# Poly[[dodecaaquabis($\mu_3$-pyridine-2,6-dicarboxylato)tetrakis($\mu_2$-pyridine-2,6-dicarboxylato)tricalcium-dieuropium(III)] 10.5-hydrate]

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In the title compound, $\{[Ca_3Eu_2(C_7H_3NO_4)_6(H_2O)_{12}]\cdot 10.5H_2O\}_n$, the $Eu^{III}$ ion is nine-coordinated by three tridentate pyridine-2,6-dicarboxylate (PDA) ligands, forming a $[Eu(PDA)_3]^{3-}$ building block. The $Ca^{2+}$ ions adopt two types of coordination geometries. One $Ca^{2+}$ ion, lying on a twofold rotation axis, is eight-coordinated by four carboxylate O atoms from four PDA ligands and four water molecules, and the other two $Ca^{2+}$ ions, each lying on an inversion center, are six-coordinated by two carboxylate O atoms from two PDA ligands and four water molecules. The carboxylate groups bridge the $Eu^{III}$ and $Ca^{2+}$ ions into a three-dimensional porous framework, with channels extending along [010] and [001] in which lattice water molecules are located. Two of the lattice water molecules are disordered over two sets of sites with equal occupancy and one water molecule is 0.25-occupied. Numerous O—H···O hydrogen bonds involving the water molecules and carboxylate O atoms are present.

## Related literature

For 3d–4f and 4d–4f metal complexes with pyridine-2,6-dicarboxylate ligands, see: Zhao et al. (2006, 2007, 2011); Zhao, Zhao et al. (2009). For Ln–Ba (Ln = lanthanide) complexes with pyridine-2,6-dicarboxylate ligands, see: Zhao, Zuo et al. (2009).
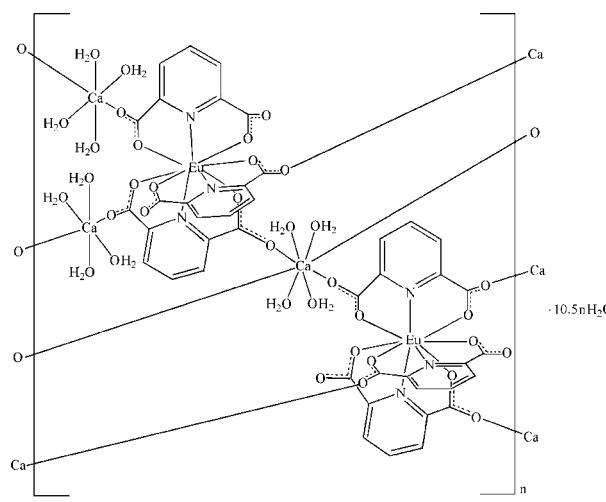
## Experimental

### Crystal data

| | |
|---|---|
| $[Ca_3Eu_2(C_7H_3NO_4)_6(H_2O)_{12}]\cdot 10.5H_2O$ | $\beta = 107.685\,(4)°$ |
| $M_r = 1820.14$ | $V = 3413.5\,(14)$ Å$^3$ |
| Monoclinic, $P2_1/c$ | $Z = 2$ |
| $a = 16.070\,(4)$ Å | Mo $K\alpha$ radiation |
| $b = 9.471\,(2)$ Å | $\mu = 2.16$ mm$^{-1}$ |
| $c = 23.540\,(6)$ Å | $T = 113$ K |
| | $0.20 \times 0.19 \times 0.16$ mm |

### Data collection

| | |
|---|---|
| Rigaku Saturn724 CCD diffractometer | 27531 measured reflections |
| Absorption correction: multi-scan (CrystalClear; Rigaku/MSC, 2009) | 6015 independent reflections |
| | 4964 reflections with $I > 2\sigma(I)$ |
| $T_{min} = 0.672$, $T_{max} = 0.724$ | $R_{int} = 0.054$ |

### Refinement

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)] = 0.042$ | H atoms treated by a mixture of independent and constrained refinement |
| $wR(F^2) = 0.094$ | |
| $S = 1.14$ | |
| 6015 reflections | $\Delta\rho_{max} = 1.31$ e Å$^{-3}$ |
| 531 parameters | $\Delta\rho_{min} = -1.29$ e Å$^{-3}$ |
| 30 restraints | |

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O13—H13A···O10$^i$ | 0.85 (1) | 1.97 (2) | 2.796 (6) | 163 (5) |
| O13—H13B···O20$^{ii}$ | 0.85 (1) | 1.85 (1) | 2.696 (6) | 175 (6) |
| O14—H14A···O16$^{iii}$ | 0.85 (1) | 1.96 (1) | 2.774 (6) | 160 (5) |
| O14—H14B···O9$^{iii}$ | 0.85 (1) | 1.91 (2) | 2.723 (5) | 160 (5) |
| O15—H15A···O21$^{iv}$ | 0.85 (1) | 1.99 (1) | 2.839 (6) | 172 (6) |
| O15—H15B···O5 | 0.85 (1) | 1.90 (1) | 2.734 (5) | 165 (5) |
| O16—H16A···O13$^{iv}$ | 0.78 (6) | 2.38 (7) | 3.079 (6) | 150 (6) |
| O16—H16B···O1$^{iv}$ | 0.84 (6) | 1.88 (7) | 2.704 (6) | 169 (6) |
| O17—H17A···O3$^{iii}$ | 0.85 (1) | 1.91 (1) | 2.745 (6) | 167 (5) |
| O17—H17B···O19$^v$ | 0.85 (1) | 1.93 (3) | 2.722 (7) | 155 (6) |
| O18—H18A···O22'$^{vi}$ | 0.85 (1) | 2.37 (6) | 2.990 (15) | 130 (6) |
| O18—H18A···O22$^{vi}$ | 0.85 (1) | 2.16 (7) | 2.657 (14) | 117 (6) |
| O18—H18B···O4$^{iii}$ | 0.85 (1) | 1.98 (2) | 2.772 (6) | 155 (5) |
| O19—H19A···O24$^{vii}$ | 0.86 (1) | 2.31 (3) | 3.12 (2) | 159 (6) |
| O19—H19B···O7$^{viii}$ | 0.85 (1) | 2.07 (4) | 2.828 (6) | 148 (6) |
| O20—H20A···O15 | 0.85 (1) | 2.04 (2) | 2.862 (6) | 161 (6) |
| O20—H20B···O23 | 0.85 (1) | 2.03 (4) | 2.758 (10) | 143 (6) |

# metal-organic compounds

| $D$—H$\cdots A$ | $D$—H | H$\cdots A$ | $D\cdots A$ | $D$—H$\cdots A$ |
|---|---|---|---|---|
| O20—H20$B\cdots$O22$^{ix}$ | 0.85 (1) | 2.32 (4) | 3.042 (13) | 143 (5) |
| O21—H21$A\cdots$O11 | 0.85 (1) | 1.94 (2) | 2.774 (6) | 167 (6) |
| O21—H21$B\cdots$O17 | 0.85 (1) | 2.42 (4) | 3.113 (7) | 138 (5) |

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

Data collection: *CrystalClear* (Rigaku/MSC, 2009); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HY2534).

## References

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# supporting information

# Poly[[dodecaaquabis(*μ*₃-pyridine-2,6-dicarboxylato)tetrakis(*μ*₂-pyridine-2,6-dicarboxylato)tricalciumdieuropium(III)] 10.5-hydrate]

## Fengjuan Shi, Jiguang Deng and Hongxing Dai

### S1. Comment

Pyridine-2,6-dicarboxylic acid (H₂PDA), as a chelating or bridging ligand, has been proven to be an efficient multidentate ligand to construct multidimensional heterometal-organic frameworks with porous structures. Especially, the lanthanide complexes based on H₂PDA show variable structure characters. The PDA anion chelating to a lanthanide ion possesses free carboxylate oxygen atoms, which can coordinate with transition metals. A systematic study of 3d–4f and 4d–4f complexes based on pyridine-2,6-dicarboxylic acid ligand has been undertaken, such as Ln–Mn (Zhao *et al.*, 2006), Ln–Co (Zhao *et al.*, 2007), Ln–Fe (Zhao *et al.*, 2011) and Ln–Ag (Zhao, Zhao *et al.*, 2009). However, the reports of heterometal-organic frameworks associated with lanthanide and alkaline earth ions are rather rare, only Ln–Ba complexes based on pyridine-2,6-dicarboxylic acid ligand were reported (Zhao, Zuo *et al.*, 2009). In this paper, we report the synthesis and crystal structure of the title compound, using the hydrothermal method with pyridine-2,6-dicarboxylic acid.

