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Solid-state structure and antimicrobial and cytotoxicity studies of a cucurbit[6]uril-like Cu_6L_4 constructed from 3,5-bis[(1*H*-tetrazol-5-yl)methyl]-4*H*-1,2,4-triazol-4-amine[1]

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[1] Dedicated to Professor Dietmar Stalke on the occasion of his 60th birthday

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3,5-Bis[(1*H*-tetrazol-5-yl)methyl]-4*H*-1,2,4-triazol-4-amine (H_2L) associates under deprotonation with $CuSO_4$ in aqueous medium to form a new waisted barrel-shaped M_6L_4 cluster, namely hexaaquatetrakis{μ_4-3,5-bis[(1*H*-tetrazol-5-yl)methyl]-4*H*-1,2,4-triazol-4-amine}-μ_4-sulfato-hexacopper(II) sulfate hydrate, $[Cu_6(SO_4)(C_6H_6N_{12})_4(H_2O)_6]SO_4{\cdot}nH_2O$ (n = ~23) (**1**). Cluster **1** resembles concave cucurbit[6]uril and has one disordered sulfate anion trapped inside the cage, which additionally stabilizes the Cu_6 unit. The Cu^{II} ions have either a square-pyramidal or a distorted octahedral geometry. The equatorial positions are filled by N atoms from the L^{2-} ligand, while the axial positions are occupied by coordinated water molecules and O atoms of the sulfate counter-ion. In the solid state, the Cu_6 clusters are connected through a large number of hydrogen bonds formed by uncoordinated water molecules and an additional sulfate anion. The compound shows good antimicrobial activity against *E. coli* tested with the Kirby Bauer approach. In addition, the cell viability towards HeLa and L-929 cells was studied.

1. Introduction

The synthesis of molecular clusters is interesting to the scientific community due to the possible applications of these clusters in different fields, as they have high potential in information storage uses (Mannini *et al.*, 2009), quantum computing devices (Leuenberger & Loss, 2001; Ardavan *et al.*, 2007) and molecular-based spintronics (Bogani & Wernsdorfer, 2008; Fedin *et al.*, 2015; Han *et al.*, 2015). Moreover, extensive studies of recent polynuclear complexes have shown that a multicore centre of transition metal ions can serve as a site for the catalytic oxidation of hydrocarbons (Roy & Manassero, 2010). Recently, polynuclear complexes of Cu^{II} were furthermore shown to have good antimicrobial, antitumoral and even antihypertensive activities (Islas *et al.*, 2014; Przyojski *et al.*, 2013). 'Direct' synthesis of such materials comprises two approaches: one is the association of predesigned building blocks into the molecular cluster (Peng *et al.*, 2017; Samanta *et al.*, 2016), while the second relates to a bridging ligand able to associate metal ions, and where the formation of molecular clusters is achieved by additional capping ligands that prevent the formation of coordination polymers (Mclellan *et al.*, 2015; Yoshizawa *et al.*, 2005; Wang *et al.*, 2016; Fujita *et al.*, 2015; Yokoyama *et al.*, 2015; Fromm, 1999; Ahlrichs *et al.*, 1996). Nevertheless, the targeted synthesis of cluster compounds remains challenging, since both approaches are not straightforward and defined through a

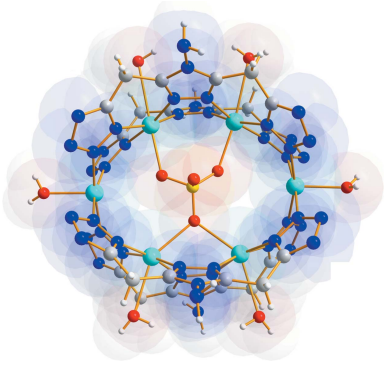

Table 1
Experimental details.

Crystal data	
Chemical formula	$[Cu_6(SO_4)(C_6H_8N_{12})(H_2O)_6]$-$SO_4{\cdot}10H_2O$ (+ solvent)
M_r	1846.52
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	200
a, b, c (Å)	20.5813 (13), 15.3333 (9), 23.4790 (14)
β (°)	115.210 (4)
V (Å^3)	6703.7 (7)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	2.04
Crystal size (mm)	0.21 × 0.17 × 0.12
Data collection	
Diffractometer	Stoe IPDS 2
Absorption correction	Integration (*X-RED32*; Stoe & Cie, 2002)
T_{min}, T_{max}	0.692, 0.949
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	75675, 11937, 7035
R_{int}	0.085
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.599
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.040, 0.112, 0.98
No. of reflections	11937
No. of parameters	1118
No. of restraints	176
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.77, −0.68

Computer programs: *X-AREA* (Stoe & Cie, 2002), *X-RED32* (Stoe & Cie, 2002), *SHELXT* (Sheldrick, 2015*a*), *SHELXL* (Sheldrick, 2015*b*), *OLEX2* (Dolomanov *et al.*, 2009), *ORTEPIII* (Burnett & Johnson, 1996) and *DIAMOND* (Brandenburg & Putz, 1999).

combination of methods. Herein we report the structure of the semi-flexible ligand 3,5-bis[(1*H*-tetrazol-5-yl)methyl]-4*H*-1,2,4-triazol-4-amine (H_2L) containing 1,2,4-triazolyl and 1*H*-tetrazolyl coordination moieties, connected through single methylene linkers, which allows the ligand to bend while binding to Cu^{II} ions, resulting in the title Cu_6L_4 cluster.

2. Experimental

Reagent-grade 1*H*-tetrazole-5-acetic acid and hydrazine hydrate were obtained from TCI. $CuSO_4{\cdot}5H_2O$, Mueller–Hinton Agar (70191) and Mueller–Hinton Broth (70192) were purchased from Sigma–Aldrich. All chemicals were used as received without further purification. Elemental analyses for C, H and N were carried out using a FLASH 2000 Organic Elemental Analyzer. IR spectra were recorded (4000–400 cm^{-1}) using a golden gate on a PerkinElmer Frontier FT–IR spectrometer. Thermogravimetric analyses (TGA) were performed under an N_2 flow at a heating rate of 10 K min^{-1} from 293 to 873 K in a Mettler Toledo SDTA 851a. Powder X-ray diffraction investigations were carried out on a Stoe STADI P diffractometer with Cu $K\alpha$ (λ = 1.5406 Å) radiation. ^{1}H NMR and ^{13}C NMR spectra were recorded, respectively, on a 400 MHz (Bruker DRX 400) and a Bruker 100 MHz spectrometer at room temperature with d_6-DMSO as the solvent and tetramethylsilane (TMS) as the internal standard. Mass spectra were performed on a Bruker ION Trap MS and HR–MS on a Bruker BioAPEXII.

2.1. Synthesis and crystallization

2.1.1. Synthesis of H_2L. 1*H*-Tetrazole-5-acetic acid (1 g, 7.8 mmol) was dissolved in hydrazine monohydrate (3 ml) at 268 K. The mixture was stirred for 5 min and then transferred to a Teflon reactor (5 ml volume) that was placed in a stainless steel bomb, tightened and heated at 393 K for 6 h. After cooling to room temeprature, the viscous liquid was transferred to an evaporating flask and water was removed using a rotary evaporator. Excess hydrazine was removed by refluxing in acetone three times. Drying under reduced pressure led to the formation of a white powder of H_2L in a yield of 86%. HR–MS: calculated 248.10; obtained: 249.1069 [M + H$^+$]. ^{1}H NMR (d_6-DMSO): 4.51 (4H, –CH_2–, *s*), 5.99 (2H, NH_2–, *s*). ^{13}C NMR (d_6-DMSO): 20.02 (–CH$_2$–), 151.26 (*tert*-$C_{triazole}$), 152.49 (*tert*-$C_{tetrazole}$). FT–IR (cm^{-1}): 3341 (*m*), 3209 (*w*), 2995 (*w*), 2961 (*m*), 1946 (*br m*), 1620 (*m*), 1575 (*m*), 1529 (*s*), 1437 (*s*), 1371 (*m*), 1314 (*w*), 1261 (*w*), 1243 (*s*), 1107 (*s*), 1058 (*s*), 1036 (*s*), 1002 (*s*), 954 (*s*), 880 (*s*), 836 (*s*), 739 (*s*), 724 (*m*), 701 (*m*), 685 (*s*), 610 (*s*), 498 (*m*), 416 (*m*).

2.1.2. Synthesis of 1. $CuSO_4{\cdot}5H_2O$ (75 mg, 0.3 mmol) was mixed in water with H_2L (49.6 mg, 0.2 mmol) at room temperature. After stirring for 6 h, a dark-blue precipitate was collected, yielding 92% of **1** based on the ligand. Crystals suitable for X-ray analysis were collected after self-diffusion of the components over a period of two weeks. FT–IR (cm^{-1}): 3217 (*br s*), 1632 (*m*), 1571 (*m*), 1496 (*m*), 1404 (*s*), 1279 (*w*), 1232 (*w*), 1083 (*s*), 1059 (*s*), 1006 (*s*), 929 (*m*), 768 (*s*), 613 (*s*), 456 (*s*). Elemental analysis calculated for $C_{24}H_{89}Cu_6N_{48}O_{37}S_2$ (%): C 13.81, H 4.30, Cu 18.26, N 32.21, O 28.36, S 3.07; found: C 13.81, H 4.40, N 31.79, S 3.12; this corresponds to the formula $[Cu_6(\mu_4\text{-}SO_4)(\mu_6\text{-}L)_4(H_2O)_6]SO_4{\cdot}23H_2O$ (M_r = 2083.18).

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. Methylene H atoms were calculated in specific positions and refined isotropically with fixed distance and displacement parameters, *i.e.* C—H = 0.97 Å and U_{iso}(H) = 1.2U_{eq}(C). Amino H atoms were restrained with N—H = 0.87 Å and U_{iso}(H) = 1.2U_{eq}(N). The H atoms of the uncoordinated and disordered water molecules were located where possible from difference density maps, refined with isotropic displacement parameters and restrained with O—H = 0.93 Å, H···H = 1.52 Å and U_{iso}(H) = 1.5U_{eq}(O). The contribution of an additional estimated total of 13 highly disordered uncoordinated water molecules was taken into account in the refinement using the *PLATON*/SQUEEZE software (Spek, 2009, 2015), resulting in a formula for the complex of $[Cu_6(\mu_4\text{-}SO_4)(\mu_6\text{-}L)_4(H_2O)_6]SO_4{\cdot}10H_2O$ (+ solvent). The coordinated SO_4^{2-} anion was split over two positions, with site-occupancy factors that refined to 0.772 (2) and 0.228 (2).

2.3. Biological tests

A disc diffusion test inspired by the Clinical and Laboratory Standards Institute® was performed to investigate the antimicrobial effect of H_2L, the Cu_6 complex and $CuSO_4{\cdot}5H_2O$ on *E. coli* ATCC® 25922 (kindly provided by the group of Professor Dr Patrice Nordmann from the University of Fribourg).

E. coli ATCC® 25922 was cultured in Mueller–Hinton Broth at 310 K and an agitation of 130 rpm overnight. Subsequently, the suspension was diluted by a factor of 100 and the bacteria proliferated at 310 K and 130 rpm until the log phase was reached. A 10^6 CFU/ml bacteria suspension was prepared by adjusting the turbidity to a 0.5 McFahrland (BioSan Densitometer DEN-1) which corresponds to 1–2 × 10^8 CFU/ml (colony forming units). 500 µl of the 10^6 CFU/ml suspension was spread evenly on a Mueller–Hinton Agar plate (14.5 cm diameter). H_2L, the Cu_6 cluster and $CuSO_4{\cdot}5H_2O$ pellets (0.6–0.7 cm diameter) were carefully deposited on top of the *E. coli* layer. Finally, the plates were kept at 310 K overnight. This test was performed in triplicate. Pellets were fabricated with a pellet press (Quick Press KBr pellet kit, Z506761 Aldrich).

Murine fibroblast cells L-929 were purchased from American Type Culture Collection (ATCC® CCL-1TM, Manassas, USA). The human cancer cells HeLa (ATCC® CCL-2TM) were kindly provided by Professor Beat Schwaller of the University of Fribourg. Both cell lines were cultured in DMEM/F-12 (Gibco®, Reinach, Switzerland). DMEM/F-12 was supplemented with 10% heat-inactivated fetal bovine serum (GE Healthcare Life Sciences, Reinach, Switzerland) and 1% Pen/Strep (Gibco® 100X solution). Cells were cultured in 25 cm^2 cell culture flasks (TPP, Trasadingen, Switzerland) under a humidified atmosphere containing 5% CO_2 at 310 K. The medium was replaced every 3–4 d. Cells were passaged after reaching near-confluence (80%) (1 ml of 0.025% trypsin and 0.01% EDTA in PBS, Gibco®) and the initial cell concentration was determined with the Trypan blue exclusion method (Strober, 2001) (0.4% Trypan blue solution T8154; Sigma–Aldrich, Schnelldorf, Germany, 10 µl + 10 µl cell suspension). The working cell concentrations were prepared by diluting cells with cell culture medium.

