

# Tris{2-methoxy-6-[4-methylphenyl]iminoethylphenolate- $\kappa^2 O,O'$ }tris(thiocyanato- $\kappa N$ )europium(III)

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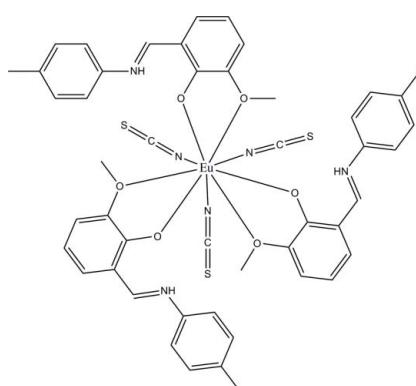
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Key indicators: single-crystal X-ray study;  $T = 296\text{ K}$ ; mean  $\sigma(\text{C}-\text{C}) = 0.008\text{ \AA}$ ;  $R$  factor = 0.045;  $wR$  factor = 0.137; data-to-parameter ratio = 15.4.

The metal center in the structure of the title compound,  $[\text{Eu}(\text{NCS})_3(\text{C}_{15}\text{H}_{15}\text{NO}_2)_3]$ , is coordinated by three Schiff base 2-methoxy-6-[4-methylphenyl]iminoethylphenolate ( $L$ ) ligands and three independent thiocyanate ions. In the crystal structure, the acidic H atom is located on the Schiff base N atom and hydrogen bonded to the phenolate O atom. The coordination environment of the  $\text{Eu}^{III}$  ion is nine-coordinate by three chelating methoxyphenolate pairs of O atoms and three N-atom terminals of the thiocyanate ions. The compound is isostructural with the  $\text{Ce}^{III}$  analogue [Liu *et al.* (2009). *Acta Cryst. E* **65**, m650].

## Related literature

For background to Schiff bases and their applications, see: Liu *et al.* (1997); Mihara *et al.* (2009). For related structures, see: Liu *et al.* (2009); Zhao *et al.* (2007). For a zigzag chain cadmium(II) complex, see: Li *et al.* (2008).



## Experimental

### Crystal data

|  |  |
|--|--|
| $[\text{Eu}(\text{NCS})_3(\text{C}_{15}\text{H}_{15}\text{NO}_2)_3]$ | $V = 5053.23 (12)\text{ \AA}^3$          |
| $M_r = 1050.04$  | $Z = 4$                                  |
| Monoclinic, $P2_1/c$   | Mo $K\alpha$ radiation                   |
| $a = 16.6445 (2)\text{ \AA}$   | $\mu = 1.42\text{ mm}^{-1}$              |
| $b = 14.2411 (2)\text{ \AA}$   | $T = 296\text{ K}$                       |
| $c = 22.1678 (3)\text{ \AA}$   | $0.31 \times 0.16 \times 0.13\text{ mm}$ |
| $\beta = 105.912 (1)^\circ$  |  |

### Data collection

|  |  |
|--|--|
| Bruker APEXII CCD area-detector diffractometer                       | 37461 measured reflections             |
| Absorption correction: multi-scan ( <i>SADABS</i> ; Sheldrick, 1996) | 8882 independent reflections           |
| $T_{\min} = 0.757$ , $T_{\max} = 0.834$                              | 6762 reflections with $I > 2\sigma(I)$ |
|  | $R_{\text{int}} = 0.046$               |

### Refinement

|                                 |   |
|---------------------------------|---|
| $R[F^2 > 2\sigma(F^2)] = 0.045$ | 577 parameters                                |
| $wR(F^2) = 0.137$               | H-atom parameters constrained                 |
| $S = 1.06$                      | $\Delta\rho_{\max} = 0.87\text{ e \AA}^{-3}$  |
| 8882 reflections                | $\Delta\rho_{\min} = -0.41\text{ e \AA}^{-3}$ |

**Table 1**  
Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ).

| $D-\text{H} \cdots A$ | $D-\text{H}$ | $\text{H} \cdots A$ | $D \cdots A$ | $D-\text{H} \cdots A$ |
|-----------------------|--------------|---------------------|--------------|-----------------------|
| N1—H1A $\cdots$ O1    | 0.86         | 1.89                | 2.588 (4)    | 138                   |
| N2—H2A $\cdots$ O3    | 0.86         | 1.89                | 2.580 (4)    | 137                   |
| N3—H3A $\cdots$ O5    | 0.86         | 1.84                | 2.550 (4)    | 138                   |

Data collection: *APEX2* (Bruker, 2006); cell refinement: *SAINT* (Bruker, 2006); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZL2242).

## References

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# supporting information

*Acta Cryst.* (2009). E65, m1651 [doi:10.1107/S1600536809049125]

## **Tris{2-methoxy-6-[(4-methylphenyl)iminiomethyl]phenolate- $\kappa^2O,O'$ }tris(thiocyanato- $\kappa N$ )europium(III)**

**Jian-Feng Liu, Jia-Lu Liu and Guo-Liang Zhao**

### **S1. Comment**

Rare earth complexes with Schiff ligands derived from *o*-vanillin have been investigated over many years. Liu *et al.* (1997) for example describe structural and chemical properties of vanilline derived complexes, and (Mihara *et al.*, 2009) investigated them as catalyststs for asymmetric  $\alpha$ -additions of isocyanides to aldehydes. Over the last years we have been engaged in the syntheses of new analogous Schiff bases derived from *o*-vanillin and their rare metal complexes. In prvious articles we have reported partial results (Zhao *et al.*, 2007; Li *et al.* 2008; Liu *et al.* 2009). Herein, we would like to describe a new Eu<sup>III</sup> complex.

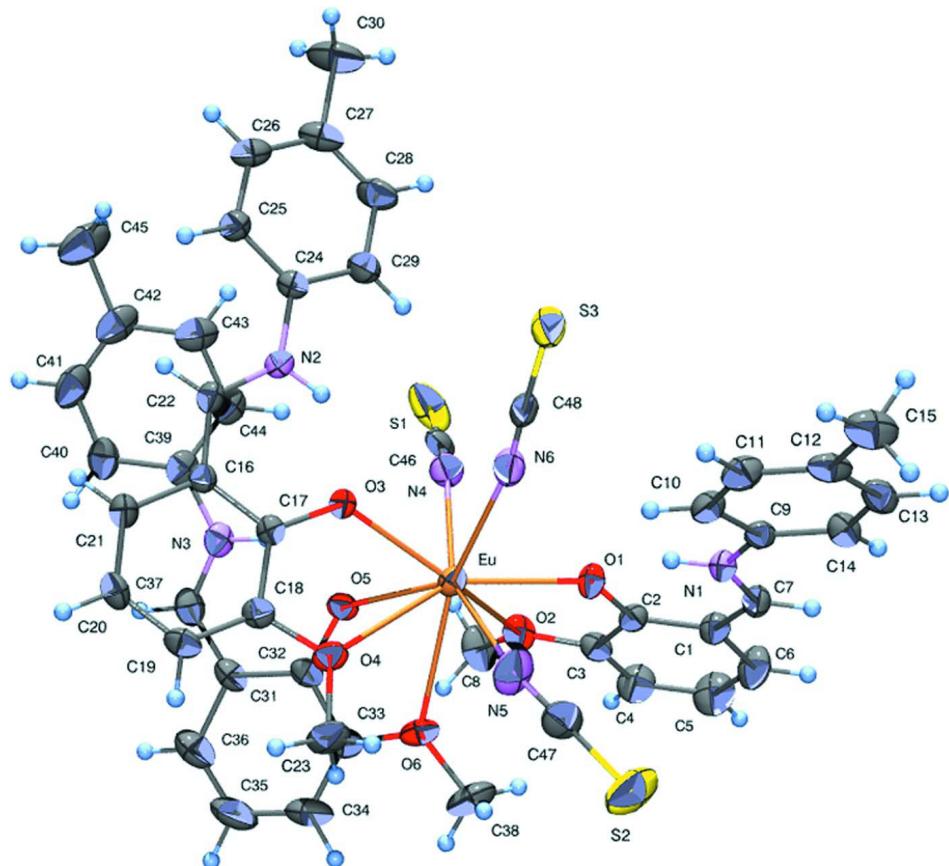
The structure of the title complex is shown in Fig. 1. The structure of [Eu(NCS)<sub>3</sub>·(C<sub>15</sub>H<sub>15</sub>NO<sub>2</sub>)<sub>3</sub>] contains three (HL) ligands and three independent thiocyanate ions. The Eu<sup>III</sup> is nine-coordinated by three *N* terminals from three thiocyanate ions and six O atoms from the HL ligands (shown in Fig. 2). The HL ligands chelate the Eu<sup>III</sup> ion with the methoxy O atoms and the deprotonated phenolic hydroxyl O atoms. The Eu—O (phenolic) bonds are 2.773 (3) - 2.839 (3) Å, which are longer than the ones between Eu<sup>III</sup> and methoxy O atoms (2.376 (3) - 2.418 (3) Å). The Eu—N bonds are 2.512 (5) - 2.566 (5) Å. The Eu—O (phenolic) and Eu—N bonds are shorter than in the isostructural Ce<sup>III</sup> complex (Liu *et al.* 2009), which can be attributed to the ionic radius decrease from Ce<sup>III</sup> to Eu<sup>III</sup> due to the lanthanide contraction. Because of the geometric and chemical environment requirements of the chelating groups, the coordination geometry deviates considerably from that of a distorted capped square antiprismatic geometry (Fig. 2). In the HL ligands, the acidic proton has been transferred from the phenolic group to the *N*-imine atom, which is involved in an intramolecular hydrogen bond. All hydrogen bonds are listed in Table 1.

