catena-Poly[[tetrakis(3,5-dimethyl-1H-pyrazole-κN²)copper(II)]-μ₂-sulfato-κ²O:O′]: crystal structure and Hirshfeld surface analysis of a Cu^{II} coordination polymer

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The title coordination polymer, [Cu(SO₄)(C₅H₈N₂)₄]ₙ, was synthesized using a one-pot reaction of copper powder, anhydrous copper(II) sulfate and 3,5-dimethyl-1H-pyrazole (Hdmpz) in acetonitrile under ambient conditions. The asymmetric unit can be described as a chain consisting of four [Cu(SO₄)(Hdmpz)₄] formula units that are connected to each other by a μ₂-sulfato-bridged ligand. The octahedral coordination geometry (O₂N₄) of all copper atoms is realized by coordination of four pyrazole ligands and two sulfate ligands. Four pyridine-like N atoms of the pyrazole ligands occupy the equatorial positions, while two oxygen atoms of two sulfate ligands are in axial positions. As a result of the sulfate ligand rotation, there is a pairwise alternation of terminal O atoms (which are not involved in coordination to the copper atom) of the SO₄ tetrahedra. The Cu···Cu distances within one asymmetric unit are in the range 7.0842 (12)–7.1554 (12) Å. The crystal structure is built up from polymeric chains packed in a parallel manner along the b-axis direction. Hirshfeld surface analysis suggests that the most important contributions to the surface contacts are from H···H (74.7%), H···O/O···H (14.8%) and H···C/C···H (8.2%) interactions.

1. Chemical context

The synthesis, structure and properties of metal complexes, including coordination polymers, is an important area of chemical research. The nature of the anion, which is part of a coordination compound, is one of several factors that has a great influence on the final structural topology of the complexes (Mondal et al., 2009; Mahmoudi et al., 2007; Kwak et al., 2008; Balic´ et al., 2018). A large number of coordination compounds have been synthesized and studied due to the development of supramolecular chemistry and the study of self-assembly of metal complexes with organic molecules, such as pyrazoles. These molecules have long been recognized as useful ligands for studying transition-metal coordination chemistry (Mihailov et al., 1974; Nicholls et al., 1971; Reedijk, 1971, 1970a,b; Reedijk & Smit, 1971; Reedijk et al., 1971; Singh et al., 1973; ten Hoedt et al., 1982). Pyrazole-based ligands are used to construct supramolecular architectures due to the presence of a pyrrole NH group in the pyrazole ring, which is not necessarily coordinated by a metal atom, but may act as a donor of hydrogen bonds. In addition, substituents on the
pyrazole ring can also be involved in hydrogen-bond interactions. These facts are very important because there is a noticeable influence of hydrogen bonding on coordination compound assembly (Di Nicola et al., 2007; Brewer et al., 2020; Burrows et al., 2011). The crystal packing of coordination polymers also depends on the different solvents employed, although not necessarily incorporating the solvents as crystallization molecules (Di Nicola et al., 2014). Reaction of a metal salt with an organic ligand is a popular way for the synthesis of coordination compounds, including metal coordination polymers (Gogoi et al., 2019; Shen et al., 2004), but there are many types of coordination compounds and the methods of synthesis are varied (House et al., 2016). In this article we report the preparation of the coordination polymer \( \text{catena-poly[\text{tetrakis}(3,5\text{-dimethyl-1H-pyrazole-}C_2\text{N_2})\text{copper(II)}]·\mu_2\text{-sulfato-}_C^\text{C}_2\text{O}_2\text{O}^\prime} \) using the direct synthesis method, which is based on oxidative dissolution of a powdered metal in the presence of an organic ligand (Kokozay et al., 2018; Li et al., 2021).

2. Structural commentary

The title coordination polymer crystallizes in the orthorhombic \( \text{Pna}_2_1 \) space group. The asymmetric unit is a chain consisting of four \([\text{Cu(Hdmpz)}_4\text{SO}_4]\) formula units (Fig. 1) that are connected to each other by a \( \mu_2\)-sulfato-bridged ligand along the \( b \)-axis direction (Fig. 2). Each mononuclear unit \([\text{Cu(Hdmpz)}_4\text{SO}_4]\) consists of four 3,5-dimethyl-1H-pyrazole molecules, which are coordinated in a monodentate way, and one sulfate ligand that is connected by one oxygen atom to the copper ion. The octahedral coordination environment of each copper atom consists of four pyridine-like nitrogen atoms of Hdmpz ligands, which occupy the equatorial positions, and two oxygen atoms of two SO₄ ligands, which are in axial positions. The difference in lengths of the axial Cu—O and equatorial Cu—N bonds is at least 0.235 Å. Bond lengths between the central atom and the nitrogen atoms in the equatorial position are approximately the same [in the range 2.028 (6) to 2.054 (6) Å]. The N1, N3, N5 and N7 nitrogen atoms slightly deviate from of the equatorial plane [by —0.088 (3) Å for N1, 0.069 (3) Å for N3, 0.067 (3) Å for N5 and —0.086 (3) Å for N7]. The Cu1 atom is out of the equatorial plane, formed by four nitrogen atoms, by 0.038 (3) Å. The N—Cu—N angles are practically right angles, in the range of 88.0 (2)—91.2 (2)°. The intermetallic Cu···Cu distances between two neighboring \([\text{Cu(Hdmpz)}_4\text{SO}_4]\) fragments within one asymmetric unit are in the range 7.0842 (12)–7.1554 (12) Å while the interchalogenic S···S distances are in the range 7.166 (2)–7.223 (2) Å. Bridging oxygen atoms of sulfate ligands, which bind \([\text{Cu(Hdmpz)}_4\text{SO}_4]\) formula units, are arranged in a spiral along the \( b \) axis (Fig. 3).

The molecular structure of the complex is stabilized by weak intramolecular hydrogen bonds in which hydrogen donors are carbon atoms (—CH₃ groups at the 3 and 5 positions of the pyrazole ring) and pyrrole-like nitrogen atoms of NH groups, while hydrogen acceptors are pyridine-like nitrogen atoms of the neighboring pyrazole ligands and O and S atoms of the sulfate ligands. Significant contributions to the hydrogen-bond network are made by N—H···O hydrogen bonds with lengths in the range of 2.022 (5) to 2.437 (4) Å.

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**Figure 1**
Representation of four \([\text{Cu(SO}_4]\text{2(Hdmpz)}_4]\) formula units in the structure of the title coordination polymer, with displacement ellipsoids at the 50% probability level.

**Figure 2**
The asymmetric unit of the title compound. Selected pyrazole ring atoms are represented as wireframes. H atoms and hydrogen bonds are omitted for clarity.
Selected intramolecular geometric parameters of hydrogen bonds are given in Table 1. The hydrogen-bond network in the asymmetric unit of the title compound is shown in Fig. 4. The torsion angle Cu1—Cu2—Cu3—Cu4 is 80.2 (2) and S1—S2—S3—S4 is 97.8 (2) and O1—O2—O5—O6, O5—O6—O9—O10 and O9—O10—O13—O14 are 36 (4), 25 (7) and 51 (3), respectively.

All pyrazole rings are oriented unsymmetrically in the mononuclear fragment. Thus, the planes of pyrazole rings N1/N2/C1/C3/C4 (pyrazole ligand near the Cu1 atom) and N9/N10/C21/C23/C24 (pyrazole ligand near the Cu2 atom) are oriented almost parallel to each other with a small deviation [plane normal to plane normal angle = 12.8 (3)]. The plane-to-plane twist angle is 4.2 (4), the plane-to-plane fold angle is 13.4 (4) and the plane-to-plane shift = 4.879 (18) Å. Within one [Cu(Hdmpz)₂SO₄] unit, pairs of pyrazole ring planes, for example N1/N2/C1/C3/C4, N7/N8/C16/C18/C19 and N3/N4/C6/C8/C9, N5/N6/C11/C13/C14, are placed in a non-parallel manner. The torsion angles N2—N1—N7—N8 and N4—N3—N5—N6 are 109.0 (6) and 111.3 (6), respectively.

### Table 1

| D—H · · · A | D—H | H · · · A | D···A | D—H · · · A |
|------------|------|-----------|-------|------------|
| N2—H2···O4 | 0.86 | 2.08      | 2.792 (7) | 139 |
| N6—H6···O3 | 0.86 | 2.04      | 2.889 (7) | 168 |
| N10—H10···O3 | 0.86 | 2.11      | 2.869 (7) | 146 |
| N12—H12···O4 | 0.86 | 2.12      | 2.951 (8) | 163 |
| N14—H14···O8 | 0.86 | 2.10      | 2.835 (7) | 143 |
| N16—H16···O5 | 0.86 | 2.44      | 2.889 (7) | 114 |
| N16—H16···O7 | 0.86 | 2.04      | 2.894 (8) | 173 |
| N18—H18···O6 | 0.86 | 2.39      | 2.866 (8) | 116 |
| N18—H18···O8 | 0.86 | 2.14      | 2.988 (7) | 169 |
| N20—H20···O9 | 0.86 | 2.41      | 2.885 (9) | 115 |
| N20—H20···O11 | 0.86 | 2.08      | 2.933 (7) | 171 |
| N22—H22···O7 | 0.86 | 2.05      | 2.828 (7) | 150 |
| N24—H24···O12 | 0.86 | 2.16      | 2.840 (8) | 135 |
| N26—H26···O16 | 0.86 | 2.02      | 2.875 (7) | 171 |
| N28—H28···O15 | 0.86 | 2.07      | 2.803 (7) | 143 |
| N30—H30···O10 | 0.86 | 2.31      | 2.817 (8) | 118 |
| N30—H30···O12 | 0.86 | 2.24      | 3.083 (6) | 165 |
| N32—H32···O11 | 0.86 | 2.12      | 2.857 (7) | 144 |
| C30—H30C···O5 | 0.96 | 2.39      | 3.213 (11) | 144 |
| C50—H50A···O6 | 0.96 | 2.23      | 3.132 (9) | 155 |
| C65—H65B···O10 | 0.96 | 2.27      | 3.192 (11) | 160 |
| C70—H70B···O10 | 0.96 | 2.35      | 3.116 (10) | 137 |

3. Supramolecular features

The crystal structure (Fig. 5) is built up from polymeric chains packed parallel along the b-axis direction. The unit-cell example N1/N2/C1/C3/C4, N7/N8/C16/C18/C19 and N3/N4/C6/C8/C9, N5/N6/C11/C13/C14, are placed in a non-parallel manner. The torsion angles N2—N1—N7—N8 and N4—N3—N5—N6 are 109.0 (6) and 111.3 (6), respectively.
dimensions can be explained because of the presence of four complex moieties in the asymmetric unit \((Z' = 4, Z = 16)\). As a result of the sulfate ligand rotation, there is a pairwise alternation of the terminal oxygen atoms (which are not involved in coordinating the copper atom) of the \(\text{SO}_4\) tetrahedra. Within one chain the intermetallic distance between two copper atoms, which are located at the edges of two neighboring asymmetric units, is 7.1625 (12) Å, while the interchalcogenic distance between the nearest sulfur atoms is 7.227 (2) Å. Polymeric chains, which are formed with the participation of bridging sulfate ligands, are stabilized by an extensive hydrogen-bond network. Neighboring chains are connected to each other by weak \(\text{C—H}/\text{C1/C1/C1} \text{N}\) and \(\text{C—H}/\text{C1/C1/C1} \text{O}\) hydrogen bonds. Geometric parameters for intermolecular hydrogen bonds are given in Table 2.

### Table 2

| Geometric parameters of intermolecular hydrogen bonds (Å, °) |
|------------------------------------------------------------|
| **C2—H2A···N16** |
| 0.96 | 3.01 | 3.722 (10) | 132 |
| **C2—H2A···O7** |
| 0.96 | 28 | 3.806 (9) | 146 |
| **C33—H33···N8** |
| 0.93 | 3.07 | 3.66 (1) | 123 |
| **C32—H32···N32** |
| 0.96 | 3.00 | 3.792 (10) | 140 |
| **C32—H32···N31** |
| 0.96 | 3.17 | 3.984 (10) | 143 |
| **C32—H32···N28** |
| 0.96 | 2.87 | 3.735 (11) | 150 |

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

4. Hirshfeld surface analysis

The Hirshfeld surface analysis was performed and the associated two-dimensional fingerprint plots generated using Crystal Explorer 17.5 software (Spackman et al., 2021), with a standard resolution of the three-dimensional \(d_{\text{norm}}\) surfaces plotted over a fixed color scale of −0.5511 (red) to 1.8416 (blue) a.u. The red spots in Fig. 6 represent short contacts and negative \(d_{\text{norm}}\) values on the surface corresponding to the interactions described above. The Hirshfeld surfaces mapped over \(d_{\text{norm}}\) are shown for the \(\text{H}···\text{H}, \text{H}···\text{O}/\text{O}···\text{H}, \text{H}···\text{C}/\text{C}···\text{H}, \text{Cu}···\text{O}/\text{O}···\text{Cu}\) and \(\text{H}···\text{N}/\text{N}···\text{H}\) contacts, the overall two-dimensional fingerprint plot and the decomposed two-dimensional fingerprint plots are given in Fig. 7. For the title coordination polymer, the most significant contributions to the overall crystal packing are from \(\text{H}···\text{H}\) (74.7%), \(\text{H}···\text{O}/\text{O}···\text{H}\) (14.8%) and \(\text{H}···\text{N}/\text{N}···\text{H}\) (8.2%) contacts. Small contributions of weak \(\text{Cu}···\text{O}/\text{O}···\text{Cu}\) (0.9%) and \(\text{N}/\text{N}···\text{O}/\text{O}···\text{N}\) (0.2%) contacts have a negligible effect on the packing. The total contribution of contacts involving hydrogen atoms is 85.9%, for O atoms is 8.4%, C atoms 4.4%, N atoms 0.7% and Cu atoms 0.5%. These values were calculated using the Crystal Explorer 17.5 software (Spackman et al., 2021). A special filter ‘by elements’ was chosen during the calculation of the contributions of selected individual interactions to the total Hirshfeld surface. Quantitative physical properties of Hirshfeld surface for the title compound were also obtained, such as the molecular volume (650.80 Å³), surface area (512.94 Å²), globularity (0.708), as well as sphericity (0.034). These properties provide significant information on the shape of the molecules and may serve in the future to identify and establish correlations with other properties.

