Crystal structure of a Tb$$^{III}$$–Cu$$^{II}$$ glycinehydroxamate 15-metallacrown-5 sulfate complex

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The core of the title complex, bis[hexaaquahemiaquapentakis(C$_2$H$_4$N$_2$O$_2$)glycinehydroxamato)sulfatopentacopper(II)terbium(III)] sulfate hexahydrate, [TbCu$_5$(SO$_4$)(GlyHA)$_5$(H$_2$O)$_6.5$]$_2$(SO$_4$)$_2$H$_2$O (I), which belongs to the 15-metallacrown-5 family, consists of five glycinehydroxamate dianions (GlyHA$^{2-}$/C$_2$H$_4$N$_2$O$_2$) and five copper(II) ions linked together forming a metallamacrocyclic moiety. The terbium(III) ion is connected to the centre of the metallamacrocycle through five hydroxamate oxygen atoms. The coordination environment of the Tb$^{3+}$ ion is completed to an octacoordination level by oxygen atoms of a bidentate sulfate and an apically coordinated water molecule, while the copper(II) atoms are square-planar, penta- or hexacoordinate due to the apical coordination of water molecules. Continuous shape calculations indicate that the coordination polyhedron of the Tb$^{3+}$ ion in I is best described as square antiprismatic. The positive charge of each pair of [TbCu$_5$(GlyHA)$_5$(H$_2$O)$_6.5$(SO$_4$)$_2$H$_2$O]$_2$ fragments is compensated by a non-coordinated sulfate anion, which is located on an inversion center with 1:1 disordered oxygen atoms. Complex I is isomorphous with the previously reported compounds [LnCu$_5$(GlyHA)$_5$(SO$_4$)(H$_2$O)$_6.5$]$_2$(SO$_4$), where Ln$^{III}$ = Pr, Nd, Sm, Eu, Gd, Dy and Ho.

1. Chemical context

Numerous research studies devoted to polynuclear 3d–4f assemblies have been stimulated by their non-trivial luminescence properties (Jankolovits et al., 2011; Maity et al., 2015), single-molecule magnet (SMM) behaviour (Dhers et al., 2016; Zangana et al., 2014) and their significant magnetocaloric effect (Pavlishchuk & Pavlishchuk, 2020; Zheng et al., 2014). The 15-metallacrown-5 complexes are 3d–4f metallamacrocyclic assemblies, which can be easily obtained from one-step reactions between an α-substituted hydroxamic acid and the corresponding salts of transition metals and lanthanides (Stemmler et al., 1999; Pavlishchuk et al., 2011, 2019). Compounds bearing 15-metallacrown-5 [LnCu$_5$]$^{3+}$ units have demonstrated the ability to serve as sensors (Zabrodina et al., 2018), can absorb and adsorb various small molecules (Lim et al., 2010; Pavlishchuk et al., 2014; Ostrowska et al., 2016) and display SMM behaviour (Wang et al., 2019, 2021; Zaleski et al., 2006; Wu et al., 2021). Taking into account the fact that 15-metallacrowns-5 are also suitable building blocks for the generation of porous coordination polymers and discrete assemblies (Pavlishchuk et al., 2017a,b, 2018), the synthesis of...
new examples of this class of metallamacrocyclic assemblies and studies of their structural features are of particular interest. Herein we report the crystal structure of the new 15-metallacrown-5 complex \([\text{TbCu}_5(\text{GlyHA})_5(\text{H}_2\text{O})_{6.5}(\text{SO}_4)]_2\) \((\text{SO}_4)\cdot 13(\text{H}_2\text{O})\) (1), which complements the previously reported series of isomorphous metallamacrocycles with Pr, Nd, Sm, Eu, Gd, Dy and Ho ions at their centres.

2. Structural commentary

Complex 1 crystallizes in the space group \(P\overline{1}\) and is isostructural with the previously reported complexes

\([\text{LnCu}_4(\text{GlyHA})_4(\text{SO}_4)(\text{H}_2\text{O})_{6.5}]_2(\text{SO}_4)\), where GlyHA\(^{2-}\) is the dianion of glycinehydroxamic acid and \(\text{Ln}^{III} = \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Dy} \) and \(\text{Ho}\) (Pavlishchuk et al., 2011). Each unit cell in 1 contains two \([\text{TbCu}_5(\text{GlyHA})_5(\text{SO}_4)(\text{H}_2\text{O})_{6.5}]^+\) 15-metallacrown-5 cations related by an inversion center, one non-coordinated sulfate anion for charge-balance and non-coordinated water molecules (Figs. 1 and 2).

The core of the \([\text{TbCu}_5(\text{GlyHA})_5(\text{SO}_4)(\text{H}_2\text{O})_{6.5}]^+\) complex cation in 1 is constructed from five copper(II) ions linked by five bridging glycinehydroxamate dianions (GlyHA\(^{2-}\)) and a terbium(III) ion bound at the centre of the metallocycle (Fig. 1). The copper(II) equatorial coordination environment in 1 is formed by two oxygen atoms (from a carboxylate and a deprotonated hydroxamate group) and two nitrogen atoms (from an amine and a deprotonated hydroxamate). The equatorial \(\text{Cu}—\text{O}_{\text{eq}}\) and \(\text{Cu}—\text{N}_{\text{eq}}\) distances range from 1.928 (3) to 1.969 (3) Å and 1.890 (4) to 2.018 (4) Å (Table 1), respectively, which is typical of aminohydroxamate 15-metallacrown-5 complexes (Stemmler et al., 1999; Pavlishchuk et al., 2011; Katkova et al., 2015; Meng et al., 2016). As a result of the apical coordination of water molecules to copper(II) ions, Cu1 has distorted square-bipyramidal coordination \([\text{Cu}1—\text{O}_{20} = 2.601 (4) \ \text{Å} \text{and Cu}1—\text{O}_{21} = 2.736 (4) \ \text{Å}](1)\), while Cu3, Cu4 and Cu5 are in square-pyramidal environments \([\text{Cu}3—\text{O}_{16} = 2.508 (4) \ \text{Å} \text{and Cu}3—\text{O}_{11} = 2.436 (3) \ \text{Å}](1)\).

Table 1

| Bond Lengths (Å) |  
|-----------------|-----------------|-----------------|-----------------|
| Cu1—N3         | 1.915 (4)       | Cu4—O8          | 1.940 (3)       |
| Cu1—O1         | 1.928 (3)       | Cu4—O7          | 1.947 (3)       |
| Cu1—O2         | 1.969 (3)       | Cu4—N10         | 2.012 (4)       |
| Cu1—N4         | 1.991 (4)       | Cu4—O17         | 2.481 (4)       |
| Cu1—O20        | 2.601 (4)       | Cu5—N1          | 1.890 (4)       |
| Cu1—O21        | 2.736 (4)       | Cu5—O9          | 1.943 (3)       |
| Cu2—N5         | 1.900 (4)       | Cu5—O10         | 1.946 (3)       |
| Cu2—O3         | 1.928 (3)       | Cu5—N2          | 2.003 (4)       |
| Cu2—O4         | 1.936 (3)       | Cu5—O18         | 2.379 (4)       |
| Cu2—N6         | 2.018 (4)       | Tb1—O9          | 2.370 (3)       |
| Cu2—O19        | 2.409 (10)      | Tb1—O1          | 2.372 (3)       |
| Cu3—N7         | 1.904 (4)       | Tb1—O15         | 2.383 (3)       |
| Cu3—O6         | 1.944 (3)       | Tb1—O3          | 2.386 (3)       |
| Cu3—O5         | 1.949 (3)       | Tb1—O7          | 2.411 (3)       |
| Cu3—N8         | 2.014 (4)       | Tb1—O5          | 2.430 (3)       |
| Cu3—O16        | 2.508 (4)       | Tb1—O12         | 2.436 (3)       |
| Cu4—N9         | 1.894 (4)       | Tb1—O11         | 2.451 (3)       |

Figure 1

The unit cell of complex 1 containing two \([\text{TbCu}_5(\text{GlyHA})_5(\text{SO}_4)(\text{H}_2\text{O})_{6.5}]^+\) metallacrown cations and non-coordinated sulfate anions (located on a inversion center with O atoms 1:1 disordered). Non-coordinated water molecules are omitted for clarity of presentation.