In the title compound, the Eu$^{III}$ ion coordinates with three PDA ligands in a tridentate mode, forming a [Eu(PDA)₃]$^{3-}$ building block. The remaining coordination sites in the [Eu(PDA)₃]$^{3-}$ unit coordinate with Ca$^{2+}$ ions. The Ca$^{2+}$ ions adopt two types of coordination geometry, as shown in Fig. 1. The coordination environments of Ca1 and Ca3 atoms are similar, each located on an inversion center and coordinated by two carboxylate O atoms and four water molecules, forming [CaO₂(H₂O)₄] building blocks. Ca2 atom lies on a twofold rotation axis and is coordinated by four carboxylate O atoms from four PDA ligands and four water molecules, forming an eight-coordinated [CaO₄(H₂O)₄] building block. Furthermore, Ca2 and Ca1 atoms are bridged by the same PDA ligand. The overall framework can be viewed as the self-assembly of three types of building blocks, [Eu(PDA)₃], [CaO₂(H₂O)₄] and [CaO₄(H₂O)₄]. Each [Eu(PDA)₃] is surrounded by two [CaO₂(H₂O)₄] units and one [CaO₄(H₂O)₄] unit in its vicinity, while each [CaO₂(H₂O)₄] or [CaO₄(H₂O)₄] unit has two [Eu(PDA)₃] and four [Eu(PDA)₃] units as the nearest neighbors. The linkers are carboxylate groups. As a result of this connection, the [CaO₂(H₂O)₄], [CaO₄(H₂O)₄] and [Eu(PDA)₃] building blocks are connected alternately by carboxylate groups, forming a three-dimensional porous framework, with channels extending along [0 1 0] and [0 0 1] (Fig. 2).

### S2. Experimental

A mixture of pyridine-2,6-dicarboxylic acid (134 mg, 0.8 mmol), calcium hydroxide (52 mg, 0.7 mmol), europium nitrate hexahydrate (89 mg, 0.2 mmol) and deionized water (10 ml) was placed in a 25 ml Teflon-lined stainless steel autoclave, which was kept at 433 K for 3 days. The resuling colorless block-shaped crystals suitable for X-ray diffraction experiment were collected and washed with deionized water and diethyl ether (yield: 170 mg).

### S3. Refinement

H atoms bonded to C atoms were positioned geometrically and refined using a riding model, with C—H = 0.95 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. H atorms of water molecules were found from difference Fourier maps and refined with a distance

restraint of O—H = 0.85 (1) Å and with $U_{iso}(H) = 1.2U_{eq}(O)$. O22 and O23 atoms were disordered over two sets of positions with occupancy factors of 0.5:0.5, respectively. The occupancy factor of the lattice water O24 was set to 0.25. H atorms of disordered water molecules O22, O23 and O24 were not included. The highest residual electron density was found 2.36 Å from H5 atom and the deepest hole 0.78 Å from Eu1 atom.
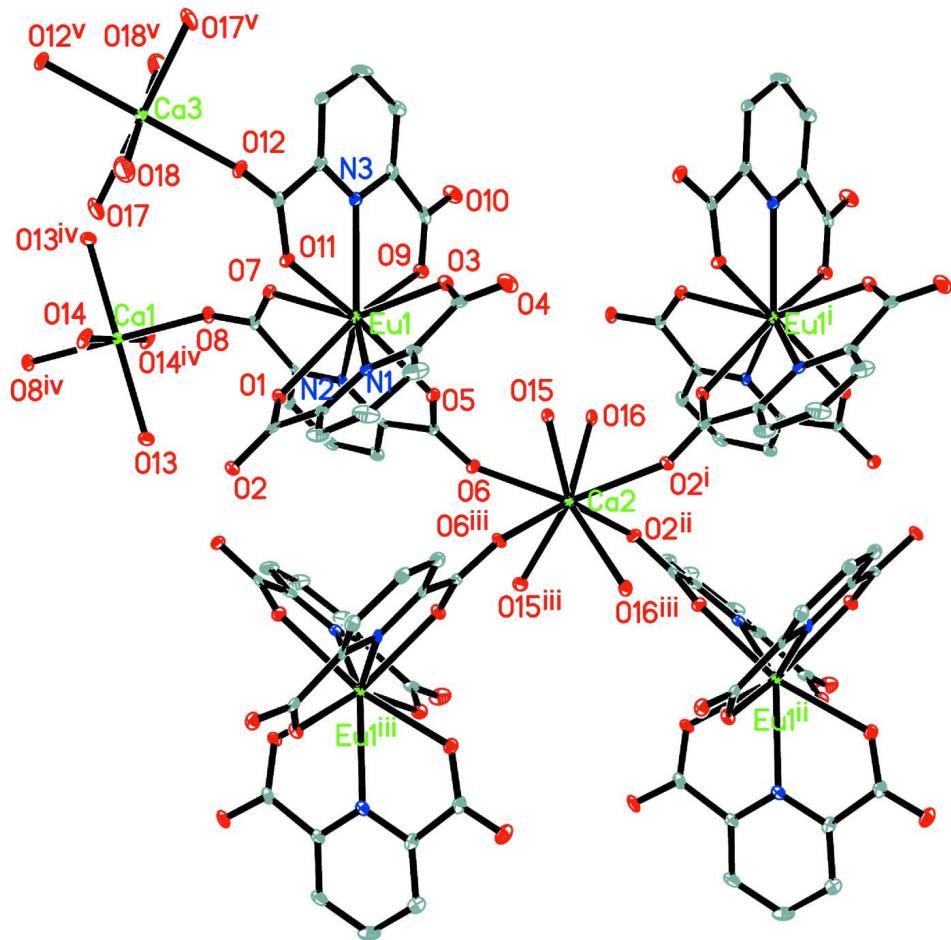


**Figure 1**

The asymmetric unit of the title compound. Displacement ellipsoids are drawn at the 30% probability level. Lattice water molecules and H atoms are omitted and C atoms are not labeled for clarity. [Symmetry codes: (i) $x$, $y+1$, $z$; (ii) $-x+1$, $y+1$, $-z+1/2$; (iii) $-x+1$, $y$, $-z+1/2$; (iv) $-x+1$, $-y$, $-z$; (v) $-x$, $-y$, $-z$.]
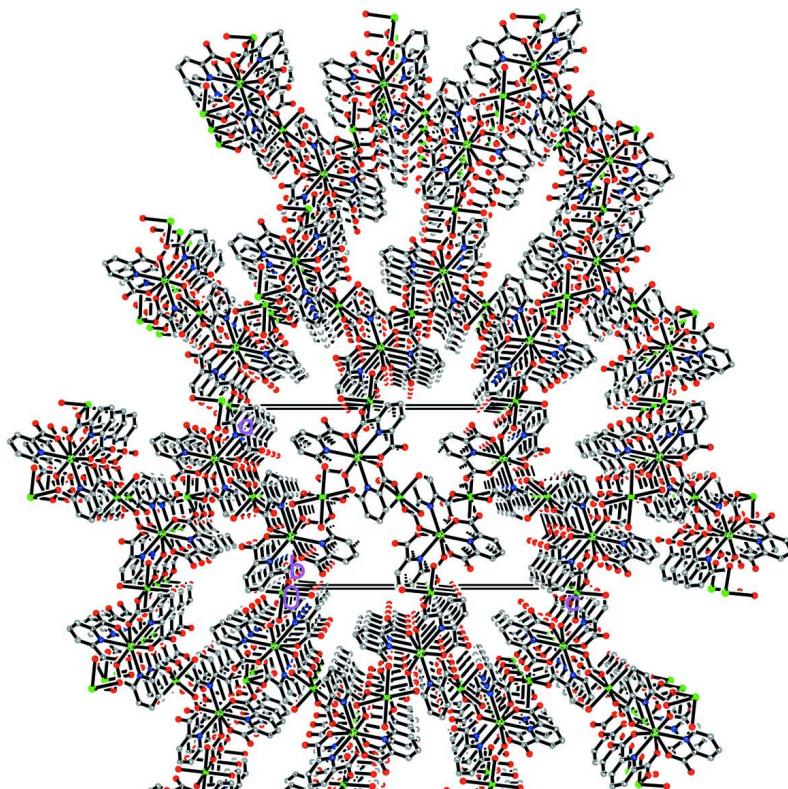
**Figure 2**

The three-dimensional structure of the title compound viewed along the *b* axis. Lattice water molecules and H atoms are omitted for clarity.