### **S2. Experimental**

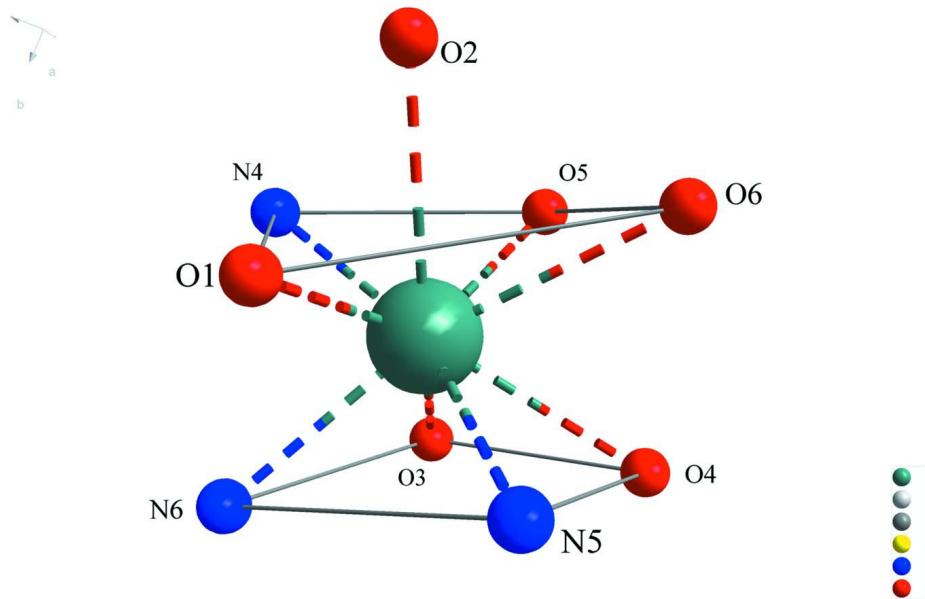
Reagents and solvents were of commercially available quality and were used without further purification. The Schiff base ligand was prepared in a high yield synthesis by condensation of *o*-vanillin and *p*-methylaniline and was recrystallized in ethanol before being used. 1 mmol Eu(NO<sub>3</sub>)<sub>3</sub> (dissolved in methanol) was added dropwise into a methanol solution with 3 mmol *N*-salicylidene-*p*-toluidine under stirring and the mixture was continuously stirred at room temperature for 8 h to obtain a purplish red solution. The deposit was filtered off and the solution was left standing for slow evaporation. Red crystal of the title compound formed after several days.

### **S3. Refinement**

The structure was solved by direct methods and successive Fourier difference synthesis and the atom numbering scheme was adopted from the isostructural Ce<sup>III</sup> complex (Liu *et al.* 2009). The H atoms bonded to C and N atoms were positioned geometrically and refined using a riding model [aliphatic C—H = 0.96 Å ( $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ ), aromatic C—H = 0.93 Å ( $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ ) and N—H = 0.86 Å with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$ ].

**Figure 1**

The molecular structure of the title complex, showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 30% probability level.

**Figure 2**

The coordination environment of the europium(III) atom, showing the distorted monocapped square antiprismatic geometry.

### Tris{2-methoxy-6-[(4-methylphenyl)iminiomethyl]phenolate- $\kappa^2O,O'$ }tris(thiocyanato- $\kappa N$ )europium(III)

#### Crystal data



$$M_r = 1050.04$$

Monoclinic,  $P2_1/c$

Hall symbol: -P 2ybc

$$a = 16.6445 (2) \text{ \AA}$$

$$b = 14.2411 (2) \text{ \AA}$$

$$c = 22.1678 (3) \text{ \AA}$$

$$\beta = 105.912 (1)^\circ$$

$$V = 5053.23 (12) \text{ \AA}^3$$

$$Z = 4$$

$$F(000) = 2136$$

$$D_x = 1.380 \text{ Mg m}^{-3}$$

Mo  $K\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 7369 reflections

$$\theta = 2.0\text{--}25.0^\circ$$

$$\mu = 1.42 \text{ mm}^{-1}$$

$$T = 296 \text{ K}$$

Block, red

$$0.31 \times 0.16 \times 0.13 \text{ mm}$$

#### Data collection

Bruker APEXII CCD area-detector

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

phi and  $\omega$  scans

Absorption correction: multi-scan

(*SADABS*; Sheldrick, 1996)

$$T_{\min} = 0.757, T_{\max} = 0.834$$

37461 measured reflections

8882 independent reflections

6762 reflections with  $I > 2\sigma(I)$

$$R_{\text{int}} = 0.046$$

$$\theta_{\max} = 25.0^\circ, \theta_{\min} = 2.0^\circ$$

$$h = -19 \rightarrow 19$$

$$k = -16 \rightarrow 16$$

$$l = -23 \rightarrow 26$$

*Refinement*Refinement on  $F^2$ 

Least-squares matrix: full

$$R[F^2 > 2\sigma(F^2)] = 0.045$$

$$wR(F^2) = 0.137$$

$$S = 1.06$$

8882 reflections

577 parameters

0 restraints

Primary atom site location: structure-invariant  
direct methodsSecondary atom site location: difference Fourier  
mapHydrogen site location: inferred from  
neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0857P)^2]$$
$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

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

$$\Delta\rho_{\max} = 0.87 \text{ e \AA}^{-3}$$

$$\Delta\rho_{\min} = -0.41 \text{ e \AA}^{-3}$$

*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 ( $\text{\AA}^2$ )*

|      | <i>x</i>      | <i>y</i>      | <i>z</i>      | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|---------------|---------------|---------------|----------------------------------|
| Eu   | 0.212188 (12) | 0.775828 (17) | 0.392808 (11) | 0.04651 (12)                     |
| C1   | -0.0555 (3)   | 0.7601 (3)    | 0.4198 (2)    | 0.0496 (12)                      |
| C2   | 0.0249 (3)    | 0.7317 (3)    | 0.4190 (2)    | 0.0419 (10)                      |
| C3   | 0.0421 (3)    | 0.6343 (3)    | 0.4173 (2)    | 0.0482 (11)                      |
| C4   | -0.0183 (4)   | 0.5697 (4)    | 0.4158 (3)    | 0.0741 (17)                      |
| H4A  | -0.0063       | 0.5062        | 0.4143        | 0.089*                           |
| C5   | -0.0979 (4)   | 0.5975 (4)    | 0.4164 (3)    | 0.089 (2)                        |
| H5A  | -0.1386       | 0.5523        | 0.4152        | 0.107*                           |
| C6   | -0.1172 (3)   | 0.6901 (4)    | 0.4186 (3)    | 0.0768 (18)                      |
| H6A  | -0.1707       | 0.7077        | 0.4194        | 0.092*                           |
| C7   | -0.0755 (3)   | 0.8557 (3)    | 0.4200 (2)    | 0.0510 (12)                      |
| H7A  | -0.1291       | 0.8720        | 0.4213        | 0.061*                           |
| C8   | 0.1514 (4)    | 0.5228 (4)    | 0.4240 (3)    | 0.0787 (18)                      |
| H8A  | 0.1088        | 0.4829        | 0.4317        | 0.118*                           |
| H8B  | 0.2006        | 0.5189        | 0.4588        | 0.118*                           |
| H8C  | 0.1645        | 0.5028        | 0.3864        | 0.118*                           |
| C9   | -0.0370 (2)   | 1.0207 (3)    | 0.41823 (19)  | 0.0417 (10)                      |
| C10  | 0.0249 (3)    | 1.0782 (4)    | 0.4082 (2)    | 0.0537 (12)                      |
| H10A | 0.0731        | 1.0522        | 0.4017        | 0.064*                           |
| C11  | 0.0150 (3)    | 1.1736 (4)    | 0.4081 (3)    | 0.0618 (13)                      |
| H11A | 0.0573        | 1.2118        | 0.4017        | 0.074*                           |
| C12  | -0.0553 (4)   | 1.2144 (3)    | 0.4170 (2)    | 0.0585 (14)                      |
| C13  | -0.1161 (3)   | 1.1561 (4)    | 0.4272 (2)    | 0.0560 (12)                      |
| H13A | -0.1642       | 1.1821        | 0.4339        | 0.067*                           |
| C14  | -0.1071 (3)   | 1.0589 (3)    | 0.4279 (2)    | 0.0512 (11)                      |