5. Database survey

A search of the Cambridge Structural Database (CSD version 5.42, update February 2021; Groom et al., 2016) for the \(\text{Cu}_2(\text{µ}_2-\text{SO}_4)(\text{Hpz})_4\) moiety [two \(\text{Cu(Hpz)}_2\) fragments connected through a bidentate-bridged \(\text{SO}_4\) ligand] revealed two hits: QITCAZ, a coordination compound based on

![Figure 6](image-url) Two projections of Hirshfeld surfaces mapped over \(d_{\text{norm}}\) showing the intermolecular interactions.

![Figure 7](image-url) The overall two-dimensional fingerprint plot and those delineated into specified interactions. Hirshfeld surface representations with the function \(d_{\text{norm}}\) plotted onto the surface for the different interactions.
4-iodo-1H-pyrazole (Song et al., 2013) and XACTUR, a 1H-pyrazole-containing complex (Shen et al., 2004). These structures are similar to the title compound. Moreover there are 23 hits for the Cu(CN)₂SO₄ moiety, where CuN₂ is the backbone of the pyrazole ring. Most similar to the title complex are two catena-[(μ₂-sulfato)bis(3,5-dimethyl-1H-pyrazole)aquacopper(II)dihydrate] complexes: EHOMEU (Wang et al., 2010) and EHOMEU01 (Gogoi et al., 2019); FITCUI, a complex based on 2-thienyl-1H-pyrazole (Pettinari et al., 2014); ZZZALD01 a tetrakis(pyrazole)sulfato-copper(II) monohydrate (Shen et al., 2004); two monohydrated tetra-pyrazole sulfato copper(II) complexes: LUNDAB (Kumar et al., 2014) and LUNDAB01 (Zerguini et al., 2019).

6. Synthesis and crystallization

The synthesis of [Cu(SO₄)(Hdmmpz)]₄ was conducted at room temperature by the oxidative dissolution method as a result of the addition of a copper powder (1.56 mmol, 0.1 g) and anhydrous copper(II) sulfate (3.1 mmol, 0.5 g) mixture to an acetonitrile (9 ml) solution of 3,5-dimethyl-1H-pyrazole (4.68 mmol, 0.45g). The mixture was stirred without heating for three h with free air access until dissolution of the copper powder and a gray–blue precipitate of the product was obtained (the precipitate weight was 0.86 g). The precipitate was filtered off and the obtained green–blue solution was analyzed. Clear, intense blue crystals of the title compound suitable for X-ray analysis were obtained by slow evaporation of the solvent at room temperature in an open vessel. The relative yield of the single-crystal portion of the product with respect to the ligand was approximately 7%. The obtained blue crystals were studied by elemental analysis (calculated for C₉H₃₂CuN₇O₄S: C 44.1%, H 5.9%, N 20.6%, found: C 44.5%, H 6.3%, N 21%). The elemental analysis data of the obtained grey–blue precipitate was: found C 36.8%, H 5.5%, N 17.2%. IR spectra of the starting 3,5-dimethyl-1H-pyrazole, grey–blue precipitate and clear, intense blue crystals of the title coordination polymer are given in the supporting information for this article.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. Refinement of the N─H bond lengths was attempted, but this provided unrealistic values. Thus, hydrogens were placed at calculated positions and refined as riding with U(eq) = 1.2U(eq) (N, C) or 1.5U(eq) (C-methyl). The crystal studied was refined as a two-component inversion twin.

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References

Balić, T., Popović, Z. & Marković, B. (2018). Inorg. Chim. Acta. 478, 32–43.
Brewer, G., Butcher, R. J. & Zavalić, P. (2020). Materials. 13, 1595.
Burrows, A. D., Kelly, D. J., Haja Mohideen, M. I., Mahon, M. F., Pop, V. M. & Richardson, C. (2011). CrystEngComm. 13, 1676–1682.
Di Nicola, C., Garau, F., Lanza, A., Monari, M., Pandolfo, L., Pettinari, C. & Zorzi, A. (2014). Inorg. Chim. Acta. 416, 186–194.
Di Nicola, C., Karbach, Y. Y., Kirillov, A. M., Monari, M., Pandolfo, L., Pettinari, C. & Pomeario, A. J. L. (2007). Inorg. Chem. 46, 221–230.
Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschnigg, H. (2009). J. Appl. Cryst. 42, 339–341.
Gogoi, A., Nashre-ul-Islam, S. M., Frontera, A. & Bhattacharyya, M. K. (2019). Inorg. Chim. Acta. 484, 133–141.
Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). Acta Cryst. B72, 171–179.
Hoedt, R. W. M. ten, Hulsbergen, F. B., Verschoor, G. C. & Reedijk, J. (1982). Inorg. Chem. 21, 2369–2373.
House, J. E. & House, K. A. (2016). Synthesis and Reactions of Coordination Compounds. Descriptive Inorganic Chemistry, ch. 21, pp. 347–370. Amsterdam: Elsevier.
Kokozay, V. N., Vasilyeva, O. Yu. & Makhankova, V. G. (2018). Direct Synthesis of Metal Complexes, edited by I. B. Kharisov, pp. 183–237. Amsterdam: Elsevier.
Kumar, V., Kundu, A., Singh, M., Ramanujachary, K. V. & Raman, A. (2014). J. Chem. Sci. 126, 1433–1442.
Kwak, H., Lee, S. H., Kim, S. H., Lee, Y. M., Lee, E. Y., Park, B. K., Kim, E. Y., Kim, C., Kim, S.-J. & Kim, Y. (2008). Eur. J. Inorg. Chem. pp. 408–415.
Li, X. & Binnemans, K. (2021). Chem. Rev. 121, 4506–4530.
Mahmoudi, G. & Morsali, A. (2007). CrystEngComm. 9, 1062–1072.
Mihailov, M. H., Mihailova, V. T. & Khalkin, V. A. (1974). *J. Inorg. Nucl. Chem.* **36**, 141–144.

Mondal, R., Basu, T., Sadhukhan, D., Chattopadhyay, T. & Bhunia, M. K. (2009). *Cryst. Growth Des.* **9**, 1095–1105.

Nicholls, D. & Warburton, B. A. (1971). *J. Inorg. Nucl. Chem.* **33**, 1041–1045.

Pettinari, C., Marchetti, F., Orbisaglia, S., Palmucci, J., Pettinari, R., Di Nicola, C., Skelton, W. B. & White, A. H. (2014). *Eur. J. Inorg. Chem.* pp. 546–558.

Reedijk, J. (1971). *Recl Trav. Chim. Pays Bas*, **90**, 117–136.

Reedijk, J. (1970a). *Recl Trav. Chim. Pays Bas*, **89**, 605–618.

Reedijk, J. (1970b). *Recl Trav. Chim. Pays Bas*, **89**, 993–1016.

Reedijk, J. & Smit, J. A. (1971). *Recl Trav. Chim. Pays Bas*, **90**, 1135–1140.

Reedijk, J., Windhorst, J. C. A., van Ham, N. H. M. & Groeneveld, W. L. (1971). *Recl Trav. Chim. Pays Bas*, **90**, 234–251.

Rigaku OD (2021). *CrysAlis PRO* Rigaku Oxford Diffraction, Yarnton, England.

Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.

Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.

Shen, W.-Z., Yi, L., Cheng, P., Yan, S.-P., Liao, D.-Z. & Jiang, Z.-H. (2004). *Inorg. Chem. Commun.* **7**, 819–822.

Singh, C. B., Satpathy, S. & Sahoo, B. (1973). *J. Inorg. Nucl. Chem.* **35**, 3947–3950.

Song, G., Sun, Q., Hou, Y.-N., Zhan, R., Wei, D.-M., Shi, Zh. & Xing, Y.-H. (2013). *Wuji Huaxue Xuebao*, **29**, 2150.

Spackman, P. R., Turner, M. J., McKinnon, J. J., Wolff, S. K., Grimwood, D. J., Jayatilaka, D. & Spackman, M. A. (2021). *J. Appl. Cryst.* **54**, 1006–1011.

Wang, S.-Q. & Jian, F.-F. (2010). *Z. Kristallogr. New Cryst. Struct.* **225**, 683–684.

Zerguini, A. L., Cherouana, A., Duparc, V. H. & Schaper, F. (2019). *Inorg. Chem. Commun.* **99**, 36–39.
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Computing details
Data collection: CrysAlis PRO (Rigaku OD, 2021); cell refinement: CrysAlis PRO (Rigaku OD, 2021); data reduction: CrysAlis PRO (Rigaku OD, 2021); program(s) used to solve structure: SHELXT2018/2 (Sheldrick, 2015a); program(s) used to refine structure: SHELXL2018/3 (Sheldrick, 2015b); molecular graphics: OLEX2 (Dolomanov et al., 2009); software used to prepare material for publication: OLEX2 (Dolomanov et al., 2009).

catena-Poly[[tetrakis(3,5-dimethyl-1H-pyrazole-κN^{2})copper(II)]-μ_2-sulfato-κ^{2}O:O′]

Crystal data
[Cu(SO_4)(C_5H_8N_2)_4]  \( D_\lambda = 1.359 \text{ Mg m}^{-3} \)
Orthorhombic, \( Pna2_1 \)  
\( a = 19.3656 \) (6) Å  
\( b = 28.4032 \) (6) Å  
\( c = 19.3456 \) (5) Å  
\( V = 10641.0 \) (5) Å³  
\( Z = 16 \)  
\( F(000) = 4560 \)

Data collection
Rigaku Oxford Diffraction Xcalibur, Eos diffractometer  
Radiation source: fine-focus sealed X-ray tube, Enhance (Mo) X-ray Source  
Graphite monochromator  
Detector resolution: 16.1593 pixels mm⁻¹  
\( \omega \) scans  
Absorption correction: multi-scan  
(CrysAlis PRO; Rigaku OD, 2021)  
\( T_{\text{min}} = 0.907, T_{\text{max}} = 1.000 \)
119732 measured reflections  
22862 independent reflections  
14389 reflections with \( I > 2\sigma(I) \)  
\( R_{\text{int}} = 0.062 \)  
\( \theta_{\text{max}} = 29.4^\circ, \theta_{\text{min}} = 1.7^\circ \)  
\( h = -26 \rightarrow 26 \)  
\( k = -39 \rightarrow 36 \)  
\( l = -22 \rightarrow 26 \)

Refinement
Refinement on \( F^2 \)  
Least-squares matrix: full  
\( R[F^2 > 2\sigma(F^2)] = 0.054 \)  
\( wR(F^2) = 0.133 \)  
\( S = 1.03 \)  
22862 reflections  
1234 parameters  
1 restraint  
Primary atom site location: dual  
Hydrogen site location: mixed  
H-atom parameters constrained
\[ w = \frac{1}{[\sigma^2(F_o^2) + (0.0546P)^2 + 4.6894P]} \]

where \( P = (F_o^2 + 2F_c^2)/3 \)

\[(\Delta/\sigma)_{\text{max}} = 0.001\]

\[\Delta \rho_{\text{max}} = 1.19 \text{ e Å}^{-3}\]

