# metal-organic compounds

## Poly[tetraaqua-$\mu_4$-bromido-di-$\mu_2$-bromido-$\mu_2$-hydroxido-di-$\mu_3$-iso-nicotinato-tetra-$\mu_2$-isonicotinato-tetracopper(I)dithulium(III)]

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A new thulium(III)–copper(I) heterometallic coordination polymer, $[Cu_4Tm_2Br_3(C_6H_4NO_2)_6(OH)(H_2O)_4]_n$, has been prepared by a hydrothermal method. The Tm and both Cu atoms lie on mirror planes. The Tm atom is seven-coordinate with a capped distorted trigonal–prismatic coordination geometry, while the Cu atoms adopt trigonal $CuBrN_2$ and tetrahedral $CuBr_3N$ coordination modes, respectively. The Cu atom in the trigonal coordination environment is disordered over two sites of equal occupancy. The crystal structure is constructed from two distinct units of dimeric $[Tm_2(\mu_2$-$OH(IN)_6(H_2O)_4]$ cores (IN = isonicotinate) and one-dimensional inorganic $[Cu_4Br_3]_n$ chains, which are linked together, forming heterometallic Cu–halide–lanthanide–organic layers.

## Related literature

For background to the structures and applications of heterometallic lanthanide–transition metal polymers, see: Benelli & Gatteschi (2002); Shibasaki & Yoshikawa (2002); Zhao *et al.* (2004*a*,*b*); Guillou *et al.* (2006); Wang *et al.* (2006). For some examples of heterometallic lanthanide–transition metal extended architectures, see: Ren *et al.* (2003); Prasad *et al.* (2007); Cheng *et al.* (2008).
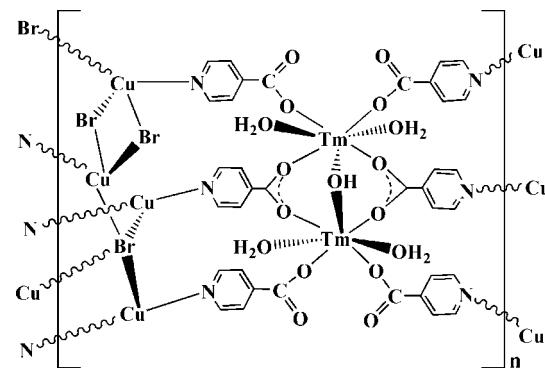


## Experimental

*Crystal data*

| | |
|---|---|
| $[Cu_4Tm_2Br_3(C_6H_4NO_2)_6(OH)$ | $V = 4458.3$ (3) Å$^3$ |
| $(H_2O)_4]$ | $Z = 4$ |
| $M_r = 1653.43$ | Mo $K\alpha$ radiation |
| Orthorhombic, $Cmcm$ | $\mu = 8.58$ mm$^{-1}$ |
| $a = 19.1815$ (2) Å | $T = 295$ (2) K |
| $b = 6.6973$ (4) Å | $0.16 \times 0.09 \times 0.08$ mm |
| $c = 34.7044$ (5) Å | |

*Data collection*

| | |
|---|---|
| Bruker APEXII area-detector diffractometer | 17231 measured reflections |
| Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996) | 2408 independent reflections |
| | 2090 reflections with $I > 2\sigma(I)$ |
| $T_{min} = 0.341$, $T_{max} = 0.547$ | $R_{int} = 0.037$ |
| (expected range = 0.313–0.503) | |

*Refinement*

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)] = 0.027$ | 6 restraints |
| $wR(F^2) = 0.064$ | H-atom parameters constrained |
| $S = 1.11$ | $\Delta\rho_{max} = 0.83$ e Å$^{-3}$ |
| 2408 reflections | $\Delta\rho_{min} = -0.87$ e Å$^{-3}$ |
| 179 parameters | |

Data collection: *APEX2* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); 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: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SJ2536).

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# supporting information

# Poly[tetraaqua-$\mu_4$-bromido-di-$\mu_2$-bromido-$\mu_2$-hydroxido-di-$\mu_3$-isonicotinato-tetra-$\mu_2$-isonicotinato-tetracopper(I)dithulium(III)]