For an MTT assay, L-929 and HeLa cells were seeded in 96-well flat-bottomed tissue culture plates (TPP, Trasadingen, Switzerland) with a concentration of 2 × 10^3 cells/well for L-929 and 2.5 × 10^3 cells/well for HeLa (in 50 µl DMEM/F-12). After 24 h of incubation, 50 µl of fresh medium containing the corresponding amount of H_2L and Cu_6 complex was added to the cells. Cells were exposed to 1, 5, 10, 20, 50 and 100 µg ml^{-1} of each molecule for 24 and 48 h. Both molecules were previously dissolved in dimethyl sulfoxide (DMSO) at a concentration of 12.5 mg ml^{-1}, resulting in a final DMSO content of 0.4% for the 100 µg ml^{-1} condition. The following controls were also supplemented with fresh medium, medium with cells, medium with cells and 0.4% DMSO. Each experiment was repeated three times with three replicates of the same material and concentration.

Cell viability was evaluated by the MTT [3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide, M5655, Sigma–Aldrich] assay, which reports the combined effects of proliferation (number of viable cells) and cellular metabolic activity (Mosmann, 1983). Briefly, 10 µl of a 5 mg ml^{-1} MTT stock solution (in CMF-PBS, Gibco®) were added to each well. After 4 h of incubation (humidified atmosphere containing 5% CO_2 at 310 K), the medium was exchanged by 100 µl DMSO to solubilize the formed formazan crystals (30 min orbital shaking at room temperature). The formazan concentration was quantified using a multimode microplate reader (Tecan, Spark®, Männedorf, Switzerland) by measuring the absorbance at 570 nm (background correction measured at 620 nm). An additional background correction was performed with the medium control.

Data analysis and treatment was performed with GraphPad *Prism 6* (https://www.graphpad.com/scientific-software/prism/), OriginLab *Origin 7.5* (https://www.originlab.com) and Adobe *Illustrator* CS6 (https://www.adobe.com/uk/products/illustrator.html).

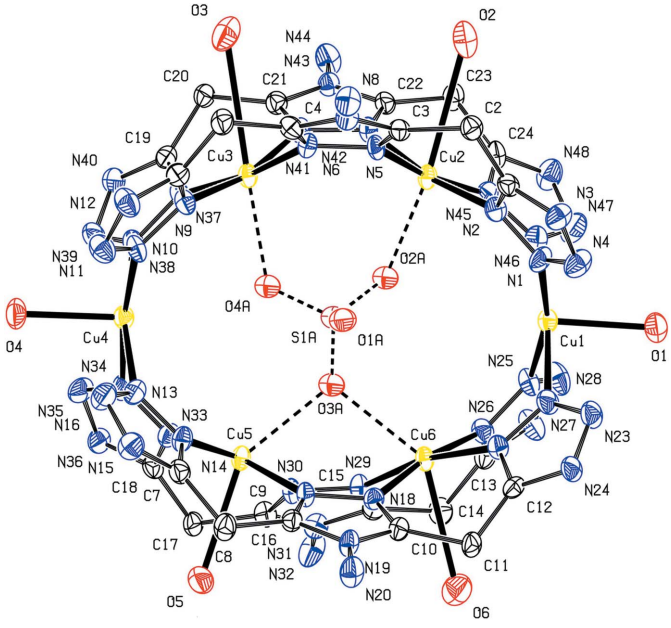

Figure 1
Structure of the hexanuclear Cu^{II} cage **1** with an M_6L_4 structure, resembling cyclic cucurbit[6]uril, with one of the two SO_4^{2-} anions entrapped. The minor sulfate disorder form, a second sulfate anion, the H atoms and the uncoordinated water molecules have been omitted for clarity. The formation of Cu_6 cluster **1** occurs with a bridging *L* ligand in a hexadentate mode. Atoms Cu2, Cu4, Cu5 and Cu6 have octahedral coordination geometries, and Cu1 and Cu4 have square-pyramidal coordination geometries.

3. Results and discussion

3.1. Structure analysis

The hexanuclear Cu^{II} compound **1** crystallizes in the monoclinic space group $P2_1/c$ with one formula unit in the asymmetric unit. The cation contains six Cu^{II} ions connected

Table 2
Selected bond lengths (Å).

Cu1—N1	2.003 (4)	Cu4—N10	2.013 (3)
Cu1—N22	2.017 (3)	Cu4—N13	2.040 (4)
Cu1—N25	2.022 (4)	Cu4—N34	1.997 (4)
Cu1—N46	2.018 (4)	Cu4—N38	2.025 (3)
Cu1—O1	2.182 (3)	Cu4—O4	2.165 (3)
Cu2—N2	1.992 (3)	Cu5—N14	1.994 (4)
Cu2—N5	1.995 (3)	Cu5—N17	1.990 (3)
Cu2—N42	2.006 (3)	Cu5—N30	2.003 (3)
Cu2—N45	1.977 (4)	Cu5—N33	1.993 (3)
Cu2—O2*A*	2.231 (11)	Cu5—O3*A*	2.346 (12)
Cu2—O2*B*	2.360 (4)	Cu5—O4*B*	2.246 (4)
Cu3—N6	1.983 (3)	Cu6—N18	2.000 (3)
Cu3—N9	1.988 (3)	Cu6—N21	1.980 (3)
Cu3—N37	1.977 (3)	Cu6—N26	1.984 (4)
Cu3—N41	1.999 (4)	Cu6—N29	1.991 (3)
Cu3—O2*B*	2.305 (4)	Cu6—O3*A*	2.386 (12)
Cu3—O4*A*	2.258 (11)	Cu6—O3*B*	2.233 (4)

by four L^{2-} ligands, which each act in a hexadentate mode, one disordered sulfate anion and six water molecules coordinating to the Cu^{II} centres. The general shape of the Cu_6 cluster corresponds to an elongated barrel, similar to curcurbit[6]uril, but with a concave instead of a convex curvature along the 'waistline'. Four Cu^{II} ions (Cu2, Cu3, Cu5 and Cu6) possess an octahedral coordination sphere, while Cu1 and Cu4 are five-coordinated in a square-pyramidal fashion. Cu1 is thus coordinated by four N atoms from tetrazole groups in equatorial positions, with Cu1—N1 = 2.003 (3) Å, Cu1—N22 = 2.017 (3) Å, Cu1—N25 = 2.022 (4) Å and Cu1—N46 = 2.018 (4) Å, while the apical position is occupied by a coordinated water molecule [Cu1—O1 = 2.182 (3) Å]. Atom Cu4 has a similar coordination, but its coordination bonds to the tetrazole N atoms (Table 2) are different in distance, varying from 1.997 (4) to 2.040 (4) Å, and its coordination by a water molecule [Cu4—O4 = 2.165 (3) Å] in the axial position is much stronger than for Cu1. Atoms Cu2 and Cu3, as well as Cu5 and Cu6, form different distances to the N-atom donors of the heterocycles, as well as to the axially coordinated water molecules and the sulfate anion (Table 2), with the most resemblances between diagonally opposite Cu^{II} ions that are bridged by the μ_4-SO_4^{2-} ligand, hence Cu2 with Cu5 and Cu3 with Cu6. Atoms Cu2 and Cu5 have short coordination bonds with tetrazole N atoms, *i.e.* Cu2—N2 and Cu5–N17 of 1.992 (3) and 1.990 (4) Å, respectively. Atoms Cu3 and Cu6 also form short bonds with the tetrazole N atoms, *i.e.* Cu3—N6 = 1.988 (3) Å and Cu6—N21 = 1.980 (3) Å. Compared with the tetrazole ring, the N atoms of the 1,2,4-triazole ring overall form longer bonds with the Cu^{II} ions, *i.e.* Cu2—N5 = 1.995 (3) Å and Cu2—N42 = 2.006 (3) Å.

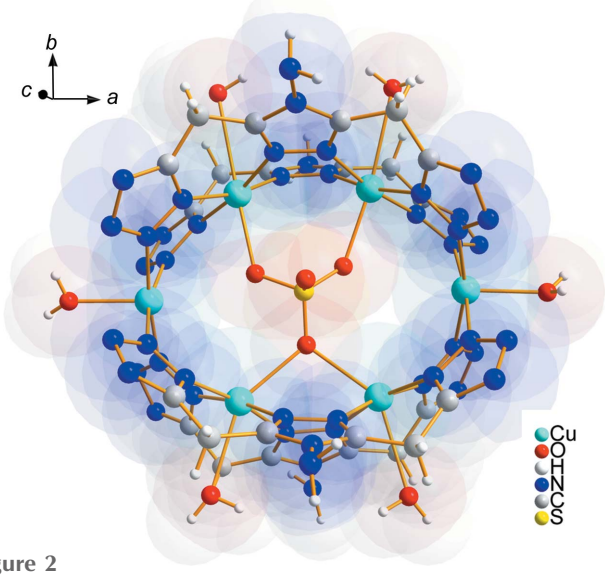

Figure 2
The formation of the inorganic cucurbit[6]uril-like structure of a hexanuclear cluster of Cu^{II} with L^{2-} by self-assembly. An SO_4^{2-} anion trapped between six Cu atoms in the hexanuclear cluster additionally stabilizes the formation of the Cu_6 fragment in a μ_4-bridging mode.

Water molecules coordinated to the Cu^{II} ions, decorating the outer face of the barrel-shape, form weak coordination bonds ranging from 2.568 (3) Å for Cu5—O5 to 2.887 (3) Å for Cu3—O3. The elongation of the Cu3—O3 bond might be explained by the presence of intermolecular hydrogen bonds between coordinated and uncoordinated water molecules around the Cu_6 barrel.

The cavity of the cage is occupied by a coordinating sulfate anion with a tetradentate bridging mode that completes the octahedral geometry of the Cu2, Cu3, Cu5 and Cu6 atoms, with distances of 2.231 (11)–2.386 (12) Å (Fig. 1). This sulfate anion is disordered over two positions by a pseudo-mirror plane that contains the Cu^{II} ions. It may play the role of a template and/or a stabilizing agent. A second, uncoordinated, sulfate anion remains outside of the cluster cavity and takes part in intramolecular hydrogen bonding with coordinated molecules of water (atoms O1, O2, O3, O4 and O5; Fig. S12 in the supporting information). This sulfate anion thus serves as a 'glue' between the hexanuclear clusters in the crystal packing, forming numerous different graph sets of hydrogen bonds and short contacts (Fig. S12).

The cavity size of the oval barrel, measured between the Cu atoms, is ~8.5 Å long and 5.6–6.7 Å wide. Within the Cu^{II} ring, the shortest distances between Cu atoms that can potentially show antiferromagnetic or ferromagnetic behaviour are 3.6055 (7) and 3.7771 (7) Å (Fig. 2). We tried several times to measure the magnetic properties of **1** but were unsuccessful because the crystals decompose quickly upon losing solvent.

3.2. Thermal stability

Thermogravimetric analyses of H_2L and **1** were performed from 298 to 873 K (Figs. S5 and S6 in the supporting information). Complex **1** is unstable and starts to lose water molecules even at room temperature, while heating over 333 K shows decomposition, which continues to 433 K, and was assigned to the loss of uncoordinated and coordinated water molecules, as well as to cleavage of the amino groups of the ligand. Further heating from 433 to 673 K gives an additional step of slow decomposition that can be assigned to complete decomposition of the organic ligand L that occurs at ~553 K for the ligand alone with a ~35–40% weight loss. Heating over 673 K leads to complete decomposition of the complex. Both