**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.** Refined as a 2-component inversion twin.

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

|  | \( x \) | \( y \) | \( z \) | \( U_{eq} \) |
|---|---|---|---|---|
| Cu1 | 0.32732 (4) | 0.08172 (3) | 0.47991 (5) | 0.0381 (2) |
| Cu2 | 0.35680 (4) | 0.33019 (3) | 0.49183 (4) | 0.0366 (2) |
| Cu3 | 0.34772 (4) | 0.57922 (3) | 0.51712 (5) | 0.0386 (2) |
| Cu4 | 0.31888 (4) | 0.83027 (3) | 0.50659 (4) | 0.0383 (2) |
| S1 | 0.38041 (9) | 0.20005 (5) | 0.50836 (11) | 0.0453 (4) |
| S2 | 0.33477 (9) | 0.45147 (5) | 0.54082 (11) | 0.0425 (5) |
| S3 | 0.29310 (9) | 0.69962 (5) | 0.48845 (12) | 0.0482 (5) |
| S4 | 0.34086 (9) | 0.94986 (5) | 0.45316 (11) | 0.0415 (4) |
| O1 | 0.3364 (2) | 0.16205 (14) | 0.4818 (3) | 0.0518 (14) |
| O2 | 0.3552 (2) | 0.24597 (13) | 0.4860 (3) | 0.0507 (13) |
| O3 | 0.3800 (3) | 0.19749 (17) | 0.5846 (3) | 0.0574 (15) |
| O4 | 0.4509 (2) | 0.19497 (15) | 0.4824 (3) | 0.0612 (15) |
| O5 | 0.3613 (2) | 0.41241 (13) | 0.4991 (3) | 0.0495 (14) |
| O6 | 0.3581 (2) | 0.49625 (14) | 0.5126 (3) | 0.0526 (14) |
| O7 | 0.2586 (2) | 0.44992 (15) | 0.5392 (3) | 0.0572 (14) |
| O8 | 0.3598 (3) | 0.44762 (16) | 0.6120 (3) | 0.0603 (16) |
| O9 | 0.3357 (2) | 0.66123 (14) | 0.5160 (4) | 0.0570 (15) |
| O10 | 0.3188 (3) | 0.74469 (14) | 0.5145 (3) | 0.0603 (15) |
| O11 | 0.2977 (3) | 0.69918 (17) | 0.4129 (3) | 0.0629 (16) |
| O12 | 0.2213 (3) | 0.69417 (17) | 0.5107 (4) | 0.0710 (16) |
| O13 | 0.3157 (2) | 0.91247 (13) | 0.4997 (3) | 0.0486 (14) |
| O14 | 0.3186 (2) | 0.99611 (14) | 0.4783 (3) | 0.0516 (14) |
| O15 | 0.3144 (3) | 0.94324 (18) | 0.3832 (3) | 0.0599 (16) |
| O16 | 0.4168 (2) | 0.94793 (16) | 0.4532 (3) | 0.0537 (14) |
| N1 | 0.4125 (3) | 0.07577 (18) | 0.5413 (3) | 0.0406 (14) |
| N2 | 0.4699 (3) | 0.10224 (17) | 0.5263 (3) | 0.0421 (13) |
| H2 | 0.471469 | 0.123444 | 0.494624 | 0.050* |
| N3 | 0.3918 (3) | 0.07707 (17) | 0.3958 (3) | 0.0371 (13) |
| N4 | 0.4314 (3) | 0.03765 (18) | 0.3906 (3) | 0.0406 (14) |
| H4 | 0.431493 | 0.015166 | 0.420404 | 0.049* |
| N5 | 0.2660 (3) | 0.08838 (18) | 0.5646 (3) | 0.0402 (14) |
| N6 | 0.2834 (3) | 0.12205 (18) | 0.6108 (3) | 0.0492 (15) |
| H6 | 0.316691 | 0.141689 | 0.604779 | 0.059* |
| N7 | 0.2437 (3) | 0.07873 (18) | 0.4170 (3) | 0.0404 (15) |