Figure 2

Structure of the \([\text{TbCu}_5(\text{GlyHA})_5(\text{SO}_4)(\text{H}_2\text{O})_{6.5}]^+\) metallacrown cations in 1. The dashed lines indicate the disorder of the non-coordinated sulfate anion. Displacement ellipsoids are shown at the 50% probability level. [Symmetry code: (i) \(x, y, z + 1\).]
The coordination environment of the Tb$^{III}$ ion is completed to an octacoordination level via the two oxygen atoms O11 [Tb1—O11 = 2.451 (3) Å] and O12 [Tb1—O12 = 2.436 (3) Å] from the bidentate sulfate anions and O15 [Tb1—O15 = 2.383 (3) Å] from a water molecule coordinated in the trans-position opposite to the SO$_4^{2-}$ ion. An analysis of selected structural parameters for complex 1 and those of isomorphous compounds with other Ln$^{III}$ ions (Table 2) reveals the influence of the lanthanide contraction. Similar behaviour was found in other series of lanthanide(III) containing metallamacrocycles (Pavlishchuk et al., 2011; Zaleski et al., 2011). According to Shape 2.1 (Casanova et al., 2005) calculations (Fig. 3, Table 3), the coordination geometry of the Tb$^{III}$ ion in 1 is a square antiprism ($D_{4d}$), which is of particular interest with respect to potential generation of lanthanide(III)-containing SMMs (Liu et al., 2018). The deviations from an idealized square-antiprismatic geometry in the [LnCu$_5$(GlyHA)$_5$(SO$_4$)(H$_2$O)$_{6.5}$](SO$_4$) complexes decrease with reduction of the deviation of the Ln$^{III}$ ion from the mean plane of the metallacrown core, which parallels the ionic radii of the Ln$^{III}$ ions (Table 3). It may be noted that, in the case of a series of related 15-metallacrown-5 complexes with octacoordinate Ln$^{III}$ ions containing bidentate carbonates or acetates instead of sulfates, the coordination of the lanthanide ions is triangular dodecahedral ($D_{2d}$) (Table 3).

The Cu···O and Ln···Cu separations for complex 1 range from 4.501 (1) to 4.577 (1) Å and 3.8398 (8) to 3.8944 (8) Å, respectively, and are typical for [LnCu$_5$]$^{3+}$ metallacrowns (Stemmler et al., 1999; Pavlishchuk et al., 2011; Katkova et al., 2015a; Meng et al., 2016). The Cu···O, Cu···N and Cu···Cu distances do not vary significantly amongst metallamacrocycles with different bidentate counter-anions (Table 2). The metallacrown moiety in 1 is close to planar, the deviation of...
Table 3
Continuous shape calculations for octacoordinated LnIII ions in I obtained with Shape 2.1 software (Casanova et al., 2005).

|          | OP-8  | HPY-8 | HBPY-8 | CU-8  | SAPR-8 | TDD-8 | JGBF-8 | JETBPY-8 |
|----------|-------|-------|--------|-------|--------|-------|--------|----------|
| Pr–SO4   | 30.846| 22.755| 15.952 | 11.561| 2.215  | 2.397 | 13.029 | 25.482   |
| Nd–SO4   | 30.677| 22.888| 15.968 | 11.587| 2.141  | 2.364 | 13.033 | 25.516   |
| Sm–SO4   | 30.387| 22.903| 15.951 | 11.630| 2.020  | 2.311 | 13.013 | 25.752   |
| Eu–SO4   | 30.516| 23.164| 16.270 | 11.783| 1.952  | 2.363 | 13.190 | 25.864   |
| Gd–SO4   | 30.465| 23.110| 16.032 | 11.570| 1.907  | 2.269 | 13.151 | 26.121   |
| Tb–SO4   | 30.381| 23.117| 16.159 | 11.666| 1.854  | 2.322 | 13.140 | 26.276   |
| Dy–SO4   | 30.357| 23.195| 16.112 | 11.613| 1.799  | 2.254 | 13.168 | 26.433   |
| Ho–SO4   | 30.272| 23.212| 16.095 | 11.588| 1.761  | 2.247 | 13.186 | 26.496   |

Octacoordinated ions: OP-8 = octagon (D8h); HPY-8 = heptagonal pyramid (C7v); HBPY-8 = hexagonal bipyramid (D4h); CU-8 = cube (Oh); SAPR-8 = square antiprism (D2d); TDD-8 = triangular dodecahedron (D3d); JGBF-8 = Johnson gyrobirotundig 126 (D3d); JETBPY-8 = Johnson elongated triangular bipyramid J4 (D3d).

3. Supramolecular features
The [LnCu5(GlyHA)3]3+ cations in complex I are non-oligomerized, which is typical for 15-metallacrown-5 complexes. The water apical to TbIII in I (O15) is involved in the formation of intramolecular hydrogen bonds (O15—H15A···O21 and O15—H15B···O16) with apically coordinated water molecules O16 and O21 on copper(II) ions Cu3 and Cu4, respectively. Intramolecular hydrogen bonds in I are also formed between the bidentate sulfate and apically coordinated water molecules O17, O18 and O20 (O17—H17A···O12, O18—H18B···O14 and O20—H20B···O11) on copper(II) ions Cu4, Cu5 and Cu1. An extended system of intermolecular hydrogen bonds [N2—H2A···O15iii, N8—H8B···O12iv, N10—H10A···O20v, O10viii···H21B—O21, O6vii···H17B—O17, O21—H21A···O18ix, O16—H16A···O17x] links adjacent [TbCu5(GlyHA)3(H2O)6.5(SO4)]3+ cations and non-coordinated sulfate anions [N4—H4A···O27ix(SO4), O18—H18B···O27(SO4), N4—H4A···O25(SO4) and O20—H20A···O25(SO4)]. Non-coordinated water molecules in I are linked by hydrogen bonds with carbonyl oxygen and amine nitrogen atoms in the glycine-hydroxamate unit from the metallacrown core (O4v···H23A—O23, O8···H24B—O24, N6—H6B···O24vii, N8—H8A···O23, N10—H10B···O22viii) and coordinated water molecules (O16—H16B···O22, O19—H19A···O24ix, O19—H19B···O24viii) or bidentate sulfate (O11ix···H24A···O24 and O13h···H23B···O23). Hydrogen-bond parameters and symmetry codes are given in Table 4.

4. Database survey
Comounds most closely related to I are its isomorphous counterparts [LnCu5(GlyHA)3(SO4)(H2O)6.5(SO4)]SO4, where GlyHA3− is the dianion of glycinehydroxyacidic acid and LnIII = Pr, Nd, Sm, Eu, Gd, Dy and Ho (Pavlishchuk et al., 2001). A search of the Cambridge Structural Database (Version 5.41, 2021; Groom et al., 2016) reveals other compounds that also feature an LnCu5(GlyHA)3 core, with counter-anions such as nitrate, acetate, chloride, lactate, carbonate, sulfate, isophthalate, terephthalate and all lanthanide ions other than radioactive Pm (Katzka et al., 2015a,b; Pavlishchuk et al., 2011, 2017a, Pavlishchuk et al., 2018, 2019; Stemmler et al., 1999; Muravyeva et al., 2016; Kreml et al., 2016). Most of
these complexes feature, similar to I, individual molecular complex cations (Katkova et al., 2015a,b; Pavlishchuk et al., 2011, 2017a, 2018, 2019; Stemmler et al., 1999; Muravyeva et al., 2016; Kremlev et al., 2016), but a small number of oligomerized examples have also been reported (Pavlishchuk et al., 2017a, 2018).