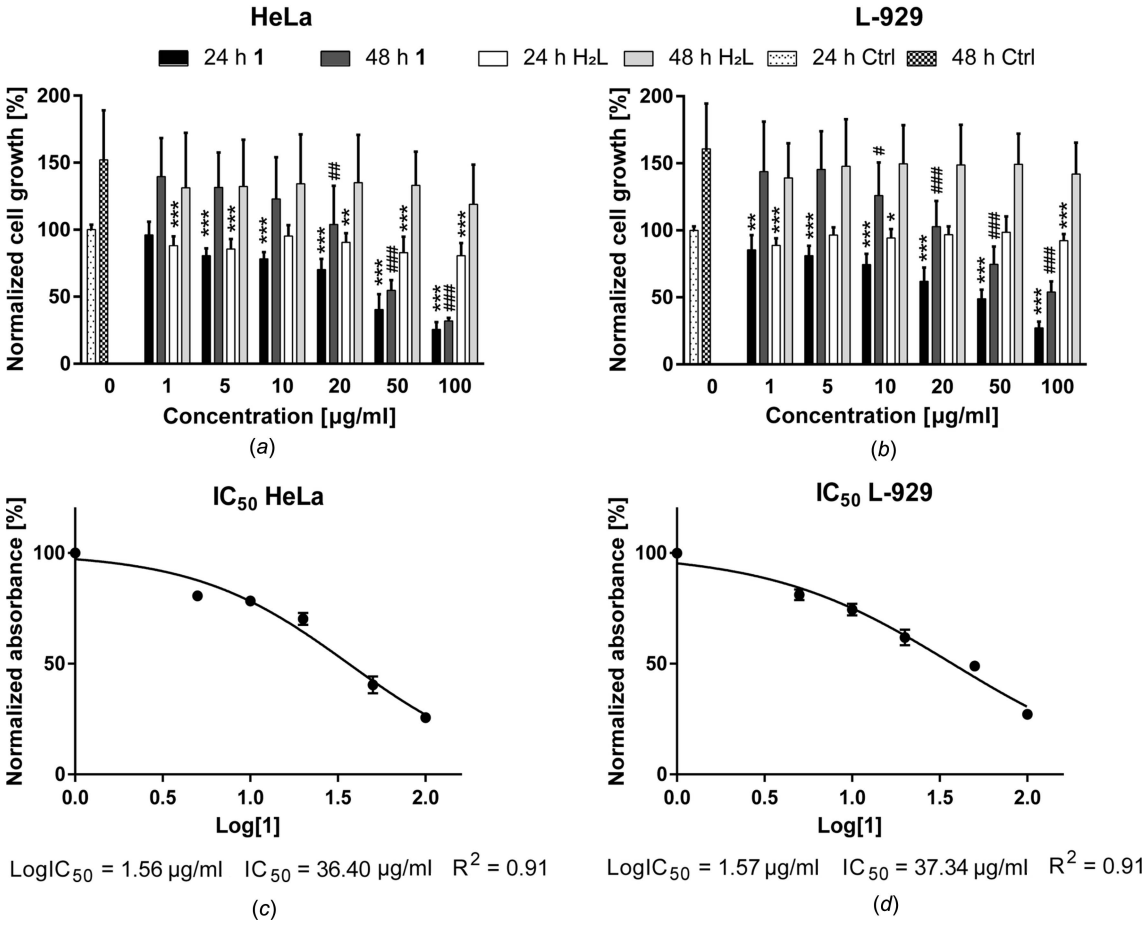

Figure 3
The effect of **1** and H_2L on HeLa and L-929 cell growth. (*a*)/(*b*) Cell growth was normalized to the 24 h Ctrl (in %); the bar chart represents the mean ±SD cell growth of three experiments (in triplicate) after 24 and 48 h of 0–100 µg ml^{-1} **1** and H_2L incubation time; statistical significance was calculated relative to the 24 (*) or 48 h (#) Ctrl (*/# $p < 0.05$, **/## $p < 0.01$ and ***/### $p < 0.001$). (*c*)/(*d*) IC_{50} determination for 24 h Cu_6 (0, 5–100 µg ml^{-1}). The graph was normalized to the largest value in each data set (100%) and $y = 0.0$ (0%) and each data point represents the mean ±s.e.m. (standard error of mean) of three experiments (in triplicate), given are the calculated values of $LogIC_{50}$, IC_{50} and R^2.

ligand and complex show good stability up to 523 K and have similar trends in their decompositions. An additional study by PXRD analysis of dried **1** at room temperature confirms that the complex starts to lose uncoordinated molecules of water at room temperature, leading to a crystalline powder that does not fit to the single-crystal structure of **1**, and of which the structure could not be resolved from the obtained data (Fig. S9 in the supporting information).

3.3. IR studies

The FT–IR spectrum of **1** (Figs. S7 and S8 in the supporting information) features a strong broad band from 3600–2900 cm^{-1} corresponding to the stretching vibrations of coordinated and uncoordinated water molecules, as well as stretching vibrations of the amino groups. Numerous hydrogen bonds between these groups and uncoordinated water molecules make it difficult to assign these functional groups precisely compared to the IR spectrum of the ligand alone (Fig. S7). The stretching vibrations of C═N at 1632 cm^{-1} and asymmetrical N═N at 1404 cm^{-1}, and the asymmetric vibrations of C—N at 1232 cm^{-1} and N—N at 1279 cm^{-1}, confirm the presence of tetrazole and triazole groups of the ligand in **1**. Asymmetrical and symmetrical vibrations of the coordinated sulfate anion feature two broad bands at 1083–1006 cm^{-1}, which indicates the lower symmetry of the sulfate anion due to a distortion from T_d to C_{3v} occurring upon coordination of the sulfate anion in μ_4-mode to four Cu^{II} ions (Nakamoto, 2008).

3.4. Antimicrobial properties

The determined ZOI (zone of inhibition) for the samples seen in Fig. S10 in the supporting information was as follows: $CuSO_4{\cdot}5H_2O$ 12 mm, *L* 1 mm and Cu_6 complex **1** 0.8 mm. Hereby, the amount of compound (and hence of copper) differed widely, ranging from 0.16–0.29 ($CuSO_4{\cdot}5H_2O$) over 0.4 (H_2L) to 0.02–0.05 mmol (**1**; for a more detailed description, see Table S2 in the supporting information), between the three compounds tested. In addition, the pellet formed with **1** is water insoluble and stayed intact. Hence, the solubility and diffusion of Cu^{II} into the environment from **1** is weaker than for $CuSO_4{\cdot}5H_2O$ and H_2L, which both dissolve completely. Therefore, one can assume that less material and thus Cu^{II}

ions of Cu_6 diffused into the agar compared to $CuSO_4{\cdot}5H_2O$ and H_2L. Still, **1** indicates a typical copper diffusion pattern, as seen for $CuSO_4{\cdot}5H_2O$. All in all, a direct comparison is difficult due to the aforementioned reasons. Nevertheless, the test demonstrates that H_2L, as well as **1** have a slight antimicrobial effect on *E. coli*. Furthermore, an increase in the ZOI was observed for **1** when a higher concentration was applied (0.5 to 0.8 mm, see Table S2). For H_2L, similar concentrations in all three cases were used and no correlation between concentration and ZOI was observed. For $CuSO_4{\cdot}5H_2O$, very high concentrations were applied. Thus, we assume that a saturation limit was reached, leading to no correlation between concentration and ZOI.

3.5. Cell viability

Figs. 3(*a*)/(*b*) depicts the normalized cell growth [normalized to the 24 h Ctrl (%)] of HeLa and L-929 incubated with 0–100 µg ml^{-1} of **1** and H_2L for 24 and 48 h. According to ISO 10993-5:2009(E) (Strober, 2001), a compound is cytotoxic when cell growth is below 70%. HeLa cell growth was reduced below 70% when exposed to more than 10 and 20 µg ml^{-1} of **1** (24 and 48 h). For L-929, cell growth was reduced below 70% when exposed to more than 10 and 50 µg ml^{-1} of **1** (24 and 48 h). This indicates a better recovery of L-929 than of HeLa. For both cell lines, no reduced cell growth below 70% was observed when incubated with 0–100 µg ml^{-1} H_2L, meaning that the ligand is not cytotoxic in this concentration range.

Comparing the effects of **1** at 24 and 48 h with each other, one can observe that in every case and for both cell lines, cell growth increased from 24 to 48 h incubation time. This observation was more prominent for L-929 than for HeLa, which supports the previously mentioned assumption that L-929 cells recover better than HeLa.

Nevertheless, HeLa cells show a significantly lower proliferation for 5–100 µg ml^{-1} of **1** (24 h, $p < 0.001$) and for 20–100 µg ml^{-1} Cu_6 (48 h, $p < 0.01/0.001$) in comparison to the 24 h Ctrl. L-929 instead demonstrates a significantly lower proliferation compared to the 24 h Ctrl for 1–100 µg ml^{-1} of **1** (24 h, $p < 0.001$) and for 10–100 µg ml^{-1} of **1** (48 h, $p < 0.05/0.001$). This suggests that regardless of the enhanced recovery of L-929 cells in comparison to HeLa cells, the L-929 cells seem to be slightly more affected by Cu_6.

For both cell lines, after 24 h incubation, the significance in proliferation compared to the 24 h Ctrl varies between the different concentrations of H_2L. After 48 h of incubation, no statistical significance in proliferation ($p > 0.05$) of both cell lines for all the different concentrations tested with H_2L is observed anymore. This supports the aforementioned conclusion, that the compound is not cytotoxic in the examined concentration range.

As the compounds were first dissolved in DMSO, we also tested the cell growth for cells cultured with 0.4% DMSO, which corresponds to the highest DMSO concentration applied to the cells (100 µg ml^{-1} condition).

Fig. S11 in the supporting information shows the difference in proliferation when cells were incubated with 0.4% DMSO. When incubated with 0.4% DMSO, a significantly lower proliferation in comparison to the 24 h Ctrl is observed after 48 h of incubation for HeLa cells. L-929 cells instead show no significantly lower proliferation after 48 h of incubation. According to ISO 10993-5:2009(E) (ISO10993-5, 2009), DMSO concentrations above 0.5% are cytotoxic. In spite of using a DMSO concentration below 0.5%, the cell growth was lower than for the control. This might influence the results given for the highest compound concentrations (100–50 µg ml^{-1}). Nevertheless, with each dilution, the DMSO content decreases (0.4, 0.2, 0.08, 0.04, 0.02 and 0.004%) and therefore the impact on the cell growth should also decrease.

Furthermore, we determined the IC_{50}, which is the half maximal inhibitory concentration. This term is preferably used when drugs are investigated. Especially when metal ions are involved, publications tend to use the term TC_{50} which stands for the half maximal toxic concentration. We decided to use the term IC_{50} throughout this manuscript. The values were determined by generating a dose-response curve, which was normalized to the largest value in each data set (100%) and y = 0.0 (0%). For the 48 h conditions, the standard deviations were high, leading to an R^2 value below 0.8. In addition, no cytotoxic cell growth in presence of H_2L was observed. Therefore, only the IC_{50} for the 24 h of **1** (HeLa and L-929) was determined (Figs. 3*c* and 3*d*).

As displayed in Figs. 3(*c*)/(*d*), the IC_{50} values for both cell lines are similar (36.4 and 37.3 µg ml^{-1}). This implies that the cytotoxicity of **1** on HeLa and L-929 is effectively the same. Other Cu^{II} compounds described in the literature have IC_{50} values ranging from 41.5 to 135 µmol l^{-1} (ISO10993-5, 2009; Schmalz *et al.*, 1998; Yamamoto *et al.*, 1998; Wataha *et al.*, 1994) for L-929. In our case, the IC_{50} for Cu^{II} was determined to be 95.5 (17.5 µ*M* Cu_6) for HeLa and 98 µ*M* (17.9 µ*M* of **1**) for L-929. Our values were thus exactly between the values found in the literature. Even still, a direct comparison between the IC_{50} values in the above-mentioned literature and our values is difficult as different cell numbers, different media and different assays were used.

A publication from van Tonder *et al.* (2015) suggests that the MTT assay is suitable for obtaining preliminary results, but due to a relatively low accuracy and high variations in IC_{50} values, supporting cell viability tests are recommended. Nevertheless, the MTT assay demonstrated that the H_2L ligand is not cytotoxic in the tested concentration range (4.03–403 µmol l^{-1}) for HeLa and L-929. Compound **1** instead shows, according to ISO 10993-5:2009(E) (ISO10993-5, 2009), cytotoxicity above 10/20 µg ml^{-1} for HeLa and 10/50 µg ml^{-1} for L-929. The IC_{50} values investigated in our study are in accordance with the IC_{50} values for Cu^{II} and L-929 cells published in the above-mentioned literature.

4. Conclusions

We report the synthesis of a novel hexanuclear cluster of Cu^{II} based on the new semi-flexible 3,5-bis[(1*H*-tetrazol-5-yl)-methyl]-4*H*-1,2,4-triazol-4-amine building block. The structure of the hexanuclear complex of Cu^{II} was determined by

single-crystal X-ray diffraction, revealing a barrel-type complex similar to cucurbit[6]uril with M_6L_4. The antimicrobial properties show good potential for combating bacterial infections. The biocompatibility tests with HeLa and L-929 show that the Cu_6 cluster is much more cytotoxic than other Cu^{II} compounds and inhibits the growth of HeLa slightly more than L-929.

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supporting information

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Solid-state structure and antimicrobial and cytotoxicity studies of a cucurbit[6]uril-like Cu_6L_4 constructed from 3,5-bis[(1*H*-tetrazol-5-yl)methyl]-4*H*-1,2,4-triazol-4-amine

Serhii Vasylevskyi, Anja Holzheu and Katharina M. Fromm

Computing details

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA* (Stoe & Cie, 2002); data reduction: *X-RED* (Stoe & Cie, 2002); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015b); molecular graphics: OLEX2 (Dolomanov *et al.*, 2009), *ORTEPIII* (Burnett & Johnson, 1996) and *DIAMOND* (Brandenburg & Putz, 1999); software used to prepare material for publication: OLEX2 (Dolomanov *et al.*, 2009).