Absolute structure: Refined as an inversion twin

Absolute structure parameter: 0.479 (15)
The table contains the Cartesian coordinates and displacement parameters for atoms N1 to N32, C1 to C8, and H8 to H32 in the crystal structure. The coordinates are given in angstroms (Å) and the displacement parameters in ångstroms squared (Å²).
| Atom | X (Å) | Y (Å) | Z (Å) | Temperature (Å²) |
|------|-------|-------|-------|------------------|
| H5B  | 0.355543 | -0.001530 | 0.590356 | 0.100* |
| H5C  | 0.411053 | -0.011900 | 0.647336 | 0.100* |
| C6   | 0.4698 (4) | 0.0382 (2) | 0.3339 (4) | 0.0493 (19) |
| C7   | 0.5150 (4) | -0.0028 (3) | 0.3150 (5) | 0.074 (3) |
| H7A  | 0.541754 | -0.012111 | 0.354541 | 0.110* |
| H7B  | 0.486784 | -0.028761 | 0.300331 | 0.110* |
| H7C  | 0.545514 | 0.006079 | 0.278111 | 0.110* |
| C8   | 0.4558 (4) | 0.0797 (2) | 0.3010 (4) | 0.057 (2) |
| H8A  | 0.475469 | 0.090205 | 0.259971 | 0.069* |
| C9   | 0.4068 (4) | 0.1032 (2) | 0.3403 (4) | 0.0433 (17) |
| C10  | 0.3741 (5) | 0.1494 (2) | 0.3269 (4) | 0.064 (2) |
| H10A | 0.370788 | 0.154240 | 0.277892 | 0.095* |
| H10B | 0.328688 | 0.150070 | 0.346832 | 0.095* |
| H10C | 0.401648 | 0.173990 | 0.346972 | 0.095* |
| C11  | 0.2429 (5) | 0.1213 (3) | 0.6671 (5) | 0.064 (2) |
| C12  | 0.2525 (5) | 0.1557 (3) | 0.7255 (5) | 0.091 (3) |
| H12A | 0.228809 | 0.144454 | 0.765843 | 0.137* |
| H12B | 0.300869 | 0.158834 | 0.735583 | 0.137* |
| H12C | 0.234159 | 0.185804 | 0.712433 | 0.137* |
| C13  | 0.1985 (5) | 0.0846 (3) | 0.6565 (5) | 0.065 (2) |
| C14  | 0.2144 (4) | 0.074778 | 0.686407 | 0.078* |
| C15  | 0.1806 (4) | 0.0235 (2) | 0.5586 (5) | 0.065 (2) |
| H15A | 0.164851 | 0.032739 | 0.513512 | 0.098* |
| H15B | 0.213211 | -0.001791 | 0.554232 | 0.098* |
| H15C | 0.141941 | 0.013189 | 0.585722 | 0.098* |
| C16  | 0.1745 (4) | 0.0393 (2) | 0.3441 (4) | 0.0472 (18) |
| C17  | 0.1537 (4) | -0.0010 (3) | 0.2990 (6) | 0.069 (3) |
| H17A | 0.183502 | -0.002395 | 0.259473 | 0.104* |
| H17B | 0.106820 | 0.003300 | 0.284058 | 0.104* |
| H17C | 0.157235 | -0.029876 | 0.324644 | 0.104* |
| C18  | 0.1448 (4) | 0.0824 (3) | 0.3581 (5) | 0.058 (2) |
| H18A | 0.103391 | 0.093839 | 0.340651 | 0.069* |
| C19  | 0.1889 (4) | 0.1050 (2) | 0.4032 (4) | 0.0492 (19) |
| C20  | 0.1813 (4) | 0.1533 (2) | 0.4351 (5) | 0.074 (3) |
| H20A | 0.150287 | 0.151529 | 0.473782 | 0.111* |
| H20B | 0.225577 | 0.164219 | 0.450522 | 0.111* |
| H20C | 0.163077 | 0.174749 | 0.401402 | 0.111* |
| C21  | 0.5111 (4) | 0.2829 (2) | 0.6214 (4) | 0.0485 (18) |
| C22  | 0.5304 (5) | 0.2404 (3) | 0.6634 (4) | 0.069 (2) |
| H22A | 0.559190 | 0.249827 | 0.701352 | 0.104* |
| H22B | 0.554996 | 0.218450 | 0.634818 | 0.104* |
| H22C | 0.489284 | 0.225722 | 0.680924 | 0.104* |
| C23  | 0.5467 (4) | 0.3217 (3) | 0.6007 (4) | 0.0514 (19) |
| H23  | 0.591877 | 0.329426 | 0.612165 | 0.062* |
| C24  | 0.5018 (4) | 0.3476 (2) | 0.5585 (4) | 0.0426 (16) |
| C25  | 0.5174 (4) | 0.3928 (2) | 0.5231 (5) | 0.060 (2) |
| H25A | 0.566328 | 0.398168 | 0.523457 | 0.090* |
| Atom | x      | y      | z      | U(eq)  |
|------|--------|--------|--------|--------|
| H25B | 0.494508 | 0.418130 | 0.546674 | 0.090* |
| H25C | 0.501375 | 0.391373 | 0.476133 | 0.090* |
| C26  | 0.5061 (4) | 0.2867 (3) | 0.3537 (4) | 0.056 (2) |
| C27  | 0.5556 (6) | 0.2466 (3) | 0.3427 (6) | 0.104 (4) |
| H27A | 0.588553 | 0.254903 | 0.307665 | 0.156* |
| H27B | 0.579403 | 0.239943 | 0.385145 | 0.156* |
| H27C | 0.530273 | 0.219273 | 0.328355 | 0.156* |
| C28  | 0.4935 (5) | 0.3277 (3) | 0.3192 (4) | 0.064 (2) |
| H28A | 0.515504 | 0.338284 | 0.279364 | 0.077* |
| C29  | 0.4408 (4) | 0.3507 (2) | 0.3557 (4) | 0.0505 (19) |
| C30  | 0.4076 (5) | 0.3971 (3) | 0.3412 (4) | 0.071 (3) |
| H30A | 0.362296 | 0.392072 | 0.322493 | 0.107* |
| H30B | 0.435085 | 0.414249 | 0.308444 | 0.107* |
| H30C | 0.404123 | 0.414809 | 0.383313 | 0.107* |
| C31  | 0.2715 (4) | 0.3463 (2) | 0.6863 (4) | 0.0489 (18) |
| C32  | 0.2785 (5) | 0.3752 (3) | 0.7511 (4) | 0.071 (2) |
| H32A | 0.260913 | 0.406319 | 0.742753 | 0.106* |
| H32B | 0.252743 | 0.360759 | 0.787763 | 0.106* |
| H32C | 0.326293 | 0.377149 | 0.763903 | 0.106* |
| C33  | 0.2287 (4) | 0.3101 (3) | 0.6676 (4) | 0.059 (2) |
| H33  | 0.195432 | 0.295838 | 0.695224 | 0.070* |
| C34  | 0.2444 (4) | 0.2987 (2) | 0.5991 (4) | 0.0462 (19) |
| C35  | 0.2102 (4) | 0.2627 (3) | 0.5545 (5) | 0.067 (2) |
| H35A | 0.227412 | 0.232031 | 0.566120 | 0.101* |
| H35B | 0.161182 | 0.263641 | 0.562070 | 0.101* |
| H35C | 0.219822 | 0.269301 | 0.506840 | 0.101* |
| C36  | 0.1892 (4) | 0.3819 (3) | 0.3860 (5) | 0.062 (2) |
| C37  | 0.1406 (5) | 0.4231 (3) | 0.3818 (6) | 0.099 (4) |
| H37A | 0.093811 | 0.411965 | 0.382856 | 0.148* |
| H37B | 0.148371 | 0.443765 | 0.420305 | 0.148* |
| H37C | 0.148481 | 0.439946 | 0.339455 | 0.148* |
| C38  | 0.1967 (5) | 0.3428 (3) | 0.3447 (5) | 0.065 (2) |
| H38  | 0.170690 | 0.335538 | 0.305757 | 0.078* |
| C39  | 0.2504 (4) | 0.3164 (2) | 0.3720 (4) | 0.0490 (19) |
| C40  | 0.2795 (5) | 0.2713 (3) | 0.3473 (5) | 0.073 (3) |
| H40A | 0.256185 | 0.261897 | 0.305781 | 0.110* |
| H40B | 0.327845 | 0.275217 | 0.338011 | 0.110* |
| H40C | 0.273345 | 0.247627 | 0.382141 | 0.110* |
| C41  | 0.4994 (4) | 0.5381 (3) | 0.6556 (4) | 0.0498 (19) |
| C42  | 0.5231 (4) | 0.4972 (3) | 0.6985 (5) | 0.077 (3) |
| H42A | 0.516980 | 0.504359 | 0.746621 | 0.116* |
| H42B | 0.571074 | 0.491173 | 0.689528 | 0.116* |
| H42C | 0.496494 | 0.469786 | 0.686875 | 0.116* |
| C43  | 0.5285 (4) | 0.5809 (3) | 0.6422 (4) | 0.056 (2) |
| H43  | 0.569799 | 0.592359 | 0.659665 | 0.067* |
| C44  | 0.4843 (4) | 0.6040 (2) | 0.5965 (4) | 0.0471 (18) |
| C45  | 0.4919 (4) | 0.6522 (2) | 0.5650 (5) | 0.070 (2) |
| H45A | 0.539299 | 0.661929 | 0.568093 | 0.104* |
|   | x   | y   | z   |      |
|---|-----|-----|-----|------|
| H45B | 0.478179 | 0.651109 | 0.517373 | 0.104* |
| H45C | 0.463279 | 0.674139 | 0.589483 | 0.104* |
| C46  | 0.4464 (4) | 0.6273 (3) | 0.3424 (4) | 0.0526 (19) |
| C47  | 0.4456 (5) | 0.6662 (3) | 0.2898 (4) | 0.078 (3) |
| H47A | 0.452922 | 0.653232 | 0.244593 | 0.117* |
| H47B | 0.401622 | 0.681892 | 0.291063 | 0.117* |
| H47C | 0.481512 | 0.688432 | 0.300053 | 0.117* |
| C48  | 0.4908 (4) | 0.5902 (3) | 0.3515 (4) | 0.056 (2) |
| H48  | 0.528511 | 0.582495 | 0.324045 | 0.068* |
| C49  | 0.4680 (4) | 0.5665 (2) | 0.4099 (4) | 0.0431 (18) |
| C50  | 0.4983 (4) | 0.5240 (2) | 0.4440 (5) | 0.066 (2) |
| H50A | 0.462492 | 0.506713 | 0.466947 | 0.098* |
| H50B | 0.532356 | 0.53715 | 0.477141 | 0.098* |
| H50C | 0.519666 | 0.504384 | 0.409681 | 0.098* |
| C51  | 0.2114 (4) | 0.5354 (2) | 0.6688 (4) | 0.0495 (19) |
| C52  | 0.1679 (4) | 0.4945 (3) | 0.6911 (6) | 0.072 (3) |
| H52A | 0.183295 | 0.466551 | 0.667829 | 0.108* |
| H52B | 0.172145 | 0.490291 | 0.740129 | 0.108* |
| H52C | 0.120465 | 0.500471 | 0.679529 | 0.108* |
| C53  | 0.2305 (4) | 0.5758 (3) | 0.7027 (4) | 0.0517 (19) |
| H53  | 0.216045 | 0.585499 | 0.746269 | 0.062* |
| C54  | 0.2752 (4) | 0.5990 (2) | 0.6595 (4) | 0.0454 (17) |
| C55  | 0.3139 (5) | 0.6447 (3) | 0.6737 (5) | 0.072 (3) |
| H55A | 0.293584 | 0.669771 | 0.647370 | 0.109* |
| H55B | 0.361446 | 0.641088 | 0.660726 | 0.109* |
| H55C | 0.311095 | 0.652069 | 0.722096 | 0.109* |
| C56  | 0.1634 (4) | 0.5951 (3) | 0.4085 (5) | 0.069 (3) |
| C57  | 0.0974 (5) | 0.6235 (3) | 0.4060 (6) | 0.105 (4) |
| H57A | 0.060225 | 0.605184 | 0.424750 | 0.157* |
| H57B | 0.103045 | 0.651724 | 0.432740 | 0.157* |
| H57C | 0.087055 | 0.631684 | 0.358930 | 0.157* |
| C58  | 0.1910 (5) | 0.5612 (3) | 0.3649 (5) | 0.078 (3) |
| H58  | 0.170809 | 0.548858 | 0.325256 | 0.094* |
| C59  | 0.2541 (4) | 0.5495 (3) | 0.3921 (5) | 0.053 (2) |
| C60  | 0.3040 (5) | 0.5152 (3) | 0.3616 (5) | 0.076 (3) |
| H60A | 0.292885 | 0.510294 | 0.313798 | 0.114* |
| H60B | 0.350055 | 0.527494 | 0.365318 | 0.114* |
| H60C | 0.301045 | 0.485884 | 0.386008 | 0.114* |
| C61  | 0.4981 (4) | 0.8783 (3) | 0.5986 (4) | 0.059 (2) |
| C62  | 0.5536 (5) | 0.9155 (3) | 0.5916 (6) | 0.096 (4) |
| H62A | 0.549922 | 0.937439 | 0.629168 | 0.143* |
| H62B | 0.547886 | 0.931859 | 0.548573 | 0.143* |
| H62C | 0.598204 | 0.900764 | 0.592679 | 0.143* |
| C63  | 0.4896 (4) | 0.8416 (3) | 0.6425 (5) | 0.062 (2) |
| H63  | 0.518563 | 0.833641 | 0.679017 | 0.075* |
| C64  | 0.4295 (4) | 0.8180 (2) | 0.6230 (4) | 0.050 (2) |
| C65  | 0.3958 (5) | 0.7755 (3) | 0.6532 (5) | 0.077 (3) |
| H65A | 0.366272 | 0.784778 | 0.690652 | 0.115* |
| Atom  | U₁₁  | U₂₂  | U₃₃  | U₁₂  | U₁₃  | U₂₃  |
|-------|------|------|------|------|------|------|
| Cu1   | 0.0354 (4) | 0.0381 (4) | 0.0408 (6) | -0.0023 (3) | -0.0030 (4) | -0.0003 (4) |
| Cu2   | 0.0354 (4) | 0.0365 (4) | 0.0380 (5) | -0.0001 (3) | 0.0027 (4)  | 0.0004 (4)  |
| Cu3   | 0.0340 (4) | 0.0375 (4) | 0.0443 (6) | -0.0002 (3) | 0.0000 (4)  | 0.0033 (4)  |
| Cu4   | 0.0361 (4) | 0.0427 (4) | 0.0363 (5) | -0.0003 (3) | -0.0013 (4) | 0.0022 (4)  |
| S1    | 0.0503 (10) | 0.0279 (7)  | 0.0578 (13) | -0.0068 (7) | 0.0034 (10) | -0.0005 (8) |
| S2    | 0.0462 (10) | 0.0256 (8)  | 0.0556 (13) | -0.0035 (7) | -0.0002 (9) | -0.0013 (8) |
|    | S3       | S4       | O1       | O2       | O3       | O4       | O5       | O6       | O7       | O8       | O9       | O10      | O11      | O12      | O13      | O14      | O15      | O16      | N1       | N2       | N3       | N4       | N5       | N6       | N7       | N8       | N9       | N10      | N11      | N12      | N13      | N14      | N15      | N16      | N17      | N18      | N19      | N20      | N21      | N22      | N23      | N24      | N25      | N26      | N27      | N28      | N29      | N30      |
|----|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
|    | 0.0541 (11) | 0.0306 (8) | 0.0598 (14) | 0.0086 (7) | 0.0045 (10) | -0.0009 (9) |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |
|      |       |       |       |       |       |       |       |       |
|------|-------|-------|-------|-------|-------|-------|-------|-------|
| N31  | 0.031 | 0.037 | 0.041 | 0.000 | 0.002 | −0.005|
| N32  | 0.039 | 0.036 | 0.054 | 0.000 | −0.002| −0.003|
| C1   | 0.040 | 0.064 | 0.061 | 0.005 | −0.012| −0.017|
| C2   | 0.048 | 0.103 | 0.076 | −0.012| −0.011| −0.011|
| C3   | 0.063 | 0.063 | 0.067 | 0.008 | −0.021| 0.002 |
| C4   | 0.055 | 0.037 | 0.050 | −0.004| −0.005| 0.001 |
| C5   | 0.081 | 0.062 | 0.057 | −0.009| −0.019| 0.009 |
| C6   | 0.041 | 0.051 | 0.056 | −0.007| 0.002 | −0.005|
| C7   | 0.064 | 0.063 | 0.093 | 0.004 | 0.014 | −0.016|
| C8   | 0.070 | 0.056 | 0.047 | −0.008| 0.012 | 0.008 |
| C9   | 0.049 | 0.043 | 0.038 | −0.014| −0.009| 0.001 |
| C10  | 0.087 | 0.043 | 0.061 | −0.007| −0.005| 0.016 |
| C11  | 0.083 | 0.055 | 0.055 | −0.011| 0.017 | −0.010|
| C12  | 0.114 | 0.092 | 0.068 | −0.018| 0.024 | −0.033|
| C13  | 0.072 | 0.062 | 0.061 | −0.011| 0.024 | −0.005|
| C14  | 0.051 | 0.039 | 0.060 | −0.003| 0.008 | −0.002|
| C15  | 0.050 | 0.057 | 0.089 | −0.022| 0.009 | −0.013|
| C16  | 0.040 | 0.054 | 0.048 | −0.007| −0.006| −0.003|
| C17  | 0.059 | 0.082 | 0.066 | −0.014| −0.012| −0.018|
| C18  | 0.039 | 0.066 | 0.069 | 0.011 | −0.009| 0.008 |
| C19  | 0.042 | 0.037 | 0.069 | 0.004 | 0.006 | 0.007 |
| C20  | 0.055 | 0.041 | 0.126 | 0.011 | 0.002 | −0.005|
| C21  | 0.057 | 0.047 | 0.042 | 0.003 | −0.012| −0.004|
| C22  | 0.088 | 0.062 | 0.057 | 0.004 | −0.025| 0.014 |
| C23  | 0.042 | 0.061 | 0.051 | 0.000 | −0.009| −0.002|
| C24  | 0.041 | 0.039 | 0.048 | 0.000 | 0.002 | −0.005|
| C25  | 0.046 | 0.059 | 0.076 | −0.018| −0.002| 0.016 |
| C26  | 0.054 | 0.063 | 0.052 | −0.005| 0.015 | −0.016|
| C27  | 0.109 | 0.095 | 0.107 | 0.024 | 0.043 | −0.019|
| C28  | 0.078 | 0.071 | 0.044 | −0.014| 0.027 | −0.009|
| C29  | 0.066 | 0.045 | 0.041 | −0.018| 0.000 | −0.004|
| C30  | 0.114 | 0.050 | 0.049 | −0.005| 0.004 | 0.010 |
| C31  | 0.059 | 0.045 | 0.043 | 0.006 | 0.013 | 0.004 |
| C32  | 0.094 | 0.073 | 0.044 | −0.006| 0.013 | −0.007|
| C33  | 0.057 | 0.060 | 0.059 | −0.003| 0.028 | 0.008 |
| C34  | 0.041 | 0.038 | 0.059 | −0.008| 0.005 | −0.003|
| C35  | 0.057 | 0.062 | 0.083 | −0.020| 0.020 | −0.013|
| C36  | 0.056 | 0.052 | 0.077 | 0.000 | −0.016| 0.017 |
| C37  | 0.088 | 0.077 | 0.131 | 0.029 | −0.039| 0.015 |
| C38  | 0.078 | 0.065 | 0.052 | −0.013| −0.027| 0.007 |
| C39  | 0.061 | 0.043 | 0.042 | −0.009| −0.007| 0.007 |
| C40  | 0.111 | 0.050 | 0.060 | −0.010| −0.014| −0.010|
| C41  | 0.049 | 0.060 | 0.040 | 0.008 | −0.005| 0.004 |
| C42  | 0.070 | 0.090 | 0.073 | 0.012 | −0.006| 0.030 |
| C43  | 0.040 | 0.072 | 0.055 | −0.001| −0.007| 0.001 |
| C44  | 0.038 | 0.047 | 0.056 | −0.005| 0.001 | −0.001|
| C45  | 0.058 | 0.051 | 0.100 | −0.012| −0.010| 0.004 |
| C46  | 0.055 | 0.054 | 0.049 | −0.009| −0.001| 0.007 |
| C47  | 0.098 (7) | 0.086 (6) | 0.050 (5) | −0.002 (5) | 0.001 (5) | 0.026 (5) |
| C48  | 0.044 (4) | 0.063 (5) | 0.062 (6) | −0.004 (4) | 0.017 (4) | −0.002 (4) |
| C49  | 0.038 (4) | 0.032 (3) | 0.060 (5) | −0.004 (3) | 0.004 (4) | −0.002 (3) |
| C50  | 0.043 (4) | 0.050 (4) | 0.104 (7) | 0.006 (4) | 0.017 (5) | 0.004 (4) |
| C51  | 0.040 (4) | 0.043 (4) | 0.065 (6) | 0.003 (3) | 0.010 (4) | 0.009 (4) |
| C52  | 0.059 (6) | 0.073 (6) | 0.084 (8) | −0.013 (4) | 0.016 (5) | 0.019 (5) |
| C53  | 0.046 (4) | 0.061 (5) | 0.048 (5) | 0.005 (4) | 0.005 (4) | 0.000 (4) |
| C54  | 0.049 (4) | 0.037 (4) | 0.050 (5) | 0.003 (3) | 0.001 (4) | −0.004 (3) |
| C55  | 0.102 (7) | 0.047 (5) | 0.068 (7) | −0.017 (4) | 0.009 (5) | −0.014 (4) |
| C56  | 0.047 (5) | 0.061 (5) | 0.099 (8) | −0.009 (4) | −0.026 (5) | 0.032 (5) |
| C57  | 0.065 (6) | 0.100 (7) | 0.149 (11) | 0.012 (6) | −0.035 (7) | 0.023 (7) |
| C58  | 0.085 (7) | 0.069 (6) | 0.081 (7) | −0.019 (5) | −0.038 (6) | 0.001 (5) |
| C59  | 0.058 (5) | 0.046 (4) | 0.055 (5) | −0.006 (4) | −0.017 (4) | 0.003 (4) |
| C60  | 0.082 (6) | 0.074 (6) | 0.072 (7) | −0.002 (5) | −0.010 (5) | −0.016 (5) |
| C61  | 0.057 (5) | 0.058 (5) | 0.060 (5) | −0.001 (4) | −0.016 (4) | −0.013 (4) |
| C62  | 0.081 (7) | 0.097 (7) | 0.109 (9) | −0.038 (6) | −0.028 (6) | −0.012 (6) |
| C63  | 0.066 (5) | 0.055 (5) | 0.065 (6) | 0.013 (4) | −0.037 (5) | −0.008 (4) |
| C64  | 0.066 (5) | 0.042 (4) | 0.042 (5) | 0.012 (4) | −0.011 (4) | 0.001 (3) |
| C65  | 0.122 (8) | 0.053 (5) | 0.055 (6) | 0.002 (5) | −0.022 (6) | 0.016 (4) |
| C66  | 0.055 (5) | 0.041 (4) | 0.046 (5) | −0.007 (3) | 0.004 (4) | −0.011 (3) |
| C67  | 0.080 (6) | 0.076 (5) | 0.047 (5) | −0.006 (4) | 0.003 (4) | 0.004 (4) |
| C68  | 0.044 (4) | 0.064 (5) | 0.056 (5) | 0.000 (4) | 0.011 (4) | −0.014 (4) |
| C69  | 0.041 (4) | 0.036 (4) | 0.050 (5) | 0.001 (3) | 0.001 (4) | −0.005 (3) |
| C70  | 0.057 (5) | 0.057 (5) | 0.086 (7) | 0.021 (4) | 0.001 (5) | 0.005 (4) |
| C71  | 0.063 (5) | 0.046 (4) | 0.040 (5) | 0.010 (4) | 0.004 (4) | 0.002 (3) |
| C72  | 0.119 (8) | 0.054 (5) | 0.066 (6) | −0.005 (5) | 0.012 (6) | −0.009 (5) |
| C73  | 0.078 (6) | 0.069 (5) | 0.043 (5) | 0.010 (4) | 0.017 (5) | 0.003 (4) |
| C74  | 0.057 (5) | 0.056 (5) | 0.061 (6) | 0.007 (4) | 0.016 (4) | 0.011 (4) |
| C75  | 0.078 (7) | 0.084 (6) | 0.096 (8) | −0.021 (5) | 0.030 (6) | 0.017 (5) |
| C76  | 0.050 (5) | 0.048 (4) | 0.059 (5) | −0.012 (4) | −0.007 (4) | −0.004 (4) |
| C77  | 0.073 (7) | 0.072 (6) | 0.126 (9) | −0.020 (5) | −0.015 (6) | −0.033 (6) |
| C78  | 0.040 (4) | 0.059 (5) | 0.065 (6) | 0.002 (4) | −0.012 (4) | 0.003 (4) |
| C79  | 0.038 (4) | 0.041 (4) | 0.055 (5) | 0.005 (3) | 0.002 (4) | 0.005 (3) |
| C80  | 0.051 (5) | 0.058 (4) | 0.095 (7) | 0.018 (3) | 0.003 (5) | −0.012 (5) |