|      |             |            |            |             |
|------|-------------|------------|------------|-------------|
| H14A | -0.1488     | 1.0204     | 0.4349     | 0.061*      |
| C15  | -0.0667 (4) | 1.3191 (4) | 0.4163 (3) | 0.0801 (18) |
| H15A | -0.0192     | 1.3490     | 0.4080     | 0.120*      |
| H15B | -0.0719     | 1.3394     | 0.4564     | 0.120*      |
| H15C | -0.1163     | 1.3358     | 0.3842     | 0.120*      |
| C16  | 0.4877 (2)  | 0.8421 (3) | 0.3996 (2) | 0.0417 (10) |
| C17  | 0.4005 (2)  | 0.8307 (3) | 0.3755 (2) | 0.0401 (10) |
| C18  | 0.3682 (3)  | 0.8078 (3) | 0.3111 (2) | 0.0466 (11) |
| C19  | 0.4192 (3)  | 0.7976 (4) | 0.2730 (2) | 0.0552 (12) |
| H19A | 0.3967      | 0.7839     | 0.2307     | 0.066*      |
| C20  | 0.5051 (3)  | 0.8079 (4) | 0.2974 (3) | 0.0600 (13) |
| H20A | 0.5395      | 0.8001     | 0.2711     | 0.072*      |
| C21  | 0.5395 (3)  | 0.8290 (4) | 0.3585 (2) | 0.0561 (13) |
| H21A | 0.5972      | 0.8349     | 0.3738     | 0.067*      |
| C22  | 0.5236 (3)  | 0.8642 (3) | 0.4622 (2) | 0.0452 (11) |
| H22A | 0.5815      | 0.8699     | 0.4763     | 0.054*      |
| C23  | 0.2420 (4)  | 0.7996 (5) | 0.2274 (2) | 0.082 (2)   |
| H23A | 0.2825      | 0.8111     | 0.2047     | 0.123*      |
| H23B | 0.1996      | 0.8472     | 0.2172     | 0.123*      |
| H23C | 0.2170      | 0.7391     | 0.2162     | 0.123*      |
| C24  | 0.5109 (3)  | 0.8965 (3) | 0.5674 (2) | 0.0447 (10) |
| C25  | 0.5932 (3)  | 0.9208 (4) | 0.5954 (2) | 0.0533 (12) |
| H25A | 0.6303      | 0.9285     | 0.5712     | 0.064*      |
| C26  | 0.6195 (3)  | 0.9335 (4) | 0.6590 (2) | 0.0630 (14) |
| H26A | 0.6749      | 0.9501     | 0.6774     | 0.076*      |
| C27  | 0.5675 (4)  | 0.9228 (4) | 0.6963 (3) | 0.0688 (15) |
| C28  | 0.4859 (4)  | 0.9002 (4) | 0.6681 (3) | 0.0739 (16) |
| H28A | 0.4488      | 0.8941     | 0.6925     | 0.089*      |
| C29  | 0.4578 (3)  | 0.8862 (4) | 0.6044 (2) | 0.0635 (14) |
| H29A | 0.4023      | 0.8696     | 0.5864     | 0.076*      |
| C30  | 0.5990 (5)  | 0.9382 (5) | 0.7666 (3) | 0.105 (2)   |
| H30A | 0.5541      | 0.9286     | 0.7854     | 0.158*      |
| H30B | 0.6196      | 1.0012     | 0.7748     | 0.158*      |
| H30C | 0.6432      | 0.8946     | 0.7842     | 0.158*      |
| C31  | 0.3719 (3)  | 0.5437 (4) | 0.3346 (2) | 0.0576 (13) |
| C32  | 0.3006 (3)  | 0.5925 (3) | 0.3394 (2) | 0.0496 (11) |
| C33  | 0.2273 (3)  | 0.5862 (4) | 0.2897 (2) | 0.0571 (12) |
| C34  | 0.2241 (5)  | 0.5321 (5) | 0.2387 (3) | 0.087 (2)   |
| H34A | 0.1750      | 0.5286     | 0.2063     | 0.105*      |
| C35  | 0.2944 (6)  | 0.4814 (6) | 0.2347 (3) | 0.103 (2)   |
| H35A | 0.2908      | 0.4432     | 0.2001     | 0.123*      |
| C36  | 0.3666 (5)  | 0.4865 (5) | 0.2794 (3) | 0.0869 (19) |
| H36A | 0.4132      | 0.4537     | 0.2753     | 0.104*      |
| C37  | 0.4482 (3)  | 0.5515 (4) | 0.3816 (3) | 0.0591 (13) |
| H37A | 0.4945      | 0.5192     | 0.3767     | 0.071*      |
| C38  | 0.0808 (4)  | 0.6303 (5) | 0.2585 (3) | 0.088 (2)   |
| H38A | 0.0801      | 0.5789     | 0.2303     | 0.133*      |
| H38B | 0.0642      | 0.6868     | 0.2347     | 0.133*      |