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*Crystal data*
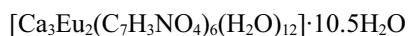
| | |
|---|---|
| [Ca₃Eu₂(C₇H₃NO₄)₆(H₂O)₁₂]·10.5H₂O | $F(000) = 1830$ |
| $M_r = 1820.14$ | $D_x = 1.771$ Mg m⁻³ |
| Monoclinic, $P2/c$ | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| Hall symbol: -P 2yc | Cell parameters from 11834 reflections |
| $a = 16.070$ (4) Å | $\theta = 1.3$–27.9° |
| $b = 9.471$ (2) Å | $\mu = 2.16$ mm⁻¹ |
| $c = 23.540$ (6) Å | $T = 113$ K |
| $\beta = 107.685$ (4)° | Prism, colorless |
| $V = 3413.5$ (14) Å³ | 0.20 × 0.19 × 0.16 mm |
| $Z = 2$ | |

*Data collection*

| | |
|---|---|
| Rigaku Saturn724 CCD diffractometer | Absorption correction: multi-scan (*CrystalClear*; Rigaku/MSC, 2009) |
| Radiation source: rotating anode | $T_{min} = 0.672$, $T_{max} = 0.724$ |
| Multilayer monochromator | 27531 measured reflections |
| Detector resolution: 14.22 pixels mm⁻¹ | 6015 independent reflections |
| $\omega$ and $\varphi$ scans | 4964 reflections with $I > 2\sigma(I)$ |
| | $R_{int} = 0.054$ |

$\theta_{max} = 25.0°$, $\theta_{min} = 1.3°$

$h = -18 \rightarrow 19$

$k = -10 \rightarrow 11$

$l = -28 \rightarrow 28$

*Refinement*

Refinement on $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.042$

$wR(F^2) = 0.094$

$S = 1.14$

6015 reflections

531 parameters

30 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0212P)^2 + 16.8621P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.002$

$\Delta\rho_{max} = 1.31$ e Å$^{-3}$

$\Delta\rho_{min} = -1.29$ e Å$^{-3}$

*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* | $U_{iso}$*/$U_{eq}$ | Occ. (<1) |
|---|---|---|---|---|---|
| Eu1 | 0.296251 (16) | 0.50554 (3) | 0.097315 (11) | 0.00952 (9) | |
| Ca1 | 0.5000 | 0.0000 | 0.0000 | 0.0113 (3) | |
| Ca2 | 0.5000 | 1.00350 (17) | 0.2500 | 0.0138 (3) | |
| Ca3 | 0.0000 | 0.0000 | 0.0000 | 0.0198 (4) | |
| O1 | 0.3736 (2) | 0.3233 (4) | 0.16621 (16) | 0.0151 (8) | |
| O2 | 0.4013 (3) | 0.2000 (4) | 0.25127 (16) | 0.0182 (9) | |
| O3 | 0.1929 (2) | 0.6789 (4) | 0.11297 (16) | 0.0174 (9) | |
| O4 | 0.1130 (3) | 0.7722 (5) | 0.16683 (18) | 0.0282 (11) | |
| O5 | 0.3886 (2) | 0.6872 (4) | 0.15705 (16) | 0.0149 (8) | |
| O6 | 0.5155 (2) | 0.8058 (4) | 0.18919 (16) | 0.0158 (9) | |
| O7 | 0.3344 (2) | 0.3313 (4) | 0.03339 (16) | 0.0140 (8) | |
| O8 | 0.4335 (2) | 0.2095 (4) | 0.00428 (16) | 0.0169 (9) | |
| O9 | 0.2999 (2) | 0.6871 (4) | 0.02212 (16) | 0.0162 (9) | |
| O10 | 0.2495 (3) | 0.7858 (4) | −0.06830 (18) | 0.0243 (10) | |
| O11 | 0.1823 (2) | 0.3273 (4) | 0.08688 (16) | 0.0159 (9) | |
| O12 | 0.0604 (3) | 0.2142 (4) | 0.03527 (18) | 0.0205 (9) | |
| O13 | 0.6116 (2) | 0.0662 (4) | 0.08852 (17) | 0.0185 (9) | |
| H13A | 0.647 (2) | 0.113 (5) | 0.075 (2) | 0.022* | |
| H13B | 0.639 (3) | 0.012 (5) | 0.1167 (18) | 0.022* | |
| O14 | 0.4145 (3) | −0.0939 (4) | 0.05348 (17) | 0.0222 (10) | |
| H14A | 0.419 (4) | −0.043 (5) | 0.0840 (16) | 0.027* | |
| H14B | 0.380 (3) | −0.162 (4) | 0.052 (2) | 0.027* | |

| | | | | |
|---|---|---|---|---|
| O15 | 0.3478 (3) | 0.9194 (4) | 0.21233 (17) | 0.0204 (9) |
| H15A | 0.306 (3) | 0.974 (5) | 0.194 (2) | 0.025* |
| H15B | 0.354 (4) | 0.854 (4) | 0.1894 (18) | 0.025* |
| O16 | 0.4648 (3) | 1.0983 (4) | 0.14661 (18) | 0.0165 (9) |
| H16A | 0.504 (4) | 1.121 (7) | 0.135 (3) | 0.020* |
| H16B | 0.437 (4) | 1.172 (7) | 0.148 (3) | 0.020* |
| O17 | 0.1405 (3) | −0.0914 (5) | 0.0396 (2) | 0.0314 (11) |
| H17A | 0.164 (3) | −0.161 (4) | 0.061 (3) | 0.038* |
| H17B | 0.179 (3) | −0.033 (5) | 0.036 (3) | 0.038* |
| O18 | −0.0140 (3) | −0.0554 (5) | 0.0933 (2) | 0.0391 (12) |
| H18A | −0.0678 (13) | −0.048 (7) | 0.090 (3) | 0.047* |
| H18B | 0.011 (3) | −0.118 (6) | 0.118 (3) | 0.047* |
| N1 | 0.2624 (3) | 0.4885 (5) | 0.19488 (18) | 0.0125 (9) |
| N2 | 0.4526 (3) | 0.5088 (4) | 0.09633 (18) | 0.0106 (9) |
| N3 | 0.1693 (3) | 0.5085 (5) | 0.00041 (19) | 0.0132 (9) |
| C1 | 0.3627 (4) | 0.2941 (6) | 0.2164 (2) | 0.0140 (12) |
| C2 | 0.2960 (4) | 0.3823 (6) | 0.2330 (2) | 0.0158 (12) |
| C3 | 0.2680 (4) | 0.3533 (7) | 0.2820 (2) | 0.0227 (14) |
| H3 | 0.2916 | 0.2765 | 0.3078 | 0.027* |
| C4 | 0.2045 (4) | 0.4396 (8) | 0.2922 (3) | 0.0292 (16) |
| H4 | 0.1838 | 0.4223 | 0.3253 | 0.035* |
| C5 | 0.1711 (4) | 0.5518 (7) | 0.2539 (3) | 0.0281 (16) |
| H5 | 0.1283 | 0.6128 | 0.2608 | 0.034* |
| C6 | 0.2015 (4) | 0.5727 (6) | 0.2057 (2) | 0.0184 (13) |
| C7 | 0.1659 (4) | 0.6849 (6) | 0.1585 (2) | 0.0170 (13) |
| C8 | 0.4686 (4) | 0.7088 (6) | 0.1610 (2) | 0.0124 (12) |
| C9 | 0.5084 (3) | 0.6070 (5) | 0.1267 (2) | 0.0119 (12) |
| C10 | 0.5932 (4) | 0.6158 (6) | 0.1249 (2) | 0.0169 (12) |
| H10 | 0.6311 | 0.6876 | 0.1464 | 0.020* |
| C11 | 0.6218 (4) | 0.5190 (6) | 0.0915 (2) | 0.0182 (13) |
| H11 | 0.6800 | 0.5233 | 0.0896 | 0.022* |
| C12 | 0.5646 (4) | 0.4142 (6) | 0.0603 (2) | 0.0165 (12) |
| H12 | 0.5832 | 0.3458 | 0.0372 | 0.020* |
| C13 | 0.4797 (3) | 0.4130 (5) | 0.0640 (2) | 0.0116 (12) |
| C14 | 0.4114 (4) | 0.3098 (6) | 0.0316 (2) | 0.0134 (12) |
| C15 | 0.2437 (4) | 0.7017 (6) | −0.0285 (3) | 0.0172 (13) |
| C16 | 0.1646 (4) | 0.6081 (6) | −0.0416 (2) | 0.0147 (12) |
| C17 | 0.0927 (4) | 0.6196 (6) | −0.0923 (2) | 0.0192 (13) |
| H17 | 0.0898 | 0.6920 | −0.1207 | 0.023* |
| C18 | 0.0254 (4) | 0.5236 (7) | −0.1002 (3) | 0.0258 (15) |
| H18 | −0.0243 | 0.5285 | −0.1346 | 0.031* |
| C19 | 0.0312 (4) | 0.4197 (6) | −0.0574 (3) | 0.0207 (14) |
| H19 | −0.0142 | 0.3524 | −0.0622 | 0.025* |
| C20 | 0.1038 (3) | 0.4157 (6) | −0.0079 (2) | 0.0137 (12) |
| C21 | 0.1156 (4) | 0.3100 (6) | 0.0415 (2) | 0.0149 (12) |
| O19 | 0.2379 (3) | 0.0820 (5) | 0.9928 (2) | 0.0386 (12) |
| H19A | 0.211 (4) | 0.121 (6) | 0.9594 (17) | 0.046* |
| H19B | 0.282 (3) | 0.132 (6) | 1.011 (2) | 0.046* |