**Geometric parameters (Å, °)**

| Cu1—O1  | 2.289 (4) | C17—H17B | 0.9600 |
| Cu1—O14′| 2.438 (4) | C17—H17C | 0.9600 |
| Cu1—N1  | 2.039 (6) | C18—H18A | 0.9300 |
| Cu1—N3  | 2.054 (6) | C18—C19 | 1.379 (11) |
| Cu1—N5  | 2.033 (6) | C19—C20 | 1.510 (10) |
| Cu1—N7  | 2.028 (6) | C20—H20A | 0.9600 |
| Cu2—O2  | 2.395 (4) | C20—H20B | 0.9602 |
| Cu2—O5  | 2.341 (4) | C20—H20C | 0.9599 |
| Cu2—N9  | 2.033 (6) | C21—C22 | 1.504 (10) |
| Cu2—N11 | 2.042 (6) | C21—C23 | 1.358 (10) |
| Cu2—N13 | 2.031 (6) | C22—H22A | 0.9600 |
| Bond                  | Distance (Å) | Bond                  | Distance (Å) | Distance (Å) |
|-----------------------|--------------|-----------------------|--------------|--------------|
| Cu2—N15               | 2.028 (6)    | C22—H22B              | 0.9600       |
| Cu3—O6                | 2.367 (4)    | C22—H22C              | 0.9600       |
| Cu3—O9                | 2.341 (4)    | C23—H23               | 0.9300       |
| Cu3—N17               | 2.041 (6)    | C23—C24               | 1.401 (10)   |
| Cu3—N19               | 2.044 (6)    | C24—C25               | 1.487 (9)    |
| Cu3—N21               | 2.040 (6)    | C25—H25A              | 0.9600       |
| Cu3—N23               | 2.058 (6)    | C25—H25B              | 0.9600       |
| Cu4—O10               | 2.435 (4)    | C25—H25C              | 0.9600       |
| Cu4—O13               | 2.339 (4)    | C26—C27               | 1.504 (11)   |
| Cu4—N25               | 2.014 (6)    | C26—C28               | 1.364 (11)   |
| Cu4—N27               | 2.045 (6)    | C27—H27A              | 0.9602       |
| Cu4—N29               | 2.031 (6)    | C27—H27B              | 0.9598       |
| Cu4—N31               | 2.030 (6)    | C27—H27C              | 0.9597       |
| S1—O1                 | 1.468 (5)    | C28—H28A              | 0.9300       |
| S1—O2                 | 1.465 (4)    | C28—C29               | 1.403 (11)   |
| S1—O3                 | 1.477 (6)    | C29—C30               | 1.493 (10)   |
| S1—O4                 | 1.462 (5)    | C30—H30A              | 0.9600       |
| S2—O5                 | 1.465 (5)    | C30—H30B              | 0.9600       |
| S2—O6                 | 1.456 (5)    | C30—H30C              | 0.9600       |
| S2—O7                 | 1.475 (5)    | C31—C32               | 1.504 (10)   |
| S2—O8                 | 1.463 (6)    | C31—C33               | 1.369 (10)   |
| S3—O9                 | 1.468 (5)    | C32—H32A              | 0.9599       |
| S3—O10                | 1.463 (5)    | C32—H32B              | 0.9602       |
| S3—O11                | 1.465 (6)    | C32—H32C              | 0.9600       |
| S3—O12                | 1.465 (5)    | C33—H33               | 0.9300       |
| S4—O13                | 1.475 (5)    | C33—C34               | 1.398 (11)   |
| S4—O14                | 1.466 (5)    | C34—C35               | 1.492 (10)   |
| S4—O15                | 1.459 (6)    | C35—H35A              | 0.9600       |
| S4—O16                | 1.473 (5)    | C35—H35B              | 0.9600       |
| N1—N2                 | 1.373 (7)    | C35—H35C              | 0.9599       |
| N1—C4                 | 1.339 (9)    | C36—C37               | 1.506 (10)   |
| N2—H2                 | 0.8600       | C36—C38               | 1.374 (11)   |
| N2—C1                 | 1.338 (9)    | C37—H37A              | 0.9596       |
| N3—N4                 | 1.361 (7)    | C37—H37B              | 0.9601       |
| N3—C9                 | 1.338 (9)    | C37—H37C              | 0.9604       |
| N4—H4                 | 0.8600       | C38—H38               | 0.9300       |
| N4—C6                 | 1.325 (9)    | C38—C39               | 1.387 (11)   |
| N5—N6                 | 1.351 (8)    | C39—C40               | 1.477 (11)   |
| N5—C14                | 1.325 (9)    | C40—H40A              | 0.9601       |
| N6—H6                 | 0.8600       | C40—H40B              | 0.9599       |
| N6—C11                | 1.343 (10)   | C40—H40C              | 0.9598       |
| N7—N8                 | 1.365 (7)    | C41—C42               | 1.500 (10)   |
| N7—C19                | 1.325 (9)    | C41—C43               | 1.364 (10)   |
| N8—H8                 | 0.8600       | C42—H42A              | 0.9600       |
| N8—C16                | 1.341 (9)    | C42—H42B              | 0.9600       |
| N9—N10                | 1.358 (7)    | C42—H42C              | 0.9600       |
| N9—C24                | 1.337 (8)    | C43—H43               | 0.9300       |
| N10—H10               | 0.8600       | C43—C44               | 1.395 (10)   |
| Bond              | Distance (Å) | Bond              | Distance (Å) |
|------------------|--------------|------------------|--------------|
| N10—C21          | 1.326 (9)    | C44—C45          | 1.505 (10)   |
| N11—N12          | 1.347 (7)    | C45—H45A        | 0.9601       |
| N11—C29          | 1.335 (9)    | C45—H45B        | 0.9600       |
| N12—H12          | 0.8600       | C45—H45C        | 0.9601       |
| N12—C26          | 1.352 (9)    | C46—C47         | 1.503 (10)   |
| N13—N14          | 1.347 (7)    | C46—C48         | 1.371 (10)   |
| N13—C34          | 1.345 (8)    | C47—H47A        | 0.9598       |
| N14—H14          | 0.8600       | C47—H47B        | 0.9607       |
| N14—C31          | 1.322 (9)    | C47—H47C        | 0.9599       |
| N15—N16          | 1.362 (7)    | C48—H48         | 0.9300       |
| N15—C39          | 1.333 (9)    | C48—C49         | 1.387 (11)   |
| N16—H16          | 0.8600       | C49—C50         | 1.495 (10)   |
| N16—C36          | 1.326 (9)    | C50—H50A        | 0.9600       |
| N17—N18          | 1.341 (7)    | C50—H50B        | 0.9600       |
| N17—C44          | 1.341 (8)    | C50—H50C        | 0.9600       |
| N18—H18          | 0.8600       | C51—C52         | 1.499 (10)   |
| N18—C41          | 1.327 (9)    | C51—C53         | 1.372 (10)   |
| N19—N20          | 1.355 (7)    | C52—H52A        | 0.9600       |
| N19—C49          | 1.315 (9)    | C52—H52B        | 0.9599       |
| N20—H20          | 0.8600       | C52—H52C        | 0.9609       |
| N20—C46          | 1.318 (9)    | C53—H53         | 0.9300       |
| N21—N22          | 1.355 (7)    | C53—C54         | 1.371 (10)   |
| N21—C54          | 1.342 (9)    | C54—C55         | 1.524 (10)   |
| N22—H22          | 0.8600       | C55—H55A        | 0.9600       |
| N22—C51          | 1.316 (9)    | C55—H55B        | 0.9600       |
| N23—N24          | 1.346 (7)    | C55—H55C        | 0.9600       |
| N23—C59          | 1.324 (10)   | C56—C57         | 1.512 (11)   |
| N24—H24          | 0.8600       | C56—C58         | 1.387 (13)   |
| N24—C56          | 1.341 (10)   | C57—H57A        | 0.9605       |
| N25—N26          | 1.344 (7)    | C57—H57B        | 0.9602       |
| N25—C64          | 1.355 (9)    | C57—H57C        | 0.9599       |
| N26—H26          | 0.8600       | C58—H58         | 0.9300       |
| N26—C61          | 1.340 (9)    | C58—C59         | 1.371 (11)   |
| N27—N28          | 1.373 (7)    | C59—C60         | 1.494 (11)   |
| N27—C69          | 1.331 (8)    | C60—H60A        | 0.9599       |
| N28—H28          | 0.8600       | C60—H60B        | 0.9604       |
| N28—C66          | 1.327 (9)    | C60—H60C        | 0.9597       |
| N29—N30          | 1.363 (7)    | C61—C62         | 1.512 (11)   |
| N29—C71          | 1.319 (9)    | C61—C63         | 1.355 (11)   |
| N30—H30          | 0.8600       | C62—H62A        | 0.9600       |
| N30—C74          | 1.332 (10)   | C62—H62B        | 0.9600       |
| N31—N32          | 1.350 (7)    | C62—H62C        | 0.9600       |
| N31—C79          | 1.354 (8)    | C63—H63         | 0.9300       |
| N32—H32          | 0.8600       | C63—C64         | 1.396 (10)   |
| N32—C76          | 1.341 (9)    | C64—C65         | 1.490 (11)   |
| C1—C2            | 1.490 (10)   | C65—H65A        | 0.9599       |
| C1—C3            | 1.364 (11)   | C65—H65B        | 0.9603       |
| C2—H2A           | 0.9605       | C65—H65C        | 0.9604       |
| Bond          | Distance (Å) | Bond          | Distance (Å) | Distance (Å) |
|--------------|-------------|--------------|-------------|-------------|
| C2—H2B       | 0.9601      | C66—C67      | 1.453 (10)  |             |
| C2—H2C       | 0.9600      | C66—C68      | 1.382 (10)  |             |
| C3—H3        | 0.9300      | C67—H67A     | 0.9600      |             |
| C3—C4        | 1.400 (11)  | C67—H67B     | 0.9599      |             |
| C4—C5        | 1.482 (10)  | C67—H67C     | 0.9605      |             |
| C5—H5A       | 0.9599      | C68—H68      | 0.9300      |             |
| C5—H5B       | 0.9605      | C68—C69      | 1.369 (11)  |             |
| C5—H5C       | 0.9609      | C69—C70      | 1.492 (10)  |             |
| C6—C7        | 1.504 (10)  | C70—H70A     | 0.9603      |             |
| C6—C8        | 1.366 (10)  | C70—H70B     | 0.9599      |             |
| C7—H7A       | 0.9604      | C70—H70C     | 0.9599      |             |
| C7—H7B       | 0.9602      | C71—C72      | 1.516 (11)  |             |
| C7—H7C       | 0.9599      | C71—C73      | 1.385 (10)  |             |
| C8—H8A       | 0.9300      | C72—H72A     | 0.9603      |             |
| C8—C9        | 1.386 (10)  | C72—H72B     | 0.9601      |             |
| C9—C10       | 1.482 (10)  | C72—H72C     | 0.9600      |             |
| C10—H10A     | 0.9600      | C73—H73      | 0.9300      |             |
| C10—H10B     | 0.9600      | C73—C74      | 1.369 (11)  |             |
| C10—H10C     | 0.9600      | C74—C75      | 1.501 (11)  |             |
| C11—C12      | 1.505 (11)  | C75—H75A     | 0.9600      |             |
| C11—C13      | 1.368 (11)  | C75—H75B     | 0.9596      |             |
| C12—H12A     | 0.9596      | C75—H75C     | 0.9600      |             |
| C12—H12B     | 0.9600      | C76—C77      | 1.505 (11)  |             |
| C12—H12C     | 0.9604      | C76—C78      | 1.365 (10)  |             |
| C13—H13      | 0.9300      | C77—H77A     | 0.9602      |             |
| C13—C14      | 1.381 (11)  | C77—H77B     | 0.9601      |             |
| C14—C15      | 1.502 (10)  | C77—H77C     | 0.9598      |             |
| C15—H15A     | 0.9599      | C78—H78      | 0.9300      |             |
| C15—H15B     | 0.9606      | C78—C79      | 1.393 (10)  |             |
| C15—H15C     | 0.9597      | C79—C80      | 1.490 (9)   |             |
| C16—C17      | 1.495 (11)  | C80—H80A     | 0.9599      |             |
| C16—C18      | 1.378 (10)  | C80—H80B     | 0.9599      |             |
| C17—H17A     | 0.9600      | C80—H80C     | 0.9600      |             |
| O1—Cu1—O14'  | 179.5 (2)   | C16—C18—C19  | 106.3 (6)   |             |
| N1—Cu1—O1    | 90.64 (19)  | C19—C18—H18A 126.8 |
| N1—Cu1—O14'  | 88.90 (19)  | N7—C19—C18  111.0 (6) |
| N1—Cu1—N3    | 88.0 (2)    | N7—C19—C20  120.5 (7) |
| N3—Cu1—O1    | 91.7 (2)    | C18—C19—C20 128.5 (7) |
| N3—Cu1—O14'  | 88.2 (2)    | C19—C20—H20A 109.4 |
| N5—Cu1—O1    | 86.5 (2)    | C19—C20—H20B 109.5 |
| N5—Cu1—O14'  | 93.6 (2)    | C19—C20—H20C 109.5 |
| N5—Cu1—N1    | 90.6 (2)    | H20A—C20—H20B 109.5 |
| N5—Cu1—N3    | 177.7 (2)   | H20A—C20—H20C 109.5 |
| N7—Cu1—O1    | 96.5 (2)    | H20B—C20—H20C 109.5 |
| N7—Cu1—O14'  | 83.98 (19)  | N10—C21—C22 120.4 (7) |
| N7—Cu1—N1    | 172.8 (2)   | N10—C21—C23 106.4 (6) |
| N7—Cu1—N3    | 90.4 (2)    | C23—C21—C22 133.2 (7) |
N7—Cu1—N5 91.2 (2) C21—C22—H22A 109.5
O5—Cu2—O2 178.8 (2) C21—C22—H22B 109.5
N9—Cu2—O2 89.05 (19) C21—C22—H22C 109.5
N9—Cu2—O5 89.76 (19) H22A—C22—H22B 109.5
N9—Cu2—N11 87.6 (2) H22A—C22—H22C 109.5
N11—Cu2—O2 84.0 (2) H22B—C22—H22C 109.5
N11—Cu2—O5 96.0 (2) C21—C23—H23 126.8
N13—Cu2—O2 89.1 (2) C21—C23—C24 106.4 (6)
N13—Cu2—O5 90.9 (2) C24—C23—H23 126.8
N15—Cu2—N9 172.4 (2) C21—C23—C24 106.4 (6)
N15—Cu2—N11 94.08 (19) C24—C23—C25 126.6 (7)
N15—Cu2—O5 87.11 (19) C24—C25—H25A 109.5
N17—Cu3—O6 85.2 (2) C24—C25—H25B 109.5
N17—Cu3—O9 97.2 (2) C24—C25—H25C 109.5
N17—Cu3—N19 85.2 (2) H25A—C25—H25B 109.5
N21—Cu3—O6 91.2 (2) H25A—C25—H25C 109.5
N21—Cu3—O9 92.4 (2) N12—C26—C27 119.2 (8)
N21—Cu3—N23 173.2 (2) N12—C26—C28 107.0 (7)
N21—Cu3—O6 92.5 (2) C28—C26—C27 133.8 (8)
N21—Cu3—O9 86.0 (2) C28—C26—C27 133.8 (8)
N21—Cu3—N23 90.1 (2) C26—C27—H27A 109.7
N21—Cu3—N19 91.7 (2) C26—C27—H27B 109.6
N21—Cu3—O6 89.9 (2) C26—C27—H27C 109.5
N21—Cu3—O9 89.4 (2) C26—C27—H27C 109.5
N21—Cu3—N17 175.7 (2) H27A—C27—H27B 109.5
N21—Cu3—N19 91.3 (2) H27A—C27—H27C 109.5
N21—Cu3—O6 88.1 (2) C29—C28—C29 106.3 (7)
N21—Cu3—O9 89.6 (2) C29—C28—C29 106.3 (7)
O13—Cu4—O10 178.39 (17) C28—C29—C30 122.0 (7)
N25—Cu4—O10 96.2 (2) C28—C29—C30 129.0 (7)
N25—Cu4—O13 84.87 (19) C29—C30—H30A 109.5
N25—Cu4—N27 89.7 (2) C29—C30—H30B 109.5
N25—Cu4—N29 91.8 (2) C29—C30—H30C 109.5
N25—Cu4—N31 175.6 (2) C30A—C30—H30B 109.5
N27—Cu4—O10 88.1 (2) H30A—C30—H30C 109.5
N27—Cu4—O13 93.1 (2) H30B—C30—H30C 109.5
N29—Cu4—O10 83.4 (2) N14—C31—C32 121.3 (7)
N29—Cu4—O13 95.3 (2) N14—C31—C33 105.4 (7)
N29—Cu4—N27 171.5 (2) C33—C31—C32 133.2 (7)
N31—Cu4—O10 88.2 (2) C31—C32—H32A 109.3
N31—Cu4—O13 90.79 (19) C31—C32—H32B 109.6
N31—Cu4—N27 89.9 (2) C31—C32—H32C 109.5
N31—Cu4—N29 89.2 (2) H32A—C32—H32B 109.5
O1—S1—O3 108.0 (3) H32A—C32—H32C 109.5
O2—S1—O1 110.5 (3) H32B—C32—H32C 109.5
O2—S1—O3 109.7 (4) C31—C33—H33 126.5
O4—S1—O1 110.5 (3) C31—C33—C34 107.0 (7)
O4—S1—O2 108.0 (3) C34—C33—H33 126.5
O4—S1—O3 110.1 (4) N13—C34—C33 109.0 (6)
O5—S2—O7 108.4 (3) N13—C34—C35 123.4 (7)
O6—S2—O5 110.2 (3) C33—C34—C35 127.6 (7)
O6—S2—O7 109.1 (3) C34—C35—H35A 109.4
O6—S2—O8 108.4 (3) C34—C35—H35B 109.4
O8—S2—O5 110.2 (3) C34—C35—H35C 109.6
O8—S2—O7 110.4 (4) H35A—C35—H35B 109.5
O10—S3—O9 109.5 (3) H35A—C35—H35C 109.5
O10—S3—O11 109.3 (4) H35B—C35—H35C 109.5
O10—S3—O12 108.3 (3) N16—C36—C37 122.1 (8)
O11—S3—O9 108.7 (4) N16—C36—C38 106.4 (7)
O11—S3—O12 110.5 (4) C38—C36—C37 131.5 (9)
O12—S3—O9 110.4 (3) C36—C37—H37A 109.4
O14—S4—O13 110.2 (3) C36—C37—H37B 109.6
O14—S4—O16 109.1 (3) C36—C37—H37C 109.5
O15—S4—O13 110.9 (3) H37A—C37—H37B 109.5
O15—S4—O14 108.6 (3) H37A—C37—H37C 109.5
O15—S4—O16 110.3 (4) H37B—C37—H37C 109.4
O16—S4—O13 107.7 (3) C36—C38—H38 126.4
S1—O1—Cu1 141.5 (3) C36—C38—C39 107.2 (7)
S1—O2—Cu2 150.2 (3) C39—C38—C39 126.4
S2—O5—Cu2 140.8 (3) C39—C38—C40 108.7 (7)
S2—O6—Cu3 146.0 (3) N15—C39—C38 122.1 (7)
S3—O9—Cu3 143.0 (3) N15—C39—C40 129.2 (8)
S3—O10—Cu4 148.4 (4) C39—C40—H40A 109.4
S4—O13—Cu4 138.1 (3) C39—C40—H40B 109.5
Cu1ii—O14—Cu1i 175.78 (12) C39—C40—H40C 109.5
S4—O14—Cu1i 26.2 (2) H40A—C40—H40B 109.5
S4—O14—Cu1ii 151.4 (3) H40A—C40—H40C 109.5
N2—N1—Cu1 119.1 (4) H40B—C40—H40C 109.5
C4—N1—Cu1 135.0 (5) N18—C41—C42 122.1 (7)
C4—N1—N2 105.4 (6) N18—C41—C43 105.9 (6)
N1—N2—H2 124.3 C43—C41—C42 132.0 (8)
C1—N2—N1 111.5 (6) C41—C42—H42A 109.5
C1—N2—H2 124.3 C41—C42—H42B 109.5
C4—N4—Cu1 117.0 (4) C41—C42—H42C 109.5