5. Synthesis and crystallization

Complex 1 was synthesized and crystallized according a general procedure described previously (Pavlishchuk et al., 2011). Single crystals were obtained by slow evaporation from an aqueous solution of 1.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 5. The structure is isomorphous with its Dy, Eu, Gd, Ho, Nd, Pr analogues (Pavlishchuk et al., 2011) and was solved by isomorphous replacement. The O19 water molecule is disordered over two mutually exclusive positions across an inversion center and was refined as half occupied.

The non-coordinated sulfate ion is located on an inversion center and the oxygen atoms are disordered over two sets of positions with half occupancy.

C—H bond distances were constrained to 0.99 for aliphatic CH2 moieties. N—H bond distances were constrained to 0.91 Å for pyramidal (sp3-hybridized) ammonium NH+ groups. Water H-atom positions were refined, and O—H distances were restrained to 0.84 (2) Å. The H···H distances within the O23 and O24 water molecules were further restrained to 1.35 (2) Å. Uiso(H) values were set to kUeq(C/N/O) with k =1.5 for OH, and 1.2 for CH2 and NH2 units, respectively.

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Crystal structure of a Tb\textsuperscript{III}–Cu\textsuperscript{II} glycinehydroxamate 15-metallacrown-5 sulfate complex

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Computing details

Data collection: APEX3 (Bruker, 2018); cell refinement: SAINT (Bruker, 2018); data reduction: SAINT (Bruker, 2018); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL2018/3 (Sheldrick, 2015), shelXle (Hübschle et al., 2011); software used to prepare material for publication: publCIF (Westrip, 2010).

Bis[hexaaquahemiaquapentakis(µ\textsubscript{3}-glycinehydroxamato)sulfatopentacopper(II)terbium(III)] sulfate hexahydrate

Crystal data

[Tb\textsubscript{2}Cu\textsubscript{5}(H\textsubscript{2}O\textsubscript{6})\textsubscript{5}(SO\textsubscript{4})\textsubscript{5}(SO\textsubscript{4})\textsubscript{6}H\textsubscript{2}O] \textsubscript{2} \textsubscript{2}(SO\textsubscript{4})\textsubscript{6}H\textsubscript{2}O

$M_r = 2464.44$

Triclinic, $P\overline{1}$

$\alpha = 9.6370$ (4) Å

$\beta = 11.5888$ (5) Å

$\gamma = 16.2367$ (6) Å

$\alpha = 99.6716$ (13)$^{\circ}$

$\beta = 91.3031$ (12)$^{\circ}$

$\gamma = 105.3123$ (12)$^{\circ}$

$V = 1719.80$ (12) Å\textsuperscript{3}

$Z = 1$

$F(000) = 1214$

$D_x = 2.380$ Mg m\textsuperscript{-3}

Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å

Cell parameters from 9965 reflections

$\theta = 4.0–79.9^{\circ}$

$\mu = 15.11$ mm\textsuperscript{-1}

$T = 150$ K

Plate, blue

$0.20 \times 0.20 \times 0.08$ mm

Data collection

Bruker AXS D8 Quest CMOS diffractometer with PhotonII charge-integrating pixel array detector (CPAD)

Radiation source: I-mu-S microsource X-ray tube

Laterally graded multilayer (Goebel) mirror monochromator

Detector resolution: 7.4074 pixels mm\textsuperscript{-1}

$\omega$ and phi scans

Absorption correction: multi-scan (SADABS; Krause et al., 2015)

$T_{\text{min}} = 0.454$, $T_{\text{max}} = 0.754$

16278 measured reflections

7029 independent reflections

6786 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.050$

$\theta_{\text{max}} = 80.3^{\circ}$, $\theta_{\text{min}} = 2.8^{\circ}$

$h = -12\rightarrow 12$

$k = -14\rightarrow 14$

$l = -19\rightarrow 15$

Refinement

Refinement on $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.041$

$wR(F^2) = 0.118$

$S = 1.10$

562 parameters

22 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

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Hydrogen site location: mixed
H atoms treated by a mixture of independent
and constrained refinement

\[ w = 1/\left(\sigma^2(F_o^2) + (0.0656P)^2 + 1.8351P\right) \]
where \( P = (F_o^2 + 2F_c^2)/3 \)
\( (\Delta/\sigma)_{\text{max}} < 0.001 \)
\[ \Delta \rho_{\text{max}} = 1.59 \text{ e Å}^{-3} \]
\[ \Delta \rho_{\text{min}} = -1.34 \text{ e Å}^{-3} \]

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.** The structure is isomorphous with its Dy, Eu, Gd, Ho, Nd, Pr analogues (AVP85_10mz121, AVP355_10mz172, AVP621_09mz411 and AVP629_10mz194, AVP65_10mz125 and AVP651_10mz191, AVP70_10mz147, AVP75_10mz148 and AVP754_10mz650), and was solved by isomorphous replacement.
The water molecule of O19 is disordered over two mutually exclusive positions across an inversion center and was refined as half occupied. The non-coordinated sulfate ion is located on an inversion center and the oxygen atoms are disordered over two sets of positions with half occupancy.
Water H atom positions were refined and O-H distances were restrained to 0.84 (2) Angstrom, respectively. Some H···H distances were further restrained to 1.35 (2) Angstrom.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

