	0.0232 (9)	0.0143 (8)	0.0023 (7)	-0.0052 (7)	-0.0077 (7)
C3	0.0141 (7)	0.0146 (7)	0.0122 (7)	-0.0036 (6)	-0.0003 (6)	-0.0025 (6)
C4	0.0157 (8)	0.0239 (9)	0.0146 (8)	0.0005 (7)	-0.0035 (6)	-0.0062 (7)
C5	0.0161 (8)	0.0239 (9)	0.0161 (8)	-0.0005 (7)	-0.0026 (6)	-0.0081 (7)
C6	0.0159 (7)	0.0172 (7)	0.0137 (7)	-0.0018 (6)	-0.0016 (6)	-0.0024 (6)
C7	0.0172 (8)	0.0162 (7)	0.0139 (7)	-0.0006 (6)	-0.0024 (6)	-0.0010 (6)
C8	0.0129 (7)	0.0167 (7)	0.0095 (7)	-0.0035 (6)	-0.0012 (5)	-0.0002 (6)
C9	0.0161 (7)	0.0151 (7)	0.0113 (7)	-0.0002 (6)	-0.0008 (6)	-0.0014 (6)
C10	0.0171 (7)	0.0162 (7)	0.0112 (7)	-0.0025 (6)	-0.0014 (6)	0.0012 (6)
C11	0.0213 (8)	0.0155 (7)	0.0129 (7)	-0.0038 (6)	-0.0018 (6)	-0.0022 (6)
C12	0.0210 (8)	0.0161 (7)	0.0116 (7)	-0.0058 (6)	-0.0011 (6)	-0.0006 (6)
C13	0.0120 (7)	0.0147 (7)	0.0103 (7)	-0.0010 (6)	-0.0014 (5)	-0.0007 (6)
C14	0.0277 (9)	0.0154 (8)	0.0126 (8)	-0.0049 (7)	-0.0027 (6)	-0.0018 (6)
C15	0.0292 (9)	0.0181 (8)	0.0133 (8)	-0.0087 (7)	-0.0025 (7)	0.0012 (6)
C16	0.0267 (10)	0.0251 (10)	0.0280 (10)	-0.0022 (8)	-0.0047 (8)	0.0073 (8)
Cl1	0.0292 (2)	0.0207 (2)	0.0281 (2)	-0.00046 (18)	-0.01003 (19)	-0.00127 (18)
Cl2	0.0274 (2)	0.0405 (3)	0.0291 (3)	-0.0046 (2)	-0.0018 (2)	0.0059 (2)

Geometric parameters (Å, °)

Eu1—O3	2.3279 (13)	C1—H1	0.9500
Eu1—O1	2.3332 (12)	C2—C3	1.395 (2)
Eu1—O2	2.3579 (12)	С2—Н2	0.9500
Eu1—O11	2.4781 (13)	C3—C4	1.400 (2)
Eu1—O7	2.4979 (13)	C3—C3 ⁱ	1.479 (3)
Eu1—O8	2.4994 (13)	C4—C5	1.376 (2)
Eu1—O5	2.5061 (14)	C4—H4	0.9500
Eu1—O4	2.5090 (14)	С5—Н5	0.9500
Eu1—O10	2.5137 (14)	C6—C7	1.381 (2)
Eu1—N6	2.9160 (16)	С6—Н6	0.9500
Eu1—N5	2.9271 (15)	C7—C8	1.394 (2)
Eu1—N4	2.9424 (16)	С7—Н7	0.9500
01—N1	1.3331 (18)	C8—C9	1.398 (2)
O2—N2	1.3365 (18)	C8—C13 ⁱⁱ	1.475 (2)
O3—N3	1.3316 (18)	C9—C10	1.376 (2)
O4—N4	1.276 (2)	С9—Н9	0.9500
O5—N4	1.268 (2)	C10—H10	0.9500