|      |               |              |              |             |
|------|---------------|--------------|--------------|-------------|
| H38C | 0.0426        | 0.6176       | 0.2830       | 0.133*      |
| C39  | 0.5297 (3)    | 0.6218 (3)   | 0.4791 (3)   | 0.0554 (13) |
| C40  | 0.6085 (3)    | 0.6166 (4)   | 0.4702 (3)   | 0.0703 (15) |
| H40A | 0.6153        | 0.5965       | 0.4320       | 0.084*      |
| C41  | 0.6768 (3)    | 0.6413 (5)   | 0.5182 (4)   | 0.086 (2)   |
| H41A | 0.7296        | 0.6382       | 0.5116       | 0.104*      |
| C42  | 0.6700 (3)    | 0.6700 (4)   | 0.5745 (4)   | 0.0795 (18) |
| C43  | 0.5901 (3)    | 0.6761 (4)   | 0.5832 (3)   | 0.0730 (16) |
| H43A | 0.5838        | 0.6971       | 0.6214       | 0.088*      |
| C44  | 0.5208 (3)    | 0.6515 (4)   | 0.5359 (3)   | 0.0631 (14) |
| H44A | 0.4679        | 0.6550       | 0.5424       | 0.076*      |
| C45  | 0.7453 (4)    | 0.7002 (6)   | 0.6284 (4)   | 0.119 (3)   |
| H45A | 0.7957        | 0.6922       | 0.6159       | 0.179*      |
| H45B | 0.7479        | 0.6622       | 0.6647       | 0.179*      |
| H45C | 0.7393        | 0.7650       | 0.6383       | 0.179*      |
| C46  | 0.3000 (3)    | 0.6760 (4)   | 0.5457 (2)   | 0.0527 (12) |
| C47  | 0.0442 (4)    | 0.8630 (5)   | 0.2737 (3)   | 0.0781 (17) |
| C48  | 0.2338 (3)    | 1.0044 (4)   | 0.4741 (3)   | 0.0538 (12) |
| S1   | 0.33288 (14)  | 0.60173 (15) | 0.60390 (8)  | 0.1038 (7)  |
| S2   | -0.05210 (12) | 0.86508 (18) | 0.23051 (12) | 0.1316 (9)  |
| S3   | 0.25269 (9)   | 1.10435 (12) | 0.51097 (9)  | 0.0882 (6)  |
| N1   | -0.0237 (2)   | 0.9224 (3)   | 0.41848 (16) | 0.0427 (9)  |
| H1A  | 0.0254        | 0.9049       | 0.4175       | 0.051*      |
| N2   | 0.4802 (2)    | 0.8774 (2)   | 0.50229 (16) | 0.0418 (8)  |
| H2A  | 0.4268        | 0.8742       | 0.4876       | 0.050*      |
| N3   | 0.4561 (2)    | 0.6018 (3)   | 0.43120 (19) | 0.0531 (10) |
| H3A  | 0.4109        | 0.6263       | 0.4357       | 0.064*      |
| N4   | 0.2777 (3)    | 0.7258 (3)   | 0.5055 (2)   | 0.0592 (11) |
| N5   | 0.1114 (3)    | 0.8592 (4)   | 0.3037 (2)   | 0.0935 (18) |
| N6   | 0.2185 (2)    | 0.9354 (3)   | 0.4477 (2)   | 0.0652 (12) |
| O1   | 0.08463 (17)  | 0.7912 (2)   | 0.42051 (16) | 0.0475 (8)  |
| O2   | 0.1224 (2)    | 0.6171 (2)   | 0.41675 (17) | 0.0593 (9)  |
| O3   | 0.35011 (16)  | 0.8406 (2)   | 0.41093 (13) | 0.0443 (7)  |
| O4   | 0.28219 (19)  | 0.8018 (3)   | 0.29336 (14) | 0.0553 (8)  |
| O5   | 0.30193 (18)  | 0.6438 (2)   | 0.38871 (14) | 0.0474 (7)  |
| O6   | 0.1634 (2)    | 0.6416 (3)   | 0.29926 (15) | 0.0611 (9)  |

Atomic displacement parameters ( $\text{\AA}^2$ )

|    | $U^{11}$     | $U^{22}$     | $U^{33}$     | $U^{12}$     | $U^{13}$     | $U^{23}$     |
|----|--------------|--------------|--------------|--------------|--------------|--------------|
| Eu | 0.03922 (15) | 0.05006 (19) | 0.04699 (18) | 0.00313 (9)  | 0.00630 (11) | 0.00323 (11) |
| C1 | 0.046 (2)    | 0.042 (3)    | 0.062 (3)    | -0.007 (2)   | 0.017 (2)    | -0.002 (2)   |
| C2 | 0.043 (2)    | 0.039 (3)    | 0.042 (3)    | -0.0024 (19) | 0.0084 (19)  | 0.001 (2)    |
| C3 | 0.060 (3)    | 0.037 (3)    | 0.049 (3)    | -0.003 (2)   | 0.018 (2)    | -0.001 (2)   |
| C4 | 0.075 (4)    | 0.041 (3)    | 0.106 (5)    | -0.011 (3)   | 0.023 (3)    | -0.005 (3)   |
| C5 | 0.083 (4)    | 0.057 (4)    | 0.131 (6)    | -0.032 (3)   | 0.038 (4)    | -0.007 (4)   |
| C6 | 0.055 (3)    | 0.058 (3)    | 0.123 (5)    | -0.015 (3)   | 0.032 (3)    | -0.004 (4)   |
| C7 | 0.041 (2)    | 0.053 (3)    | 0.061 (3)    | 0.000 (2)    | 0.017 (2)    | -0.008 (2)   |

|     |             |             |             |              |              |              |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| C8  | 0.097 (4)   | 0.040 (3)   | 0.110 (5)   | 0.022 (3)    | 0.045 (4)    | 0.012 (3)    |
| C9  | 0.043 (2)   | 0.043 (3)   | 0.036 (2)   | 0.0028 (19)  | 0.0059 (18)  | 0.000 (2)    |
| C10 | 0.045 (2)   | 0.053 (3)   | 0.056 (3)   | 0.000 (2)    | 0.002 (2)    | -0.001 (2)   |
| C11 | 0.061 (3)   | 0.048 (3)   | 0.069 (4)   | -0.010 (2)   | 0.005 (2)    | 0.002 (3)    |
| C12 | 0.078 (3)   | 0.047 (3)   | 0.038 (3)   | 0.006 (3)    | -0.005 (2)   | -0.002 (2)   |
| C13 | 0.066 (3)   | 0.048 (3)   | 0.053 (3)   | 0.011 (2)    | 0.015 (2)    | -0.003 (2)   |
| C14 | 0.058 (3)   | 0.043 (3)   | 0.054 (3)   | 0.003 (2)    | 0.018 (2)    | 0.003 (2)    |
| C15 | 0.112 (5)   | 0.043 (3)   | 0.074 (4)   | 0.001 (3)    | 0.005 (3)    | -0.002 (3)   |
| C16 | 0.042 (2)   | 0.043 (3)   | 0.043 (3)   | -0.0041 (18) | 0.0156 (19)  | -0.002 (2)   |
| C17 | 0.045 (2)   | 0.034 (2)   | 0.042 (3)   | -0.0011 (18) | 0.0140 (19)  | 0.0045 (19)  |
| C18 | 0.053 (2)   | 0.046 (3)   | 0.041 (3)   | -0.005 (2)   | 0.013 (2)    | 0.006 (2)    |
| C19 | 0.071 (3)   | 0.059 (3)   | 0.036 (3)   | -0.003 (2)   | 0.015 (2)    | 0.000 (2)    |
| C20 | 0.062 (3)   | 0.074 (4)   | 0.055 (3)   | -0.001 (3)   | 0.034 (3)    | -0.003 (3)   |
| C21 | 0.044 (2)   | 0.070 (4)   | 0.057 (3)   | -0.001 (2)   | 0.019 (2)    | -0.005 (3)   |
| C22 | 0.037 (2)   | 0.046 (3)   | 0.054 (3)   | -0.0017 (18) | 0.015 (2)    | 0.001 (2)    |
| C23 | 0.068 (3)   | 0.139 (6)   | 0.031 (3)   | -0.019 (4)   | 0.001 (2)    | 0.018 (3)    |
| C24 | 0.052 (2)   | 0.039 (3)   | 0.042 (3)   | 0.0001 (19)  | 0.013 (2)    | -0.002 (2)   |
| C25 | 0.048 (2)   | 0.058 (3)   | 0.054 (3)   | -0.009 (2)   | 0.014 (2)    | -0.007 (2)   |
| C26 | 0.069 (3)   | 0.055 (3)   | 0.056 (3)   | -0.009 (3)   | 0.002 (3)    | -0.010 (3)   |
| C27 | 0.104 (4)   | 0.053 (3)   | 0.047 (3)   | -0.013 (3)   | 0.017 (3)    | -0.009 (3)   |
| C28 | 0.098 (4)   | 0.083 (4)   | 0.048 (3)   | -0.024 (3)   | 0.032 (3)    | -0.013 (3)   |
| C29 | 0.064 (3)   | 0.070 (4)   | 0.062 (3)   | -0.016 (3)   | 0.025 (3)    | -0.016 (3)   |
| C30 | 0.161 (7)   | 0.099 (6)   | 0.050 (4)   | -0.034 (5)   | 0.020 (4)    | -0.015 (4)   |
| C31 | 0.072 (3)   | 0.053 (3)   | 0.054 (3)   | 0.004 (2)    | 0.027 (3)    | -0.007 (2)   |
| C32 | 0.066 (3)   | 0.045 (3)   | 0.041 (3)   | -0.001 (2)   | 0.019 (2)    | 0.005 (2)    |
| C33 | 0.067 (3)   | 0.055 (3)   | 0.046 (3)   | -0.004 (2)   | 0.009 (2)    | 0.003 (2)    |
| C34 | 0.111 (5)   | 0.091 (5)   | 0.049 (4)   | -0.024 (4)   | 0.006 (3)    | -0.021 (3)   |
| C35 | 0.135 (6)   | 0.105 (6)   | 0.072 (5)   | -0.016 (5)   | 0.034 (5)    | -0.044 (4)   |
| C36 | 0.112 (5)   | 0.079 (5)   | 0.079 (5)   | 0.003 (4)    | 0.044 (4)    | -0.019 (4)   |
| C37 | 0.065 (3)   | 0.042 (3)   | 0.076 (4)   | 0.014 (2)    | 0.029 (3)    | 0.003 (3)    |
| C38 | 0.071 (4)   | 0.090 (5)   | 0.078 (4)   | -0.011 (3)   | -0.023 (3)   | 0.007 (4)    |
| C39 | 0.055 (3)   | 0.040 (3)   | 0.067 (3)   | 0.014 (2)    | 0.010 (2)    | 0.011 (2)    |
| C40 | 0.060 (3)   | 0.062 (4)   | 0.091 (4)   | 0.022 (3)    | 0.025 (3)    | 0.005 (3)    |
| C41 | 0.050 (3)   | 0.080 (5)   | 0.121 (6)   | 0.018 (3)    | 0.010 (3)    | 0.005 (4)    |
| C42 | 0.062 (3)   | 0.053 (4)   | 0.104 (5)   | 0.012 (3)    | -0.010 (3)   | 0.012 (4)    |
| C43 | 0.080 (4)   | 0.049 (3)   | 0.075 (4)   | 0.010 (3)    | -0.005 (3)   | 0.001 (3)    |
| C44 | 0.059 (3)   | 0.049 (3)   | 0.077 (4)   | 0.011 (2)    | 0.013 (3)    | 0.010 (3)    |
| C45 | 0.077 (4)   | 0.100 (5)   | 0.146 (7)   | 0.008 (4)    | -0.028 (4)   | 0.000 (5)    |
| C46 | 0.061 (3)   | 0.061 (3)   | 0.037 (3)   | 0.017 (2)    | 0.017 (2)    | -0.006 (3)   |
| C47 | 0.084 (4)   | 0.082 (4)   | 0.060 (4)   | 0.028 (3)    | 0.006 (3)    | 0.009 (3)    |
| C48 | 0.036 (2)   | 0.057 (3)   | 0.071 (3)   | -0.008 (2)   | 0.020 (2)    | -0.007 (3)   |
| S1  | 0.1488 (16) | 0.1137 (15) | 0.0626 (10) | 0.0676 (13)  | 0.0518 (10)  | 0.0386 (10)  |
| S2  | 0.0849 (12) | 0.1219 (17) | 0.148 (2)   | 0.0366 (12)  | -0.0365 (12) | -0.0150 (15) |
| S3  | 0.0592 (8)  | 0.0801 (11) | 0.1363 (15) | -0.0291 (7)  | 0.0455 (9)   | -0.0507 (11) |
| N1  | 0.0374 (17) | 0.043 (2)   | 0.048 (2)   | 0.0043 (16)  | 0.0115 (15)  | 0.0024 (17)  |
| N2  | 0.0366 (17) | 0.043 (2)   | 0.043 (2)   | -0.0041 (15) | 0.0067 (15)  | -0.0012 (17) |
| N3  | 0.049 (2)   | 0.045 (2)   | 0.064 (3)   | 0.0140 (17)  | 0.0140 (19)  | 0.004 (2)    |
| N4  | 0.061 (3)   | 0.068 (3)   | 0.048 (3)   | 0.012 (2)    | 0.012 (2)    | 0.009 (2)    |