|   | x    | y    | z    | U(eq) | Occ. (<1) |
|---|------|------|------|-------|-----------|
| C1| 0.4433 (5) | 0.2625 (4) | 0.5042 (3) | 0.0167 (8) |
| C2| 0.3610 (5) | 0.2938 (4) | 0.5788 (3) | 0.0195 (9) |
| H2C| 0.320220 | 0.220082 | 0.602893 | 0.023* |
| H2D| 0.427084 | 0.354919 | 0.622292 | 0.023* |
| C3| 0.6783 (5) | 0.0423 (4) | 0.2493 (3) | 0.0158 (8) |
| C4| 0.6931 (6) | -0.0360 (5) | 0.3110 (3) | 0.0235 (10) |
| H4C| 0.794720 | -0.038433 | 0.316648 | 0.028* |
| H4D| 0.632740 | -0.119964 | 0.290399 | 0.028* |
| C5| 0.7890 (5) | 0.3483 (4) | 0.0317 (3) | 0.0175 (9) |
| C6| 0.8858 (5) | 0.2707 (4) | -0.0019 (3) | 0.0221 (10) |
| H6C| 0.874472 | 0.253424 | -0.063895 | 0.027* |
| H6D| 0.987712 | 0.315424 | 0.015213 | 0.027* |
| C7| 0.5254 (5) | 0.6985 (4) | 0.1304 (3) | 0.0159 (8) |
| C8| 0.6022 (5) | 0.7507 (4) | 0.0594 (3) | 0.0179 (9) |
| H8C| 0.532673 | 0.736705 | 0.010561 | 0.022* |
| H8D| 0.643978 | 0.839491 | 0.076935 | 0.022* |
| C9| 0.2149 (5) | 0.5808 (4) | 0.3895 (3) | 0.0163 (9) |
| C10| 0.1644 (5) | 0.6898 (4) | 0.3802 (3) | 0.0222 (10) |
| H10C| 0.058903 | 0.664428 | 0.366493 | 0.027* |
| H10D| 0.184336 | 0.748022 | 0.434014 | 0.027* |
| Cu1| 0.57451 (7) | 0.15475 (6) | 0.38923 (4) | 0.01792 (16) |
| Cu2| 0.71639 (7) | 0.16393 (6) | 0.12404 (4) | 0.01884 (16) |
| Cu3| 0.68477 (7) | 0.53540 (6) | 0.08031 (4) | 0.01553 (15) |
| Cu4| 0.34975 (7) | 0.64627 (6) | 0.24858 (4) | 0.01548 (15) |
| Cu5| 0.28203 (7) | 0.39948 (6) | 0.44370 (4) | 0.01615 (15) |
| Tb1| 0.48345 (2) | 0.35681 (2) | 0.24306 (2) | 0.01322 (9) |
| N1| 0.4245 (4) | 0.3141 (3) | 0.4416 (2) | 0.0171 (7) |
| Atom | X       | Y       | Z       | U1     | U2     | U3     | U12    | U13    | U23    |
|------|---------|---------|---------|--------|--------|--------|--------|--------|--------|
| N2   | 0.2431  | 0.3430  | 0.5530  | 0.0195 | 0.023  |
| H2A  | 0.2365  | 0.4062  | 0.5928  |        |        |        |        |        |        |
| H2B  | 0.1577  | 0.2843  | 0.5476  |        |        |        |        |        |        |
| N3   | 0.6105  | 0.1242  | 0.2732  | 0.0178 | 0.0215 |
| N4   | 0.6482  | 0.0108  | 0.3943  |        |        |        |        |        |        |
| H4A  | 0.7247  | 0.0319  | 0.4328  | 0.026  |
| H4B  | 0.5779  | -0.0487 | 0.4106  | 0.026  |
| N5   | 0.7027  | 0.3075  | 0.0865  | 0.0166 |
| N6   | 0.8492  | 0.1541  | 0.0304  | 0.0171 |
| H6A  | 0.9313  | 0.1394  | 0.0495  | 0.021  |
| H6B  | 0.8054  | 0.0916  | -0.0116 | 0.021  |
| N7   | 0.5575  | 0.6039  | 0.1480  | 0.0172 |
| N8   | 0.7190  | 0.6918  | 0.0356  | 0.0159 |
| H8A  | 0.8059  | 0.7427  | 0.0570  | 0.019  |
| H8B  | 0.7203  | 0.6761  | -0.0211 | 0.019  |
| N9   | 0.2929  | 0.5471  | 0.3302  | 0.0173 |
| N10  | 0.2378  | 0.7509  | 0.3133  | 0.022  |
| H10A | 0.2987  | 0.8242  | 0.3365  | 0.027  |
| H10B | 0.1710  | 0.7639  | 0.2780  | 0.027  |
| O1   | 0.5000  | 0.2882  | 0.3716  | 0.016  |
| O2   | 0.5244  | 0.1896  | 0.5060  | 0.019  |
| O3   | 0.6029  | 0.1998  | 0.2163  | 0.019  |
| O4   | 0.7336  | 0.0300  | 0.1769  | 0.019  |
| O5   | 0.6158  | 0.3809  | 0.1186  | 0.015  |
| O6   | 0.7979  | 0.4510  | 0.0074  | 0.018  |
| O7   | 0.4861  | 0.5537  | 0.2123  | 0.016  |
| O8   | 0.4330  | 0.7478  | 0.1689  | 0.019  |
| O9   | 0.3463  | 0.4493  | 0.3393  | 0.017  |
| O10  | 0.1827  | 0.5265  | 0.4519  | 0.019  |
| O11  | 0.2853  | 0.1696  | 0.2229  | 0.023  |
| O12  | 0.2734  | 0.3216  | 0.1464  | 0.020  |
| O13  | 0.1448  | 0.1123  | 0.0876  | 0.025  |
| O14  | 0.0575  | 0.2189  | 0.2058  | 0.031  |
| O15  | 0.7222  | 0.4609  | 0.3006  | 0.018  |
| O16  | 0.767   | 0.430   | 0.331   | 0.028  |
| O17  | 0.562   | 0.617   | 0.269   | 0.028  |
| O18  | 0.455   | 0.312   | 0.156   | 0.033  |
| O19  | 0.472   | -0.003  | 0.060   | 0.071  |
| O20  | 0.552   | 0.02    | -0.021  | 0.071  |
|   |   |   |   |   |   |
|---|---|---|---|---|---|
| O20 | 0.3102 (4) | 0.0221 (3) | 0.3519 (3) | 0.0283 (8) |   |
| H20A | 0.236 (5) | 0.022 (7) | 0.377 (4) | 0.043* |   |
| H20B | 0.291 (8) | 0.063 (6) | 0.318 (4) | 0.043* |   |
| O21 | 0.8274 (4) | 0.3337 (4) | 0.3966 (2) | 0.0308 (8) |   |
| H21A | 0.909 (4) | 0.320 (7) | 0.392 (5) | 0.046* |   |
| H21B | 0.841 (8) | 0.380 (6) | 0.443 (3) | 0.046* |   |
| O22 | 0.9749 (5) | 0.8150 (4) | 0.2711 (3) | 0.0361 (9) |   |
| H22A | 0.972 (9) | 0.855 (7) | 0.319 (2) | 0.054* |   |
| H22B | 0.980 (9) | 0.857 (6) | 0.234 (4) | 0.054* |   |
| O23 | 0.9394 (4) | 0.9116 (3) | 0.1345 (2) | 0.0243 (7) |   |
| H23A | 0.876 (4) | 0.947 (5) | 0.150 (4) | 0.036* |   |
| H23B | 1.011 (4) | 0.968 (4) | 0.126 (4) | 0.036* |   |
| O24 | 0.3431 (7) | 0.9430 (4) | 0.1264 (3) | 0.0523 (14) |   |
| H24A | 0.328 (11) | 0.998 (6) | 0.163 (4) | 0.079* |   |
| H24B | 0.368 (10) | 0.893 (6) | 0.152 (4) | 0.079* |   |
| O25 | 0.1618 (8) | 0.0365 (9) | 0.4920 (5) | 0.0357 (19) | 0.5 |
| O26 | −0.0300 (9) | −0.0158 (7) | 0.5820 (5) | 0.0339 (17) | 0.5 |
| O27 | −0.0484 (9) | 0.1032 (7) | 0.4781 (5) | 0.0333 (17) | 0.5 |
| O28 | −0.0592 (9) | −0.1078 (7) | 0.4360 (5) | 0.0346 (17) | 0.5 |
| S1 | 0.18461 (12) | 0.20240 (10) | 0.16476 (7) | 0.0195 (2) |   |
| S2 | 0.000000 | 0.000000 | 0.500000 | 0.0199 (3) |   |