| | | | | | |
|---|---|---|---|---|---|
| O20 | 0.2972 (3) | 0.9062 (5) | 0.3187 (2) | 0.0351 (12) | |
| H20A | 0.314 (4) | 0.890 (7) | 0.2883 (16) | 0.042* | |
| H20B | 0.253 (3) | 0.960 (6) | 0.309 (2) | 0.042* | |
| O21 | 0.1986 (3) | 0.0862 (5) | 0.15634 (18) | 0.0290 (11) | |
| H21A | 0.196 (4) | 0.152 (4) | 0.1311 (18) | 0.035* | |
| H21B | 0.176 (4) | 0.011 (3) | 0.139 (2) | 0.035* | |
| O22 | 0.1015 (10) | 0.9136 (14) | 0.8459 (6) | 0.049 (4) | 0.50 |
| O23 | 0.1373 (5) | 0.9971 (10) | 0.2459 (3) | 0.030 (2) | 0.50 |
| O22′ | 0.1367 (9) | 0.9633 (14) | 0.8406 (7) | 0.049 (4) | 0.50 |
| O23′ | 0.0826 (8) | 1.1594 (14) | 0.2299 (5) | 0.066 (4) | 0.50 |
| O24 | 0.8088 (12) | 0.744 (2) | 0.1251 (9) | 0.039 (5) | 0.25 |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Eu1 | 0.00769 (14) | 0.00855 (14) | 0.01199 (14) | −0.00043 (12) | 0.00250 (10) | −0.00100 (12) |
| Ca1 | 0.0110 (7) | 0.0095 (7) | 0.0141 (7) | 0.0012 (7) | 0.0049 (6) | −0.0014 (7) |
| Ca2 | 0.0153 (8) | 0.0103 (8) | 0.0120 (7) | 0.000 | −0.0018 (6) | 0.000 |
| Ca3 | 0.0147 (8) | 0.0103 (8) | 0.0264 (9) | −0.0014 (7) | −0.0059 (7) | −0.0002 (7) |
| O1 | 0.015 (2) | 0.014 (2) | 0.016 (2) | 0.0042 (16) | 0.0041 (16) | −0.0006 (16) |
| O2 | 0.021 (2) | 0.014 (2) | 0.015 (2) | 0.0040 (17) | −0.0005 (17) | 0.0014 (17) |
| O3 | 0.014 (2) | 0.018 (2) | 0.020 (2) | 0.0036 (17) | 0.0044 (17) | −0.0012 (17) |
| O4 | 0.023 (2) | 0.036 (3) | 0.025 (2) | 0.016 (2) | 0.0068 (19) | −0.003 (2) |
| O5 | 0.009 (2) | 0.014 (2) | 0.021 (2) | −0.0012 (16) | 0.0038 (16) | −0.0036 (16) |
| O6 | 0.010 (2) | 0.013 (2) | 0.022 (2) | −0.0035 (16) | 0.0008 (16) | −0.0036 (17) |
| O7 | 0.012 (2) | 0.013 (2) | 0.018 (2) | −0.0009 (16) | 0.0071 (16) | −0.0035 (16) |
| O8 | 0.023 (2) | 0.013 (2) | 0.017 (2) | 0.0045 (17) | 0.0090 (17) | −0.0017 (16) |
| O9 | 0.014 (2) | 0.016 (2) | 0.018 (2) | 0.0002 (17) | 0.0050 (17) | 0.0032 (16) |
| O10 | 0.021 (2) | 0.026 (2) | 0.027 (2) | 0.0012 (19) | 0.0096 (19) | 0.0131 (19) |
| O11 | 0.010 (2) | 0.015 (2) | 0.020 (2) | −0.0034 (16) | 0.0012 (17) | −0.0025 (16) |
| O12 | 0.015 (2) | 0.013 (2) | 0.032 (2) | −0.0064 (17) | 0.0043 (18) | −0.0052 (17) |
| O13 | 0.015 (2) | 0.021 (2) | 0.018 (2) | −0.0004 (18) | 0.0024 (17) | 0.0034 (17) |
| O14 | 0.033 (3) | 0.018 (2) | 0.019 (2) | −0.0128 (19) | 0.014 (2) | −0.0057 (17) |
| O15 | 0.019 (2) | 0.013 (2) | 0.023 (2) | 0.0057 (18) | −0.0025 (18) | −0.0045 (17) |
| O16 | 0.019 (2) | 0.010 (2) | 0.020 (2) | 0.0020 (18) | 0.0057 (18) | −0.0018 (17) |
| O17 | 0.015 (2) | 0.016 (2) | 0.061 (3) | 0.0024 (18) | 0.007 (2) | 0.014 (2) |
| O18 | 0.042 (3) | 0.028 (3) | 0.046 (3) | 0.007 (2) | 0.012 (3) | 0.005 (2) |
| N1 | 0.010 (2) | 0.013 (2) | 0.014 (2) | −0.001 (2) | 0.0023 (18) | −0.005 (2) |
| N2 | 0.012 (2) | 0.006 (2) | 0.014 (2) | −0.001 (2) | 0.0042 (18) | 0.0029 (19) |
| N3 | 0.011 (2) | 0.013 (2) | 0.017 (2) | 0.000 (2) | 0.0055 (18) | −0.004 (2) |
| C1 | 0.017 (3) | 0.012 (3) | 0.011 (3) | −0.008 (2) | 0.001 (2) | −0.003 (2) |
| C2 | 0.011 (3) | 0.018 (3) | 0.015 (3) | −0.003 (2) | −0.002 (2) | −0.006 (2) |
| C3 | 0.019 (3) | 0.034 (4) | 0.014 (3) | −0.003 (3) | 0.003 (3) | 0.003 (3) |
| C4 | 0.017 (3) | 0.052 (4) | 0.019 (3) | 0.004 (3) | 0.008 (3) | 0.005 (3) |
| C5 | 0.016 (3) | 0.052 (4) | 0.019 (3) | 0.001 (3) | 0.009 (3) | −0.010 (3) |
| C6 | 0.009 (3) | 0.023 (3) | 0.019 (3) | −0.001 (2) | −0.003 (2) | −0.007 (2) |
| C7 | 0.010 (3) | 0.022 (3) | 0.017 (3) | 0.001 (3) | 0.001 (2) | −0.007 (2) |
| C8 | 0.014 (3) | 0.010 (3) | 0.011 (3) | 0.000 (2) | 0.001 (2) | 0.002 (2) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C9 | 0.010 (3) | 0.009 (3) | 0.016 (3) | 0.002 (2) | 0.002 (2) | 0.005 (2) |
| C10 | 0.013 (3) | 0.018 (3) | 0.020 (3) | −0.001 (2) | 0.004 (2) | 0.005 (2) |
| C11 | 0.012 (3) | 0.020 (3) | 0.022 (3) | 0.005 (2) | 0.005 (2) | 0.008 (2) |
| C12 | 0.015 (3) | 0.015 (3) | 0.021 (3) | 0.004 (2) | 0.009 (2) | 0.003 (2) |
| C13 | 0.012 (3) | 0.008 (3) | 0.015 (3) | 0.004 (2) | 0.005 (2) | 0.006 (2) |
| C14 | 0.017 (3) | 0.010 (3) | 0.013 (3) | 0.002 (2) | 0.006 (2) | 0.005 (2) |
| C15 | 0.020 (3) | 0.012 (3) | 0.023 (3) | 0.007 (2) | 0.010 (3) | 0.001 (2) |
| C16 | 0.015 (3) | 0.014 (3) | 0.019 (3) | 0.006 (2) | 0.012 (2) | 0.001 (2) |
| C17 | 0.015 (3) | 0.025 (3) | 0.020 (3) | 0.004 (3) | 0.008 (3) | 0.003 (3) |
| C18 | 0.014 (3) | 0.039 (4) | 0.020 (3) | 0.007 (3) | −0.002 (2) | −0.002 (3) |
| C19 | 0.013 (3) | 0.018 (3) | 0.025 (3) | 0.000 (3) | −0.002 (3) | −0.009 (3) |
| C20 | 0.011 (3) | 0.013 (3) | 0.019 (3) | 0.000 (2) | 0.006 (2) | −0.006 (2) |
| C21 | 0.013 (3) | 0.010 (3) | 0.023 (3) | 0.000 (2) | 0.008 (3) | −0.004 (2) |
| O19 | 0.032 (3) | 0.038 (3) | 0.048 (3) | −0.013 (2) | 0.014 (2) | −0.013 (2) |
| O20 | 0.038 (3) | 0.035 (3) | 0.031 (3) | 0.010 (2) | 0.008 (2) | −0.011 (2) |
| O21 | 0.029 (3) | 0.016 (2) | 0.031 (3) | −0.002 (2) | −0.007 (2) | 0.0055 (19) |
| O22 | 0.070 (11) | 0.046 (9) | 0.048 (7) | 0.012 (7) | 0.041 (7) | 0.017 (6) |
| O23 | 0.023 (5) | 0.048 (6) | 0.017 (4) | −0.007 (5) | 0.003 (4) | −0.005 (4) |
| O22′ | 0.040 (8) | 0.041 (8) | 0.071 (9) | −0.001 (6) | 0.025 (6) | 0.026 (6) |
| O23′ | 0.068 (8) | 0.085 (10) | 0.045 (7) | −0.036 (7) | 0.018 (6) | −0.015 (6) |
| O24 | 0.034 (6) | 0.040 (6) | 0.043 (6) | 0.003 (5) | 0.013 (5) | 0.003 (5) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Eu1—O5 | 2.423 (4) | O14—H14A | 0.85 (1) |
| Eu1—O7 | 2.434 (4) | O14—H14B | 0.85 (1) |
| Eu1—O1 | 2.435 (4) | O15—H15A | 0.85 (1) |
| Eu1—O3 | 2.441 (4) | O15—H15B | 0.85 (1) |
| Eu1—O11 | 2.447 (4) | O16—H16A | 0.78 (6) |
| Eu1—O9 | 2.481 (4) | O16—H16B | 0.84 (6) |
| Eu1—N2 | 2.520 (4) | O17—H17A | 0.85 (1) |
| Eu1—N1 | 2.521 (4) | O17—H17B | 0.85 (1) |
| Eu1—N3 | 2.557 (4) | O18—H18A | 0.85 (1) |
| Ca1—O8ⁱ | 2.270 (4) | O18—H18B | 0.85 (1) |
| Ca1—O8 | 2.270 (4) | N1—C6 | 1.345 (7) |
| Ca1—O14ⁱ | 2.305 (4) | N1—C2 | 1.347 (7) |
| Ca1—O14 | 2.305 (4) | N2—C9 | 1.338 (7) |
| Ca1—O13ⁱ | 2.383 (4) | N2—C13 | 1.340 (7) |
| Ca1—O13 | 2.383 (4) | N3—C20 | 1.339 (7) |
| Ca1—H13A | 2.70 (5) | N3—C16 | 1.353 (7) |
| Ca1—H14A | 2.70 (4) | C1—C2 | 1.501 (8) |
| Ca2—O6ⁱⁱ | 2.415 (4) | C2—C3 | 1.387 (8) |
| Ca2—O6 | 2.415 (4) | C3—C4 | 1.383 (9) |
| Ca2—O2ⁱⁱⁱ | 2.451 (4) | C3—H3 | 0.9500 |
| Ca2—O2ⁱᵛ | 2.451 (4) | C4—C5 | 1.391 (9) |
| Ca2—O15ⁱⁱ | 2.466 (4) | C4—H4 | 0.9500 |
| Ca2—O15 | 2.466 (4) | C5—C6 | 1.379 (8) |
| Ca2—O16ⁱⁱ | 2.493 (4) | C5—H5 | 0.9500 |