|    |             |             |             |              |              |              |
|----|-------------|-------------|-------------|--------------|--------------|--------------|
| N5 | 0.065 (3)   | 0.131 (5)   | 0.076 (4)   | 0.032 (3)    | 0.005 (3)    | 0.038 (3)    |
| N6 | 0.052 (2)   | 0.057 (3)   | 0.093 (3)   | -0.004 (2)   | 0.029 (2)    | -0.014 (3)   |
| O1 | 0.0397 (15) | 0.0340 (17) | 0.072 (2)   | -0.0014 (12) | 0.0208 (15)  | 0.0004 (15)  |
| O2 | 0.066 (2)   | 0.0378 (18) | 0.076 (2)   | 0.0080 (16)  | 0.0216 (17)  | 0.0007 (17)  |
| O3 | 0.0363 (14) | 0.056 (2)   | 0.0420 (17) | -0.0025 (13) | 0.0138 (13)  | -0.0035 (15) |
| O4 | 0.0519 (18) | 0.073 (2)   | 0.0360 (18) | -0.0073 (16) | 0.0040 (14)  | 0.0065 (16)  |
| O5 | 0.0531 (17) | 0.0491 (19) | 0.0367 (17) | 0.0077 (14)  | 0.0069 (13)  | -0.0026 (15) |
| O6 | 0.062 (2)   | 0.070 (2)   | 0.0397 (19) | -0.0064 (18) | -0.0051 (15) | 0.0018 (17)  |

*Geometric parameters ( $\text{\AA}$ ,  $\text{^{\circ}}$ )*

|          |           |          |            |
|----------|-----------|----------|------------|
| Eu—O1    | 2.376 (3) | C23—H23C | 0.9600     |
| Eu—O3    | 2.404 (3) | C24—C29  | 1.369 (6)  |
| Eu—O5    | 2.418 (3) | C24—C25  | 1.383 (6)  |
| Eu—N5    | 2.512 (5) | C24—N2   | 1.420 (5)  |
| Eu—N4    | 2.538 (4) | C25—C26  | 1.369 (7)  |
| Eu—N6    | 2.566 (5) | C25—H25A | 0.9300     |
| Eu—O6    | 2.773 (3) | C26—C27  | 1.359 (7)  |
| Eu—O4    | 2.786 (3) | C26—H26A | 0.9300     |
| Eu—O2    | 2.839 (3) | C27—C28  | 1.368 (8)  |
| C1—C2    | 1.403 (6) | C27—C30  | 1.519 (8)  |
| C1—C7    | 1.402 (7) | C28—C29  | 1.374 (7)  |
| C1—C6    | 1.427 (7) | C28—H28A | 0.9300     |
| C2—O1    | 1.299 (5) | C29—H29A | 0.9300     |
| C2—C3    | 1.419 (6) | C30—H30A | 0.9600     |
| C3—C4    | 1.356 (7) | C30—H30B | 0.9600     |
| C3—O2    | 1.362 (5) | C30—H30C | 0.9600     |
| C4—C5    | 1.385 (8) | C31—C32  | 1.405 (7)  |
| C4—H4A   | 0.9300    | C31—C37  | 1.409 (7)  |
| C5—C6    | 1.361 (8) | C31—C36  | 1.452 (8)  |
| C5—H5A   | 0.9300    | C32—O5   | 1.310 (5)  |
| C6—H6A   | 0.9300    | C32—C33  | 1.406 (7)  |
| C7—N1    | 1.289 (6) | C33—C34  | 1.356 (8)  |
| C7—H7A   | 0.9300    | C33—O6   | 1.386 (6)  |
| C8—O2    | 1.422 (6) | C34—C35  | 1.398 (10) |
| C8—H8A   | 0.9600    | C34—H34A | 0.9300     |
| C8—H8B   | 0.9600    | C35—C36  | 1.333 (9)  |
| C8—H8C   | 0.9600    | C35—H35A | 0.9300     |
| C9—C14   | 1.357 (6) | C36—H36A | 0.9300     |
| C9—C10   | 1.380 (6) | C37—N3   | 1.289 (6)  |
| C9—N1    | 1.417 (6) | C37—H37A | 0.9300     |
| C10—C11  | 1.369 (7) | C38—O6   | 1.433 (6)  |
| C10—H10A | 0.9300    | C38—H38A | 0.9600     |
| C11—C12  | 1.369 (8) | C38—H38B | 0.9600     |
| C11—H11A | 0.9300    | C38—H38C | 0.9600     |
| C12—C13  | 1.376 (7) | C39—C44  | 1.376 (7)  |
| C12—C15  | 1.503 (7) | C39—C40  | 1.380 (7)  |
| C13—C14  | 1.392 (7) | C39—N3   | 1.413 (6)  |