**Atomic displacement parameters (Å²)**

| U₁₁ | U₂₂ | U₃₃ | U₁₂ | U₁₃ | U₂₃ |
|-----|-----|-----|-----|-----|-----|
| C1  | 0.0163 (19) | 0.0162 (19) | 0.019 (2) | 0.0070 (16) | 0.0042 (17) | 0.0016 (17) |
| C2  | 0.024 (2) | 0.025 (2) | 0.016 (2) | 0.0143 (18) | 0.0049 (17) | 0.0080 (18) |
| C3  | 0.0152 (19) | 0.0150 (19) | 0.019 (2) | 0.0092 (16) | 0.0030 (16) | 0.0011 (17) |
| C4  | 0.034 (3) | 0.024 (2) | 0.019 (2) | 0.020 (2) | 0.0063 (19) | 0.0025 (19) |
| C5  | 0.018 (2) | 0.019 (2) | 0.016 (2) | 0.0074 (17) | 0.0045 (17) | 0.0023 (17) |
| C6  | 0.025 (2) | 0.018 (2) | 0.025 (2) | 0.0068 (18) | 0.0113 (19) | 0.0018 (18) |
| C7  | 0.0150 (19) | 0.0126 (19) | 0.019 (2) | 0.0023 (15) | 0.0009 (16) | 0.0027 (17) |
| C8  | 0.018 (2) | 0.017 (2) | 0.021 (2) | 0.0078 (16) | 0.0038 (17) | 0.0055 (17) |
| C9  | 0.018 (2) | 0.0165 (19) | 0.017 (2) | 0.0114 (16) | 0.0011 (16) | −0.0027 (17) |
| C10 | 0.029 (2) | 0.024 (2) | 0.022 (2) | 0.0194 (19) | 0.0081 (19) | 0.0066 (19) |
| Cu1 | 0.0252 (3) | 0.0179 (3) | 0.0165 (3) | 0.0146 (3) | 0.0054 (3) | 0.0048 (3) |
| Cu2 | 0.0252 (3) | 0.0152 (3) | 0.0212 (4) | 0.0122 (3) | 0.0111 (3) | 0.0051 (3) |
| Cu3 | 0.0188 (3) | 0.0136 (3) | 0.0167 (3) | 0.0074 (2) | 0.0067 (2) | 0.0039 (2) |
| Cu4 | 0.0173 (3) | 0.0138 (3) | 0.0189 (3) | 0.0090 (2) | 0.0052 (2) | 0.0045 (2) |
| Cu5 | 0.0188 (3) | 0.0174 (3) | 0.0169 (3) | 0.0111 (3) | 0.0069 (2) | 0.0053 (3) |
| Tb1 | 0.01436 (14) | 0.01192 (14) | 0.01535 (15) | 0.00683 (10) | 0.00396 (10) | 0.00235 (10) |
| N1  | 0.0233 (18) | 0.0181 (17) | 0.0138 (18) | 0.0112 (15) | 0.0065 (14) | 0.0044 (14) |
| N2  | 0.0220 (19) | 0.0194 (18) | 0.020 (2) | 0.0106 (15) | 0.0073 (15) | 0.0036 (15) |
| N3  | 0.0234 (19) | 0.0150 (17) | 0.0201 (19) | 0.0111 (15) | 0.0070 (15) | 0.0071 (15) |
| N4  | 0.029 (2) | 0.0223 (19) | 0.020 (2) | 0.0157 (16) | 0.0087 (16) | 0.0072 (16) |
| N5  | 0.0159 (17) | 0.0179 (17) | 0.0169 (18) | 0.0087 (14) | 0.0056 (14) | −0.0016 (15) |
| N6  | 0.0171 (17) | 0.0183 (18) | 0.0193 (19) | 0.0092 (14) | 0.0060 (14) | 0.0053 (15) |
| N7  | 0.0192 (18) | 0.0170 (17) | 0.0174 (18) | 0.0075 (14) | 0.0036 (15) | 0.0043 (15) |
### Geometric parameters (Å, °)

|   | C1—N1 | C1—O2 | C1—C2 | C2—N2 | C2—H2C | C2—H2D | C3—N3 | C3—O4 | C3—C4 | C4—N4 | C4—H4C | C4—H4D |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
|   | 1.294 (6) | 1.298 (5) | 1.509 (6) | 1.480 (6) | 0.9900 | 0.9900 | 1.301 (5) | 1.304 (6) | 1.488 (7) | 1.488 (6) | 0.9900 | 0.9900 |