| | | | |
|---|---|---|---|
| Ca2—O16 | 2.493 (4) | C6—C7 | 1.519 (8) |
| Ca2—H15B | 2.74 (5) | C8—C9 | 1.519 (7) |
| Ca3—O12 | 2.292 (4) | C9—C10 | 1.378 (8) |
| Ca3—O12$^v$ | 2.292 (4) | C10—C11 | 1.375 (8) |
| Ca3—O17$^v$ | 2.332 (4) | C10—H10 | 0.9500 |
| Ca3—O17 | 2.332 (4) | C11—C12 | 1.400 (8) |
| Ca3—O18 | 2.334 (5) | C11—H11 | 0.9500 |
| Ca3—O18$^v$ | 2.334 (5) | C12—C13 | 1.392 (8) |
| Ca3—H17B | 2.76 (4) | C12—H12 | 0.9500 |
| Ca3—H18A | 2.70 (5) | C13—C14 | 1.495 (8) |
| O1—C1 | 1.276 (6) | C15—C16 | 1.502 (8) |
| O2—C1 | 1.243 (6) | C16—C17 | 1.390 (8) |
| O2—Ca2$^{vi}$ | 2.451 (4) | C17—C18 | 1.381 (8) |
| O3—C7 | 1.274 (7) | C17—H17 | 0.9500 |
| O4—C7 | 1.243 (7) | C18—C19 | 1.392 (9) |
| O5—C8 | 1.277 (6) | C18—H18 | 0.9500 |
| O6—C8 | 1.244 (6) | C19—C20 | 1.375 (8) |
| O7—C14 | 1.267 (6) | C19—H19 | 0.9500 |
| O8—C14 | 1.257 (6) | C20—C21 | 1.501 (8) |
| O9—C15 | 1.266 (7) | O19—H19A | 0.86 (1) |
| O10—C15 | 1.254 (7) | O19—H19B | 0.85 (1) |
| O11—C21 | 1.274 (6) | O20—H20A | 0.85 (1) |
| O12—C21 | 1.247 (7) | O20—H20B | 0.85 (1) |
| O13—H13A | 0.85 (1) | O21—H21A | 0.85 (1) |
| O13—H13B | 0.85 (1) | O21—H21B | 0.85 (1) |
| | | | |
| O5—Eu1—O7 | 127.97 (12) | O12$^v$—Ca3—H17B | 107.2 (11) |
| O5—Eu1—O1 | 91.03 (12) | O17$^v$—Ca3—H17B | 163.3 (7) |
| O7—Eu1—O1 | 75.97 (12) | O17—Ca3—H17B | 16.7 (7) |
| O5—Eu1—O3 | 76.07 (12) | O18—Ca3—H17B | 94.3 (12) |
| O7—Eu1—O3 | 149.31 (12) | O18$^v$—Ca3—H17B | 85.7 (12) |
| O1—Eu1—O3 | 127.54 (13) | O12—Ca3—H18A | 95.3 (15) |
| O5—Eu1—O11 | 148.83 (13) | O12$^v$—Ca3—H18A | 84.7 (15) |
| O7—Eu1—O11 | 77.98 (12) | O17$^v$—Ca3—H18A | 78.7 (7) |
| O1—Eu1—O11 | 78.07 (12) | O17—Ca3—H18A | 101.3 (7) |
| O3—Eu1—O11 | 87.52 (13) | O18—Ca3—H18A | 17.5 (8) |
| O5—Eu1—O9 | 77.22 (12) | O18$^v$—Ca3—H18A | 162.5 (8) |
| O7—Eu1—O9 | 87.93 (12) | H17B—Ca3—H18A | 111.7 (14) |
| O1—Eu1—O9 | 148.04 (13) | C1—O1—Eu1 | 125.7 (3) |
| O3—Eu1—O9 | 78.80 (13) | C1—O2—Ca2$^{vi}$ | 137.0 (4) |
| O11—Eu1—O9 | 125.83 (12) | C7—O3—Eu1 | 125.3 (3) |
| O5—Eu1—N2 | 63.91 (13) | C8—O5—Eu1 | 125.6 (3) |
| O7—Eu1—N2 | 64.10 (13) | C8—O6—Ca2 | 137.2 (4) |
| O1—Eu1—N2 | 72.89 (13) | C14—O7—Eu1 | 124.2 (3) |
| O3—Eu1—N2 | 135.96 (13) | C14—O8—Ca1 | 153.3 (3) |
| O11—Eu1—N2 | 136.48 (13) | C15—O9—Eu1 | 125.7 (4) |
| O9—Eu1—N2 | 75.26 (13) | C21—O11—Eu1 | 125.9 (3) |
| O5—Eu1—N1 | 77.31 (13) | C21—O12—Ca3 | 153.5 (4) |