|          |             |               |           |
|----------|-------------|---------------|-----------|
| C13—H13A | 0.9300      | C40—C41       | 1.374 (8) |
| C14—H14A | 0.9300      | C40—H40A      | 0.9300    |
| C15—H15A | 0.9600      | C41—C42       | 1.347 (9) |
| C15—H15B | 0.9600      | C41—H41A      | 0.9300    |
| C15—H15C | 0.9600      | C42—C43       | 1.399 (9) |
| C16—C22  | 1.389 (6)   | C42—C45       | 1.536 (9) |
| C16—C17  | 1.413 (6)   | C43—C44       | 1.374 (7) |
| C16—C21  | 1.429 (6)   | C43—H43A      | 0.9300    |
| C17—O3   | 1.305 (5)   | C44—H44A      | 0.9300    |
| C17—C18  | 1.418 (6)   | C45—H45A      | 0.9600    |
| C18—C19  | 1.359 (7)   | C45—H45B      | 0.9600    |
| C18—O4   | 1.380 (5)   | C45—H45C      | 0.9600    |
| C19—C20  | 1.390 (7)   | C46—N4        | 1.121 (6) |
| C19—H19A | 0.9300      | C46—S1        | 1.641 (6) |
| C20—C21  | 1.352 (7)   | C47—N5        | 1.135 (7) |
| C20—H20A | 0.9300      | C47—S2        | 1.626 (6) |
| C21—H21A | 0.9300      | C48—N6        | 1.137 (6) |
| C22—N2   | 1.304 (5)   | C48—S3        | 1.628 (6) |
| C22—H22A | 0.9300      | N1—H1A        | 0.8600    |
| C23—O4   | 1.431 (6)   | N2—H2A        | 0.8600    |
| C23—H23A | 0.9600      | N3—H3A        | 0.8600    |
| C23—H23B | 0.9600      |               |           |
| <br>     |             |               |           |
| O1—Eu—O3 | 143.27 (10) | O4—C23—H23A   | 109.5     |
| O1—Eu—O5 | 133.32 (10) | O4—C23—H23B   | 109.5     |
| O3—Eu—O5 | 74.53 (10)  | H23A—C23—H23B | 109.5     |
| O1—Eu—N5 | 73.04 (14)  | O4—C23—H23C   | 109.5     |
| O3—Eu—N5 | 110.57 (15) | H23A—C23—H23C | 109.5     |
| O5—Eu—N5 | 128.62 (15) | H23B—C23—H23C | 109.5     |
| O1—Eu—N4 | 86.82 (13)  | C29—C24—C25   | 118.8 (4) |
| O3—Eu—N4 | 79.07 (12)  | C29—C24—N2    | 118.4 (4) |
| O5—Eu—N4 | 73.48 (12)  | C25—C24—N2    | 122.7 (4) |
| N5—Eu—N4 | 157.03 (16) | C26—C25—C24   | 119.5 (5) |
| O1—Eu—N6 | 73.71 (11)  | C26—C25—H25A  | 120.2     |
| O3—Eu—N6 | 70.59 (11)  | C24—C25—H25A  | 120.2     |
| O5—Eu—N6 | 139.54 (12) | C27—C26—C25   | 122.2 (5) |
| N5—Eu—N6 | 83.44 (18)  | C27—C26—H26A  | 118.9     |
| N4—Eu—N6 | 80.30 (15)  | C25—C26—H26A  | 118.9     |
| O1—Eu—O6 | 99.07 (10)  | C26—C27—C28   | 117.9 (5) |
| O3—Eu—O6 | 117.38 (10) | C26—C27—C30   | 120.6 (6) |
| O5—Eu—O6 | 59.55 (10)  | C28—C27—C30   | 121.5 (6) |
| N5—Eu—O6 | 75.07 (16)  | C27—C28—C29   | 121.3 (5) |
| N4—Eu—O6 | 120.07 (12) | C27—C28—H28A  | 119.3     |
| N6—Eu—O6 | 158.50 (13) | C29—C28—H28A  | 119.3     |
| O1—Eu—O4 | 142.12 (10) | C24—C29—C28   | 120.3 (5) |
| O3—Eu—O4 | 59.59 (9)   | C24—C29—H29A  | 119.8     |
| O5—Eu—O4 | 71.15 (11)  | C28—C29—H29A  | 119.8     |
| N5—Eu—O4 | 69.46 (14)  | C27—C30—H30A  | 109.5     |

|              |             |               |           |
|--------------|-------------|---------------|-----------|
| N4—Eu—O4     | 131.00 (12) | C27—C30—H30B  | 109.5     |
| N6—Eu—O4     | 106.60 (12) | H30A—C30—H30B | 109.5     |
| O6—Eu—O4     | 66.42 (10)  | C27—C30—H30C  | 109.5     |
| O1—Eu—O2     | 58.09 (9)   | H30A—C30—H30C | 109.5     |
| O3—Eu—O2     | 143.34 (10) | H30B—C30—H30C | 109.5     |
| O5—Eu—O2     | 75.55 (10)  | C32—C31—C37   | 120.9 (5) |
| N5—Eu—O2     | 104.53 (16) | C32—C31—C36   | 119.0 (5) |
| N4—Eu—O2     | 72.46 (13)  | C37—C31—C36   | 120.1 (5) |
| N6—Eu—O2     | 124.88 (12) | O5—C32—C31    | 121.2 (4) |
| O6—Eu—O2     | 61.96 (10)  | O5—C32—C33    | 120.2 (4) |
| O4—Eu—O2     | 127.55 (10) | C31—C32—C33   | 118.6 (5) |
| C2—C1—C7     | 120.6 (4)   | C34—C33—O6    | 126.5 (5) |
| C2—C1—C6     | 118.9 (5)   | C34—C33—C32   | 121.1 (5) |
| C7—C1—C6     | 120.6 (5)   | O6—C33—C32    | 112.3 (4) |
| O1—C2—C1     | 122.5 (4)   | C33—C34—C35   | 120.2 (6) |
| O1—C2—C3     | 118.7 (4)   | C33—C34—H34A  | 119.9     |
| C1—C2—C3     | 118.8 (4)   | C35—C34—H34A  | 119.9     |
| C4—C3—O2     | 126.9 (4)   | C36—C35—C34   | 121.7 (6) |
| C4—C3—C2     | 120.7 (5)   | C36—C35—H35A  | 119.2     |
| O2—C3—C2     | 112.4 (4)   | C34—C35—H35A  | 119.2     |
| C3—C4—C5     | 120.7 (5)   | C35—C36—C31   | 119.3 (6) |
| C3—C4—H4A    | 119.7       | C35—C36—H36A  | 120.3     |
| C5—C4—H4A    | 119.7       | C31—C36—H36A  | 120.3     |
| C6—C5—C4     | 120.9 (5)   | N3—C37—C31    | 122.3 (4) |
| C6—C5—H5A    | 119.6       | N3—C37—H37A   | 118.8     |
| C4—C5—H5A    | 119.6       | C31—C37—H37A  | 118.8     |
| C5—C6—C1     | 120.1 (5)   | O6—C38—H38A   | 109.5     |
| C5—C6—H6A    | 119.9       | O6—C38—H38B   | 109.5     |
| C1—C6—H6A    | 119.9       | H38A—C38—H38B | 109.5     |
| N1—C7—C1     | 123.6 (4)   | O6—C38—H38C   | 109.5     |
| N1—C7—H7A    | 118.2       | H38A—C38—H38C | 109.5     |
| C1—C7—H7A    | 118.2       | H38B—C38—H38C | 109.5     |
| O2—C8—H8A    | 109.5       | C44—C39—C40   | 119.5 (5) |
| O2—C8—H8B    | 109.5       | C44—C39—N3    | 117.4 (4) |
| H8A—C8—H8B   | 109.5       | C40—C39—N3    | 123.0 (5) |
| O2—C8—H8C    | 109.5       | C41—C40—C39   | 119.5 (6) |
| H8A—C8—H8C   | 109.5       | C41—C40—H40A  | 120.2     |
| H8B—C8—H8C   | 109.5       | C39—C40—H40A  | 120.2     |
| C14—C9—C10   | 119.9 (4)   | C42—C41—C40   | 122.2 (6) |
| C14—C9—N1    | 122.4 (4)   | C42—C41—H41A  | 118.9     |
| C10—C9—N1    | 117.7 (4)   | C40—C41—H41A  | 118.9     |
| C11—C10—C9   | 119.7 (5)   | C41—C42—C43   | 118.1 (5) |
| C11—C10—H10A | 120.2       | C41—C42—C45   | 123.2 (7) |
| C9—C10—H10A  | 120.2       | C43—C42—C45   | 118.6 (7) |
| C12—C11—C10  | 121.9 (5)   | C44—C43—C42   | 120.7 (6) |
| C12—C11—H11A | 119.1       | C44—C43—H43A  | 119.6     |
| C10—C11—H11A | 119.1       | C42—C43—H43A  | 119.6     |
| C11—C12—C13  | 117.7 (5)   | C43—C44—C39   | 119.8 (5) |