## Guo-Ming Wang, Zeng-Xin Li, Qing-Hua Zheng and Hui-Luan Liu

## S1. Comment

The rational design and synthesis of heterometallic lanthanide(Ln)–transition metal(TM) compounds have attracted increasing attention in recent years, not only because of their intriguing variety of architectures and topologies but also owing to their potential applications in luminescence, magnetism, bimetallic catalysis, and molecular adsorption. (Benelli & Gatteschi, 2002; Shibasaki & Yoshikawa, 2002; Zhao *et al.*, 2004*a*,*b*; Guillou *et al.*, 2006; Wang *et al.*, 2006). So far, most work has been focused on the assembly of homometallic Ln and TM compounds, while the construction of heterometallic Ln–TM extented architectures is still a challenge (Ren *et al.*, 2003; Prasad *et al.*, 2007; Cheng *et al.*, 2008). This may be attributed to the different competitive reactions of Ln and TM metals with the same ligand, which often results in the formation of the homometallic compounds rather than heterometallic ones. Generally, the Ln ions prefer O-donors, while TM ions have stronger tendency to coordinate to N-donors. Therefore, isonicotinic acid (HIN) has been chosen here as the multifunctional bridging ligand to construct new hetero-Ln–TM complexes. The title compound [$Tm_2Cu_4Br_3(\mu2\text{-}OH)(C_6H_4NO_2)_6(H_2O)_4$]$_n$ (1) is reported here and displays novel two-dimensional coordination features.

In the asymmetric unit, the Tm1 atom, occupying a special position on a mirror plane (Fig. 1), is seven-coordinated and has a capped trigonal–prismatic coordination environment comprising two coordinated water molecules, one $\mu_2$-OH and four carboxylate oxygen atoms from four IN$^-$ ligands. The Tm—O bond lengths range from 2.193 (2) to 2.449 (5) Å. Both Cu1 and Cu2 atoms occupy special positions on two crystallographic mirror planes, one perpendicular ($z = 0$) and the other parallel to the $c$ axis. The Cu1 atom is three-coordinate with one $\mu_4$-Br1 and two N atoms from two bridging IN$^-$ moieties, while the Cu2 center is coordinated to one $\mu_4$-Br1, two $\mu_2$-Br2 atoms and one N atom from one IN$^-$ ligand that defines a distorted tetrahedral geometry. The Cu—N and Cu—Br distances are in the range 1.928 (3)–2.020 (4) Å and 2.518 (9)–2.688 (7) Å, respectively. Although copper(II) salts were used as starting materials, the Cu centers in the product are in the +1 oxidation state. This is attributed to a reduction reaction occurring under the hydrothermal conditions used.

The framework of 1 is constructed from two subunits, dimeric [$Tm_2(\mu_2\text{-}OH)(IN^-)_6$] (Tm$_2$) cores and inorganic [$Cu_4Br_3$]$_n$ chains. As shown in Fig. 2, two crystallographically identical Tm(III) ions are linked by one bridging hydroxo group and six IN$^-$ ligands to form the dimeric Tm$_2$ fragment, in which the IN$^-$ ligand adopts two different coordination modes. The Tm$\cdots$Tm distance is 4.071 (1) Å. The Cu(I) centers, however, are bridged by $\mu_4$-Br and $\mu_2$-Br atoms to form one-dimensional inorganic [$Cu_4Br_3$]$_n$ chains (Fig. 3). Interestingly, such one-dimensional copper halide chains appear to be constructed directly from corner- and edge-sharing tetrahedral Cu(2)Br$_3$N units, decorated by the trigonal Cu(1)BrN$_2$ groups protruding outside the chain. In addition, the Cu$\cdots$Cu distance within the copper(I) halide chains is 2.688 (7) Å, less than twice the van der Waals radius of the Cu(I) ion (1.4 Å), indicating a strong Cu$\cdots$Cu interaction. The linkages between dimeric Tm$_2$ and inorganic [$Cu_4Br_3$]$_n$ motifs through N—Cu bonds give rise to a novel two-dimensional hetero-

Tm—Cu framework (Fig. 4). Adjacent sheets are further packed to form a three-dimensional supramolecular framework through O—H···O hydrogen bonds.

## S2. Experimental

The title compound was synthesized under mild hydrothermal conditions. Typically, a mixture of $Tm_2O_3$ (0.5 mmol, 0.193 g), $CuBr_2$ (0.089 g, 0.40 mmol), HIN (2.00 mmol, 0.247 g) and $H_2O$ (8 ml) was sealed in a 25 ml Teflon-lined steel autoclave and heated under autogenous pressure at 443 K for 8 days. The yellow block-like crystals obtained were recovered by filtration, washed with distilled water and dried in air.

## S3. Refinement

H atoms bound to C atoms were placed in calculated positions, with C—H distances of 0.93 Å. All other H atoms were located in a difference Fourier map and treated as riding, with fixed $U_{iso}(H) = 1.2U_{eq}(O)$. The H4 and H6C atoms lie close to a mirror plane, and were treated as disordered with constrained site occupancy factors of 0.25 and 0.5, respectively. Atom Cu1 was refined as disordered over two positions, each with 50% site occupancy.
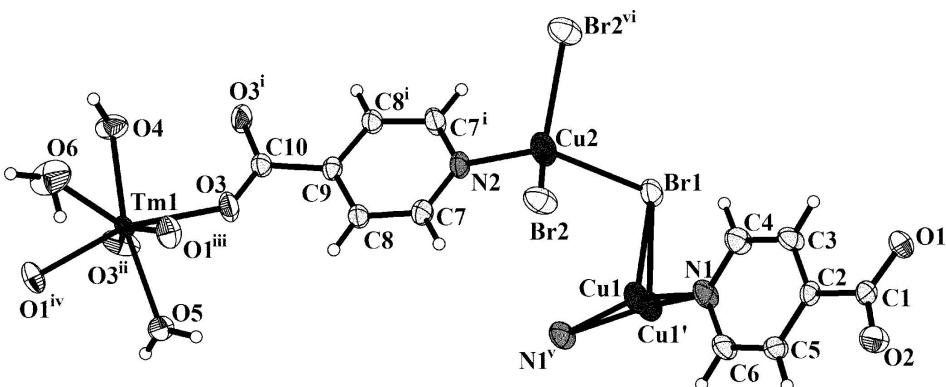