| | | | |
|---|---|---|---|
| O7—Eu1—N1 | 133.20 (13) | Ca1—O13—H13A | 103 (4) |
| O1—Eu1—N1 | 63.64 (13) | Ca1—O13—H13B | 127 (4) |
| O3—Eu1—N1 | 63.93 (13) | H13A—O13—H13B | 111 (4) |
| O11—Eu1—N1 | 71.66 (13) | Ca1—O14—H14A | 109 (3) |
| O9—Eu1—N1 | 138.80 (13) | Ca1—O14—H14B | 141 (3) |
| N2—Eu1—N1 | 120.06 (13) | H14A—O14—H14B | 111 (5) |
| O5—Eu1—N3 | 133.78 (14) | Ca2—O15—H15A | 122 (4) |
| O7—Eu1—N3 | 74.84 (13) | Ca2—O15—H15B | 99 (4) |
| O1—Eu1—N3 | 135.19 (13) | H15A—O15—H15B | 110 (5) |
| O3—Eu1—N3 | 74.49 (13) | Ca2—O16—H16A | 118 (5) |
| O11—Eu1—N3 | 63.13 (13) | Ca2—O16—H16B | 103 (4) |
| O9—Eu1—N3 | 62.70 (13) | H16A—O16—H16B | 106 (6) |
| N2—Eu1—N3 | 121.28 (13) | Ca3—O17—H17A | 137 (4) |
| N1—Eu1—N3 | 118.61 (14) | Ca3—O17—H17B | 111 (4) |
| O8<sup>i</sup>—Ca1—O8 | 179.999 (2) | H17A—O17—H17B | 111 (5) |
| O8<sup>i</sup>—Ca1—O14<sup>i</sup> | 86.94 (14) | Ca3—O18—H18A | 107 (4) |
| O8—Ca1—O14<sup>i</sup> | 93.06 (14) | Ca3—O18—H18B | 131 (5) |
| O8<sup>i</sup>—Ca1—O14 | 93.07 (14) | H18A—O18—H18B | 112 (6) |
| O8—Ca1—O14 | 86.93 (14) | C6—N1—C2 | 119.0 (5) |
| O14<sup>i</sup>—Ca1—O14 | 180.0 | C6—N1—Eu1 | 120.3 (4) |
| O8<sup>i</sup>—Ca1—O13<sup>i</sup> | 88.30 (14) | C2—N1—Eu1 | 120.0 (4) |
| O8—Ca1—O13<sup>i</sup> | 91.70 (14) | C9—N2—C13 | 119.5 (5) |
| O14<sup>i</sup>—Ca1—O13<sup>i</sup> | 92.24 (14) | C9—N2—Eu1 | 120.8 (3) |
| O14—Ca1—O13<sup>i</sup> | 87.76 (14) | C13—N2—Eu1 | 119.7 (3) |
| O8<sup>i</sup>—Ca1—O13 | 91.70 (14) | C20—N3—C16 | 119.0 (5) |
| O8—Ca1—O13 | 88.30 (14) | C20—N3—Eu1 | 120.1 (3) |
| O14<sup>i</sup>—Ca1—O13 | 87.76 (14) | C16—N3—Eu1 | 120.8 (3) |
| O14—Ca1—O13 | 92.24 (14) | O2—C1—O1 | 125.8 (5) |
| O13<sup>i</sup>—Ca1—O13 | 180.0 | O2—C1—C2 | 118.6 (5) |
| O8<sup>i</sup>—Ca1—H13A | 92.6 (12) | O1—C1—C2 | 115.5 (5) |
| O8—Ca1—H13A | 87.4 (12) | N1—C2—C3 | 122.4 (5) |
| O14<sup>i</sup>—Ca1—H13A | 70.1 (6) | N1—C2—C1 | 114.5 (5) |
| O14—Ca1—H13A | 109.9 (6) | C3—C2—C1 | 123.0 (5) |
| O13<sup>i</sup>—Ca1—H13A | 162.2 (6) | C4—C3—C2 | 118.0 (6) |
| O13—Ca1—H13A | 17.8 (6) | C4—C3—H3 | 121.0 |
| O8<sup>i</sup>—Ca1—H14A | 103.8 (11) | C2—C3—H3 | 121.0 |
| O8—Ca1—H14A | 76.2 (11) | C3—C4—C5 | 119.9 (6) |
| O14<sup>i</sup>—Ca1—H14A | 162.7 (6) | C3—C4—H4 | 120.0 |
| O14—Ca1—H14A | 17.3 (6) | C5—C4—H4 | 120.0 |
| O13<sup>i</sup>—Ca1—H14A | 101.5 (10) | C6—C5—C4 | 118.6 (6) |
| O13—Ca1—H14A | 78.5 (10) | C6—C5—H5 | 120.7 |
| H13A—Ca1—H14A | 95.5 (12) | C4—C5—H5 | 120.7 |
| O6<sup>ii</sup>—Ca2—O6 | 78.34 (19) | N1—C6—C5 | 122.0 (6) |
| O6<sup>ii</sup>—Ca2—O2<sup>iii</sup> | 113.44 (13) | N1—C6—C7 | 114.2 (5) |
| O6—Ca2—O2<sup>iii</sup> | 141.21 (12) | C5—C6—C7 | 123.6 (5) |
| O6<sup>ii</sup>—Ca2—O2<sup>iv</sup> | 141.21 (12) | O4—C7—O3 | 126.0 (5) |
| O6—Ca2—O2<sup>iv</sup> | 113.44 (13) | O4—C7—C6 | 118.2 (5) |
| O2<sup>iii</sup>—Ca2—O2<sup>iv</sup> | 81.20 (19) | O3—C7—C6 | 115.8 (5) |

| | | | |
|---|---|---|---|
| O6ⁱⁱ—Ca2—O15ⁱⁱ | 78.83 (13) | O6—C8—O5 | 126.2 (5) |
| O6—Ca2—O15ⁱⁱ | 72.14 (13) | O6—C8—C9 | 117.9 (5) |
| O2ⁱⁱⁱ—Ca2—O15ⁱⁱ | 144.61 (14) | O5—C8—C9 | 115.9 (5) |
| O2ⁱᵛ—Ca2—O15ⁱⁱ | 71.03 (13) | N2—C9—C10 | 122.3 (5) |
| O6ⁱⁱ—Ca2—O15 | 72.14 (13) | N2—C9—C8 | 113.8 (5) |
| O6—Ca2—O15 | 78.83 (13) | C10—C9—C8 | 123.9 (5) |
| O2ⁱⁱⁱ—Ca2—O15 | 71.03 (13) | C11—C10—C9 | 118.8 (5) |
| O2ⁱᵛ—Ca2—O15 | 144.61 (14) | C11—C10—H10 | 120.6 |
| O15ⁱⁱ—Ca2—O15 | 142.3 (2) | C9—C10—H10 | 120.6 |
| O6ⁱⁱ—Ca2—O16ⁱⁱ | 74.59 (13) | C10—C11—C12 | 119.5 (5) |
| O6—Ca2—O16ⁱⁱ | 145.52 (14) | C10—C11—H11 | 120.3 |
| O2ⁱⁱⁱ—Ca2—O16ⁱⁱ | 70.74 (13) | C12—C11—H11 | 120.3 |
| O2ⁱᵛ—Ca2—O16ⁱⁱ | 77.45 (14) | C13—C12—C11 | 118.2 (5) |
| O15ⁱⁱ—Ca2—O16ⁱⁱ | 81.92 (14) | C13—C12—H12 | 120.9 |
| O15—Ca2—O16ⁱⁱ | 111.92 (14) | C11—C12—H12 | 120.9 |
| O6ⁱⁱ—Ca2—O16 | 145.52 (14) | N2—C13—C12 | 121.6 (5) |
| O6—Ca2—O16 | 74.59 (13) | N2—C13—C14 | 114.7 (5) |
| O2ⁱⁱⁱ—Ca2—O16 | 77.45 (14) | C12—C13—C14 | 123.7 (5) |
| O2ⁱᵛ—Ca2—O16 | 70.74 (13) | O8—C14—O7 | 124.7 (5) |
| O15ⁱⁱ—Ca2—O16 | 111.91 (14) | O8—C14—C13 | 118.5 (5) |
| O15—Ca2—O16 | 81.92 (14) | O7—C14—C13 | 116.8 (5) |
| O16ⁱⁱ—Ca2—O16 | 137.8 (2) | O10—C15—O9 | 125.4 (5) |
| O6ⁱⁱ—Ca2—H15B | 71.4 (11) | O10—C15—C16 | 118.1 (5) |
| O6—Ca2—H15B | 61.0 (6) | O9—C15—C16 | 116.5 (5) |
| O2ⁱⁱⁱ—Ca2—H15B | 86.9 (6) | N3—C16—C17 | 121.9 (5) |
| O2ⁱᵛ—Ca2—H15B | 147.2 (11) | N3—C16—C15 | 114.0 (5) |
| O15ⁱⁱ—Ca2—H15B | 128.1 (6) | C17—C16—C15 | 124.1 (5) |
| O15—Ca2—H15B | 17.9 (6) | C18—C17—C16 | 118.5 (6) |
| O16ⁱⁱ—Ca2—H15B | 126.9 (9) | C18—C17—H17 | 120.7 |
| O16—Ca2—H15B | 76.9 (12) | C16—C17—H17 | 120.7 |
| O12—Ca3—O12ᵛ | 180.00 (9) | C17—C18—C19 | 119.3 (5) |
| O12—Ca3—O17ᵛ | 93.91 (15) | C17—C18—H18 | 120.3 |
| O12ᵛ—Ca3—O17ᵛ | 86.09 (15) | C19—C18—H18 | 120.3 |
| O12—Ca3—O17 | 86.09 (15) | C20—C19—C18 | 119.1 (6) |
| O12ᵛ—Ca3—O17 | 93.91 (15) | C20—C19—H19 | 120.5 |
| O17ᵛ—Ca3—O17 | 180.0 (3) | C18—C19—H19 | 120.5 |
| O12—Ca3—O18 | 90.53 (16) | N3—C20—C19 | 122.1 (5) |
| O12ᵛ—Ca3—O18 | 89.48 (16) | N3—C20—C21 | 114.6 (5) |
| O17ᵛ—Ca3—O18 | 95.84 (18) | C19—C20—C21 | 123.3 (5) |
| O17—Ca3—O18 | 84.16 (18) | O12—C21—O11 | 125.4 (5) |
| O12—Ca3—O18ᵛ | 89.47 (16) | O12—C21—C20 | 118.5 (5) |
| O12ᵛ—Ca3—O18ᵛ | 90.53 (16) | O11—C21—C20 | 116.1 (5) |
| O17ᵛ—Ca3—O18ᵛ | 84.16 (18) | H19A—O19—H19B | 109 (5) |
| O17—Ca3—O18ᵛ | 95.84 (18) | H20A—O20—H20B | 110 (5) |
| O18—Ca3—O18ᵛ | 180.0 | H21A—O21—H21B | 111 (4) |
| O12—Ca3—H17B | 72.8 (11) | | |
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| O5—Eu1—O1—C1 | 78.5 (4) | O11—Eu1—N3—C20 | 1.3 (4) |