**N8** 0.0212 (18) 0.0104 (15) 0.0183 (18) 0.0060 (14) 0.0061 (14) 0.0057 (14)

**N9** 0.0202 (18) 0.0166 (17) 0.0185 (19) 0.0108 (14) 0.0029 (15) 0.0032 (15)

**N10** 0.0212 (19) 0.0169 (18) 0.034 (2) 0.0125 (15) 0.0102 (17) 0.0039 (17)

**O1** 0.0207 (15) 0.0205 (15) 0.0148 (15) 0.0141 (12) 0.0090 (12) 0.0057 (12)

**O2** 0.0277 (17) 0.0195 (15) 0.0172 (16) 0.0146 (13) 0.0065 (13) 0.0050 (13)

**O3** 0.0307 (17) 0.0187 (15) 0.0182 (16) 0.0155 (13) 0.0121 (13) 0.0095 (13)

**O4** 0.0251 (16) 0.0183 (15) 0.0197 (16) 0.0123 (13) 0.0084 (13) 0.0041 (13)

**O5** 0.0193 (14) 0.0119 (13) 0.0197 (16) 0.0103 (11) 0.0064 (12) 0.0031 (12)

**O6** 0.0271 (17) 0.0166 (14) 0.0172 (16) 0.0107 (13) 0.0104 (13) 0.0053 (12)

**O7** 0.0180 (14) 0.0154 (14) 0.0205 (16) 0.0086 (12) 0.0114 (12) 0.0067 (12)

**O8** 0.0201 (15) 0.0193 (15) 0.0238 (17) 0.0120 (12) 0.0072 (13) 0.0070 (13)

**O9** 0.0204 (15) 0.0178 (15) 0.0210 (16) 0.0168 (12) 0.0109 (12) 0.0065 (13)

**O10** 0.0280 (17) 0.0209 (15) 0.0172 (16) 0.0160 (13) 0.0094 (13) 0.0081 (13)

**O11** 0.0247 (17) 0.0219 (16) 0.0246 (18) 0.0061 (13) −0.0008 (14) 0.0042 (14)

**O12** 0.0253 (16) 0.0174 (15) 0.0180 (16) 0.0028 (13) 0.0002 (13) 0.0058 (13)

**O13** 0.0280 (17) 0.0206 (16) 0.0241 (18) 0.0028 (14) 0.0013 (14) 0.0010 (14)

**O14** 0.0210 (17) 0.043 (2) 0.0267 (19) 0.0086 (16) 0.0047 (14) −0.0019 (16)

**O15** 0.0178 (15) 0.0222 (16) 0.0167 (16) 0.0076 (12) 0.0016 (12) 0.0044 (13)

**O16** 0.0190 (16) 0.0268 (17) 0.0287 (19) 0.0047 (14) 0.0044 (14) 0.0029 (15)

**O17** 0.0281 (17) 0.0224 (16) 0.0183 (16) 0.0111 (14) 0.0040 (14) 0.0043 (14)

**O18** 0.0261 (17) 0.0227 (17) 0.0236 (18) 0.0066 (14) 0.0045 (14) 0.0040 (14)

**O19** 0.038 (5) 0.064 (6) 0.026 (4) −0.007 (4) −0.001 (4) 0.005 (4)

**O20** 0.0309 (19) 0.0200 (17) 0.035 (2) 0.0066 (15) 0.0100 (16) 0.0063 (15)

**O21** 0.0287 (19) 0.044 (2) 0.0241 (19) 0.0232 (17) 0.0003 (15) −0.0036 (16)

**O22** 0.047 (2) 0.036 (2) 0.032 (2) 0.0236 (19) −0.0020 (19) 0.0038 (17)

**O23** 0.0215 (16) 0.0173 (15) 0.035 (2) 0.0072 (13) 0.0068 (15) 0.0026 (14)

**O24** 0.090 (4) 0.039 (2) 0.037 (2) 0.043 (3) −0.015 (2) −0.008 (2)

**O25** 0.023 (4) 0.058 (5) 0.034 (4) 0.014 (4) 0.007 (3) 0.022 (4)

**O26** 0.042 (4) 0.034 (4) 0.025 (4) 0.011 (3) 0.007 (3) 0.002 (3)

**O27** 0.038 (4) 0.030 (4) 0.041 (5) 0.018 (3) 0.007 (3) 0.018 (3)

**O28** 0.044 (5) 0.026 (4) 0.033 (4) 0.009 (3) 0.004 (3) 0.003 (3)

**S1** 0.0186 (5) 0.0195 (5) 0.0200 (5) 0.0044 (4) 0.0019 (4) 0.0037 (4)

**S2** 0.0189 (7) 0.0180 (7) 0.0235 (8) 0.0071 (6) −0.0005 (6) 0.0026 (6)
| Bond              | Length (Å) | Bond Angle (°) | Other Bond Angle (°) |
|------------------|------------|----------------|----------------------|
| C5—N5            | 1.295 (6)  |                |                      |
| C5—O6            | 1.298 (6)  |                |                      |
| C5—C6            | 1.509 (6)  |                |                      |
| C6—N6            | 1.491 (6)  |                |                      |
| C6—H6C           | 0.9900     |                |                      |
| C6—H6D           | 0.9900     |                |                      |
| C7—N7            | 1.288 (6)  |                |                      |
| C7—O8            | 1.298 (5)  |                |                      |
| C7—C8            | 1.509 (6)  |                |                      |
| C8—N8            | 1.489 (5)  |                |                      |
| C8—H8C           | 0.9900     |                |                      |
| C8—H8D           | 0.9900     |                |                      |
| C9—O10           | 1.282 (6)  |                |                      |
| C9—N9            | 1.306 (6)  |                |                      |
| C9—C10           | 1.498 (6)  |                |                      |
| C10—N10          | 1.487 (7)  |                |                      |
| C10—H10C         | 0.9900     |                |                      |
| C10—H10D         | 0.9900     |                |                      |
| Cu1—N3           | 1.915 (4)  |                |                      |
| Cu1—O1           | 1.928 (3)  |                |                      |
| Cu1—O2           | 1.969 (3)  |                |                      |
| Cu1—N4           | 1.991 (4)  |                |                      |
| Cu1—O20          | 2.601 (4)  |                |                      |
| Cu1—O21          | 2.736 (4)  |                |                      |
| Cu2—N5           | 1.900 (4)  |                |                      |
| Cu2—O3           | 1.928 (3)  |                |                      |
| Cu2—O4           | 1.936 (3)  |                |                      |
| Cu2—N6           | 2.018 (4)  |                |                      |
| Cu2—O19          | 2.409 (10) |                |                      |
| Cu3—N7           | 1.904 (4)  |                |                      |
| Cu3—O6           | 1.944 (3)  |                |                      |
| Cu3—O5           | 1.949 (3)  |                |                      |
| Cu3—N8           | 2.014 (4)  |                |                      |
| Cu3—O16          | 2.508 (4)  |                |                      |
| Cu4—N9           | 1.894 (4)  |                |                      |
| Cu4—O8           | 1.940 (3)  |                |                      |
| Cu4—O7           | 1.947 (3)  |                |                      |
| Cu4—N10          | 2.012 (4)  |                |                      |
| Cu4—O17          | 2.481 (4)  |                |                      |
| Cu5—N1           | 1.890 (4)  |                |                      |
| Cu5—O9           | 1.943 (3)  |                |                      |
| Cu5—O10          | 1.946 (3)  |                |                      |

| Bond Angle        | Value (°) | Bond Angle        | Value (°) |
|-------------------|-----------|-------------------|-----------|
| C5—N5—C6         | 125.3 (4) | O5—Tb1—O11       | 112.83 (11) |
| N1—C1—O2         | 114.2 (4) | O12—Tb1—O11      | 57.34 (11)  |
| O2—C1—C2         | 120.5 (4) | O9—Tb1—S1        | 83.26 (8)   |
| N2—C2—C1         | 110.0 (4) | O1—Tb1—S1        | 102.84 (8)  |
| N2—C2—H2C        | 109.7     | O15—Tb1—S1       | 174.96 (8)  |
| Bond Pairs | Angle (°) | Error (°) |
|-----------|-----------|-----------|
| C1—C2—H2C | 109.7 | |
| N2—C2—H2D | 109.7 | |
| C1—C2—H2D | 109.7 | |
| H2C—C2—H2D | 108.2 | |
| N3—C3—O4 | 123.0 (4) | |
| N3—C3—C4 | 115.9 (4) | |
| O4—C3—C4 | 121.1 (4) | |
| C3—C4—N4 | 111.1 (4) | |
| C3—C4—H4C | 109.4 | |
| N4—C4—H4C | 109.4 | |
| C3—C4—H4D | 109.4 | |
| N4—C4—H4D | 109.4 | |
| H4C—C4—H4D | 108.0 | |
| N5—C5—O6 | 123.7 (4) | |
| N5—C5—C6 | 116.0 (4) | |
| O6—C5—C6 | 120.3 (4) | |
| N6—C6—C5 | 110.5 (4) | |
| N6—C6—H6C | 109.5 | |
| C5—C6—H6C | 109.5 | |
| N6—C6—H6D | 109.5 | |
| C5—C6—H6D | 109.5 | |
| H6C—C6—H6D | 108.1 | |
| N7—C7—C8 | 115.5 (4) | |
| O8—C7—C8 | 120.4 (4) | |
| N8—C8—C7 | 109.8 (4) | |
| N8—C8—H8C | 109.7 | |
| C7—C8—H8C | 109.7 | |
| N8—C8—H8D | 109.7 | |
| O10—C9—N9 | 123.8 (4) | |
| O10—C9—C10 | 121.2 (4) | |
| N9—C9—C10 | 115.0 (4) | |
| N10—C10—C9 | 111.3 (4) | |
| N10—C10—H10C | 109.4 | |
| C9—C10—H10C | 109.4 | |
| N10—C10—H10D | 109.4 | |
| C9—C10—H10D | 109.4 | |
| H10C—C10—H10D | 108.0 | |
| N3—Cu1—O1 | 90.36 (14) | |
| N3—Cu1—O2 | 175.68 (15) | |
| O1—Cu1—O2 | 86.12 (13) | |
| N3—Cu1—N4 | 83.85 (16) | |
| O1—Cu1—N4 | 173.91 (15) | |
| O2—Cu1—N4 | 99.57 (15) | |
| N3—Cu1—O20 | 89.10 (15) | |
| O1—Cu1—O20 | 85.07 (13) | |
| Bond               | Angle (°) (E)  |
|--------------------|---------------|
| O2—Cu1—O20        | 88.10 (14)    |
| N4—Cu1—O20        | 92.89 (15)    |
| N3—Cu1—O21        | 82.42 (14)    |
| O1—Cu1—O21        | 80.09 (13)    |
| O2—Cu1—O21        | 99.41 (13)    |
| N4—Cu1—O21        | 100.98 (15)   |
| O20—Cu1—O21       | 162.82 (12)   |
| N5—Cu2—O3         | 89.51 (15)    |
| N5—Cu2—O4         | 172.53 (15)   |
| O3—Cu2—O4         | 84.79 (13)    |
| N5—Cu2—N6         | 83.61 (16)    |
| O3—Cu2—N6         | 171.24 (15)   |
| N4—Cu2—O3         | 101.58 (15)   |
| N5—Cu2—O19        | 92.3 (3)      |
| O3—Cu2—O19        | 97.4 (3)      |
| N5—Cu2—N6         | 93.2 (3)      |
| O3—Cu2—N6         | 88.3 (3)      |
| N6—Cu2—O19        | 174.11 (15)   |
| N7—Cu3—O5         | 91.24 (15)    |
| N7—Cu3—O5         | 171.24 (15)   |
| N7—Cu3—O5         | 96.61 (14)    |
| O6—Cu3—O5         | 84.79 (13)    |
| O7—Cu3—N8         | 82.67 (16)    |
| O6—Cu3—O5         | 100.63 (14)   |
| O5—Cu3—N8         | 169.87 (14)   |
| N7—Cu3—O16        | 96.61 (14)    |
| O6—Cu3—O16        | 103.81 (14)   |
| O5—Cu3—N8         | 172.67 (15)   |
| N9—Cu4—O8         | 89.19 (15)    |
| O8—Cu4—O7         | 85.34 (13)    |
| O9—Cu4—N10        | 83.73 (17)    |
| O8—Cu4—N10        | 100.54 (16)   |
| N10—Cu4—O17       | 165.82 (17)   |
| N9—Cu4—O17        | 90.56 (14)    |
| O8—Cu4—O17        | 94.98 (13)    |
| O7—Cu4—O17        | 97.53 (13)    |
| N10—Cu4—O17       | 94.81 (15)    |
| N1—Cu5—O9         | 88.98 (14)    |
| N1—Cu5—O10        | 163.89 (16)   |
| O9—Cu5—O10        | 85.41 (13)    |
| N1—Cu5—N2         | 83.21 (16)    |
| O9—Cu5—N2         | 171.78 (14)   |
| O10—Cu5—N2        | 101.44 (14)   |
| N1—Cu5—O18        | 104.51 (15)   |
| O9—Cu5—O18        | 93.14 (13)    |
| O10—Cu5—O18       | 90.88 (14)    |
| N2—Cu5—O18        | 91.31 (15)    |
| O9—Tb1—O1         | 71.67 (10)    |