supporting information

O6—N4	1.220 (2)	C11—C12	1.378 (2)
O7—N5	1.2717 (19)	C11—H11	0.9500
08—N5	1 2680 (19)	C12—C13	1 393 (2)
00 N5	1.2000(1))	C_{12} U_{12}	0.0500
09—N3	1.220(2)		0.9300
010—N6	1.270 (2)	013-014	1.395 (2)
O11—N6	1.276 (2)	$C13-C8^{m}$	1.475 (2)
O12—N6	1.217 (2)	C14—C15	1.374 (2)
N1—C5	1.344 (2)	C14—H14	0.9500
N1—C1	1.349 (2)	С15—Н15	0.9500
N2—C6	1.348 (2)	C16—C11	1.767 (2)
N2-C10	1 351 (2)	C16—C12	1 773 (2)
N3C11	1.345(2)	C16—H16A	0.9900
N2 C15	1.345(2) 1.240(2)		0.9900
	1.349(2)	Сто—птов	0.9900
C1C2	1.376 (3)		
O3—Eu1—O1	85.10 (4)	C5—N1—C1	120.97 (15)
O3—Eu1—O2	154.66 (5)	O2—N2—C6	119.71 (14)
01 - Fu1 - 02	83 73 (4)	$\Omega^2 - N^2 - C_{10}$	118 95 (14)
$03 - F_{11} - 011$	86 31 (5)	C6 N2 C10	121.33(15)
$01 = E_{11} = 011$	122.68(4)	O_{2}^{2} N2 C11	121.35(13) 110.85(14)
O_1 Eu1 O_1	122.06(4)	$O_2 = N_2 = C_{15}$	119.65 (14)
	80.76 (5)	03-N3-C15	119.01 (15)
O3—Eu1—O7	72.54 (4)	CII—N3—CI5	121.12 (15)
O1—Eu1—O7	151.35 (4)	O6—N4—O5	122.25 (17)
O2—Eu1—O7	123.72 (4)	O6—N4—O4	122.21 (17)
O11—Eu1—O7	74.46 (5)	O5—N4—O4	115.54 (15)
O3—Eu1—O8	123.44 (4)	O6—N4—Eu1	177.07 (15)
O1—Eu1—O8	148.50 (4)	O5—N4—Eu1	57.72 (9)
O2—Eu1—O8	74.50 (4)	O4—N4—Eu1	57.89 (9)
011—Eu1—08	76 41 (5)	09—N5—08	122.22 (16)
$07 - F_{11} - 08$	51.03(4)	09 - N5 - 07	122.22(10) 121.86(15)
O_{2}^{2} Eu1 O_{2}^{2}	125 27 (5)	08 N5 07	121.00(13) 115.00(14)
01 En1 05	123.27(5)	$00 \text{ N5} \text{ E}^{-1}$	113.90(14)
01—Eu1—03	79.17 (5)	O_{2} N_{2} E_{1}	1/4.99 (12)
02—Eul—OS	/4.59 (5)	O8—N5—Eul	58.05 (8)
OII—EuI—O5	144.99 (5)	O'/—N5—Eul	58.00 (8)
O7—Eu1—O5	99.04 (5)	O12—N6—O10	122.03 (18)
O8—Eu1—O5	73.32 (5)	012—N6—011	121.27 (17)
O3—Eu1—O4	74.83 (5)	O10—N6—O11	116.70 (15)
O1—Eu1—O4	78.66 (5)	O12—N6—Eu1	177.57 (16)
O2—Eu1—O4	124.69 (5)	O10-N6-Eu1	59.16 (9)
O11—Eu1—O4	150.55 (5)	O11—N6—Eu1	57.57 (9)
O7—Eu1—O4	78.35 (5)	N1—C1—C2	120.10(17)
08—Fu1—O4	95 14 (5)	N1—C1—H1	120.0
05—Fu1—O4	50.81 (5)	C2-C1-H1	120.0
$O_3 = E_{\mu 1} = O_1 O_1 O_2$	76 78 (5)	C_1 C_2 C_3	121.05 (17)
01 = 010	70.70(3)	$C_1 = C_2 = C_3$	121.03(17)
$O_1 = Eu_1 = O_1 O_1 O_1 O_1 O_1 O_1 O_1 O_1 O_1 O_1$	/ 1.43 (4) 79 12 (5)	$C_1 = C_2 = \Pi_2$	119.3
	/8.12 (5)	$C_3 - C_2 - H_2$	119.5
011—Eu1—O10	51.46 (4)	C2—C3—C4	116.71 (16)
O7—Eu1—O10	118.58 (5)	$C2-C3-C3^{1}$	121.90 (19)