**Figure 1**

The molecular structure of 1, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) -x, y, z; (ii) x, y, 1/2 - z; (iii) x, 1 - y, 1 - z; (iv) x, 1 - y, -1/2 + z; (v) x, 2 - y, 1 - z; (vi) -x, 1 - y, 1 - z].
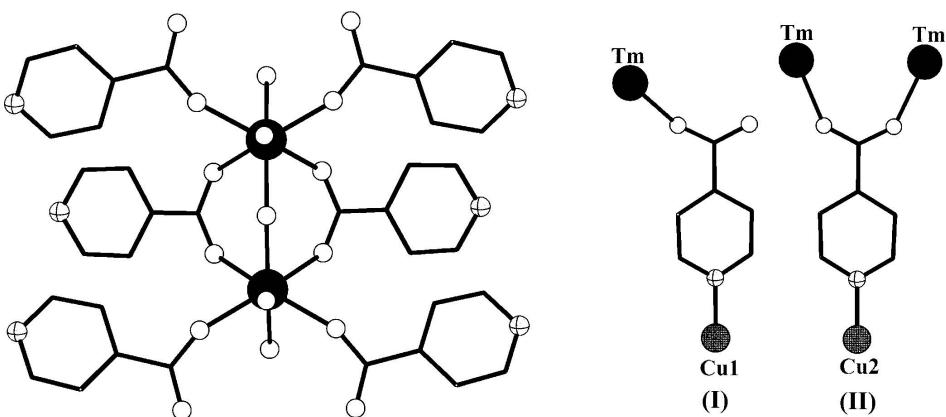


**Figure 2**

Dimeric [Tm₂($\mu$2-OH)(IN)₆] fragment and the coordination modes of IN⁻ found in 1.