Hexaaquatetrakis{μ_4-3,5-bis[(1*H*-tetrazol-5-yl)methyl]-4*H*-1,2,4-triazol-4-amine}-μ_4-sulfato-hexacopper(II) sulfate 23-hydrate

Crystal data

$[Cu_6(SO_4)(C_6H_6N_{12})_4(H_2O)_6]SO_4\cdot 10H_2O$
M_r = 1846.52
Monoclinic, $P2_1/c$
a = 20.5813 (13) Å
b = 15.3333 (9) Å
c = 23.4790 (14) Å
β = 115.210 (4)°
V = 6703.7 (7) Å^3
Z = 4
$F(000)$ = 3736
D_x = 1.830 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 18583 reflections
θ = 1.6–25.5°
μ = 2.04 mm^{-1}
T = 200 K
Prism, dark-blue
0.21 × 0.17 × 0.12 mm

Data collection

Stoe IPDS 2 diffractometer
Detector resolution: 6.67 pixels mm^{-1}
rotation method scans
Absorption correction: integration (X-RED32; Stoe & Cie, 2002)
T_{min} = 0.692, T_{max} = 0.949
75675 measured reflections
11937 independent reflections
7035 reflections with $I > 2\sigma(I)$
R_{int} = 0.085
θ_{max} = 25.2°, θ_{min} = 1.1°
$h = -24 \rightarrow 24$
$k = -18 \rightarrow 18$
$l = -27 \rightarrow 27$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.112
S = 0.98
11937 reflections
1118 parameters
176 restraints
Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0576P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.77$ e Å^{-3}
$\Delta\rho_{min} = -0.68$ 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.

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

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Cu2	0.34169 (2)	0.94511 (3)	0.51407 (2)	0.01911 (13)	
Cu3	0.15553 (2)	0.94268 (3)	0.48676 (2)	0.01875 (13)	
Cu4	0.03048 (2)	0.75462 (3)	0.46919 (2)	0.02020 (12)	
Cu5	0.15603 (2)	0.57343 (3)	0.49131 (2)	0.01914 (13)	
Cu6	0.34438 (2)	0.57584 (3)	0.51164 (2)	0.01856 (13)	
Cu1	0.46862 (2)	0.75936 (3)	0.52936 (2)	0.01959 (12)	
O4	−0.08058 (15)	0.7573 (2)	0.45497 (17)	0.0337 (8)	
H4A	−0.1203 (16)	0.739 (3)	0.4301 (19)	0.051*	
H4B	−0.087 (2)	0.798 (2)	0.475 (2)	0.051*	
O1	0.57991 (15)	0.7524 (2)	0.54217 (15)	0.0304 (7)	
H1A	0.606 (2)	0.746 (3)	0.5803 (10)	0.046*	
H1B	0.601 (2)	0.785 (3)	0.5284 (17)	0.046*	
N45	0.38702 (17)	0.9172 (2)	0.45707 (16)	0.0220 (8)	
N46	0.43928 (18)	0.8589 (2)	0.46723 (18)	0.0264 (8)	
N47	0.4659 (2)	0.8694 (3)	0.42610 (19)	0.0342 (9)	
N48	0.4306 (2)	0.9349 (3)	0.38669 (19)	0.0331 (9)	
N42	0.26230 (17)	0.9983 (2)	0.43834 (16)	0.0211 (8)	
N41	0.19117 (17)	0.9962 (2)	0.42775 (17)	0.0223 (8)	
N43	0.19771 (17)	1.0473 (2)	0.34424 (16)	0.0203 (7)	
N44	0.1808 (2)	1.0732 (3)	0.28216 (19)	0.0302 (9)	
H44A	0.178 (3)	1.1291 (13)	0.282 (2)	0.036*	
H44B	0.1404 (16)	1.051 (3)	0.2567 (19)	0.036*	
N37	0.06885 (17)	0.9103 (2)	0.41063 (17)	0.0213 (8)	
N38	0.02156 (18)	0.8451 (2)	0.40341 (17)	0.0231 (8)	
N39	−0.03218 (18)	0.8484 (2)	0.34789 (18)	0.0270 (8)	
N40	−0.02175 (18)	0.9167 (2)	0.31612 (17)	0.0265 (8)	
N9	0.10773 (17)	0.9139 (2)	0.54225 (17)	0.0221 (8)	
N10	0.05807 (18)	0.8516 (2)	0.53291 (17)	0.0235 (8)	
N11	0.0350 (2)	0.8560 (2)	0.57624 (18)	0.0301 (9)	
N12	0.0689 (2)	0.9211 (2)	0.61589 (19)	0.0308 (9)	
N6	0.23412 (17)	0.9910 (2)	0.56354 (16)	0.0204 (8)	
N5	0.30533 (17)	0.9902 (2)	0.57481 (16)	0.0197 (7)	
N7	0.29731 (18)	1.0384 (2)	0.65820 (16)	0.0221 (8)	
N8	0.3136 (2)	1.0664 (3)	0.72024 (18)	0.0281 (8)	
H8A	0.315 (2)	1.1226 (13)	0.721 (2)	0.034*	

H8B	0.3533 (16)	1.041 (3)	0.743 (2)	0.034*
N2	0.42977 (17)	0.9116 (2)	0.58985 (16)	0.0206 (8)
N1	0.47696 (18)	0.8469 (2)	0.59544 (17)	0.0248 (8)
N4	0.52881 (19)	0.8480 (2)	0.65210 (18)	0.0313 (9)
N3	0.51719 (18)	0.9126 (2)	0.68520 (17)	0.0279 (9)
N21	0.43624 (17)	0.5997 (2)	0.58547 (17)	0.0224 (8)
N22	0.48594 (18)	0.6596 (2)	0.59016 (17)	0.0233 (8)
N23	0.54339 (18)	0.6490 (2)	0.64263 (17)	0.0269 (8)
N24	0.53270 (18)	0.5813 (2)	0.67414 (17)	0.0250 (8)
N18	0.31056 (17)	0.5301 (2)	0.57414 (16)	0.0191 (7)
N17	0.24085 (17)	0.5347 (2)	0.56794 (16)	0.0204 (7)
N19	0.30881 (17)	0.4814 (2)	0.65999 (16)	0.0210 (7)
N20	0.3279 (2)	0.4506 (3)	0.72113 (19)	0.0304 (9)
H20A	0.3664 (15)	0.4763 (15)	0.7459 (18)	0.037*
H20B	0.331 (2)	0.3945 (11)	0.719 (2)	0.037*
N14	0.11200 (17)	0.6045 (2)	0.54958 (17)	0.0221 (8)
N13	0.06116 (18)	0.6647 (2)	0.53992 (17)	0.0241 (8)
N16	0.0422 (2)	0.6639 (2)	0.58634 (19)	0.0303 (9)
N15	0.0813 (2)	0.6036 (2)	0.62822 (18)	0.0290 (8)
N34	0.01511 (17)	0.6565 (2)	0.40891 (17)	0.0243 (8)
N33	0.06417 (17)	0.5948 (2)	0.41573 (17)	0.0226 (8)
N36	−0.02844 (18)	0.5771 (2)	0.32470 (17)	0.0249 (8)
N35	−0.04036 (18)	0.6464 (2)	0.35451 (18)	0.0284 (9)
N30	0.19161 (17)	0.5241 (2)	0.43079 (16)	0.0212 (8)
N29	0.26087 (17)	0.5296 (2)	0.43695 (16)	0.0204 (7)
N31	0.19542 (18)	0.4691 (2)	0.34746 (16)	0.0227 (8)
N32	0.1766 (2)	0.4314 (3)	0.28794 (19)	0.0341 (10)
H32A	0.183 (2)	0.3717 (17)	0.274 (2)	0.041*
H32B	0.1386 (18)	0.460 (3)	0.264 (2)	0.041*
N26	0.38642 (18)	0.6060 (2)	0.45224 (17)	0.0234 (8)
N25	0.43317 (18)	0.6712 (2)	0.45863 (17)	0.0244 (8)
N28	0.4495 (2)	0.6705 (3)	0.41052 (19)	0.0330 (9)
N27	0.4146 (2)	0.6055 (2)	0.37183 (18)	0.0314 (9)
C24	0.3826 (2)	0.9629 (3)	0.4065 (2)	0.0230 (9)
C23	0.3303 (2)	1.0348 (3)	0.3756 (2)	0.0244 (9)
H23A	0.353866	1.091559	0.391880	0.029*
H23B	0.316309	1.033442	0.329688	0.029*
C22	0.2653 (2)	1.0276 (3)	0.3869 (2)	0.0205 (9)
C21	0.1530 (2)	1.0255 (3)	0.3710 (2)	0.0213 (9)
C20	0.0729 (2)	1.0310 (3)	0.3401 (2)	0.0212 (9)
H20C	0.056082	1.035241	0.293922	0.025*
H20D	0.057201	1.084138	0.354655	0.025*
C19	0.0402 (2)	0.9522 (2)	0.3555 (2)	0.0206 (9)
C6	0.1133 (2)	0.9553 (3)	0.5942 (2)	0.0238 (9)
C5	0.1645 (2)	1.0283 (3)	0.6255 (2)	0.0256 (10)
H5A	0.140940	1.084716	0.608227	0.031*
H5B	0.177426	1.027713	0.671179	0.031*
C4	0.2307 (2)	1.0199 (3)	0.6152 (2)	0.0217 (9)

C3	0.3430 (2)	1.0193 (2)	0.63226 (19)	0.0197 (9)	
C2	0.4229 (2)	1.0261 (3)	0.6635 (2)	0.0227 (9)	
H2A	0.439561	1.028068	0.709698	0.027*	
H2B	0.438103	1.080716	0.650186	0.027*	
C1	0.4564 (2)	0.9495 (2)	0.6463 (2)	0.0207 (9)	
C13	0.3755 (2)	0.5674 (3)	0.3981 (2)	0.0228 (9)	
C14	0.3253 (2)	0.4918 (3)	0.3704 (2)	0.0259 (10)	
H14A	0.308442	0.491780	0.324092	0.031*	
H14B	0.351433	0.436544	0.386947	0.031*	
C15	0.2621 (2)	0.4969 (2)	0.3859 (2)	0.0216 (9)	
C16	0.1521 (2)	0.4874 (3)	0.3763 (2)	0.0218 (9)	
C17	0.0736 (2)	0.4715 (3)	0.3498 (2)	0.0227 (9)	
H17A	0.064271	0.417518	0.368203	0.027*	
H17B	0.054608	0.463140	0.303667	0.027*	
C18	0.0357 (2)	0.5469 (2)	0.36349 (19)	0.0204 (9)	
C7	0.1242 (2)	0.5680 (3)	0.6051 (2)	0.0232 (9)	
C8	0.1788 (2)	0.4993 (3)	0.6365 (2)	0.0261 (10)	
H8C	0.195692	0.504253	0.682632	0.031*	
H8D	0.156250	0.441257	0.623435	0.031*	
C9	0.2412 (2)	0.5064 (2)	0.6207 (2)	0.0199 (9)	
C10	0.3503 (2)	0.4969 (2)	0.6291 (2)	0.0213 (9)	
C11	0.4296 (2)	0.4797 (3)	0.6543 (2)	0.0226 (9)	
H11A	0.450069	0.472725	0.700640	0.027*	
H11B	0.437771	0.424769	0.636172	0.027*	
C12	0.4662 (2)	0.5529 (2)	0.6383 (2)	0.0201 (9)	
S1B	0.24045 (8)	0.75503 (10)	0.48194 (10)	0.0284 (3)	0.755 (2)
O1B	0.2185 (2)	0.7452 (3)	0.4133 (2)	0.0401 (9)	0.755 (2)
O2B	0.2466 (2)	0.8474 (2)	0.4973 (2)	0.0273 (4)	0.755 (2)
O3B	0.3099 (2)	0.7129 (2)	0.5156 (2)	0.0343 (10)	0.755 (2)
O4B	0.18460 (19)	0.7154 (2)	0.49574 (19)	0.0291 (5)	0.755 (2)
S1A	0.2517 (3)	0.7609 (3)	0.5162 (3)	0.0275 (4)	0.245 (2)
O1A	0.2778 (6)	0.7650 (7)	0.5824 (6)	0.0282 (14)	0.245 (2)
O2A	0.2964 (6)	0.8106 (7)	0.4925 (6)	0.0281 (5)	0.245 (2)
O3A	0.2457 (7)	0.6704 (7)	0.4947 (6)	0.0287 (5)	0.245 (2)
O4A	0.1782 (6)	0.7983 (7)	0.4889 (6)	0.0284 (5)	0.245 (2)
S2	0.27448 (6)	0.27338 (8)	0.58561 (6)	0.0353 (3)	
O7	0.25755 (18)	0.3385 (2)	0.53471 (18)	0.0456 (9)	
O8	0.22216 (17)	0.2821 (3)	0.61310 (17)	0.0502 (9)	
O9	0.27087 (18)	0.1859 (2)	0.55897 (18)	0.0455 (9)	
O10	0.34706 (16)	0.2908 (2)	0.63516 (17)	0.0492 (9)	
O3	0.13046 (18)	1.1281 (2)	0.48525 (18)	0.0416 (9)	
H3A	0.111 (2)	1.150 (3)	0.4493 (13)	0.062*	
H3B	0.1715 (15)	1.149 (3)	0.504 (2)	0.062*	
O2	0.37854 (17)	1.1264 (2)	0.52280 (17)	0.0404 (8)	
H2C	0.4240 (8)	1.131 (3)	0.5526 (14)	0.061*	
H2D	0.3533 (17)	1.151 (3)	0.537 (2)	0.061*	
O6	0.37999 (19)	0.4051 (2)	0.51440 (19)	0.0426 (9)	
H6A	0.400 (3)	0.366 (3)	0.503 (3)	0.064*	