|               |            |               |            |
|---------------|------------|---------------|------------|
| C11—C12—C15   | 122.1 (5)  | C43—C44—H44A  | 120.1      |
| C13—C12—C15   | 120.3 (5)  | C39—C44—H44A  | 120.1      |
| C12—C13—C14   | 121.3 (5)  | C42—C45—H45A  | 109.5      |
| C12—C13—H13A  | 119.3      | C42—C45—H45B  | 109.5      |
| C14—C13—H13A  | 119.3      | H45A—C45—H45B | 109.5      |
| C9—C14—C13    | 119.5 (5)  | C42—C45—H45C  | 109.5      |
| C9—C14—H14A   | 120.3      | H45A—C45—H45C | 109.5      |
| C13—C14—H14A  | 120.3      | H45B—C45—H45C | 109.5      |
| C12—C15—H15A  | 109.5      | N4—C46—S1     | 179.1 (5)  |
| C12—C15—H15B  | 109.5      | N5—C47—S2     | 178.2 (7)  |
| H15A—C15—H15B | 109.5      | N6—C48—S3     | 178.2 (5)  |
| C12—C15—H15C  | 109.5      | C7—N1—C9      | 128.5 (4)  |
| H15A—C15—H15C | 109.5      | C7—N1—H1A     | 115.7      |
| H15B—C15—H15C | 109.5      | C9—N1—H1A     | 115.7      |
| C22—C16—C17   | 121.4 (4)  | C22—N2—C24    | 127.4 (4)  |
| C22—C16—C21   | 119.8 (4)  | C22—N2—H2A    | 116.3      |
| C17—C16—C21   | 118.8 (4)  | C24—N2—H2A    | 116.3      |
| O3—C17—C16    | 121.5 (4)  | C37—N3—C39    | 128.1 (4)  |
| O3—C17—C18    | 120.2 (4)  | C37—N3—H3A    | 115.9      |
| C16—C17—C18   | 118.3 (4)  | C39—N3—H3A    | 115.9      |
| C19—C18—O4    | 126.3 (4)  | C46—N4—Eu     | 157.0 (4)  |
| C19—C18—C17   | 121.4 (4)  | C47—N5—Eu     | 145.2 (5)  |
| O4—C18—C17    | 112.2 (4)  | C48—N6—Eu     | 169.8 (4)  |
| C18—C19—C20   | 119.8 (5)  | C2—O1—Eu      | 131.6 (3)  |
| C18—C19—H19A  | 120.1      | C3—O2—C8      | 118.3 (4)  |
| C20—C19—H19A  | 120.1      | C3—O2—Eu      | 115.3 (3)  |
| C21—C20—C19   | 121.5 (5)  | C8—O2—Eu      | 126.3 (3)  |
| C21—C20—H20A  | 119.2      | C17—O3—Eu     | 126.8 (3)  |
| C19—C20—H20A  | 119.2      | C18—O4—C23    | 116.7 (4)  |
| C20—C21—C16   | 120.2 (4)  | C18—O4—Eu     | 114.2 (3)  |
| C20—C21—H21A  | 119.9      | C23—O4—Eu     | 128.7 (3)  |
| C16—C21—H21A  | 119.9      | C32—O5—Eu     | 126.6 (3)  |
| N2—C22—C16    | 123.1 (4)  | C33—O6—C38    | 118.9 (4)  |
| N2—C22—H22A   | 118.4      | C33—O6—Eu     | 115.3 (3)  |
| C16—C22—H22A  | 118.5      | C38—O6—Eu     | 125.7 (4)  |
| <br>          |            |               |            |
| C7—C1—C2—O1   | 2.4 (8)    | O4—Eu—N5—C47  | 135.1 (10) |
| C6—C1—C2—O1   | -179.4 (5) | O2—Eu—N5—C47  | 10.0 (10)  |
| C7—C1—C2—C3   | -178.5 (4) | O1—Eu—N6—C48  | 154 (3)    |
| C6—C1—C2—C3   | -0.3 (8)   | O3—Eu—N6—C48  | -17 (3)    |
| O1—C2—C3—C4   | 179.9 (5)  | O5—Eu—N6—C48  | 15 (3)     |
| C1—C2—C3—C4   | 0.8 (8)    | N5—Eu—N6—C48  | -132 (3)   |
| O1—C2—C3—O2   | -0.8 (6)   | N4—Eu—N6—C48  | 65 (3)     |
| C1—C2—C3—O2   | -179.9 (4) | O6—Eu—N6—C48  | -133 (2)   |
| O2—C3—C4—C5   | -179.8 (6) | O4—Eu—N6—C48  | -65 (3)    |
| C2—C3—C4—C5   | -0.6 (9)   | O2—Eu—N6—C48  | 125 (3)    |
| C3—C4—C5—C6   | -0.1 (11)  | C1—C2—O1—Eu   | -161.0 (3) |
| C4—C5—C6—C1   | 0.6 (11)   | C3—C2—O1—Eu   | 19.9 (6)   |

|                 |            |                |            |
|-----------------|------------|----------------|------------|
| C2—C1—C6—C5     | -0.4 (9)   | O3—Eu—O1—C2    | -156.8 (3) |
| C7—C1—C6—C5     | 177.8 (6)  | O5—Eu—O1—C2    | -26.2 (4)  |
| C2—C1—C7—N1     | 1.1 (8)    | N5—Eu—O1—C2    | 101.3 (4)  |
| C6—C1—C7—N1     | -177.1 (5) | N4—Eu—O1—C2    | -89.9 (4)  |
| C14—C9—C10—C11  | -0.1 (7)   | N6—Eu—O1—C2    | -170.7 (4) |
| N1—C9—C10—C11   | -179.5 (4) | O6—Eu—O1—C2    | 30.1 (4)   |
| C9—C10—C11—C12  | -0.6 (8)   | O4—Eu—O1—C2    | 93.1 (4)   |
| C10—C11—C12—C13 | 1.0 (8)    | O2—Eu—O1—C2    | -18.6 (4)  |
| C10—C11—C12—C15 | -179.5 (5) | C4—C3—O2—C8    | -9.5 (8)   |
| C11—C12—C13—C14 | -0.7 (8)   | C2—C3—O2—C8    | 171.3 (4)  |
| C15—C12—C13—C14 | 179.8 (5)  | C4—C3—O2—Eu    | 166.7 (5)  |
| C10—C9—C14—C13  | 0.4 (7)    | C2—C3—O2—Eu    | -12.6 (5)  |
| N1—C9—C14—C13   | 179.8 (4)  | O1—Eu—O2—C3    | 15.0 (3)   |
| C12—C13—C14—C9  | 0.0 (8)    | O3—Eu—O2—C3    | 153.1 (3)  |
| C22—C16—C17—O3  | 0.2 (7)    | O5—Eu—O2—C3    | -170.7 (3) |
| C21—C16—C17—O3  | 179.2 (4)  | N5—Eu—O2—C3    | -43.9 (3)  |
| C22—C16—C17—C18 | -179.8 (4) | N4—Eu—O2—C3    | 112.4 (3)  |
| C21—C16—C17—C18 | -0.8 (6)   | N6—Eu—O2—C3    | 48.2 (4)   |
| O3—C17—C18—C19  | 179.5 (4)  | O6—Eu—O2—C3    | -107.8 (3) |
| C16—C17—C18—C19 | -0.5 (7)   | O4—Eu—O2—C3    | -119.0 (3) |
| O3—C17—C18—O4   | 2.1 (6)    | O1—Eu—O2—C8    | -169.3 (5) |
| C16—C17—C18—O4  | -178.0 (4) | O3—Eu—O2—C8    | -31.1 (5)  |
| O4—C18—C19—C20  | 178.4 (5)  | O5—Eu—O2—C8    | 5.0 (4)    |
| C17—C18—C19—C20 | 1.3 (8)    | N5—Eu—O2—C8    | 131.8 (4)  |
| C18—C19—C20—C21 | -0.8 (9)   | N4—Eu—O2—C8    | -71.9 (4)  |
| C19—C20—C21—C16 | -0.6 (9)   | N6—Eu—O2—C8    | -136.1 (4) |
| C22—C16—C21—C20 | -179.6 (5) | O6—Eu—O2—C8    | 67.9 (4)   |
| C17—C16—C21—C20 | 1.3 (8)    | O4—Eu—O2—C8    | 56.8 (4)   |
| C17—C16—C22—N2  | -1.2 (7)   | C16—C17—O3—Eu  | -157.3 (3) |
| C21—C16—C22—N2  | 179.8 (4)  | C18—C17—O3—Eu  | 22.6 (6)   |
| C29—C24—C25—C26 | 0.3 (7)    | O1—Eu—O3—C17   | -160.9 (3) |
| N2—C24—C25—C26  | -176.6 (4) | O5—Eu—O3—C17   | 54.1 (3)   |
| C24—C25—C26—C27 | 0.2 (8)    | N5—Eu—O3—C17   | -71.9 (4)  |
| C25—C26—C27—C28 | -1.1 (9)   | N4—Eu—O3—C17   | 129.8 (3)  |
| C25—C26—C27—C30 | -179.6 (6) | N6—Eu—O3—C17   | -146.8 (4) |
| C26—C27—C28—C29 | 1.7 (9)    | O6—Eu—O3—C17   | 11.4 (4)   |
| C30—C27—C28—C29 | -179.9 (6) | O4—Eu—O3—C17   | -22.9 (3)  |
| C25—C24—C29—C28 | 0.2 (8)    | O2—Eu—O3—C17   | 90.4 (3)   |
| N2—C24—C29—C28  | 177.3 (5)  | C19—C18—O4—C23 | -10.6 (8)  |
| C27—C28—C29—C24 | -1.3 (9)   | C17—C18—O4—C23 | 166.7 (5)  |
| C37—C31—C32—O5  | -2.5 (8)   | C19—C18—O4—Eu  | 163.0 (4)  |
| C36—C31—C32—O5  | 178.9 (5)  | C17—C18—O4—Eu  | -19.7 (5)  |
| C37—C31—C32—C33 | 176.7 (5)  | O1—Eu—O4—C18   | 160.7 (3)  |
| C36—C31—C32—C33 | -1.8 (7)   | O3—Eu—O4—C18   | 21.3 (3)   |
| O5—C32—C33—C34  | -178.8 (5) | O5—Eu—O4—C18   | -61.4 (3)  |
| C31—C32—C33—C34 | 1.9 (8)    | N5—Eu—O4—C18   | 152.2 (4)  |
| O5—C32—C33—O6   | 2.5 (6)    | N4—Eu—O4—C18   | -15.5 (4)  |
| C31—C32—C33—O6  | -176.8 (4) | N6—Eu—O4—C18   | 76.0 (3)   |