**(a)**



**(b)**
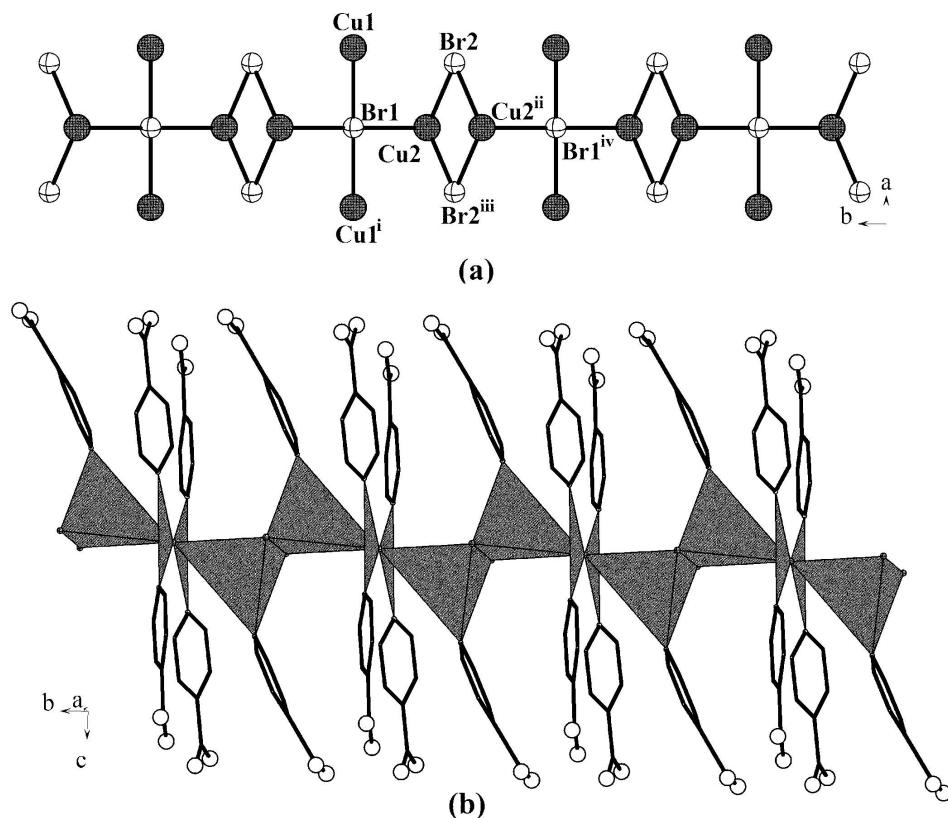
**Figure 3**

One-dimensional infinite $[Cu_4Br_3]_n$ chains along *b* axis (*a*), and polyhedral view of the $[Cu_4Br_3N_6]_n$ chains. [Symmetry codes: (i) -*x*, 2 - *y*, 1 - *z*; (ii) *x*, 1 - *y*, 1 - *z*; (iii) -*x*, 1 - *y*, 1 - *z*; (iv) *x*, -1 + *y*, *z*].
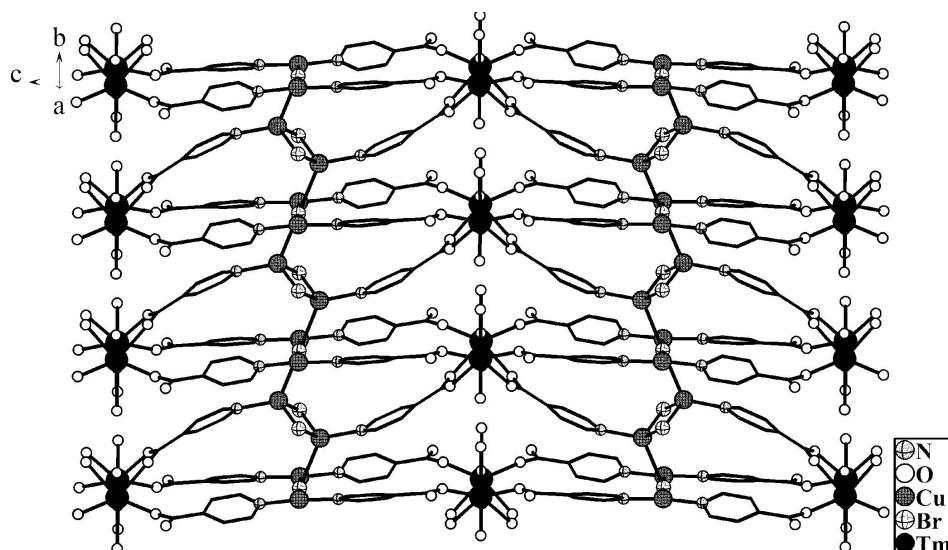


**Figure 4**

View of the two-dimensional layer structure of 1.

**Poly[tetraaqua-*μ*₄-bromido-di-*μ*₂-bromido-*μ*₂-hydroxido-di-*μ*₃- isonicotinato-tetra-*μ*₂-isonicotinato-tetracopper(I)dithulium(III)]**

*Crystal data*

| | |
|---|---|
| [Cu₄Tm₂Br₃(C₆H₄NO₂)₆(OH)(H₂O)₄] | $F(000) = 3144$ |
| $M_r = 1653.43$ | $D_x = 2.463$ Mg m⁻³ |
| Orthorhombic, *Cmcm* | Mo *Kα* radiation, $\lambda = 0.71073$ Å |
| Hall symbol: -C 2c 2 | Cell parameters from 6070 reflections |
| $a = 19.1815$ (2) Å | $\theta = 2.1–26.5°$ |
| $b = 6.6973$ (4) Å | $\mu = 8.58$ mm⁻¹ |
| $c = 34.7044$ (5) Å | $T = 295$ K |
| $V = 4458.3$ (3) Å³ | Block, yellow |
| $Z = 4$ | 0.16 × 0.09 × 0.08 mm |

*Data collection*

| | |
|---|---|
| Bruker APEXII area-detector diffractometer | 17231 measured reflections |
| Radiation source: fine-focus sealed tube | 2408 independent reflections |
| Graphite monochromator | 2090 reflections with $I > 2\sigma(I)$ |
| *φ* and *ω* scans | $R_{int} = 0.037$ |
| Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996) | $\theta_{max} = 26.5°$, $\theta_{min} = 2.1°$ |
| | $h = -24 \rightarrow 24$ |
| $T_{min} = 0.341$, $T_{max} = 0.547$ | $k = -8 \rightarrow 8$ |
| | $l = -43 \rightarrow 42$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Hydrogen site location: inferred from neighbouring sites |
| Least-squares matrix: full | |
| $R[F^2 > 2\sigma(F^2)] = 0.027$ | H-atom parameters constrained |
| $wR(F^2) = 0.064$ | $w = 1/[\sigma^2(F_o^2) + (0.0288P)^2 + 11.1134P]$ |
| $S = 1.11$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| 2408 reflections | $(\Delta/\sigma)_{max} = 0.001$ |
| 179 parameters | $\Delta\rho_{max} = 0.83$ e Å⁻³ |
| 6 restraints | $\Delta\rho_{min} = -0.87$ e Å⁻³ |
| Primary atom site location: structure-invariant direct methods | Extinction correction: *SHELXL97* (Sheldrick, 2008), Fc*=kFc[1+0.001xFc²λ³/sin(2θ)]⁻¹ᐟ⁴ |
| Secondary atom site location: difference Fourier map | Extinction coefficient: 0.00119 (4) |