H14C	0.5612 (16)	0.743 (3)	0.873 (2)	0.064*	
H14D	0.497 (2)	0.7689 (18)	0.829 (2)	0.064*	
H6B	0.349 (2)	0.381 (3)	0.523 (3)	0.064*	
O5	0.11926 (17)	0.41395 (19)	0.49395 (17)	0.0346 (8)	
H5C	0.0898 (17)	0.375 (2)	0.482 (2)	0.052*	
H5D	0.1621 (11)	0.390 (3)	0.511 (2)	0.052*	
O12	0.3824 (3)	0.8881 (3)	0.7409 (2)	0.0706 (14)	
H12A	0.391 (4)	0.847 (3)	0.722 (3)	0.106*	
H12B	0.388 (4)	0.889 (4)	0.7785 (15)	0.106*	
O13	0.2943 (2)	0.2544 (4)	0.3536 (2)	0.0862 (17)	
H13A	0.277 (4)	0.285 (4)	0.373 (3)	0.129*	
H13B	0.285 (4)	0.251 (5)	0.3154 (14)	0.129*	
O14	0.5214 (2)	0.7264 (3)	0.8449 (2)	0.0607 (11)	
O15	0.4135 (2)	0.6269 (3)	0.7438 (2)	0.0608 (11)	
H15A	0.4507 (18)	0.652 (3)	0.771 (2)	0.091*	
H15B	0.3761 (19)	0.6193 (15)	0.749 (3)	0.091*	
O16	−0.1842 (2)	0.7556 (3)	0.2775 (2)	0.0634 (11)	
H16A	−0.199 (3)	0.747 (5)	0.309 (2)	0.095*	
H16B	−0.1410 (15)	0.758 (5)	0.284 (3)	0.095*	
O17	−0.06364 (18)	0.7556 (2)	0.62144 (18)	0.0423 (8)	
H17C	−0.035 (2)	0.755 (4)	0.6609 (10)	0.063*	
H17D	−0.040 (3)	0.732 (4)	0.604 (2)	0.063*	
O18	0.0991 (2)	0.8891 (2)	0.25728 (19)	0.0497 (10)	
H18A	0.076 (3)	0.852 (3)	0.267 (3)	0.075*	
H18B	0.100 (3)	0.897 (4)	0.2224 (16)	0.075*	
O19	0.6564 (2)	0.7521 (2)	0.75150 (19)	0.0560 (10)	
H19A	0.620 (2)	0.742 (3)	0.7141 (11)	0.084*	
H19B	0.644 (3)	0.7556 (13)	0.7830 (13)	0.084*	
O20	0.3690 (4)	0.7572 (4)	0.6492 (3)	0.0637 (16)	0.755 (2)
H20E	0.398 (5)	0.724 (6)	0.677 (6)	0.095*	0.755 (2)
H20F	0.330 (3)	0.743 (6)	0.619 (3)	0.095*	0.755 (2)
O21	0.4173 (8)	0.7515 (10)	0.6759 (9)	0.046 (4)	0.245 (2)
H21A	0.457 (2)	0.747 (6)	0.706 (3)	0.069*	0.245 (2)
H21B	0.393 (11)	0.709 (15)	0.677 (7)	0.069*	0.245 (2)
O11	0.2062 (3)	0.2837 (4)	0.4078 (2)	0.0775 (14)	
H11C	0.221 (4)	0.306 (4)	0.4446 (17)	0.116*	
H11D	0.213 (4)	0.2282 (15)	0.417 (3)	0.116*	

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu2	0.0130 (3)	0.0261 (3)	0.0152 (3)	0.00082 (19)	0.0031 (2)	0.0010 (2)
Cu3	0.0141 (3)	0.0241 (3)	0.0161 (3)	−0.00153 (19)	0.0046 (2)	−0.0004 (2)
Cu4	0.0156 (2)	0.0222 (3)	0.0205 (3)	−0.00101 (19)	0.0055 (2)	−0.0015 (2)
Cu5	0.0132 (3)	0.0254 (3)	0.0157 (3)	0.00111 (19)	0.0031 (2)	−0.0002 (2)
Cu6	0.0130 (3)	0.0248 (3)	0.0156 (3)	−0.00196 (19)	0.0039 (2)	−0.0004 (2)
Cu1	0.0153 (2)	0.0227 (3)	0.0190 (3)	−0.00066 (19)	0.0056 (2)	−0.0009 (2)
O4	0.0165 (14)	0.0371 (19)	0.045 (2)	−0.0034 (13)	0.0104 (15)	−0.0149 (15)

O1	0.0221 (16)	0.0379 (19)	0.0315 (18)	−0.0009 (13)	0.0116 (14)	0.0046 (15)
N45	0.0168 (18)	0.0251 (18)	0.019 (2)	0.0015 (14)	0.0022 (15)	0.0035 (15)
N46	0.0221 (19)	0.032 (2)	0.025 (2)	0.0015 (15)	0.0107 (17)	0.0016 (16)
N47	0.030 (2)	0.040 (2)	0.036 (3)	0.0121 (17)	0.0169 (19)	0.0098 (18)
N48	0.029 (2)	0.043 (2)	0.030 (2)	0.0086 (17)	0.0159 (18)	0.0102 (18)
N42	0.0136 (17)	0.0276 (19)	0.020 (2)	−0.0009 (13)	0.0057 (15)	0.0012 (15)
N41	0.0155 (17)	0.0266 (18)	0.020 (2)	0.0011 (13)	0.0027 (15)	0.0014 (15)
N43	0.0174 (17)	0.0242 (18)	0.0164 (19)	0.0012 (13)	0.0045 (15)	0.0038 (14)
N44	0.024 (2)	0.042 (2)	0.019 (2)	−0.0044 (17)	0.0040 (17)	0.0080 (19)
N37	0.0165 (18)	0.0241 (18)	0.022 (2)	−0.0047 (14)	0.0067 (16)	−0.0003 (15)
N38	0.0178 (18)	0.0275 (19)	0.021 (2)	−0.0042 (14)	0.0057 (16)	−0.0024 (15)
N39	0.0191 (18)	0.0275 (19)	0.028 (2)	−0.0053 (15)	0.0033 (17)	0.0011 (16)
N40	0.0188 (19)	0.0266 (19)	0.028 (2)	−0.0004 (14)	0.0038 (16)	0.0008 (16)
N9	0.0187 (18)	0.0257 (18)	0.023 (2)	−0.0054 (14)	0.0097 (16)	−0.0043 (15)
N10	0.0182 (18)	0.0293 (19)	0.026 (2)	−0.0077 (14)	0.0120 (16)	−0.0034 (16)
N11	0.032 (2)	0.033 (2)	0.031 (2)	−0.0073 (16)	0.0192 (19)	−0.0051 (17)
N12	0.031 (2)	0.034 (2)	0.035 (2)	−0.0089 (16)	0.0205 (19)	−0.0085 (17)
N6	0.0150 (17)	0.0259 (18)	0.020 (2)	0.0027 (13)	0.0069 (15)	0.0018 (15)
N5	0.0110 (16)	0.0264 (18)	0.0174 (19)	−0.0023 (13)	0.0020 (14)	0.0027 (14)
N7	0.0211 (18)	0.0262 (18)	0.018 (2)	0.0001 (14)	0.0077 (15)	−0.0020 (15)
N8	0.026 (2)	0.035 (2)	0.022 (2)	−0.0011 (17)	0.0087 (17)	−0.0087 (18)
N2	0.0180 (18)	0.0248 (18)	0.0159 (19)	−0.0020 (14)	0.0042 (15)	−0.0016 (15)
N1	0.0168 (18)	0.0274 (19)	0.022 (2)	0.0065 (14)	0.0003 (16)	0.0014 (15)
N4	0.026 (2)	0.033 (2)	0.025 (2)	0.0069 (16)	0.0009 (18)	−0.0036 (17)
N3	0.0226 (19)	0.0281 (19)	0.021 (2)	0.0037 (15)	−0.0017 (16)	−0.0051 (16)
N21	0.0174 (18)	0.0244 (18)	0.024 (2)	−0.0016 (14)	0.0076 (16)	−0.0008 (15)
N22	0.0180 (18)	0.0251 (18)	0.022 (2)	−0.0033 (14)	0.0033 (16)	−0.0004 (15)
N23	0.0174 (18)	0.032 (2)	0.026 (2)	−0.0028 (15)	0.0038 (17)	0.0029 (16)
N24	0.0154 (17)	0.0275 (19)	0.024 (2)	−0.0027 (14)	0.0009 (16)	0.0036 (16)
N18	0.0157 (17)	0.0197 (16)	0.0189 (19)	0.0003 (13)	0.0046 (15)	−0.0009 (15)
N17	0.0126 (16)	0.0256 (18)	0.022 (2)	−0.0012 (13)	0.0062 (15)	0.0002 (15)
N19	0.0143 (17)	0.0313 (18)	0.0139 (19)	0.0040 (14)	0.0026 (14)	0.0073 (15)
N20	0.0221 (19)	0.043 (2)	0.023 (2)	0.0044 (16)	0.0067 (17)	0.0138 (18)
N14	0.0160 (18)	0.0277 (18)	0.019 (2)	0.0028 (14)	0.0042 (15)	0.0023 (15)
N13	0.0203 (18)	0.0256 (19)	0.026 (2)	0.0042 (14)	0.0090 (16)	−0.0002 (15)
N16	0.029 (2)	0.032 (2)	0.034 (2)	0.0082 (16)	0.0172 (18)	0.0073 (17)
N15	0.031 (2)	0.032 (2)	0.029 (2)	0.0036 (16)	0.0175 (18)	0.0047 (17)
N34	0.0147 (17)	0.0298 (19)	0.022 (2)	0.0020 (14)	0.0014 (16)	0.0004 (16)
N33	0.0181 (18)	0.0236 (18)	0.023 (2)	0.0025 (14)	0.0052 (16)	−0.0015 (15)
N36	0.0170 (18)	0.0260 (19)	0.022 (2)	−0.0003 (14)	−0.0004 (16)	−0.0049 (16)
N35	0.0201 (19)	0.0260 (19)	0.026 (2)	0.0043 (15)	−0.0027 (17)	−0.0007 (16)
N30	0.0126 (17)	0.0271 (18)	0.022 (2)	−0.0016 (13)	0.0050 (15)	−0.0002 (15)
N29	0.0154 (17)	0.0296 (18)	0.0167 (19)	−0.0014 (14)	0.0073 (15)	−0.0028 (15)
N31	0.0227 (18)	0.0257 (18)	0.0178 (19)	−0.0003 (14)	0.0068 (15)	−0.0062 (15)
N32	0.025 (2)	0.046 (2)	0.024 (2)	0.0069 (17)	0.0038 (17)	−0.0188 (18)
N26	0.0200 (18)	0.0250 (18)	0.023 (2)	−0.0038 (14)	0.0075 (16)	−0.0037 (16)
N25	0.0198 (18)	0.0307 (19)	0.024 (2)	−0.0072 (14)	0.0112 (16)	−0.0038 (16)
N28	0.029 (2)	0.045 (2)	0.031 (2)	−0.0109 (17)	0.0192 (19)	−0.0083 (19)