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| O7—Eu1—O1—C1 | −152.5 (4) | O9—Eu1—N3—C20 | −179.1 (4) |
| O3—Eu1—O1—C1 | 5.4 (5) | N2—Eu1—N3—C20 | 131.3 (4) |
| O11—Eu1—O1—C1 | −72.0 (4) | N1—Eu1—N3—C20 | −46.0 (4) |
| O9—Eu1—O1—C1 | 145.6 (4) | O5—Eu1—N3—C16 | 30.0 (5) |
| N2—Eu1—O1—C1 | 140.8 (4) | O7—Eu1—N3—C16 | −98.5 (4) |
| N1—Eu1—O1—C1 | 3.2 (4) | O1—Eu1—N3—C16 | −149.5 (4) |
| N3—Eu1—O1—C1 | −101.8 (4) | O3—Eu1—N3—C16 | 82.3 (4) |
| O5—Eu1—O3—C7 | −84.6 (4) | O11—Eu1—N3—C16 | 177.5 (4) |
| O7—Eu1—O3—C7 | 129.9 (4) | O9—Eu1—N3—C16 | −2.9 (4) |
| O1—Eu1—O3—C7 | −4.2 (5) | N2—Eu1—N3—C16 | −52.5 (4) |
| O11—Eu1—O3—C7 | 68.7 (4) | N1—Eu1—N3—C16 | 130.2 (4) |
| O9—Eu1—O3—C7 | −164.0 (4) | Ca2vi—O2—C1—O1 | −8.5 (9) |
| N2—Eu1—O3—C7 | −109.3 (4) | Ca2vi—O2—C1—C2 | 170.7 (3) |
| N1—Eu1—O3—C7 | −2.1 (4) | Eu1—O1—C1—O2 | 179.0 (4) |
| N3—Eu1—O3—C7 | 131.4 (4) | Eu1—O1—C1—C2 | −0.2 (6) |
| O7—Eu1—O5—C8 | −0.5 (5) | C6—N1—C2—C3 | 2.3 (8) |
| O1—Eu1—O5—C8 | 72.5 (4) | Eu1—N1—C2—C3 | −168.5 (4) |
| O3—Eu1—O5—C8 | −159.0 (4) | C6—N1—C2—C1 | 179.4 (5) |
| O11—Eu1—O5—C8 | 140.8 (4) | Eu1—N1—C2—C1 | 8.6 (6) |
| O9—Eu1—O5—C8 | −77.5 (4) | O2—C1—C2—N1 | 175.2 (5) |
| N2—Eu1—O5—C8 | 2.1 (4) | O1—C1—C2—N1 | −5.5 (7) |
| N1—Eu1—O5—C8 | 135.1 (4) | O2—C1—C2—C3 | −7.8 (8) |
| N3—Eu1—O5—C8 | −107.2 (4) | O1—C1—C2—C3 | 171.5 (5) |
| O6ii—Ca2—O6—C8 | 66.7 (5) | N1—C2—C3—C4 | −1.5 (9) |
| O2iii—Ca2—O6—C8 | −46.3 (6) | C1—C2—C3—C4 | −178.3 (5) |
| O2iv—Ca2—O6—C8 | −152.2 (5) | C2—C3—C4—C5 | −0.2 (9) |
| O15ii—Ca2—O6—C8 | 148.6 (5) | C3—C4—C5—C6 | 1.1 (10) |
| O15—Ca2—O6—C8 | −7.1 (5) | C2—N1—C6—C5 | −1.3 (8) |
| O16ii—Ca2—O6—C8 | 105.5 (5) | Eu1—N1—C6—C5 | 169.5 (4) |
| O16—Ca2—O6—C8 | −91.7 (5) | C2—N1—C6—C7 | −177.7 (5) |
| O5—Eu1—O7—C14 | 9.2 (4) | Eu1—N1—C6—C7 | −7.0 (6) |
| O1—Eu1—O7—C14 | −71.0 (4) | C4—C5—C6—N1 | −0.4 (9) |
| O3—Eu1—O7—C14 | 145.0 (4) | C4—C5—C6—C7 | 175.7 (6) |
| O11—Eu1—O7—C14 | −151.5 (4) | Eu1—O3—C7—O4 | −179.7 (4) |
| O9—Eu1—O7—C14 | 81.2 (4) | Eu1—O3—C7—C6 | −0.5 (7) |
| N2—Eu1—O7—C14 | 6.6 (4) | N1—C6—C7—O4 | −175.9 (5) |
| N1—Eu1—O7—C14 | −101.4 (4) | C5—C6—C7—O4 | 7.8 (9) |
| N3—Eu1—O7—C14 | 143.4 (4) | N1—C6—C7—O3 | 4.9 (7) |
| O14i—Ca1—O8—C14 | −123.5 (8) | C5—C6—C7—O3 | −171.4 (5) |
| O14—Ca1—O8—C14 | 56.5 (8) | Ca2—O6—C8—O5 | −0.2 (9) |
| O13i—Ca1—O8—C14 | 144.1 (8) | Ca2—O6—C8—C9 | 178.4 (3) |
| O13—Ca1—O8—C14 | −35.9 (8) | Eu1—O5—C8—O6 | 176.3 (4) |
| O5—Eu1—O9—C15 | −157.9 (4) | Eu1—O5—C8—C9 | −2.3 (6) |
| O7—Eu1—O9—C15 | 72.4 (4) | C13—N2—C9—C10 | 1.6 (8) |
| O1—Eu1—O9—C15 | 131.3 (4) | Eu1—N2—C9—C10 | −176.9 (4) |
| O3—Eu1—O9—C15 | −79.8 (4) | C13—N2—C9—C8 | 179.7 (4) |
| O11—Eu1—O9—C15 | −1.2 (5) | Eu1—N2—C9—C8 | 1.2 (6) |
| N2—Eu1—O9—C15 | 136.1 (4) | O6—C8—C9—N2 | −178.1 (4) |