*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 (Å²)*

| | *x* | *y* | *z* | $U_{iso}*/U_{eq}$ | Occ. (<1) |
|---|---|---|---|---|---|
| Tm1 | 0.106107 (10) | −0.00154 (3) | 0.2500 | 0.01935 (10) | |
| Cu1 | 0.1384 (6) | 1.0000 | 0.5000 | 0.037 (3) | 0.50 |

| | | | | | |
|---|---|---|---|---|---|
| Cu1′ | 0.1361 (6) | 1.064 (2) | 0.4997 (8) | 0.038 (2) | 0.25 |
| Cu2 | 0.0000 | 0.63637 (13) | 0.47157 (2) | 0.0465 (2) | |
| Br1 | 0.0000 | 1.0000 | 0.5000 | 0.0344 (2) | |
| Br2 | 0.11106 (3) | 0.5000 | 0.5000 | 0.04244 (17) | |
| O1 | 0.16098 (14) | 1.0892 (4) | 0.69667 (7) | 0.0352 (6) | |
| O2 | 0.27354 (15) | 1.1077 (5) | 0.68216 (7) | 0.0475 (8) | |
| O3 | 0.05791 (13) | 0.2265 (5) | 0.29248 (8) | 0.0390 (7) | |
| O4 | 0.0000 | −0.1250 (8) | 0.2500 | 0.0389 (13) | |
| H4 | 0.0000 | −0.2788 | 0.2600 | 0.047* | 0.50 |
| O5 | 0.19308 (19) | 0.2314 (6) | 0.2500 | 0.0365 (9) | |
| H5 | 0.2041 | 0.2871 | 0.2699 | 0.044* | |
| O6 | 0.1159 (2) | −0.3688 (7) | 0.2500 | 0.0647 (15) | |
| H6B | 0.1529 | −0.2988 | 0.2500 | 0.078* | |
| H6C | 0.1278 | −0.4859 | 0.2380 | 0.078* | 0.50 |
| C1 | 0.2117 (2) | 1.0891 (6) | 0.67359 (9) | 0.0278 (8) | |
| C2 | 0.19342 (19) | 1.0649 (5) | 0.63145 (9) | 0.0244 (7) | |
| C3 | 0.1278 (2) | 1.0044 (6) | 0.62013 (11) | 0.0307 (8) | |
| H3A | 0.0932 | 0.9823 | 0.6384 | 0.037* | |
| C4 | 0.1139 (2) | 0.9771 (6) | 0.58161 (12) | 0.0344 (10) | |
| H4A | 0.0702 | 0.9295 | 0.5744 | 0.041* | |
| C5 | 0.2424 (2) | 1.0999 (6) | 0.60318 (10) | 0.0303 (8) | |
| H5A | 0.2873 | 1.1397 | 0.6098 | 0.036* | |
| C6 | 0.2246 (2) | 1.0755 (6) | 0.56502 (10) | 0.0323 (8) | |
| H6A | 0.2580 | 1.1008 | 0.5462 | 0.039* | |
| C7 | 0.0597 (2) | 0.5415 (6) | 0.39568 (11) | 0.0307 (9) | |
| H7A | 0.1015 | 0.5754 | 0.4076 | 0.037* | |
| C8 | 0.06218 (19) | 0.4538 (5) | 0.35956 (11) | 0.0260 (8) | |
| H8A | 0.1047 | 0.4302 | 0.3475 | 0.031* | |
| C9 | 0.0000 | 0.4016 (7) | 0.34159 (13) | 0.0216 (10) | |
| C10 | 0.0000 | 0.2775 (8) | 0.30518 (13) | 0.0240 (10) | |
| N1 | 0.16080 (18) | 1.0165 (5) | 0.55395 (9) | 0.0340 (8) | |
| N2 | 0.0000 | 0.5802 (7) | 0.41440 (12) | 0.0275 (9) | |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Tm1 | 0.01730 (14) | 0.02826 (15) | 0.01249 (13) | 0.00208 (9) | 0.000 | 0.000 |
| Cu1 | 0.0466 (19) | 0.052 (8) | 0.0131 (15) | 0.000 | 0.000 | 0.000 (8) |
| Cu1′ | 0.047 (2) | 0.051 (7) | 0.0145 (17) | −0.004 (4) | 0.0008 (16) | 0.001 (5) |
| Cu2 | 0.0465 (4) | 0.0686 (6) | 0.0243 (4) | 0.000 | 0.000 | −0.0111 (4) |
| Br1 | 0.0271 (4) | 0.0500 (5) | 0.0260 (4) | 0.000 | 0.000 | −0.0129 (3) |
| Br2 | 0.0286 (3) | 0.0619 (4) | 0.0368 (4) | 0.000 | 0.000 | 0.0074 (3) |
| O1 | 0.0438 (16) | 0.0448 (16) | 0.0171 (13) | −0.0065 (14) | 0.0069 (11) | 0.0009 (12) |
| O2 | 0.0406 (17) | 0.081 (2) | 0.0212 (14) | −0.0224 (17) | −0.0013 (12) | −0.0077 (15) |
| O3 | 0.0250 (13) | 0.0570 (18) | 0.0348 (15) | 0.0037 (13) | 0.0023 (11) | −0.0254 (13) |
| O4 | 0.023 (3) | 0.033 (3) | 0.061 (4) | 0.000 | 0.000 | 0.000 |
| O5 | 0.046 (2) | 0.051 (2) | 0.0127 (17) | −0.021 (2) | 0.000 | 0.000 |
| O6 | 0.053 (3) | 0.027 (2) | 0.113 (5) | 0.008 (2) | 0.000 | 0.000 |