C9—N3—Cu1 137.1 (5) H42A—C42—H42B 109.5
C9—N3—N4 105.9 (6) H42A—C42—H42C 109.5
N3—N4—H4 124.2 H42B—C42—H42C 109.5
C6—N4—N3 111.6 (6) C41—C43—H43 126.7
C6—N4—H4 124.2 C41—C43—C44 106.7 (7)
N6—N5—Cu1 116.9 (4) C44—C43—H43 126.7
C14—N5—Cu1 137.0 (5) N17—C44—C43 109.1 (6)
C14—N5—N6 105.7 (6) N17—C44—C45 122.3 (7)
N5—N6—H6 123.9 C43—C44—C45 128.6 (7)
| Bond                  | Value (°) | Bond                  | Value (°) | Bond                  | Value (°) |
|-----------------------|-----------|-----------------------|-----------|-----------------------|-----------|
| C11—N6—N5            | 112.3 (6) | C44—C45—H45A         | 109.4     |                       |           |
| C11—N6—H6            | 123.9     | C44—C45—H45B         | 109.5     |                       |           |
| N8—N7—Cu1            | 117.5 (4) | C44—C45—H45C         | 109.5     |                       |           |
| C19—N7—Cu1           | 137.5 (5) | H45A—C45—H45B        | 109.5     |                       |           |
| C19—N7—N8            | 104.8 (6) | H45A—C45—H45C        | 109.5     |                       |           |
| N7—N8—H8             | 124.0     | H45B—C45—H45C        | 109.5     |                       |           |
| C16—N8—N7            | 112.0 (6) | N20—C46—C47          | 122.3 (7) |                       |           |
| C16—N8—H8            | 124.0     | N20—C46—C48          | 106.4 (7) |                       |           |
| N10—N9—Cu2           | 118.5 (4) | C48—C46—C47          | 131.2 (8) |                       |           |
| C24—N9—Cu2           | 135.4 (5) | C46—C47—H47A         | 109.5     |                       |           |
| C24—N9—N10           | 104.5 (5) | C46—C47—H47B         | 109.4     |                       |           |
| N9—N10—H10           | 123.6     | C46—C47—H47C         | 109.6     |                       |           |
| C21—N10—N9           | 112.9 (6) | H47A—C47—H47B        | 109.4     |                       |           |
| C21—N10—H10          | 123.6     | H47A—C47—H47C        | 109.5     |                       |           |
| N12—N11—Cu2          | 116.3 (4) | H47B—C47—H47C        | 109.4     |                       |           |
| C29—N11—Cu2          | 136.8 (5) | C46—C48—H48          | 126.9     |                       |           |
| C29—N11—N12          | 106.9 (6) | C46—C48—C49          | 106.2 (7) |                       |           |
| N11—N12—H12          | 124.6     | C49—C48—H48          | 126.9     |                       |           |
| N11—N12—C26          | 110.8 (6) | N19—C49—C48          | 109.7 (6) |                       |           |
| C26—N12—H12          | 124.6     | N19—C49—C50          | 121.5 (7) |                       |           |
| N14—N13—Cu2          | 118.9 (4) | C48—C49—C50          | 128.8 (7) |                       |           |
| C34—N13—Cu2          | 135.7 (5) | C49—C50—H50A         | 109.5     |                       |           |
| C34—N13—N14          | 104.7 (6) | C49—C50—H50B         | 109.5     |                       |           |
| N13—N14—H14          | 123.1     | C49—C50—H50C         | 109.5     |                       |           |
| C31—N14—N13          | 113.9 (6) | H50A—C50—H50B        | 109.5     |                       |           |
| C31—N14—H14          | 123.1     | H50A—C50—H50C        | 109.5     |                       |           |
| N16—N15—Cu2          | 117.2 (5) | H50B—C50—H50C        | 109.5     |                       |           |
| C39—N15—Cu2          | 136.0 (5) | N22—C51—C52          | 122.4 (7) |                       |           |
| C39—N15—N16          | 106.5 (6) | N22—C51—C53          | 106.0 (6) |                       |           |
| N15—N16—H16          | 124.4     | C53—C51—C52          | 131.5 (8) |                       |           |
| C36—N16—N15          | 111.3 (6) | C51—C52—H52A         | 109.4     |                       |           |
| C36—N16—H16          | 124.4     | C51—C52—H52B         | 109.5     |                       |           |
| N18—N17—Cu3          | 119.4 (4) | C51—C52—H52C         | 109.5     |                       |           |
| C44—N17—Cu3          | 135.2 (5) | H52A—C52—H52B        | 109.5     |                       |           |
| C44—N17—N18          | 105.1 (6) | H52A—C52—H52C        | 109.5     |                       |           |
| N17—N18—H18          | 123.4     | H52B—C52—H52C        | 109.5     |                       |           |
| C41—N18—N17          | 113.1 (6) | C51—C53—H53          | 126.9     |                       |           |
| C41—N18—H18          | 123.4     | C51—C53—C54          | 106.3 (7) |                       |           |
| N20—N19—Cu3          | 116.8 (4) | C54—C53—C55          | 126.9     |                       |           |
| C49—N19—Cu3          | 137.3 (5) | N21—C54—C53          | 110.6 (6) |                       |           |
| C49—N19—N20          | 105.9 (6) | N21—C54—C55          | 121.8 (7) |                       |           |
| N19—N20—H20          | 124.1     | C53—C54—C55          | 127.6 (7) |                       |           |
| C46—N20—N19          | 111.8 (6) | C54—C55—H55A         | 109.5     |                       |           |
| C46—N20—H20          | 124.1     | C54—C55—H55B         | 109.5     |                       |           |
| N22—N21—Cu3          | 119.5 (4) | C54—C55—H55C         | 109.5     |                       |           |
| C54—N21—Cu3          | 135.7 (5) | H55A—C55—H55B        | 109.5     |                       |           |
| C54—N21—N22          | 103.7 (6) | H55A—C55—H55C        | 109.5     |                       |           |
| N21—N22—H22          | 123.4     | H55B—C55—H55C        | 109.5     |                       |           |
| Bond                  | Distance (Å) | Torsion Angle (°) | Bond                  | Distance (Å) | Torsion Angle (°) |
|-----------------------|--------------|-------------------|-----------------------|--------------|-------------------|
| C51—N22—N21           | 113.2 (6)    |                   | N24—C56—C57           | 121.8 (10)   |                   |
| C51—N22—H22           | 123.4        |                   | N24—C56—C58           | 105.5 (7)    |                   |
| N24—N23—Cu3           | 119.3 (5)    |                   | C58—C56—C57           | 132.6 (9)    |                   |
| C59—N23—Cu3           | 135.0 (5)    |                   | C56—C57—H57A          | 109.4        |                   |
| C59—N23—N24           | 105.7 (6)    |                   | C56—C57—H57B          | 109.4        |                   |
| N23—N24—H24           | 124.0        |                   | C56—C57—H57C          | 109.7        |                   |
| C56—N24—N23           | 111.9 (7)    |                   | H57A—C57—H57B         | 109.5        |                   |
| C56—N24—H24           | 124.0        |                   | H57A—C57—H57C         | 109.4        |                   |
| N26—N25—Cu4           | 119.4 (4)    |                   | H57B—C57—H57C         | 109.5        |                   |
| N26—N25—C64           | 105.1 (6)    |                   | C56—C58—H58           | 126.9        |                   |
| C64—N25—Cu4           | 135.5 (5)    |                   | C59—C58—C56           | 106.2 (8)    |                   |
| N25—N26—H26           | 123.6        |                   | C59—C58—H58           | 126.9        |                   |
| C61—N26—N25           | 112.8 (6)    |                   | N23—C59—C58           | 110.7 (8)    |                   |
| C61—N26—H26           | 123.6        |                   | N23—C59—C60           | 123.7 (7)    |                   |
| C68—N27—Cu4           | 118.3 (4)    |                   | C58—C59—C60           | 125.6 (8)    |                   |
| C69—N27—Cu4           | 135.8 (5)    |                   | C59—C60—H60A          | 109.4        |                   |
| C69—N27—N28           | 105.9 (6)    |                   | C59—C60—H60B          | 109.5        |                   |
| N27—N28—H28           | 123.9        |                   | C59—C60—H60C          | 109.5        |                   |
| C66—N28—N27           | 112.2 (6)    |                   | H60A—C60—H60B         | 109.5        |                   |
| C66—N28—H28           | 123.9        |                   | H60A—C60—H60C         | 109.5        |                   |
| C66—N29—Cu4           | 117.1 (4)    |                   | H60B—C60—H60C         | 109.5        |                   |
| C71—N29—Cu4           | 138.3 (5)    |                   | N26—C61—C62           | 121.3 (8)    |                   |
| C71—N29—N30           | 104.5 (6)    |                   | N26—C61—C63           | 105.9 (7)    |                   |
| N29—N30—H30           | 124.0        |                   | C63—C61—C62           | 132.8 (8)    |                   |
| C74—N30—N29           | 112.0 (6)    |                   | C61—C62—H62A          | 109.5        |                   |
| C74—N30—H30           | 124.0        |                   | C61—C62—H62B          | 109.5        |                   |
| N32—N31—Cu4           | 119.4 (4)    |                   | C61—C62—H62C          | 109.5        |                   |
| N32—N31—C79           | 105.4 (5)    |                   | H62A—C62—H62B         | 109.5        |                   |
| C79—N31—Cu4           | 134.2 (5)    |                   | H62A—C62—H62C         | 109.5        |                   |
| N31—N32—H32           | 123.9        |                   | H62B—C62—H62C         | 109.5        |                   |
| C76—N32—N31           | 112.3 (6)    |                   | C61—C63—H63           | 126.2        |                   |
| C76—N32—H32           | 123.9        |                   | C61—C63—C64           | 107.6 (7)    |                   |
| N2—C1—C2              | 119.3 (8)    |                   | C64—C63—H63           | 126.2        |                   |
| N2—C1—C3              | 106.9 (7)    |                   | N25—C64—C63           | 108.6 (7)    |                   |
| C3—C1—C2              | 133.8 (8)    |                   | N25—C64—C65           | 121.0 (7)    |                   |
| C1—C2—H2A             | 109.3        |                   | C63—C64—C65           | 130.4 (7)    |                   |
| C1—C2—H2B             | 109.4        |                   | C64—C65—H65A          | 109.6        |                   |
| C1—C2—H2C             | 109.6        |                   | C64—C65—H65B          | 109.5        |                   |
| C1—C2—H2C             | 109.5        |                   | C64—C65—H65C          | 109.4        |                   |
| C1—C3—H3              | 126.6        |                   | H65A—C65—H65B         | 109.5        |                   |
| C1—C3—C4              | 106.8 (7)    |                   | N28—C66—C67           | 123.4 (7)    |                   |
| C4—C3—H3              | 126.6        |                   | N28—C66—C68           | 104.4 (7)    |                   |
| N1—C4—C3              | 109.5 (7)    |                   | C68—C66—C67           | 132.1 (8)    |                   |
| N1—C4—C5              | 123.2 (7)    |                   | C66—C67—H67A          | 109.7        |                   |
| C3—C4—C5              | 127.3 (8)    |                   | C66—C67—H67B          | 109.4        |                   |
| C4—C5—H5A             | 109.4        |                   | C66—C67—H67C          | 109.4        |                   |
| C4—C5—H5B       | 109.6 | H67A—C67—H67B       | 109.5 |
|------------------|-------|----------------------|-------|
| C4—C5—H5C       | 109.6 | H67A—C67—H67C       | 109.5 |
| H5A—C5—H5B      | 109.5 | H67B—C67—H67C       | 109.5 |
| H5A—C5—H5C      | 109.5 | C66—C68—H68         | 125.5 |
| H5B—C5—H5C      | 109.3 | C69—C68—C66         | 109.1 (7) |
| N4—C6—C7        | 121.2 (7) | C69—C68—H68       | 125.5 |
| N4—C6—C8        | 106.6 (7) | N27—C69—C68       | 108.4 (7) |
| C8—C6—C7        | 132.1 (8) | N27—C69—C70       | 121.9 (7) |
| C6—C7—H7A       | 109.4 | C68—C69—C70         | 129.7 (7) |
| C6—C7—H7B       | 109.6 | C69—C70—H70A        | 109.4 |
| C6—C7—H7C       | 109.5 | C69—C70—H70B        | 109.4 |
| H7A—C7—H7B      | 109.4 | C69—C70—H70C        | 109.6 |
| H7A—C7—H7C      | 109.5 | H70A—C70—H70B       | 109.5 |
| H7B—C7—H7C      | 109.5 | H70A—C70—H70C       | 109.5 |
| C6—C8—H8A       | 126.4 | H70B—C70—H70C       | 109.5 |
| C6—C8—C9        | 107.2 (7) | N29—C71—C72       | 120.3 (7) |
| C9—C8—H8A       | 126.4 | N29—C71—C73        | 111.4 (7) |
| N3—C9—C8        | 108.8 (6) | C73—C71—C72      | 128.3 (7) |
| N3—C9—C10       | 122.6 (7) | C71—C72—H72A     | 109.5 |
| C8—C9—C10       | 128.6 (7) | C71—C72—H72B     | 109.5 |
| C9—C10—H10A     | 109.1 | C71—C72—H72C       | 109.5 |
| C9—C10—H10B     | 109.8 | H72A—C72—H72B      | 109.4 |
| C9—C10—H10C     | 109.6 | H72A—C72—H72C      | 109.5 |
| H10A—C10—H10B   | 109.5 | H72B—C72—H72C      | 109.5 |
| H10A—C10—H10C   | 109.5 | C71—C73—H73        | 127.2 |
| H10B—C10—H10C   | 109.5 | C74—C73—C71        | 105.6 (7) |
| N6—C11—C12      | 121.8 (7) | C74—C73—H73   | 127.2 |
| N6—C11—C13      | 104.9 (7) | N30—C74—C73  | 106.6 (7) |
| C13—C11—C12     | 133.3 (8) | N30—C74—C75  | 121.0 (8) |
| C11—C12—H12A    | 109.6 | C73—C74—C75        | 132.4 (8) |
| C11—C12—H12B    | 109.4 | C74—C75—H75A       | 109.4 |
| C11—C12—H12C    | 109.5 | C74—C75—H75B       | 109.7 |
| H12A—C12—H12B   | 109.5 | C74—C75—H75C       | 109.3 |
| H12A—C12—H12C   | 109.5 | H75A—C75—H75B       | 109.5 |
| H12B—C12—H12C   | 109.4 | H75A—C75—H75C       | 109.5 |
| C11—C13—H13     | 126.2 | H75B—C75—H75C       | 109.5 |
| C11—C13—C14     | 107.7 (7) | N32—C76—C77   | 121.2 (7) |
| C14—C13—H13     | 126.2 | N32—C76—C78        | 106.2 (6) |
| N5—C14—C13      | 109.4 (7) | C78—C76—C77  | 132.6 (8) |
| N5—C14—C15      | 122.5 (7) | C76—C77—H77A  | 109.4 |
| C13—C14—C15     | 128.1 (7) | C76—C77—H77B  | 109.5 |
| C14—C15—H15A    | 109.3 | C76—C77—H77C       | 109.6 |
| C14—C15—H15B    | 109.6 | H77A—C77—H77B       | 109.4 |
| C14—C15—H15C    | 109.5 | H77A—C77—H77C       | 109.5 |
| H15A—C15—H15B   | 109.5 | H77B—C77—H77C       | 109.5 |
| H15A—C15—H15C   | 109.5 | C76—C78—H78        | 126.4 |
| H15B—C15—H15C   | 109.4 | C76—C78—C79        | 107.1 (7) |
| N8—C16—C17      | 121.2 (7) | C79—C78—H78   | 126.4 |
N8—C16—C18 105.8 (6)  N31—C79—C78 108.9 (6)
C18—C16—C17 133.0 (7)  N31—C79—C80 122.6 (6)
C16—C17—H17A 109.5  C78—C79—C80 128.5 (7)
C16—C17—H17B 109.5  N31—C79—C80A 109.5
C16—C17—H17C 109.5  C79—C80—H80B 109.5
H17A—C17—H17B 109.5  C79—C80—H80C 109.5
H17A—C17—H17C 109.5  H80A—C80—H80B 109.5
H17B—C17—H17C 109.5  H80A—C80—H80C 109.5
C16—C18—H18A 126.8  H80B—C80—H80C 109.5