N27	0.032 (2)	0.038 (2)	0.029 (2)	−0.0143 (17)	0.0181 (18)	−0.0110 (18)
C24	0.015 (2)	0.032 (2)	0.023 (2)	−0.0029 (17)	0.0095 (18)	0.0009 (19)
C23	0.018 (2)	0.033 (2)	0.020 (2)	0.0027 (17)	0.0061 (18)	0.0078 (19)
C22	0.016 (2)	0.021 (2)	0.022 (2)	−0.0020 (15)	0.0056 (18)	0.0011 (18)
C21	0.019 (2)	0.022 (2)	0.022 (2)	−0.0008 (16)	0.0079 (18)	−0.0024 (18)
C20	0.016 (2)	0.023 (2)	0.020 (2)	0.0008 (16)	0.0034 (17)	0.0026 (18)
C19	0.018 (2)	0.021 (2)	0.021 (2)	0.0022 (16)	0.0074 (18)	−0.0014 (17)
C6	0.023 (2)	0.022 (2)	0.028 (3)	0.0002 (16)	0.0119 (19)	−0.0017 (18)
C5	0.023 (2)	0.027 (2)	0.029 (3)	−0.0010 (17)	0.014 (2)	−0.0087 (19)
C4	0.023 (2)	0.022 (2)	0.020 (2)	−0.0039 (16)	0.0096 (19)	−0.0020 (18)
C3	0.017 (2)	0.019 (2)	0.018 (2)	−0.0013 (15)	0.0023 (17)	−0.0001 (17)
C2	0.019 (2)	0.025 (2)	0.021 (2)	−0.0011 (17)	0.0048 (18)	−0.0019 (18)
C1	0.018 (2)	0.021 (2)	0.019 (2)	−0.0034 (16)	0.0039 (18)	−0.0018 (17)
C13	0.018 (2)	0.028 (2)	0.021 (2)	0.0007 (17)	0.0066 (19)	−0.0043 (18)
C14	0.024 (2)	0.031 (2)	0.024 (2)	−0.0019 (17)	0.0112 (19)	−0.0058 (19)
C15	0.020 (2)	0.022 (2)	0.022 (2)	−0.0003 (16)	0.0078 (19)	−0.0035 (17)
C16	0.021 (2)	0.027 (2)	0.018 (2)	−0.0027 (16)	0.0084 (18)	−0.0043 (17)
C17	0.014 (2)	0.024 (2)	0.024 (2)	−0.0013 (16)	0.0030 (17)	−0.0028 (18)
C18	0.016 (2)	0.021 (2)	0.019 (2)	−0.0043 (16)	0.0027 (17)	−0.0015 (17)
C7	0.018 (2)	0.025 (2)	0.024 (3)	−0.0025 (17)	0.0062 (19)	0.0010 (18)
C8	0.022 (2)	0.033 (2)	0.026 (3)	0.0029 (17)	0.013 (2)	0.0080 (19)
C9	0.018 (2)	0.021 (2)	0.021 (2)	0.0014 (15)	0.0092 (18)	0.0027 (17)
C10	0.016 (2)	0.023 (2)	0.023 (2)	0.0015 (15)	0.0059 (18)	0.0018 (17)
C11	0.014 (2)	0.028 (2)	0.021 (2)	0.0021 (16)	0.0031 (17)	0.0059 (18)
C12	0.018 (2)	0.020 (2)	0.020 (2)	0.0046 (16)	0.0057 (18)	0.0008 (17)
S1B	0.0269 (6)	0.0212 (5)	0.0348 (8)	0.0000 (5)	0.0107 (7)	0.0028 (7)
O1B	0.0427 (16)	0.0369 (16)	0.0334 (16)	−0.0018 (14)	0.0094 (14)	0.0001 (15)
O2B	0.0257 (8)	0.0204 (7)	0.0345 (9)	0.0002 (7)	0.0116 (8)	0.0015 (8)
O3B	0.031 (2)	0.022 (2)	0.045 (3)	0.0097 (17)	0.011 (2)	−0.0018 (19)
O4B	0.0273 (8)	0.0217 (7)	0.0356 (9)	−0.0010 (7)	0.0108 (8)	0.0022 (8)
S1A	0.0265 (7)	0.0208 (7)	0.0338 (9)	−0.0002 (6)	0.0115 (8)	0.0018 (9)
O1A	0.029 (2)	0.022 (2)	0.031 (2)	0.001 (2)	0.010 (2)	0.001 (2)
O2A	0.0266 (9)	0.0211 (8)	0.0347 (10)	−0.0003 (8)	0.0112 (9)	0.0019 (9)
O3A	0.0271 (9)	0.0214 (8)	0.0350 (10)	−0.0004 (8)	0.0108 (9)	0.0024 (9)
O4A	0.0268 (8)	0.0213 (8)	0.0350 (9)	−0.0002 (7)	0.0110 (8)	0.0020 (9)
S2	0.0229 (5)	0.0358 (6)	0.0424 (7)	0.0008 (5)	0.0092 (5)	0.0002 (5)
O7	0.042 (2)	0.0314 (17)	0.059 (2)	0.0052 (14)	0.0173 (18)	0.0091 (17)
O8	0.0274 (17)	0.073 (2)	0.046 (2)	−0.0038 (17)	0.0120 (16)	−0.0084 (19)
O9	0.0369 (19)	0.0260 (16)	0.071 (3)	0.0011 (14)	0.0202 (18)	0.0023 (16)
O10	0.0243 (17)	0.060 (2)	0.053 (2)	−0.0029 (15)	0.0066 (16)	−0.0056 (19)
O3	0.0292 (19)	0.049 (2)	0.040 (2)	0.0107 (16)	0.0077 (16)	−0.0038 (17)
O2	0.0249 (17)	0.057 (2)	0.039 (2)	−0.0054 (16)	0.0137 (15)	0.0009 (17)
O6	0.038 (2)	0.041 (2)	0.049 (2)	0.0051 (16)	0.0197 (18)	−0.0030 (17)
O5	0.0250 (17)	0.0311 (17)	0.041 (2)	−0.0032 (13)	0.0080 (16)	0.0051 (15)
O12	0.135 (4)	0.040 (2)	0.040 (3)	0.013 (2)	0.040 (3)	0.0083 (19)
O13	0.044 (2)	0.168 (5)	0.040 (3)	0.018 (3)	0.012 (2)	−0.009 (3)
O14	0.058 (3)	0.053 (2)	0.088 (3)	−0.015 (2)	0.047 (2)	−0.024 (2)
O15	0.046 (2)	0.063 (3)	0.062 (3)	0.0017 (19)	0.011 (2)	−0.018 (2)

O16	0.047 (2)	0.068 (3)	0.056 (3)	−0.001 (2)	0.004 (2)	0.008 (2)
O17	0.0356 (19)	0.043 (2)	0.053 (2)	−0.0005 (15)	0.0238 (17)	−0.0047 (18)
O18	0.073 (3)	0.044 (2)	0.047 (3)	−0.0085 (18)	0.039 (2)	−0.0054 (18)
O19	0.045 (2)	0.055 (2)	0.044 (2)	0.0016 (17)	−0.0039 (18)	−0.0049 (18)
O20	0.076 (5)	0.069 (4)	0.045 (4)	−0.005 (4)	0.025 (3)	−0.003 (3)
O21	0.023 (8)	0.048 (9)	0.057 (11)	0.004 (7)	0.008 (8)	0.001 (8)
O11	0.066 (3)	0.120 (4)	0.056 (3)	−0.026 (3)	0.035 (3)	−0.014 (3)

Geometric parameters (Å, º)

Cu1—N1	2.003 (4)	N34—N33	1.342 (4)
Cu1—N22	2.017 (3)	N34—N35	1.310 (5)
Cu1—N25	2.022 (4)	N33—C18	1.332 (5)
Cu1—N46	2.018 (4)	N36—N35	1.350 (5)
Cu1—O1	2.182 (3)	N36—C18	1.327 (5)
Cu2—N2	1.992 (3)	N30—N29	1.373 (4)
Cu2—N5	1.995 (3)	N30—C16	1.314 (5)
Cu2—N42	2.006 (3)	N29—C15	1.310 (5)
Cu2—N45	1.977 (4)	N31—N32	1.406 (5)
Cu2—O2A	2.231 (11)	N31—C15	1.350 (5)
Cu2—O2B	2.360 (4)	N31—C16	1.360 (5)
Cu3—N6	1.983 (3)	N32—H32A	0.995 (15)
Cu3—N9	1.988 (3)	N32—H32B	0.86 (2)
Cu3—N37	1.977 (3)	N26—N25	1.350 (5)
Cu3—N41	1.999 (4)	N26—C13	1.331 (5)
Cu3—O2B	2.305 (4)	N25—N28	1.309 (5)
Cu3—O4A	2.258 (11)	N28—N27	1.334 (5)
Cu4—N10	2.013 (3)	N27—C13	1.340 (5)
Cu4—N13	2.040 (4)	C24—C23	1.495 (6)
Cu4—N34	1.997 (4)	C23—H23A	0.9900
Cu4—N38	2.025 (3)	C23—H23B	0.9900
Cu4—O4	2.165 (3)	C23—C22	1.476 (6)
Cu5—N14	1.994 (4)	C21—C20	1.494 (5)
Cu5—N17	1.990 (3)	C20—H20C	0.9900
Cu5—N30	2.003 (3)	C20—H20D	0.9900
Cu5—N33	1.993 (3)	C20—C19	1.500 (5)
Cu5—O3A	2.346 (12)	C6—C5	1.497 (6)
Cu5—O4B	2.246 (4)	C5—H5A	0.9900
Cu6—N18	2.000 (3)	C5—H5B	0.9900
Cu6—N21	1.980 (3)	C5—C4	1.487 (6)
Cu6—N26	1.984 (4)	C3—C2	1.493 (5)
Cu6—N29	1.991 (3)	C2—H2A	0.9900
Cu6—O3A	2.386 (12)	C2—H2B	0.9900
Cu6—O3B	2.233 (4)	C2—C1	1.502 (6)
O4—H4A	0.823 (19)	C13—C14	1.503 (6)
O4—H4B	0.826 (19)	C14—H14A	0.9900
O1—H1A	0.829 (19)	C14—H14B	0.9900
O1—H1B	0.811 (19)	C14—C15	1.495 (6)

N45—N46	1.340 (5)	C16—C17	1.483 (5)
N45—C24	1.347 (5)	C17—H17A	0.9900
N46—N47	1.307 (5)	C17—H17B	0.9900
N47—N48	1.349 (5)	C17—C18	1.505 (5)
N48—C24	1.331 (5)	C7—C8	1.485 (6)
N42—N41	1.377 (4)	C8—H8C	0.9900
N42—C22	1.314 (5)	C8—H8D	0.9900
N41—C21	1.306 (5)	C8—C9	1.485 (6)
N43—N44	1.404 (5)	C10—C11	1.503 (5)
N43—C22	1.357 (5)	C11—H11A	0.9900
N43—C21	1.357 (5)	C11—H11B	0.9900
N44—H44A	0.859 (19)	C11—C12	1.489 (6)
N44—H44B	0.86 (2)	S1B—O1B	1.484 (5)
N37—N38	1.355 (4)	S1B—O2B	1.454 (4)
N37—C19	1.337 (5)	S1B—O3B	1.457 (4)
N38—N39	1.303 (5)	S1B—O4B	1.454 (4)
N39—N40	1.354 (5)	S1A—O1A	1.414 (14)
N40—C19	1.331 (5)	S1A—O2A	1.475 (13)
N9—N10	1.346 (4)	S1A—O3A	1.463 (12)
N9—C6	1.337 (5)	S1A—O4A	1.483 (12)
N10—N11	1.295 (5)	S2—O7	1.480 (4)
N11—N12	1.340 (5)	S2—O8	1.479 (4)
N12—C6	1.330 (5)	S2—O9	1.469 (3)
N6—N5	1.374 (4)	S2—O10	1.475 (3)
N6—C4	1.322 (5)	O3—H3A	0.835 (19)
N5—C3	1.315 (5)	O3—H3B	0.835 (19)
N7—N8	1.415 (5)	O2—H2C	0.902 (18)
N7—C4	1.341 (5)	O2—H2D	0.819 (19)
N7—C3	1.352 (5)	O6—H6A	0.829 (19)
N8—H8A	0.863 (19)	O6—H6B	0.842 (19)
N8—H8B	0.86 (2)	O5—H5C	0.808 (19)
N2—N1	1.355 (5)	O5—H5D	0.876 (15)
N2—C1	1.332 (5)	O12—H12A	0.828 (19)
N1—N4	1.304 (5)	O12—H12B	0.840 (19)
N4—N3	1.342 (5)	O13—H13A	0.83 (2)
N3—C1	1.321 (5)	O13—H13B	0.83 (2)
N21—N22	1.344 (4)	O14—H14C	0.837 (19)
N21—C12	1.334 (5)	O14—H14D	0.814 (19)
N22—N23	1.304 (5)	O15—H15A	0.855 (19)
N23—N24	1.345 (5)	O15—H15B	0.836 (19)
N24—C12	1.337 (5)	O16—H16A	0.912 (12)
N18—N17	1.381 (4)	O16—H16B	0.835 (19)
N18—C10	1.301 (5)	O17—H17C	0.861 (19)
N17—C9	1.310 (5)	O17—H17D	0.840 (19)
N19—N20	1.399 (5)	O18—H18A	0.835 (19)
N19—C9	1.357 (5)	O18—H18B	0.832 (19)
N19—C10	1.357 (5)	O19—H19A	0.895 (17)
N20—H20A	0.853 (19)	O19—H19B	0.883 (17)

N20—H20B	0.865 (16)	O20—H20E	0.84 (2)
N14—N13	1.341 (4)	O20—H20F	0.85 (2)
N14—C7	1.339 (5)	O21—H21A	0.83 (2)
N13—N16	1.305 (5)	O21—H21B	0.831 (15)
N16—N15	1.340 (5)	O11—H11C	0.86 (2)
N15—C7	1.337 (5)	O11—H11D	0.87 (2)