| | | | | | |
|---|---|---|---|---|---|
| C1 | 0.039 (2) | 0.031 (2) | 0.0138 (16) | −0.0086 (17) | 0.0020 (15) | 0.0005 (15) |
| C2 | 0.034 (2) | 0.0235 (16) | 0.0161 (16) | −0.0035 (15) | −0.0005 (14) | −0.0006 (14) |
| C3 | 0.0290 (18) | 0.042 (2) | 0.0207 (18) | −0.0027 (17) | 0.0035 (15) | 0.0043 (15) |
| C4 | 0.030 (2) | 0.050 (3) | 0.024 (2) | −0.0011 (18) | −0.0018 (16) | −0.0005 (17) |
| C5 | 0.0307 (19) | 0.039 (2) | 0.0211 (18) | −0.0088 (17) | 0.0013 (15) | −0.0008 (17) |
| C6 | 0.033 (2) | 0.045 (2) | 0.0188 (18) | −0.0045 (18) | 0.0048 (15) | −0.0001 (17) |
| C7 | 0.028 (2) | 0.040 (2) | 0.024 (2) | −0.0044 (16) | −0.0016 (15) | −0.0091 (16) |
| C8 | 0.0226 (18) | 0.032 (2) | 0.0229 (18) | −0.0003 (14) | 0.0006 (14) | −0.0065 (15) |
| C9 | 0.029 (2) | 0.018 (2) | 0.018 (2) | 0.000 | 0.000 | 0.0000 (19) |
| C10 | 0.024 (2) | 0.028 (3) | 0.020 (2) | 0.000 | 0.000 | −0.003 (2) |
| N1 | 0.0339 (18) | 0.051 (2) | 0.0176 (15) | 0.0022 (15) | 0.0003 (13) | 0.0007 (14) |
| N2 | 0.034 (2) | 0.030 (2) | 0.018 (2) | 0.000 | 0.000 | −0.0048 (19) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Tm1—O4 | 2.197 (2) | O3—C10 | 1.243 (3) |
| Tm1—O1$^i$ | 2.208 (2) | O4—Tm1$^{ix}$ | 2.197 (2) |
| Tm1—O1$^{ii}$ | 2.208 (2) | O4—H4 | 1.0867 |
| Tm1—O5 | 2.284 (4) | O5—H5 | 0.8127 |
| Tm1—O3$^{iii}$ | 2.315 (2) | O6—H6B | 0.8504 |
| Tm1—O3 | 2.315 (2) | O6—H6C | 0.9163 |
| Tm1—O6 | 2.467 (5) | C1—C2 | 1.512 (5) |
| Tm1—H6B | 2.1833 | C2—C5 | 1.379 (5) |
| Cu1—N1 | 1.924 (4) | C2—C3 | 1.380 (5) |
| Cu1—N1$^{iv}$ | 1.924 (4) | C3—C4 | 1.375 (5) |
| Cu1—Br1 | 2.654 (12) | C3—H3A | 0.9300 |
| Cu1′—N1 | 1.97 (3) | C4—N1 | 1.342 (5) |
| Cu1′—N1$^{iv}$ | 2.00 (3) | C4—H4A | 0.9300 |
| Cu1′—Br1 | 2.645 (12) | C5—C6 | 1.377 (5) |
| Cu2—N2 | 2.020 (4) | C5—H5A | 0.9300 |
| Cu2—Br2 | 2.5191 (7) | C6—N1 | 1.342 (5) |
| Cu2—Br2$^v$ | 2.5191 (7) | C6—H6A | 0.9300 |
| Cu2—Br1 | 2.6275 (9) | C7—N2 | 1.341 (4) |
| Cu2—Cu2$^v$ | 2.6889 (17) | C7—C8 | 1.385 (6) |
| Br1—Cu2$^{vi}$ | 2.6276 (9) | C7—H7A | 0.9300 |
| Br1—Cu1′$^{vi}$ | 2.645 (12) | C8—C9 | 1.391 (4) |
| Br1—Cu1′$^{vii}$ | 2.645 (12) | C8—H8A | 0.9300 |
| Br1—Cu1′$^{iv}$ | 2.645 (12) | C9—C8$^{vii}$ | 1.391 (4) |
| Br1—Cu1$^{vi}$ | 2.654 (12) | C9—C10 | 1.512 (7) |
| Br2—Cu2$^v$ | 2.5191 (7) | C10—O3$^{vii}$ | 1.243 (3) |
| O1—C1 | 1.260 (4) | N1—Cu1′$^{iv}$ | 2.00 (3) |
| O1—Tm1$^{viii}$ | 2.208 (2) | N2—C7$^{vii}$ | 1.341 (4) |
| O2—C1 | 1.230 (5) | | |
| | | | |
| O4—Tm1—O1$^i$ | 109.97 (10) | Cu1′$^{vi}$—Br1—Cu1′$^{iv}$ | 161.3 (7) |
| O4—Tm1—O1$^{ii}$ | 109.97 (10) | Cu1′$^{vii}$—Br1—Cu1′$^{iv}$ | 180.000 (4) |
| O1$^i$—Tm1—O1$^{ii}$ | 113.85 (14) | Cu2$^{vi}$—Br1—Cu1$^{vi}$ | 90.0 |
| O4—Tm1—O5 | 159.04 (17) | Cu2—Br1—Cu1$^{vi}$ | 90.000 (2) |