|                 |             |                |            |
|-----------------|-------------|----------------|------------|
| O6—C33—C34—C35  | 178.4 (6)   | O6—Eu—O4—C18   | −125.6 (3) |
| C32—C33—C34—C35 | −0.1 (9)    | O2—Eu—O4—C18   | −114.9 (3) |
| C33—C34—C35—C36 | −1.9 (12)   | O1—Eu—O4—C23   | −26.6 (5)  |
| C34—C35—C36—C31 | 1.9 (12)    | O3—Eu—O4—C23   | −166.0 (5) |
| C32—C31—C36—C35 | −0.1 (9)    | O5—Eu—O4—C23   | 111.3 (5)  |
| C37—C31—C36—C35 | −178.6 (6)  | N5—Eu—O4—C23   | −35.1 (5)  |
| C32—C31—C37—N3  | 1.1 (8)     | N4—Eu—O4—C23   | 157.2 (5)  |
| C36—C31—C37—N3  | 179.6 (5)   | N6—Eu—O4—C23   | −111.3 (5) |
| C44—C39—C40—C41 | −0.1 (8)    | O6—Eu—O4—C23   | 47.1 (5)   |
| N3—C39—C40—C41  | 176.9 (5)   | O2—Eu—O4—C23   | 57.8 (5)   |
| C39—C40—C41—C42 | 0.7 (9)     | C31—C32—O5—Eu  | 154.9 (4)  |
| C40—C41—C42—C43 | −1.3 (10)   | C33—C32—O5—Eu  | −24.3 (6)  |
| C40—C41—C42—C45 | −178.6 (6)  | O1—Eu—O5—C32   | 94.5 (4)   |
| C41—C42—C43—C44 | 1.4 (9)     | O3—Eu—O5—C32   | −113.6 (3) |
| C45—C42—C43—C44 | 178.8 (6)   | N5—Eu—O5—C32   | −9.4 (4)   |
| C42—C43—C44—C39 | −0.9 (8)    | N4—Eu—O5—C32   | 163.5 (4)  |
| C40—C39—C44—C43 | 0.2 (8)     | N6—Eu—O5—C32   | −144.7 (3) |
| N3—C39—C44—C43  | −177.0 (5)  | O6—Eu—O5—C32   | 22.2 (3)   |
| C1—C7—N1—C9     | 179.7 (4)   | O4—Eu—O5—C32   | −51.0 (3)  |
| C14—C9—N1—C7    | 8.8 (7)     | O2—Eu—O5—C32   | 87.9 (3)   |
| C10—C9—N1—C7    | −171.8 (5)  | C34—C33—O6—C38 | 12.3 (8)   |
| C16—C22—N2—C24  | 177.3 (4)   | C32—C33—O6—C38 | −169.1 (5) |
| C29—C24—N2—C22  | −164.6 (5)  | C34—C33—O6—Eu  | −163.4 (5) |
| C25—C24—N2—C22  | 12.3 (7)    | C32—C33—O6—Eu  | 15.2 (5)   |
| C31—C37—N3—C39  | −174.4 (5)  | O1—Eu—O6—C33   | −153.9 (3) |
| C44—C39—N3—C37  | −160.3 (5)  | O3—Eu—O6—C33   | 30.8 (3)   |
| C40—C39—N3—C37  | 22.6 (8)    | O5—Eu—O6—C33   | −18.5 (3)  |
| O1—Eu—N4—C46    | 94.1 (10)   | N5—Eu—O6—C33   | 136.5 (3)  |
| O3—Eu—N4—C46    | −120.0 (10) | N4—Eu—O6—C33   | −62.3 (3)  |
| O5—Eu—N4—C46    | −43.0 (10)  | N6—Eu—O6—C33   | 137.8 (4)  |
| N5—Eu—N4—C46    | 122.6 (10)  | O4—Eu—O6—C33   | 62.8 (3)   |
| N6—Eu—N4—C46    | 168.1 (11)  | O2—Eu—O6—C33   | −107.6 (3) |
| O6—Eu—N4—C46    | −4.5 (11)   | O1—Eu—O6—C38   | 30.8 (4)   |
| O4—Eu—N4—C46    | −88.3 (10)  | O3—Eu—O6—C38   | −144.6 (4) |
| O2—Eu—N4—C46    | 36.6 (10)   | O5—Eu—O6—C38   | 166.2 (4)  |
| O1—Eu—N5—C47    | −39.5 (9)   | N5—Eu—O6—C38   | −38.8 (4)  |
| O3—Eu—N5—C47    | 179.2 (9)   | N4—Eu—O6—C38   | 122.4 (4)  |
| O5—Eu—N5—C47    | 92.9 (9)    | N6—Eu—O6—C38   | −37.5 (6)  |
| N4—Eu—N5—C47    | −69.3 (12)  | O4—Eu—O6—C38   | −112.6 (4) |
| N6—Eu—N5—C47    | −114.4 (10) | O2—Eu—O6—C38   | 77.0 (4)   |
| O6—Eu—N5—C47    | 65.1 (9)    |                |            |

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ )

| $D\text{—H}\cdots A$ | $D\text{—H}$ | $H\cdots A$ | $D\cdots A$ | $D\text{—H}\cdots A$ |
|----------------------|--------------|-------------|-------------|----------------------|
| N1—H1A…O1            | 0.86         | 1.89        | 2.588 (4)   | 138                  |
| N2—H2A…O3            | 0.86         | 1.89        | 2.580 (4)   | 137                  |
| N3—H3A…O5            | 0.86         | 1.84        | 2.550 (4)   | 138                  |