N45—Cu2—N42	85.92 (14)	N35—N34—Cu4	126.1 (3)
N45—Cu2—N5	171.00 (13)	N35—N34—N33	109.4 (3)
N45—Cu2—N2	92.10 (14)	N34—N33—Cu5	127.0 (3)
N45—Cu2—O2B	110.28 (14)	C18—N33—Cu5	127.5 (3)
N45—Cu2—O2A	85.3 (3)	C18—N33—N34	105.4 (3)
N42—Cu2—O2B	78.81 (13)	C18—N36—N35	105.4 (3)
N42—Cu2—O2A	94.1 (3)	N34—N35—N36	108.8 (3)
N5—Cu2—N42	94.64 (14)	N29—N30—Cu5	125.4 (3)
N5—Cu2—O2B	78.60 (14)	C16—N30—Cu5	126.2 (3)
N5—Cu2—O2A	103.6 (3)	C16—N30—N29	108.2 (3)
N2—Cu2—N42	169.92 (13)	N30—N29—Cu6	125.6 (3)
N2—Cu2—N5	85.79 (14)	C15—N29—Cu6	126.6 (3)
N2—Cu2—O2B	111.08 (14)	C15—N29—N30	107.7 (3)
N2—Cu2—O2A	95.6 (3)	C15—N31—N32	124.4 (4)
N41—Cu3—O2B	79.21 (14)	C15—N31—C16	107.3 (3)
N41—Cu3—O4A	106.5 (3)	C16—N31—N32	128.3 (3)
N37—Cu3—N41	86.13 (14)	N31—N32—H32A	133 (3)
N37—Cu3—N9	91.66 (14)	N31—N32—H32B	103 (3)
N37—Cu3—N6	171.29 (14)	H32A—N32—H32B	117 (4)
N37—Cu3—O2B	108.53 (14)	N25—N26—Cu6	126.7 (3)
N37—Cu3—O4A	82.7 (3)	C13—N26—Cu6	128.4 (3)
N9—Cu3—N41	167.29 (14)	C13—N26—N25	104.9 (3)
N9—Cu3—O2B	113.29 (14)	N26—N25—Cu1	125.2 (3)
N9—Cu3—O4A	85.6 (3)	N28—N25—Cu1	125.4 (3)
N6—Cu3—N41	94.51 (14)	N28—N25—N26	109.3 (3)
N6—Cu3—N9	85.81 (14)	N25—N28—N27	109.4 (3)
N6—Cu3—O2B	80.09 (14)	N28—N27—C13	105.5 (4)
N6—Cu3—O4A	105.4 (3)	N45—C24—C23	125.2 (4)
N38—Cu4—O4	97.03 (13)	N48—C24—N45	111.0 (4)
N38—Cu4—N13	168.37 (14)	N48—C24—C23	123.8 (4)
N10—Cu4—O4	92.61 (13)	C24—C23—H23A	109.2
N10—Cu4—N38	88.05 (14)	C24—C23—H23B	109.2
N10—Cu4—N13	90.17 (14)	H23A—C23—H23B	107.9
N13—Cu4—O4	94.53 (14)	C22—C23—C24	112.1 (3)
N34—Cu4—O4	93.84 (13)	C22—C23—H23A	109.2
N34—Cu4—N38	92.29 (14)	C22—C23—H23B	109.2
N34—Cu4—N10	173.45 (13)	N42—C22—N43	108.6 (3)
N34—Cu4—N13	88.18 (14)	N42—C22—C23	126.3 (4)
N17—Cu5—N14	86.03 (14)	N43—C22—C23	125.0 (4)
N17—Cu5—N33	171.09 (14)	N41—C21—N43	109.0 (3)
N17—Cu5—N30	94.81 (14)	N41—C21—C20	125.0 (4)

N17—Cu5—O4B	97.79 (14)	N43—C21—C20	126.0 (4)
N17—Cu5—O3A	77.5 (3)	C21—C20—H20C	109.5
N14—Cu5—N30	170.75 (14)	C21—C20—H20D	109.5
N14—Cu5—O4B	85.61 (14)	C21—C20—C19	110.8 (3)
N14—Cu5—O3A	114.0 (3)	H20C—C20—H20D	108.1
N33—Cu5—N14	92.05 (14)	C19—C20—H20C	109.5
N33—Cu5—N30	85.71 (14)	C19—C20—H20D	109.5
N33—Cu5—O4B	90.72 (14)	N37—C19—C20	124.2 (4)
N33—Cu5—O3A	111.1 (3)	N40—C19—N37	111.9 (4)
N30—Cu5—O4B	103.36 (14)	N40—C19—C20	123.9 (4)
N30—Cu5—O3A	75.1 (3)	N9—C6—C5	124.9 (4)
N21—Cu6—N18	85.60 (14)	N12—C6—N9	110.8 (4)
N21—Cu6—N29	168.77 (14)	N12—C6—C5	124.3 (4)
N21—Cu6—N26	91.87 (14)	C6—C5—H5A	109.4
N21—Cu6—O3B	89.51 (14)	C6—C5—H5B	109.4
N21—Cu6—O3A	117.5 (3)	H5A—C5—H5B	108.0
N18—Cu6—O3B	94.78 (14)	C4—C5—C6	111.0 (3)
N18—Cu6—O3A	78.4 (3)	C4—C5—H5A	109.4
N29—Cu6—N18	94.69 (14)	C4—C5—H5B	109.4
N29—Cu6—O3B	101.64 (14)	N6—C4—N7	109.0 (4)
N29—Cu6—O3A	73.5 (3)	N6—C4—C5	126.0 (4)
N26—Cu6—N18	171.84 (13)	N7—C4—C5	125.0 (4)
N26—Cu6—N29	86.29 (14)	N5—C3—N7	108.5 (3)
N26—Cu6—O3B	92.95 (15)	N5—C3—C2	124.9 (4)
N26—Cu6—O3A	109.6 (3)	N7—C3—C2	126.6 (4)
N46—Cu1—O1	96.32 (13)	C3—C2—H2A	109.6
N46—Cu1—N25	91.14 (14)	C3—C2—H2B	109.6
N1—Cu1—O1	100.80 (13)	C3—C2—C1	110.5 (3)
N1—Cu1—N46	87.33 (14)	H2A—C2—H2B	108.1
N1—Cu1—N22	91.68 (14)	C1—C2—H2A	109.6
N1—Cu1—N25	165.14 (14)	C1—C2—H2B	109.6
N22—Cu1—O1	90.37 (13)	N2—C1—C2	124.5 (4)
N22—Cu1—N46	173.30 (14)	N3—C1—N2	111.7 (4)
N22—Cu1—N25	88.13 (14)	N3—C1—C2	123.8 (4)
N25—Cu1—O1	94.06 (13)	N26—C13—N27	110.8 (4)
Cu4—O4—H4A	140 (3)	N26—C13—C14	124.2 (4)
Cu4—O4—H4B	109 (3)	N27—C13—C14	125.0 (4)
H4A—O4—H4B	108 (3)	C13—C14—H14A	109.4
Cu1—O1—H1A	108 (3)	C13—C14—H14B	109.4
Cu1—O1—H1B	128 (3)	H14A—C14—H14B	108.0
H1A—O1—H1B	107 (3)	C15—C14—C13	111.3 (3)
N46—N45—Cu2	126.7 (3)	C15—C14—H14A	109.4
N46—N45—C24	104.6 (3)	C15—C14—H14B	109.4
C24—N45—Cu2	127.6 (3)	N29—C15—N31	108.8 (3)
N45—N46—Cu1	127.2 (3)	N29—C15—C14	126.9 (4)
N47—N46—Cu1	122.4 (3)	N31—C15—C14	124.3 (4)
N47—N46—N45	110.1 (3)	N30—C16—N31	107.9 (3)
N46—N47—N48	109.0 (3)	N30—C16—C17	126.3 (4)

C24—N48—N47	105.3 (4)	N31—C16—C17	125.8 (4)
N41—N42—Cu2	123.5 (3)	C16—C17—H17A	109.5
C22—N42—Cu2	127.9 (3)	C16—C17—H17B	109.5
C22—N42—N41	107.7 (3)	C16—C17—C18	110.7 (3)
N42—N41—Cu3	124.1 (3)	H17A—C17—H17B	108.1
C21—N41—Cu3	127.6 (3)	C18—C17—H17A	109.5
C21—N41—N42	107.9 (3)	C18—C17—H17B	109.5
C22—N43—N44	123.5 (3)	N33—C18—C17	123.8 (3)
C21—N43—N44	129.2 (3)	N36—C18—N33	111.0 (4)
C21—N43—C22	106.7 (3)	N36—C18—C17	125.2 (4)
N43—N44—H44A	106 (3)	N14—C7—C8	124.6 (4)
N43—N44—H44B	110 (3)	N15—C7—N14	110.0 (4)
H44A—N44—H44B	111 (5)	N15—C7—C8	125.4 (4)
N38—N37—Cu3	128.4 (3)	C7—C8—H8C	109.2
C19—N37—Cu3	127.7 (3)	C7—C8—H8D	109.2
C19—N37—N38	103.7 (3)	H8C—C8—H8D	107.9
N37—N38—Cu4	125.7 (3)	C9—C8—C7	112.1 (4)
N39—N38—Cu4	123.6 (3)	C9—C8—H8C	109.2
N39—N38—N37	110.7 (3)	C9—C8—H8D	109.2
N38—N39—N40	108.4 (3)	N17—C9—N19	109.1 (3)
C19—N40—N39	105.3 (3)	N17—C9—C8	127.1 (4)
N10—N9—Cu3	127.2 (3)	N19—C9—C8	123.8 (4)
C6—N9—Cu3	128.2 (3)	N18—C10—N19	109.0 (3)
C6—N9—N10	104.5 (3)	N18—C10—C11	125.4 (4)
N9—N10—Cu4	126.8 (3)	N19—C10—C11	125.7 (4)
N11—N10—Cu4	122.7 (3)	C10—C11—H11A	109.6
N11—N10—N9	110.1 (3)	C10—C11—H11B	109.6
N10—N11—N12	109.1 (3)	H11A—C11—H11B	108.1
C6—N12—N11	105.5 (4)	C12—C11—C10	110.4 (3)
N5—N6—Cu3	124.2 (3)	C12—C11—H11A	109.6
C4—N6—Cu3	128.2 (3)	C12—C11—H11B	109.6
C4—N6—N5	107.2 (3)	N21—C12—N24	110.8 (4)
N6—N5—Cu2	124.0 (3)	N21—C12—C11	123.9 (4)
C3—N5—Cu2	127.9 (3)	N24—C12—C11	125.3 (4)
C3—N5—N6	108.0 (3)	O2B—S1B—O1B	108.8 (3)
C4—N7—N8	123.8 (3)	O2B—S1B—O3B	109.6 (3)
C4—N7—C3	107.4 (3)	O3B—S1B—O1B	108.6 (3)
C3—N7—N8	128.6 (3)	O4B—S1B—O1B	107.2 (3)
N7—N8—H8A	108 (3)	O4B—S1B—O2B	110.2 (2)
N7—N8—H8B	105 (3)	O4B—S1B—O3B	112.3 (2)
H8A—N8—H8B	115 (5)	Cu3—O2B—Cu2	101.20 (12)
N1—N2—Cu2	128.1 (3)	S1B—O2B—Cu2	129.7 (2)
C1—N2—Cu2	127.5 (3)	S1B—O2B—Cu3	127.5 (2)
C1—N2—N1	104.4 (3)	S1B—O3B—Cu6	130.5 (2)
N2—N1—Cu1	126.5 (3)	S1B—O4B—Cu5	127.7 (2)
N4—N1—Cu1	124.1 (3)	O1A—S1A—O2A	112.7 (7)
N4—N1—N2	109.4 (3)	O1A—S1A—O3A	111.0 (8)
N1—N4—N3	109.2 (3)	O1A—S1A—O4A	107.3 (8)

C1—N3—N4	105.4 (3)	O2A—S1A—O4A	108.8 (7)
N22—N21—Cu6	127.4 (3)	O3A—S1A—O2A	109.5 (8)
C12—N21—Cu6	127.3 (3)	O3A—S1A—O4A	107.3 (7)
C12—N21—N22	104.8 (3)	S1A—O2A—Cu2	131.2 (7)
N21—N22—Cu1	124.1 (3)	Cu5—O3A—Cu6	102.8 (4)
N23—N22—Cu1	125.4 (3)	S1A—O3A—Cu5	124.1 (8)
N23—N22—N21	110.1 (3)	S1A—O3A—Cu6	125.4 (7)
N22—N23—N24	108.7 (3)	S1A—O4A—Cu3	123.5 (7)
C12—N24—N23	105.5 (3)	O8—S2—O7	109.1 (2)
N17—N18—Cu6	125.1 (3)	O9—S2—O7	108.7 (2)
C10—N18—Cu6	126.6 (3)	O9—S2—O8	110.7 (2)
C10—N18—N17	108.1 (3)	O9—S2—O10	110.6 (2)
N18—N17—Cu5	125.6 (3)	O10—S2—O7	109.0 (2)
C9—N17—Cu5	127.1 (3)	O10—S2—O8	108.7 (2)
C9—N17—N18	107.2 (3)	H3A—O3—H3B	108 (3)
C9—N19—N20	123.5 (3)	H2C—O2—H2D	106 (3)
C9—N19—C10	106.5 (3)	H6A—O6—H6B	107 (3)
C10—N19—N20	129.9 (3)	H5C—O5—H5D	109 (3)
N19—N20—H20A	108 (3)	H12A—O12—H12B	127 (4)
N19—N20—H20B	106 (3)	H13A—O13—H13B	131 (5)
H20A—N20—H20B	116 (4)	H14C—O14—H14D	110 (3)
N13—N14—Cu5	126.7 (3)	H15A—O15—H15B	123 (4)
C7—N14—Cu5	128.0 (3)	H16A—O16—H16B	123 (4)
C7—N14—N13	105.2 (3)	H17C—O17—H17D	104 (3)
N14—N13—Cu4	123.5 (3)	H18A—O18—H18B	128 (4)
N16—N13—Cu4	126.0 (3)	H19A—O19—H19B	114 (3)
N16—N13—N14	110.0 (3)	H20E—O20—H20F	128 (5)
N13—N16—N15	108.7 (3)	H21A—O21—H21B	108 (3)
C7—N15—N16	106.1 (4)	H11C—O11—H11D	101 (3)
N33—N34—Cu4	124.2 (3)		