Cu1—N1—N2—C1  −174.0 (5)  N15—N16—C36—C37  −178.2 (8)
Cu1—N1—C4—C3  172.4 (6)  N15—N16—C36—C38  1.6 (9)
Cu1—N1—C4—C5  −9.5 (12)  N16—N15—C39—C38  1.3 (8)
Cu1—N3—N4—C6  178.9 (5)  N16—N15—C39—C40  −179.1 (7)
Cu1—N3—C9—C8  −179.3 (5)  N16—C36—C38—C39  −0.7 (9)
Cu1—N3—C9—C10  0.8 (11)  N17—N18—C41—C42  −178.0 (7)
Cu1—N5—N6—C11  −175.4 (5)  N17—N18—C41—C43  0.4 (9)
Cu1—N5—C14—C13  173.2 (6)  N18—N17—C44—C43  −0.1 (8)
Cu1—N5—C14—C15  −7.5 (12)  N18—N17—C44—C45  −180.0 (7)
Cu1—N7—N8—C16  175.9 (5)  N18—C46—C48—C49  0.0 (9)
Cu1—N7—C19—C18  −174.7 (6)  N20—N19—C49—C50  1.9 (8)
Cu1—N7—C19—C20  5.7 (12)  N20—N19—C49—C50  179.4 (7)
Cu2—N9—N10—C21  −164.1 (5)  N20—C46—C48—C49  0.0 (9)
Cu2—N9—C24—C23  16.4 (11)  N21—N22—C51—C52  −175.8 (7)
Cu2—N11—N12—C26  −176.7 (5)  N21—N22—C51—C52  2.0 (8)
Cu2—N11—C29—C28  176.4 (6)  N22—N21—C54—C55  −0.7 (8)
Cu2—N11—C29—C30  −2.8 (12)  N22—N21—C54—C55  178.3 (7)
Cu2—N13—N14—C31  −173.2 (5)  N22—C51—C53—C54  −2.3 (8)
Cu2—N13—C34—C33  170.5 (5)  N23—N24—C56—C57  −177.0 (7)
Cu2—N13—C34—C35  −11.9 (11)  N23—N24—C56—C57  1.5 (9)
Cu2—N15—N16—C36  173.1 (5)  N24—N23—C59—C58  0.4 (9)
Cu2—N15—C39—C38  −172.1 (6)  N24—N23—C59—C58  179.1 (7)
Cu2—N15—C39—C40  7.4 (12)  N24—N23—C59—C60  179.1 (7)
Cu3—N17—N18—C41  174.2 (5)  N24—C56—C58—C59  −1.2 (10)
Cu3—N17—C44—C43  −173.2 (5)  N25—N26—C61—C62  178.9 (7)
Cu3—N17—C44—C45  6.9 (12)  N25—N26—C61—C62  0.8 (9)
Cu3—N19—N20—C46  −179.8 (5)  N26—N25—C64—C63  1.0 (8)
Cu3—N19—C49—C48  179.1 (5)  N26—N25—C64—C63  −179.7 (7)
Cu3—N19—C49—C50  −3.5 (12)  N26—C61—C63—C64  −0.1 (9)
Cu3—N21—N22—C51  169.4 (5)  N27—N28—C66—C67  −175.1 (7)
Cu3—N21—C54—C53  −168.5 (5)  N27—N28—C66—C67  1.9 (8)
Cu3—N21—C54—C55  10.6 (11)  N28—N27—C69—C68  0.3 (8)
Cu3—N23—N24—C56  176.5 (5)  N28—N27—C69—C70  179.0 (6)
Cu3—N23—C59—C58  −176.8 (6)  N28—C66—C68—C69  −1.6 (8)
Cu3—N23—C59—C60  1.9 (12)  N29—N30—C74—C73  1.0 (9)
Cu4—N25—N26—C61  −178.7 (5)  N29—N30—C74—C75  179.5 (7)
Cu4—N25—C64—C63  178.0 (5)  N29—C71—C73—C74  0.9 (9)
Cu4—N25—C64—C65 −2.7 (12) N30—N29—C71—C72 179.5 (7)
Cu4—N27—N28—C66 178.2 (4) N30—N29—C71—C73 −0.3 (8)
Cu4—N27—C69—C68 −179.2 (5) N31—N32—C76—C77 178.7 (8)
Cu4—N27—C69—C70 −0.5 (11) N31—N32—C76—C78 0.2 (9)
Cu4—N29—N30—C74 −177.8 (5) N32—N31—C79—C78 0.8 (8)
Cu4—N29—C71—C72 −4.0 (12) N32—N31—C79—C80 −178.5 (7)
Cu4—N29—C71—C73 176.2 (6) N32—C76—C78—C79 0.4 (9)
Cu4—N31—N32—C76 169.6 (5) C1—C3—C4—C5 −0.8 (9)
Cu4—N31—C79—C80 −167.3 (5) C1—C3—C4—N1 178.7 (9)
O1—S1—O2—Cu2 170.6 (6) C4—N1—N2—C1 178.7 (9)
O2—S1—O1—Cu1 177.8 (5) C6—C8—C9—N3 −0.3 (8)
O3—S1—O2—Cu2 51.6 (8) C6—C8—C9—C10 −179.6 (7)
O4—S1—O1—Cu1 58.3 (7) C7—C6—C8—C9 176.2 (8)
O4—S1—O2—Cu2 −68.4 (8) C9—N3—N4—C6 178.7 (9)
O5—S2—O6—Cu3 170.8 (5) C9—N3—N4—C6 178.7 (9)
O6—S2—O5—Cu2 −177.9 (4) C12—C11—C13—C14 −178.9 (10)
O7—S2—O5—Cu2 −58.5 (6) C14—N5—N6—C11 1.9 (8)
O7—S2—O6—Cu3 51.8 (7) C16—C18—C19—C20 179.9 (8)
O8—S2—O5—Cu2 62.5 (5) C16—C18—C19—C20 179.9 (8)
O8—S2—O6—Cu3 −68.5 (7) C17—C16—C18—C19 −179.0 (9)
O9—S3—O10—Cu4 166.2 (6) C19—N7—N8—C16 0.2 (8)
O10—S3—O9—Cu3 177.9 (5) C21—C23—C24—C25 176.1 (8)
O11—S3—O9—Cu3 −62.7 (7) C21—C23—C24—C25 176.1 (8)
O11—S3—O10—Cu4 47.1 (7) C22—C21—C23—C24 −179.6 (7)
O12—S3—O9—Cu3 58.7 (7) C22—C21—C23—C24 −179.6 (7)
O12—S3—O10—Cu4 −73.3 (8) C24—N9—N10—C26 1.7 (8)
O13—S4—O14—Cu1ii 163.1 (6) C26—C28—C29—N11 0.1 (9)
O13—S4—O14—Cu1i −9.3 (4) C26—C28—C29—N11 0.1 (9)
O14—S4—O13—Cu4 178.2 (4) C27—C26—C28—C29 −179.5 (10)
O15—S4—O13—Cu4 57.9 (5) C29—N11—N12—C26 1.2 (8)
O15—S4—O14—Cu1ii −75.2 (8) C31—C33—C34—C35 −177.6 (7)
O15—S4—O14—Cu1i 112.4 (6) C32—C31—C33—C34 177.3 (8)
O16—S4—O13—Cu4 −62.9 (5) C34—N13—N14—C31 −1.5 (8)
O16—S4—O14—Cu1i −127.3 (6) C36—C38—C39—N15 −0.4 (10)
O16—S4—O14—Cu1ii 45.1 (8) C36—C38—C39—C40 −179.9 (8)
N1—N2—C1—C2 −178.3 (7) C37—C36—C38—C39 179.1 (9)
N1—N2—C1—C3 0.5 (8) C39—N15—N16—C36 −1.8 (8)
N2—N1—C4—C3 1.0 (8) C41—C43—C44—N17 0.3 (9)
N2—N1—C4—C5 179.1 (7) C41—C43—C44—C45 −179.8 (8)
N2—C1—C3—C4 0.1 (9) C42—C41—C43—C44 177.7 (9)
N3—N4—C6—C7 −176.6 (6) C44—N17—N18—C41 −0.2 (8)
N3—N4—C6—C8 0.8 (8) C46—C48—C49—N19 −1.3 (9)
N4—N3—C9—C8 0.0 (8) C46—C48—C49—C50 −178.5 (8)
N4—N3—C9—C10 −179.9 (6) C47—C46—C48—C49 177.9 (8)
N4—C6—C8—C9 −0.8 (9) C49—N19—N20—C46 −2.0 (8)
N5—N6—C11—C12 −179.9 (8) C51—C53—C54—N21 1.9 (9)
N5—N6—C11—C13 1.3 (9) C51—C53—C54—C55 −177.0 (7)
N6—N5—C14—C13 1.7 (8) C52—C51—C53—C54 175.2 (8)
N6—N5—C14—C15 −179.1 (7) C54—N21—N22—C51 −0.8 (8)
N6—C11—C13—C14 −0.2 (10) C56—C58—C59—N23 0.5 (10)
N7—N8—C16—C17 178.9 (7) C56—C58—C59—C60 −178.2 (8)
N7—N8—C16—C18 0.1 (8) C57—C56—C58—C59 177.0 (9)
N8—N7—C19—C18 −0.5 (8) C59—N23—N24—C56 −1.2 (8)
N8—N7—C19—C20 180.0 (7) C61—C63—C64—C56 −1.2 (8)
N8—C16—C18—C19 −0.4 (9) C61—C63—C64—N25 0.6 (9)
N8—C16—C18—C19 −0.4 (9) C61—C63—C64—N25 −179.8 (9)
N9—N10—C21—C22 −176.0 (6) C62—C61—C63—C64 −177.9 (9)
N9—N10—C21—C22 −176.0 (6) C62—C61—C63—N25 0.6 (9)
N10—N9—C24—C23 −179.1 (7) C64—N25—N26—C61 −1.2 (8)
N10—N9—C24—C23 −179.1 (7) C64—N25—N26—C61 −1.2 (8)
N10—C21—C23—C24 2.3 (9) C66—C68—C69—N27 0.9 (9)
N10—C21—C23—C24 2.3 (9) C66—C68—C69—N27 −17.7 (7)
N11—N12—C26—C27 −179.0 (8) C69—N27—N28—C66 −1.4 (7)
N11—N12—C26—C27 −179.0 (8) C69—N27—N28—C66 −1.4 (7)
N11—N12—C26—C28 −1.1 (9) C71—N29—N30—C74 −0.4 (8)
N12—N11—C29—C28 0.7 (8) C71—N29—N30—C74 −0.4 (8)
N12—N11—C29—C28 0.7 (8) C71—N29—N30—C74 −0.4 (8)
N12—N11—C29—C30 180.0 (7) C71—N29—N30—C74 1.1 (9)
N12—H12···O4 0.86 2.12 2.951 (8) 163
N12—H12···O4 0.86 2.12 2.951 (8) 163
N14—N13—C31—C32 0.9 (8) C77—C76—C78—C79 −177.9 (9)
N14—N13—C31—C32 0.9 (8) C77—C76—C78—C79 −177.9 (9)
N14—N13—C31—C33 178.5 (7) C79—N31—N32—C76 −0.6 (8)
N14—N13—C31—C33 178.5 (7) C79—N31—N32—C76 −0.6 (8)
N14—N13—C31—C34 −0.8 (9)
N14—C31—C33—C34 −0.8 (9)