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| N1—Eu1—O9—C15 | −104.8 (4) | O5—C8—C9—N2 | 0.6 (7) |
| N3—Eu1—O9—C15 | −1.6 (4) | O6—C8—C9—C10 | −0.1 (8) |
| O5—Eu1—O11—C21 | 133.3 (4) | O5—C8—C9—C10 | 178.7 (5) |
| O7—Eu1—O11—C21 | −77.0 (4) | N2—C9—C10—C11 | −1.0 (8) |
| O1—Eu1—O11—C21 | −155.0 (4) | C8—C9—C10—C11 | −178.9 (5) |
| O3—Eu1—O11—C21 | 75.8 (4) | C9—C10—C11—C12 | −0.1 (8) |
| O9—Eu1—O11—C21 | 1.5 (5) | C10—C11—C12—C13 | 0.6 (8) |
| N2—Eu1—O11—C21 | −106.3 (4) | C9—N2—C13—C12 | −1.0 (7) |
| N1—Eu1—O11—C21 | 139.1 (4) | Eu1—N2—C13—C12 | 177.5 (4) |
| N3—Eu1—O11—C21 | 1.9 (4) | C9—N2—C13—C14 | −179.4 (4) |
| O17ᵛ—Ca3—O12—C21 | −129.5 (8) | Eu1—N2—C13—C14 | −0.9 (6) |
| O17—Ca3—O12—C21 | 50.5 (8) | C11—C12—C13—N2 | 0.0 (8) |
| O18—Ca3—O12—C21 | 134.6 (8) | C11—C12—C13—C14 | 178.2 (5) |
| O18ᵛ—Ca3—O12—C21 | −45.4 (8) | Ca1—O8—C14—O7 | −107.4 (8) |
| O5—Eu1—N1—C6 | 85.5 (4) | Ca1—O8—C14—C13 | 73.3 (9) |
| O7—Eu1—N1—C6 | −143.7 (4) | Eu1—O7—C14—O8 | 171.1 (4) |
| O1—Eu1—N1—C6 | −176.9 (4) | Eu1—O7—C14—C13 | −9.5 (6) |
| O3—Eu1—N1—C6 | 4.9 (4) | N2—C13—C14—O8 | −174.2 (5) |
| O11—Eu1—N1—C6 | −91.5 (4) | C12—C13—C14—O8 | 7.5 (8) |
| O9—Eu1—N1—C6 | 32.4 (5) | N2—C13—C14—O7 | 6.5 (7) |
| N2—Eu1—N1—C6 | 134.8 (4) | C12—C13—C14—O7 | −171.9 (5) |
| N3—Eu1—N1—C6 | −47.8 (4) | Eu1—O9—C15—O10 | −173.7 (4) |
| O5—Eu1—N1—C2 | −103.9 (4) | Eu1—O9—C15—C16 | 5.3 (7) |
| O7—Eu1—N1—C2 | 26.9 (5) | C20—N3—C16—C17 | 2.0 (8) |
| O1—Eu1—N1—C2 | −6.3 (4) | Eu1—N3—C16—C17 | −174.3 (4) |
| O3—Eu1—N1—C2 | 175.6 (4) | C20—N3—C16—C15 | −177.5 (5) |
| O11—Eu1—N1—C2 | 79.2 (4) | Eu1—N3—C16—C15 | 6.3 (6) |
| O9—Eu1—N1—C2 | −156.9 (3) | O10—C15—C16—N3 | 171.7 (5) |
| N2—Eu1—N1—C2 | −54.5 (4) | O9—C15—C16—N3 | −7.4 (7) |
| N3—Eu1—N1—C2 | 122.9 (4) | O10—C15—C16—C17 | −7.7 (8) |
| O5—Eu1—N2—C9 | −1.6 (3) | O9—C15—C16—C17 | 173.2 (5) |
| O7—Eu1—N2—C9 | 176.1 (4) | N3—C16—C17—C18 | −1.8 (9) |
| O1—Eu1—N2—C9 | −101.5 (4) | C15—C16—C17—C18 | 177.6 (5) |
| O3—Eu1—N2—C9 | 25.3 (4) | C16—C17—C18—C19 | 0.6 (9) |
| O11—Eu1—N2—C9 | −151.8 (3) | C17—C18—C19—C20 | 0.4 (9) |
| O9—Eu1—N2—C9 | 81.1 (4) | C16—N3—C20—C19 | −1.0 (8) |
| N1—Eu1—N2—C9 | −57.2 (4) | Eu1—N3—C20—C19 | 175.3 (4) |
| N3—Eu1—N2—C9 | 125.5 (4) | C16—N3—C20—C21 | −180.0 (5) |
| O5—Eu1—N2—C13 | 179.9 (4) | Eu1—N3—C20—C21 | −3.7 (6) |
| O7—Eu1—N2—C13 | −2.4 (3) | C18—C19—C20—N3 | −0.2 (9) |
| O1—Eu1—N2—C13 | 80.0 (4) | C18—C19—C20—C21 | 178.7 (5) |
| O3—Eu1—N2—C13 | −153.2 (3) | Ca3—O12—C21—O11 | −98.7 (9) |
| O11—Eu1—N2—C13 | 29.7 (4) | Ca3—O12—C21—C20 | 81.6 (9) |
| O9—Eu1—N2—C13 | −97.3 (4) | Eu1—O11—C21—O12 | 175.9 (4) |
| N1—Eu1—N2—C13 | 124.4 (4) | Eu1—O11—C21—C20 | −4.4 (7) |
| N3—Eu1—N2—C13 | −53.0 (4) | N3—C20—C21—O12 | −175.2 (5) |
| O5—Eu1—N3—C20 | −146.2 (4) | C19—C20—C21—O12 | 5.8 (8) |
| O7—Eu1—N3—C20 | 85.3 (4) | N3—C20—C21—O11 | 5.1 (7) |

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| O1—Eu1—N3—C20 | 34.3 (5) | C19—C20—C21—O11 | −173.9 (5) |
| O3—Eu1—N3—C20 | −93.9 (4) | | |

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

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O13—H13*A*···O10ᵛⁱⁱ | 0.85 (1) | 1.97 (2) | 2.796 (6) | 163 (5) |
| O13—H13*B*···O20ᵛⁱⁱⁱ | 0.85 (1) | 1.85 (1) | 2.696 (6) | 175 (6) |
| O14—H14*A*···O16ᵛⁱ | 0.85 (1) | 1.96 (2) | 2.774 (6) | 160 (5) |
| O14—H14*B*···O9ᵛⁱ | 0.85 (1) | 1.91 (2) | 2.723 (5) | 160 (5) |
| O15—H15*A*···O21ⁱⁱⁱ | 0.85 (1) | 1.99 (1) | 2.839 (6) | 172 (6) |
| O15—H15*B*···O5 | 0.85 (1) | 1.90 (1) | 2.734 (5) | 165 (5) |
| O16—H16*A*···O13ⁱⁱⁱ | 0.78 (6) | 2.38 (7) | 3.079 (6) | 150 (6) |
| O16—H16*B*···O1ⁱⁱⁱ | 0.84 (6) | 1.88 (7) | 2.704 (6) | 169 (6) |
| O17—H17*A*···O3ᵛⁱ | 0.85 (1) | 1.91 (1) | 2.745 (6) | 167 (5) |
| O17—H17*B*···O19ⁱˣ | 0.85 (1) | 1.93 (3) | 2.722 (7) | 155 (6) |
| O18—H18*A*···O22ᵛˣ | 0.85 (1) | 2.37 (6) | 2.990 (15) | 130 (6) |
| O18—H18*A*···O22ˣ | 0.85 (1) | 2.16 (7) | 2.657 (14) | 117 (6) |
| O18—H18*B*···O4ᵛⁱ | 0.85 (1) | 1.98 (2) | 2.772 (6) | 155 (5) |
| O19—H19*A*···O24ˣⁱ | 0.86 (1) | 2.31 (3) | 3.12 (2) | 159 (6) |
| O19—H19*B*···O7ˣⁱⁱ | 0.85 (1) | 2.07 (4) | 2.828 (6) | 148 (6) |
| O20—H20*A*···O15 | 0.85 (1) | 2.04 (2) | 2.862 (6) | 161 (6) |
| O20—H20*B*···O23 | 0.85 (1) | 2.03 (4) | 2.758 (10) | 143 (6) |
| O20—H20*B*···O22ᵛˣⁱⁱⁱ | 0.85 (1) | 2.32 (4) | 3.042 (13) | 143 (5) |
| O21—H21*A*···O11 | 0.85 (1) | 1.94 (2) | 2.774 (6) | 167 (6) |
| O21—H21*B*···O17 | 0.85 (1) | 2.42 (4) | 3.113 (7) | 138 (5) |

Symmetry codes: (iii) *x*, *y*+1, *z*; (vi) *x*, *y*−1, *z*; (vii) −*x*+1, −*y*+1, −*z*; (viii) −*x*+1, *y*−1, −*z*+1/2; (ix) *x*, *y*, *z*−1; (x) −*x*, −*y*+1, −*z*+1; (xi) −*x*+1, −*y*+1, −*z*+1; (xii) *x*, *y*, *z*+1; (xiii) *x*, −*y*+2, *z*−1/2.