| | | | |
|---|---|---|---|
| O1ⁱ—Tm1—O5 | 80.41 (9) | Cu1′—Br1—Cu1ᵛⁱ | 170.7 (3) |
| O1ⁱⁱ—Tm1—O5 | 80.41 (9) | Cu1′ⁱᵛ—Br1—Cu1ᵛⁱ | 170.7 (3) |
| O4—Tm1—O3ⁱⁱⁱ | 83.02 (12) | Cu2ᵛⁱ—Br1—Cu1 | 90.000 (2) |
| O1ⁱ—Tm1—O3ⁱⁱⁱ | 154.05 (11) | Cu2—Br1—Cu1 | 90.0 |
| O1ⁱⁱ—Tm1—O3ⁱⁱⁱ | 80.34 (10) | Cu1′ᵛⁱ—Br1—Cu1 | 170.7 (3) |
| O5—Tm1—O3ⁱⁱⁱ | 80.85 (11) | Cu1′ᵛⁱⁱ—Br1—Cu1 | 170.7 (3) |
| O4—Tm1—O3 | 83.02 (12) | Cu1ᵛⁱ—Br1—Cu1 | 180.000 (1) |
| O1ⁱ—Tm1—O3 | 80.34 (10) | Cu2—Br2—Cu2ᵛ | 64.51 (4) |
| O1ⁱⁱ—Tm1—O3 | 154.05 (11) | C1—O1—Tm1ᵛⁱⁱⁱ | 154.2 (3) |
| O5—Tm1—O3 | 80.85 (11) | C10—O3—Tm1 | 139.8 (3) |
| O3ⁱⁱⁱ—Tm1—O3 | 79.09 (15) | Tm1—O4—Tm1ⁱˣ | 135.8 (3) |
| O4—Tm1—O6 | 72.25 (17) | Tm1—O4—H4 | 110.9 |
| O1ⁱ—Tm1—O6 | 72.46 (9) | Tm1ⁱˣ—O4—H4 | 110.9 |
| O1ⁱⁱ—Tm1—O6 | 72.46 (9) | Tm1—O5—H5 | 120.2 |
| O5—Tm1—O6 | 128.71 (15) | Tm1—O6—H6B | 60.9 |
| O3ⁱⁱⁱ—Tm1—O6 | 133.49 (10) | Tm1—O6—H6C | 150.7 |
| O3—Tm1—O6 | 133.49 (10) | H6B—O6—H6C | 105.4 |
| O4—Tm1—H6B | 92.1 | O2—C1—O1 | 126.2 (3) |
| O1ⁱ—Tm1—H6B | 64.0 | O2—C1—C2 | 117.9 (3) |
| O1ⁱⁱ—Tm1—H6B | 64.0 | O1—C1—C2 | 115.9 (3) |
| O5—Tm1—H6B | 108.8 | C5—C2—C3 | 118.0 (3) |
| O3ⁱⁱⁱ—Tm1—H6B | 140.0 | C5—C2—C1 | 120.8 (3) |
| O3—Tm1—H6B | 140.0 | C3—C2—C1 | 121.2 (3) |
| O6—Tm1—H6B | 19.9 | C4—C3—C2 | 119.5 (4) |
| Cu1′ⁱᵛ—Cu1—N1 | 93 (4) | C4—C3—H3A | 120.2 |
| Cu1′ⁱᵛ—Cu1—N1ⁱᵛ | 89 (4) | C2—C3—H3A | 120.2 |
| N1—Cu1—N1ⁱᵛ | 154.2 (7) | N1—C4—C3 | 122.6 (4) |
| Cu1′ⁱᵛ—Cu1—Br1 | 84 (3) | N1—C4—H4A | 118.7 |
| N1—Cu1—Br1 | 102.9 (4) | C3—C4—H4A | 118.7 |
| N1ⁱᵛ—Cu1—Br1 | 102.9 (4) | C6—C5—C2 | 119.7 (3) |
| Cu1′ⁱᵛ—Cu1′—N1 | 79 (4) | C6—C5—H5A | 120.2 |
| Cu1′ⁱᵛ—Cu1′—N1ⁱᵛ | 76 (4) | C2—C5—H5A | 120.2 |
| N1—Cu1′—N1ⁱᵛ | 142.3 (6) | N1—C6—C5 | 122.4 (4) |
| Cu1′ⁱᵛ—Cu1′—Br1 | 80.7 (3) | N1—C6—H6A | 118.8 |
| N1—Cu1′—Br1 | 102.0 (9) | C5—C6—H6A | 118.8 |
| N1ⁱᵛ—Cu1′—Br1 | 101.2 (9) | N2—C7—C8 | 123.3 (4) |
| N2—Cu2—Br2 | 108.50 (6) | N2—C7—H7A | 118.3 |
| N2—Cu2—Br2ᵛ | 108.50 (7) | C8—C7—H7A | 118.3 |
| Br2—Cu2—Br2ᵛ | 115.49 (4) | C7—C8—C9 | 118.9 (4) |
| N2—Cu2—Br1 | 122.79 (14) | C7—C8—H8A | 120.6 |
| Br2—Cu2—Br1 | 100.894 (19) | C9—C8—H8A | 120.6 |
| Br2ᵛ—Cu2—Br1 | 100.894 (19) | C8—C9—C8ᵛⁱⁱ | 118.1 (5) |
| N2—Cu2—Cu2ᵛ | 126.47 (15) | C8—C9—C10 | 120.8 (2) |
| Br2—Cu2—Cu2ᵛ | 57.744 (18) | C8ᵛⁱⁱ—C9—C10 | 120.8 (2) |
| Br2ᵛ—Cu2—Cu2ᵛ | 57.744 (18) | O3—C10—O3ᵛⁱⁱ | 126.7 (5) |
| Br1—Cu2—Cu2ᵛ | 110.74 (4) | O3—C10—C9 | 116.6 (2) |
| Cu2ᵛⁱ—Br1—Cu2 | 180.0 | O3ᵛⁱⁱ—C10—C9 | 116.6 (2) |
| Cu2ᵛⁱ—Br1—Cu1′ᵛⁱ | 98.6 (4) | C4—N1—C6 | 117.7 (3) |