Symmetry codes: (i) x, y−1, z; (ii) x, y+1, z.

Hydrogen-bond geometry (Å, °)

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|-----|-------|-------|---------|
| N2—H2···O4 | 0.86 | 2.08 | 2.792 (7) | 139 |
| N6—H6···O3 | 0.86 | 2.04 | 2.889 (7) | 168 |
| N10—H10···O3 | 0.86 | 2.11 | 2.869 (7) | 146 |
| N12—H12···O4 | 0.86 | 2.12 | 2.951 (8) | 163 |
| N14—H14···O8 | 0.86 | 2.10 | 2.835 (7) | 143 |
| N16—H16···O5 | 0.86 | 2.44 | 2.889 (7) | 114 |
| N16—H16···O7 | 0.86 | 2.04 | 2.894 (8) | 173 |
| N18—H18···O6 | 0.86 | 2.39 | 2.866 (8) | 116 |
| N18—H18···O8 | 0.86 | 2.14 | 2.988 (7) | 169 |
| N20—H20···S3 | 0.86 | 2.76 | 3.504 (6) | 146 |
| N20—H20···O9 | 0.86 | 2.41 | 2.885 (9) | 115 |
| N20—H20···O11 | 0.86 | 2.08 | 2.933 (7) | 171 |
| N22—H22···O7 | 0.86 | 2.05 | 2.828 (7) | 150 |
| N24—H24···O12 | 0.86 | 2.16 | 2.840 (8) | 135 |
| N26—H26···O16 | 0.86 | 2.02 | 2.875 (7) | 171 |
| N28—H28···O15 | 0.86 | 2.07 | 2.803 (7) | 143 |
| N30—H30···O10 | 0.86 | 2.31 | 2.817 (8) | 118 |
| N30—H30···O12 | 0.86 | 2.24 | 3.083 (8) | 165 |
|       |        |        |        |        |
|-------|--------|--------|--------|--------|
| N32—H32···O11 | 0.86   | 2.12   | 2.857 (7) | 144   |
| C30—H30···O5   | 0.96   | 2.39   | 3.213 (11) | 144  |
| C50—H50···O6   | 0.96   | 2.23   | 3.124 (9)  | 155  |
| C65—H65B···O10  | 0.96   | 2.27   | 3.192 (11) | 160  |
| C70—H70B···O10  | 0.96   | 2.35   | 3.116 (10) | 137  |
| C2—H2A···N16iii | 0.96   | 3.01   | 3.722 (10) | 132  |
| C2—H2A···O7iii  | 0.96   | 28     | 3.806 (9)  | 146  |
| C53—H53···N8iv  | 0.93   | 3.07   | 3.66 (1)   | 123  |
| C32—H32B···N32v | 0.96   | 3.00   | 3.792 (10) | 140  |
| C32—H32B···N31v  | 0.96   | 3.17   | 3.984 (10) | 143  |
| C32—H32B···N28v  | 0.96   | 2.87   | 3.735 (11) | 150  |

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