Cu—N10—H10B 109.7
H10A—N10—H10B 108.2
N1—O1—Cu1 106.2 (2)
N1—O1—Tb1 125.6 (2)
Cu1—O1—Tb1 126.24 (14)
C1—O2—Cu1 104.0 (3)
N3—O3—Cu2 108.6 (2)
N3—O3—Tb1 122.4 (2)
Cu2—O3—Tb1 128.77 (15)
C3—O4—Cu2 107.7 (3)
N5—O5—Cu3 107.1 (2)
N5—O5—Tb1 124.1 (2)
Cu3—O5—Tb1 123.88 (13)
C5—O6—Cu3 107.0 (3)
N7—O7—Cu4 107.2 (2)
N7—O7—Tb1 124.7 (2)
Cu4—O7—Tb1 125.89 (14)
C7—O8—Cu4 106.9 (3)
N9—O9—Cu5 107.2 (2)
N9—O9—Tb1 126.2 (2)
Cu5—O9—Tb1 126.55 (14)
C9—O10—Cu5 107.4 (3)
S1—O11—Tb1 99.41 (17)
S1—O12—Tb1 100.02 (16)
Tb1—O15—H15A 121 (4)
Tb1—O15—H15B 118 (4)
H15A—O15—H15B 107 (6)
Cu3—O16—H16A 122 (5)
Cu3—O16—H16B 114 (5)
H16A—O16—H16B 102 (7)
Cu4—O17—H17A 92 (5)
Cu4—O17—H17B 111 (5)
H17A—O17—H17B 103 (6)
Cu5—O18—H18A 120 (5)
Cu5—O18—H18B 115 (5)
H18A—O18—H18B 107 (7)
Cu2—O19—H19A 99 (10)
Cu2—O19—H19B 113 (10)
H19A—O19—H19B 135 (10)
Cu1—O20—H20A 131 (5)
Cu1—O20—H20B 95 (5)
H20A—O20—H20B 93 (7)
Cu1—O21—H21A 124 (5)
Cu1—O21—H21B 110 (5)
H21A—O21—H21B 101 (7)
H22A—O22—H22B 113 (8)
H23A—O23—H23B 105 (3)
H24A—O24—H24B 108 (3)
| Bond                  | Angle (°) (RMS) | Bond                  | Angle (°) (RMS) | Bond                  | Angle (°) (RMS) |
|----------------------|-----------------|----------------------|-----------------|----------------------|-----------------|
| O9—Tb1—O15          | 100.80 (11)     | O14—S1—O13           | 110.9 (2)       |                     |                 |
| O1—Tb1—O15          | 75.87 (11)      | O14—S1—O11           | 111.0 (2)       |                     |                 |
| O9—Tb1—O3           | 144.63 (11)     | O13—S1—O11           | 111.6 (2)       |                     |                 |
| O1—Tb1—O3           | 73.91 (10)      | O14—S1—O12           | 110.1 (2)       |                     |                 |
| O15—Tb1—O3          | 78.22 (11)      | O13—S1—O12           | 110.3 (2)       |                     |                 |
| O9—Tb1—O7           | 70.65 (10)      | O11—S1—O12           | 102.68 (19)     |                     |                 |
| O1—Tb1—O7           | 131.81 (10)     | O14—S1—Tb1           | 118.92 (16)     |                     |                 |
| O15—Tb1—O7          | 82.82 (11)      | O13—S1—Tb1           | 130.15 (15)     |                     |                 |
| O3—Tb1—O7           | 142.47 (10)     | O11—S1—Tb1           | 51.82 (13)      |                     |                 |
| O9—Tb1—O5           | 143.39 (10)     | O12—S1—Tb1           | 51.24 (13)      |                     |                 |
| O1—Tb1—O5           | 139.79 (10)     | O26—S2—O26           | 180.0           |                     |                 |
| O15—Tb1—O5          | 77.50 (11)      | O26—S2—O28           | 114.8 (5)       |                     |                 |
| O3—Tb1—O5           | 71.55 (10)      | O26—S2—O28           | 65.2 (5)        |                     |                 |
| O7—Tb1—O5           | 72.88 (10)      | O26—S2—O28           | 65.2 (5)        |                     |                 |
| O9—Tb1—O12          | 83.74 (11)      | O26—S2—O28           | 114.8 (5)       |                     |                 |
| O1—Tb1—O12          | 129.16 (11)     | O28—S2—O28           | 180.0           |                     |                 |
| O15—Tb1—O12         | 153.99 (11)     | O26—S2—O27           | 68.7 (5)        |                     |                 |
| O3—Tb1—O12          | 112.70 (11)     | O26—S2—O27           | 111.3 (5)       |                     |                 |
| O7—Tb1—O12          | 74.50 (11)      | O28—S2—O27           | 70.8 (5)        |                     |                 |
| O5—Tb1—O12          | 83.70 (11)      | O28—S2—O27           | 109.2 (5)       |                     |                 |
| O9—Tb1—O11          | 88.43 (11)      | O26—S2—O25           | 69.6 (5)        |                     |                 |
| O1—Tb1—O11          | 77.71 (11)      | O26—S2—O25           | 110.4 (5)       |                     |                 |
| O15—Tb1—O11         | 147.49 (12)     | O28—S2—O25           | 73.6 (5)        |                     |                 |
| O3—Tb1—O11          | 76.51 (12)      | O28—S2—O25           | 106.4 (5)       |                     |                 |
| O7—Tb1—O11          | 129.39 (11)     | O27—S2—O25           | 104.2 (5)       |                     |                 |
| N1—C1—C2—N2         | 18.5 (6)        | O10—C9—N9—Cu4        | −173.1 (3)      |                     |                 |
| O2—C1—C2—N2         | −161.5 (4)      | C10—C9—N9—Cu4        | 6.7 (5)         |                     |                 |
| N3—C3—C4—N4         | −9.9 (6)        | O7—Cu4—N9—C9         | 167.0 (4)       |                     |                 |
| O4—C3—C4—N4         | 168.5 (4)       | N10—Cu4—N9—C9        | −0.7 (4)        |                     |                 |
| N5—C5—C6—N6         | 5.8 (6)         | O17—Cu4—N9—C9        | −95.5 (3)       |                     |                 |
| O6—C5—C6—N6         | −176.2 (4)      | O7—Cu4—N9—O9         | −2.8 (3)        |                     |                 |
| N7—C7—C8—N8         | −10.1 (5)       | N10—Cu4—N9—O9        | −170.5 (3)      |                     |                 |
| O8—C7—C8—N8         | 170.5 (4)       | O17—Cu4—N9—O9        | 94.8 (3)        |                     |                 |
| O10—C9—C10—N10      | 168.9 (4)       | C9—C10—N10—Cu4       | 9.8 (5)         |                     |                 |
| N9—C9—C10—N10       | −10.9 (6)       | C1—N1—O1—Cu1         | 11.7 (4)        |                     |                 |
| O2—C1—N1—O1         | −0.6 (6)        | Cu5—N1—O1—Cu1        | −159.6 (2)      |                     |                 |
| C2—C1—N1—O1         | 179.4 (4)       | C1—N1—O1—Tb1         | 176.5 (3)       |                     |                 |
| O2—C1—N1—Cu5        | 171.2 (3)       | Cu5—N1—O1—Tb1        | 5.2 (5)         |                     |                 |
| C2—C1—N1—Cu5        | −8.8 (5)        | N1—C1—O2—Cu1         | −10.6 (5)       |                     |                 |
| O9—Cu5—N1—C1        | 175.3 (4)       | C2—C1—O2—Cu1         | 169.4 (3)       |                     |                 |
| O10—Cu5—N1—C1       | 105.8 (6)       | C3—N3—O3—Cu2         | −5.7 (4)        |                     |                 |
| N2—Cu5—N1—C1        | −2.1 (4)        | Cu1—N3—O3—Cu2        | 158.1 (2)       |                     |                 |
| O18—Cu5—N1—C1       | −91.7 (4)       | C3—N3—O3—Tb1         | 179.5 (3)       |                     |                 |
| O9—Cu5—N1—O1        | −13.6 (3)       | Cu1—N3—O3—Tb1        | −16.7 (5)       |                     |                 |
| O10—Cu5—N1—O1       | −83.1 (6)       | N3—C3—O4—Cu2         | 7.1 (5)         |                     |                 |
| N2—Cu5—N1—O1        | 169.0 (3)       | C4—C3—O4—Cu2         | −171.2 (4)      |                     |                 |
| O18—Cu5—N1—O1       | 79.4 (3)        | C5—N5—O5—Cu3         | −9.7 (4)        |                     |                 |
C1—C2—N2—Cu5       −19.1 (5)       Cu2—N5—O5—Cu3       164.1 (2)
O4—C3—N3—O3         −1.0 (6)         C5—N5—O5—Tb1        −165.6 (3)
C4—C3—N3—O3         177.4 (4)        Cu2—N5—O5—Tb1        8.2 (4)
O4—C3—N3—Cu1        −166.2 (3)       N5—C5—O6—Cu3         8.8 (5)
C4—C3—N3—Cu1        12.2 (5)         C6—C5—O6—Cu3        −169.1 (3)
C3—C4—N4—Cu1        3.3 (5)          C7—N7—O7—Cu4         3.2 (4)
O6—C5—N5—O5         0.7 (6)          Cu3—N7—O7—Cu4       −171.6 (2)
O4—C3—N3—Cu1        −166.2 (3)       C5—N5—O5—Tb1       −167.2 (3)
C4—C3—N3—Cu1        12.2 (5)         Cu2—N5—O5—Tb1       −7.7 (5)
C3—C4—N4—Cu1        3.3 (5)          N5—C5—O6—Cu3        8.8 (4)
N6—Cu2—N5—C5        −9.4 (3)         C9—N9—O9—Cu5        −0.7 (4)
C19—Cu2—N5—C5       −97.4 (4)        Cu4—N9—O9—Tb1       169.3 (2)
O6—Cu2—N5—C5        −173.6 (3)       C9—N9—O9—Tb1       177.4 (3)
C6—C5—N5—Cu2        4.4 (5)          Cu4—N9—O9—Tb1       −12.5 (5)
O3—Cu2—N5—C5        165.2 (4)        N9—C9—O10—Cu5       4.2 (5)
N6—Cu2—N5—C5        −9.4 (3)         C10—C9—O10—Cu5      −175.6 (4)
C19—Cu2—N5—C5       −97.4 (4)        C10—C9—O10—Cu5      −110.9 (2)
O8—C7—N7—O7         0.3 (6)          Tb1—O11—S1—O14      124.81 (18)
C8—C7—N7—O7         −179.1 (4)       Tb1—O11—S1—O13      6.7 (2)
O8—C7—N7—Cu3        175.5 (3)        Tb1—O11—S1—O12      111.5 (2)
C8—C7—N7—Cu3        −3.9 (5)         Tb1—O12—S1—O14      −125.78 (18)
C7—C8—N8—Cu3        18.0 (4)         Tb1—O12—S1—O13      −6.7 (2)
O10—C9—N9—O9         −2.5 (6)        C10—C9—O10—Cu5      4.2 (5)
C10—C9—N9—O9         177.3 (4)