124.05 (5)	C4—C3—C3 ⁱ	121.39 (19)
141.62 (5)	C5—C4—C3	120.72 (17)
140.06 (5)	С5—С4—Н4	119.6
81.12 (5)	C3—C4—H4	119.6
96.98 (5)	N1-C5-C4	120.42 (16)
77.77 (5)	N1—C5—H5	119.8
25.77 (4)	С4—С5—Н5	119.8
96.99 (5)	N2—C6—C7	120.21 (16)
100.24 (5)	N2—C6—H6	119.9
152.34 (5)	С7—С6—Н6	119.9
155.82 (5)	C6—C7—C8	120.18 (16)
25.70 (4)	С6—С7—Н7	119.9
97.96 (4)	С8—С7—Н7	119.9
164.53 (4)	C7—C8—C9	117.82 (15)
98.86 (4)	C7—C8—C13 ⁱⁱ	123.07 (15)
72.75 (4)	C9—C8—C13 ⁱⁱ	119.09 (15)
25.58 (4)	C10—C9—C8	120.41 (16)
25.50 (4)	С10—С9—Н9	119.8
86.78 (5)	С8—С9—Н9	119.8
87.47 (5)	N2—C10—C9	120.05 (16)
124.04 (4)	N2—C10—H10	120.0
98.47 (4)	С9—С10—Н10	120.0
100.07 (5)	N3—C11—C12	119.90 (16)
76.92 (4)	N3—C11—H11	120.0
99.44 (5)	C12—C11—H11	120.0
160.06 (5)	C11—C12—C13	120.50 (16)
89.34 (5)	C11—C12—H12	119.7
84.39 (5)	C13—C12—H12	119.7
25.32 (5)	C12—C13—C14	117.84 (15)
25.52 (5)	C12—C13—C8 ⁱⁱⁱ	120.62 (15)
148.34 (5)	C14—C13—C8 ⁱⁱⁱ	121.50 (15)
173.61 (5)	C15—C14—C13	119.88 (16)
87.60 (4)	C15—C14—H14	120.1
129.42 (10)	C13—C14—H14	120.1
125.13 (10)	N3—C15—C14	120.59 (17)
127.65 (10)	N3—C15—H15	119.7
96.59 (10)	C14—C15—H15	119.7
96.97 (10)	Cl1—C16—Cl2	111.26 (12)
96.43 (10)	Cl1—C16—H16A	109.4
96.46 (10)	Cl2—C16—H16A	109.4
95.15 (10)	Cl1—C16—H16B	109.4
96.66 (10)	Cl2—C16—H16B	109.4
119.59 (14)	H16A—C16—H16B	108.0
119.42 (15)		
	124.05 (5) 141.62 (5) 140.06 (5) 81.12 (5) 96.98 (5) 77.77 (5) 25.77 (4) 96.99 (5) 100.24 (5) 152.34 (5) 155.82 (5) 25.70 (4) 97.96 (4) 164.53 (4) 98.86 (4) 72.75 (4) 25.58 (4) 25.50 (4) 86.78 (5) 87.47 (5) 124.04 (4) 98.47 (4) 100.07 (5) 76.92 (4) 99.44 (5) 160.06 (5) 89.34 (5) 84.39 (5) 25.52 (5) 148.34 (5) 173.61 (5) 87.60 (4) 129.42 (10) 125.13 (10) 127.65 (10) 96.46 (10) 95.15 (10) 96.66 (10) 119.59 (14) 119.42 (15)	124.05 (5) $C4-C3-C3^i$ 141.62 (5) $C5-C4-C3$ 140.06 (5) $C5-C4-H4$ 81.12 (5) $C3-C4-H4$ 96.98 (5) N1-C5-C4 77.77 (5) N1-C5-H5 25.77 (4) $C4-C5-H5$ 96.99 (5) N2-C6-C7 100.24 (5) N2-C6-H6 152.34 (5) C7-C6-H6 155.82 (5) C6-C7-C8 25.70 (4) C6-C7-H7 97.96 (4) C8-C7-H7 164.53 (4) C7-C8-C9 98.86 (4) C7-C8-C13 ⁱⁱ 72.75 (4) C9-C8-C13 ⁱⁱ 25.58 (4) C10-C9-H9 86.78 (5) C8-C9-H9 87.47 (5) N2-C10-H10 98.47 (4) C9-C10-H10 100.07 (5) N3-C11-C12 76.92 (4) N3-C11-H11 99.44 (5) C12-C13-H12 89.34 (5) C13-C12-H12 84.39 (5) C13-C12-H12 25.32 (5) C12-C13-C8 ⁱⁱⁱ 173.61 (5) C15-C14-H14 129.42 (10) C13-C14-H14 129.42 (10) C13-C14-H14

Symmetry codes: (i) -*x*+3, -*y*+1, -*z*+1; (ii) *x*, *y*, *z*+1; (iii) *x*, *y*, *z*-1.

D—H···A	<i>D</i> —Н	$H \cdots A$	$D \cdots A$	D—H···A	
C5—H5…O7 ^{iv}	0.95	2.41	3.081 (2)	128	
С9—Н9…О9 [°]	0.95	2.57	3.286 (2)	132	
C12—H12…O2 ^{vi}	0.95	2.44	3.309 (2)	152	
C16—H16 <i>B</i> ···O12 ^v	0.99	2.42	3.242 (3)	140	
C16—H16A…O8	0.99	2.55	3.307 (3)	133	
C16—H16A····O9	0.99	2.50	3.086 (3)	118	

Hydrogen-bond geometry (Å, °)

Symmetry codes: (iv) *x*+1, *y*, *z*; (v) -*x*+1, -*y*+2, -*z*+2; (vi) -*x*+2, -*y*+2, -*z*+1.