| | | | |
|---|---|---|---|
| Cu2—Br1—Cu1$'^{vi}$ | 81.4 (4) | C4—N1—Cu1 | 122.3 (4) |
| Cu2$^{vi}$—Br1—Cu1$'^{vii}$ | 81.4 (4) | C6—N1—Cu1 | 119.9 (4) |
| Cu2—Br1—Cu1$'^{vii}$ | 98.6 (4) | C4—N1—Cu1′ | 123.7 (5) |
| Cu2$^{vi}$—Br1—Cu1′ | 81.4 (4) | C6—N1—Cu1′ | 116.5 (5) |
| Cu2—Br1—Cu1′ | 98.6 (4) | C4—N1—Cu1$'^{iv}$ | 117.0 (5) |
| Cu1$'^{vi}$—Br1—Cu1′ | 180.0 (13) | C6—N1—Cu1$'^{iv}$ | 124.3 (5) |
| Cu1$'^{vii}$—Br1—Cu1′ | 161.3 (7) | C7—N2—C7$^{vii}$ | 117.2 (4) |
| Cu2$^{vi}$—Br1—Cu1$'^{iv}$ | 98.6 (4) | C7—N2—Cu2 | 120.8 (2) |
| Cu2—Br1—Cu1$'^{iv}$ | 81.4 (4) | C7$^{vii}$—N2—Cu2 | 120.8 (2) |

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

## Hydrogen-bond geometry (Å, °)

| D—H⋯A | D—H | H⋯A | D⋯A | D—H⋯A |
|---|---|---|---|---|
| O5—H5⋯O2$^{x}$ | 0.81 | 1.86 | 2.667 (3) | 175 |

Symmetry code: (x) $-x+1/2$, $-y+3/2$, $-z+1$.