Cu2—N45—N46—Cu1	18.6 (5)	N18—C10—C11—C12	41.1 (6)
Cu2—N45—N46—N47	−167.6 (3)	N17—N18—C10—N19	−1.4 (4)
Cu2—N45—C24—N48	167.7 (3)	N17—N18—C10—C11	179.2 (4)
Cu2—N45—C24—C23	−13.0 (6)	N19—C10—C11—C12	−138.1 (4)
Cu2—N42—N41—Cu3	1.6 (4)	N20—N19—C9—N17	177.8 (4)
Cu2—N42—N41—C21	−171.5 (3)	N20—N19—C9—C8	−3.6 (6)
Cu2—N42—C22—N43	171.9 (3)	N20—N19—C10—N18	−176.3 (4)
Cu2—N42—C22—C23	−5.7 (6)	N20—N19—C10—C11	3.0 (7)
Cu2—N5—C3—N7	−176.3 (3)	N14—N13—N16—N15	0.9 (5)
Cu2—N5—C3—C2	1.5 (6)	N14—C7—C8—C9	29.7 (6)
Cu2—N2—N1—Cu1	−4.2 (5)	N13—N14—C7—N15	1.1 (4)
Cu2—N2—N1—N4	177.9 (3)	N13—N14—C7—C8	−177.7 (4)
Cu2—N2—C1—N3	−177.7 (3)	N13—N16—N15—C7	−0.2 (5)
Cu2—N2—C1—C2	0.9 (6)	N16—N15—C7—N14	−0.6 (5)
Cu3—N41—C21—N43	−173.0 (3)	N16—N15—C7—C8	178.2 (4)
Cu3—N41—C21—C20	4.9 (6)	N15—C7—C8—C9	−148.9 (4)
Cu3—N37—N38—Cu4	−4.4 (5)	N34—N33—C18—N36	0.5 (5)

Cu3—N37—N38—N39	174.7 (3)	N34—N33—C18—C17	177.8 (4)
Cu3—N37—C19—N40	−174.6 (3)	N33—N34—N35—N36	0.2 (5)
Cu3—N37—C19—C20	4.2 (6)	N35—N34—N33—Cu5	−175.6 (3)
Cu3—N9—N10—Cu4	12.4 (5)	N35—N34—N33—C18	−0.4 (4)
Cu3—N9—N10—N11	−175.1 (3)	N35—N36—C18—N33	−0.4 (5)
Cu3—N9—C6—N12	175.0 (3)	N35—N36—C18—C17	−177.7 (4)
Cu3—N9—C6—C5	−7.2 (6)	N30—N29—C15—N31	−1.1 (4)
Cu3—N6—N5—Cu2	3.0 (4)	N30—N29—C15—C14	177.7 (4)
Cu3—N6—N5—C3	−173.8 (3)	N30—C16—C17—C18	39.2 (6)
Cu3—N6—C4—N7	173.6 (3)	N29—N30—C16—N31	0.1 (5)
Cu3—N6—C4—C5	−4.6 (6)	N29—N30—C16—C17	−177.9 (4)
Cu4—N38—N39—N40	179.5 (3)	N31—C16—C17—C18	−138.5 (4)
Cu4—N10—N11—N12	172.6 (3)	N32—N31—C15—N29	179.1 (4)
Cu4—N13—N16—N15	−170.6 (3)	N32—N31—C15—C14	0.3 (6)
Cu4—N34—N33—Cu5	10.2 (5)	N32—N31—C16—N30	−178.6 (4)
Cu4—N34—N33—C18	−174.6 (3)	N32—N31—C16—C17	−0.6 (7)
Cu4—N34—N35—N36	174.2 (3)	N26—N25—N28—N27	−0.3 (5)
Cu5—N17—C9—N19	176.3 (3)	N26—C13—C14—C15	32.6 (6)
Cu5—N17—C9—C8	−2.3 (6)	N25—N26—C13—N27	1.0 (5)
Cu5—N14—N13—Cu4	−11.8 (5)	N25—N26—C13—C14	−178.4 (4)
Cu5—N14—N13—N16	176.4 (3)	N25—N28—N27—C13	0.9 (5)
Cu5—N14—C7—N15	−176.5 (3)	N28—N27—C13—N26	−1.1 (5)
Cu5—N14—C7—C8	4.7 (6)	N28—N27—C13—C14	178.2 (4)
Cu5—N33—C18—N36	175.7 (3)	N27—C13—C14—C15	−146.6 (4)
Cu5—N33—C18—C17	−7.0 (6)	C24—N45—N46—Cu1	−172.7 (3)
Cu5—N30—N29—Cu6	7.2 (5)	C24—N45—N46—N47	1.1 (4)
Cu5—N30—N29—C15	−174.5 (3)	C24—C23—C22—N42	34.4 (6)
Cu5—N30—C16—N31	175.1 (3)	C24—C23—C22—N43	−142.9 (4)
Cu5—N30—C16—C17	−2.9 (6)	C22—N42—N41—Cu3	171.9 (3)
Cu6—N21—N22—Cu1	14.9 (5)	C22—N42—N41—C21	−1.2 (4)
Cu6—N21—N22—N23	−171.7 (3)	C22—N43—C21—N41	1.6 (4)
Cu6—N21—C12—N24	171.4 (3)	C22—N43—C21—C20	−176.4 (4)
Cu6—N21—C12—C11	−8.9 (6)	C21—N43—C22—N42	−2.3 (4)
Cu6—N18—N17—Cu5	8.5 (4)	C21—N43—C22—C23	175.3 (4)
Cu6—N18—N17—C9	−173.6 (3)	C21—C20—C19—N37	34.6 (6)
Cu6—N18—C10—N19	174.0 (3)	C21—C20—C19—N40	−146.7 (4)
Cu6—N18—C10—C11	−5.3 (6)	C19—N37—N38—Cu4	−179.8 (3)
Cu6—N29—C15—N31	177.2 (3)	C19—N37—N38—N39	−0.7 (4)
Cu6—N29—C15—C14	−4.0 (6)	C6—N9—N10—Cu4	−172.1 (3)
Cu6—N26—N25—Cu1	−3.3 (5)	C6—N9—N10—N11	0.4 (4)
Cu6—N26—N25—N28	179.4 (3)	C6—C5—C4—N6	36.1 (6)
Cu6—N26—C13—N27	−178.8 (3)	C6—C5—C4—N7	−141.8 (4)
Cu6—N26—C13—C14	1.9 (6)	C4—N6—N5—Cu2	176.1 (3)
Cu1—N46—N47—N48	173.1 (3)	C4—N6—N5—C3	−0.7 (4)
Cu1—N1—N4—N3	−177.7 (3)	C4—N7—C3—N5	0.3 (4)
Cu1—N22—N23—N24	173.1 (3)	C4—N7—C3—C2	−177.5 (4)
Cu1—N25—N28—N27	−177.6 (3)	C3—N7—C4—N6	−0.7 (4)
N45—N46—N47—N48	−1.0 (5)	C3—N7—C4—C5	177.5 (4)

N45—C24—C23—C22	−24.6 (6)	C3—C2—C1—N2	36.9 (6)
N46—N45—C24—N48	−0.8 (5)	C3—C2—C1—N3	−144.8 (4)
N46—N45—C24—C23	178.4 (4)	C1—N2—N1—Cu1	177.2 (3)
N46—N47—N48—C24	0.4 (5)	C1—N2—N1—N4	−0.7 (4)
N47—N48—C24—N45	0.3 (5)	C13—N26—N25—Cu1	176.9 (3)
N47—N48—C24—C23	−179.0 (4)	C13—N26—N25—N28	−0.4 (4)
N48—C24—C23—C22	154.6 (4)	C13—C14—C15—N29	−31.9 (6)
N42—N41—C21—N43	−0.3 (4)	C13—C14—C15—N31	146.7 (4)
N42—N41—C21—C20	177.7 (4)	C15—N31—C16—N30	−0.7 (5)
N41—N42—C22—N43	2.1 (4)	C15—N31—C16—C17	177.3 (4)
N41—N42—C22—C23	−175.5 (4)	C16—N30—N29—Cu6	−177.7 (3)
N41—C21—C20—C19	−39.6 (6)	C16—N30—N29—C15	0.6 (4)
N43—C21—C20—C19	138.1 (4)	C16—N31—C15—N29	1.1 (5)
N44—N43—C22—N42	−174.3 (4)	C16—N31—C15—C14	−177.7 (4)
N44—N43—C22—C23	3.3 (6)	C16—C17—C18—N33	−33.5 (6)
N44—N43—C21—N41	173.0 (4)	C16—C17—C18—N36	143.4 (4)
N44—N43—C21—C20	−5.0 (7)	C18—N36—N35—N34	0.1 (5)
N37—N38—N39—N40	0.3 (5)	C7—N14—N13—Cu4	170.6 (3)
N38—N37—C19—N40	0.8 (4)	C7—N14—N13—N16	−1.2 (4)
N38—N37—C19—C20	179.7 (4)	C7—C8—C9—N17	−31.5 (6)
N38—N39—N40—C19	0.2 (4)	C7—C8—C9—N19	150.1 (4)
N39—N40—C19—N37	−0.6 (5)	C9—N19—C10—N18	0.4 (5)
N39—N40—C19—C20	−179.5 (4)	C9—N19—C10—C11	179.8 (4)
N9—N10—N11—N12	−0.3 (5)	C10—N18—N17—Cu5	−176.0 (3)
N9—C6—C5—C4	−29.7 (6)	C10—N18—N17—C9	1.9 (4)
N10—N9—C6—N12	−0.4 (5)	C10—N19—C9—N17	0.8 (5)
N10—N9—C6—C5	177.4 (4)	C10—N19—C9—C8	179.4 (4)
N10—N11—N12—C6	0.0 (5)	C10—C11—C12—N21	−33.3 (6)
N11—N12—C6—N9	0.3 (5)	C10—C11—C12—N24	146.4 (4)
N11—N12—C6—C5	−177.5 (4)	C12—N21—N22—Cu1	−172.6 (3)
N12—C6—C5—C4	147.8 (4)	C12—N21—N22—N23	0.8 (4)
N6—N5—C3—N7	0.3 (4)	O1B—S1B—O2B—Cu2	−81.0 (4)
N6—N5—C3—C2	178.1 (4)	O1B—S1B—O2B—Cu3	81.9 (4)
N5—N6—C4—N7	0.9 (4)	O1B—S1B—O3B—Cu6	−56.9 (4)
N5—N6—C4—C5	−177.4 (4)	O1B—S1B—O4B—Cu5	68.1 (3)
N5—C3—C2—C1	−38.2 (6)	O2B—S1B—O3B—Cu6	−175.7 (3)
N7—C3—C2—C1	139.2 (4)	O2B—S1B—O4B—Cu5	−173.6 (3)
N8—N7—C4—N6	−176.5 (3)	O3B—S1B—O2B—Cu2	37.5 (4)
N8—N7—C4—C5	1.8 (6)	O3B—S1B—O2B—Cu3	−159.6 (3)
N8—N7—C3—N5	175.8 (4)	O3B—S1B—O4B—Cu5	−51.1 (4)
N8—N7—C3—C2	−2.0 (7)	O4B—S1B—O2B—Cu2	161.6 (3)
N2—N1—N4—N3	0.2 (5)	O4B—S1B—O2B—Cu3	−35.4 (4)
N1—N2—C1—N3	0.9 (5)	O4B—S1B—O3B—Cu6	61.5 (4)
N1—N2—C1—C2	179.5 (4)	O1A—S1A—O2A—Cu2	−47.2 (11)
N1—N4—N3—C1	0.4 (5)	O1A—S1A—O3A—Cu5	74.2 (10)
N4—N3—C1—N2	−0.8 (5)	O1A—S1A—O3A—Cu6	−69.9 (11)
N4—N3—C1—C2	−179.4 (4)	O1A—S1A—O4A—Cu3	75.1 (9)
N21—N22—N23—N24	−0.2 (4)	O2A—S1A—O3A—Cu5	−160.8 (8)

N22—N21—C12—N24	−1.2 (4)	O2A—S1A—O3A—Cu6	55.2 (11)
N22—N21—C12—C11	178.5 (4)	O2A—S1A—O4A—Cu3	−47.2 (11)
N22—N23—N24—C12	−0.5 (4)	O3A—S1A—O2A—Cu2	−171.2 (8)
N23—N24—C12—N21	1.1 (5)	O3A—S1A—O4A—Cu3	−165.6 (8)
N23—N24—C12—C11	−178.6 (4)	O4A—S1A—O2A—Cu2	71.8 (11)
N18—N17—C9—N19	−1.6 (4)	O4A—S1A—O3A—Cu5	−42.8 (11)
N18—N17—C9—C8	179.8 (4)	O4A—S1A—O3A—Cu6	173.1 (8)