Symmetry code: (i) −x, −y, −z + 1.

Hydrogen-bond geometry (Å, °)

| D—H···A   | D—H  | H···A   | D···A  | D—H···A  |
|-----------|------|--------|--------|---------|
| O24—H24B·O8 | 0.84 (2) | 2.01 (3) | 2.807 (5) | 159 (7) |
| O24—H24A·O11 i | 0.84 (2) | 2.21 (3) | 3.015 (5) | 162 (7) |
| O23—H23B·O13 iii | 0.85 (2) | 2.02 (3) | 2.853 (5) | 166 (6) |
| O23—H23A·O4 ii | 0.84 (2) | 1.89 (2) | 2.734 (5) | 176 (7) |
| O22—H22B·O23 | 0.84 (2) | 1.89 (3) | 2.701 (6) | 162 (8) |
| O22—H22A·O26 viii | 0.84 (2) | 2.18 (4) | 2.968 (9) | 155 (8) |
| O22—H22A·O28 viii | 0.84 (2) | 1.92 (3) | 2.733 (9) | 161 (8) |
| O21—H21B·O10 vii | 0.83 (2) | 1.91 (3) | 2.728 (5) | 165 (8) |
| O21—H21A·O18 vii | 0.84 (2) | 1.94 (3) | 2.765 (5) | 167 (7) |
| O20—H20B·O11 | 0.83 (2) | 2.14 (3) | 2.960 (5) | 168 (7) |
| O20—H20A·O26 v | 0.83 (2) | 2.09 (3) | 2.916 (9) | 170 (7) |
| O20—H20A·O25 | 0.83 (2) | 2.02 (5) | 2.719 (9) | 142 (7) |
| O19—H19B·O24 v | 0.84 (2) | 2.07 (9) | 2.866 (11) | 157 (22) |
| O19—H19A·O24 v | 0.84 (2) | 1.72 (7) | 2.535 (12) | 162 (21) |
| O18—H18B·O14 | 0.83 (2) | 1.90 (2) | 2.732 (5) | 173 (7) |
| O18—I18A·O26 v | 0.84 (2) | 2.04 (3) | 2.857 (9) | 163 (7) |
| O18—I18A·O27 | 0.84 (2) | 1.91 (4) | 2.648 (9) | 146 (6) |
| O17—I17B·O6 vi | 0.83 (2) | 1.90 (2) | 2.730 (5) | 176 (7) |
| Bond                  | Distances          | Angles           |
|----------------------|--------------------|------------------|
| O17—H17A···O12       | 0.83 (2) 2.10 (3)  | 2.905 (5) 163 (6) |
| O16—H16B···O22       | 0.84 (2) 1.89 (2)  | 2.721 (6) 173 (7) |
| O16—H16A···O17A      | 0.84 (2) 1.95 (2)  | 2.784 (5) 172 (7) |
| O15—H15B···O16       | 0.84 (2) 1.86 (2)  | 2.692 (5) 170 (6) |
| O15—H15A···O21       | 0.84 (2) 1.85 (3)  | 2.668 (5) 166 (6) |
| N10—H10B···O22A      | 0.91 2.13          | 2.920 (6) 145    |
| N10—H10A···O20B      | 0.91 2.24          | 2.987 (5) 139    |
| N8—H8B···O12A        | 0.91 2.04          | 2.937 (5) 168    |
| N8—H8A···O23         | 0.91 2.20          | 3.031 (5) 152    |
| N6—H6B···O13A        | 0.91 2.64          | 3.363 (5) 137    |
| N6—H6B···O24A        | 0.91 2.24          | 2.984 (6) 139    |
| N6—H6A···O13A        | 0.91 2.25          | 3.158 (5) 175    |
| N4—H4B···O2A         | 0.91 2.33          | 3.182 (5) 156    |
| N4—H4A···O27A        | 0.91 2.18          | 3.037 (9) 156    |
| N4—H4A···O25A        | 0.91 2.01          | 2.789 (9) 143    |
| N2—H2B···O27         | 0.91 2.55          | 3.418 (9) 159    |
| N2—H2B···O28A        | 0.91 2.08          | 2.868 (9) 144    |
| N2—H2A···O15A        | 0.91 2.07          | 2.946 (5) 162    |

Symmetry codes: (i) −x, −y, −z+1; (ii) x, y+1, z; (iii) x+1, y+1, z; (iv) −x+1, −y+1, −z+1; (v) x+1, y, z; (vi) −x+1, −y+1, −z; (vii) x, y+1, z; (viii) x−1, y, z; (ix) −x+1, −y, −z; (x) −x+1, −y, −z+1.