Incorporation of in situ generated 3,3′-(sulfanediy1)bis(1-methyl-1,3-imidazolidine-2-thione) into a one-dimensional Cu\(^{1}\) coordination polymer with sulfur-bridged \{Cu\(^{1}\)\(_4\)S\(_{10}\}\)\(_n\) central cores

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The reaction of [Cu(CH\(_3\)CN)\(_4\)](BF\(_4\)) with 1-methyl-1,3-imidazolidine-2-thione [SC\(_3\)H\(_4\)(NMe)NH], under aerobic conditions at room temperature, yielded an unusual one-dimensional coordination polymer, namely, catena-poly[[[(1-methyl-1,3-imidazolidine-2-thione-κ\(S\))copper(I)]·μ-(1-methyl-1,3-imidazolidine-2-thione)-κ\(S\)S-copper(I)-μ-[3,3′-(sulfanediy1)bis(1-methyl-1,3-imidazolidine-2-thione)]·κ\(S\)S,‘S:‘S,‘S] bis(tetrafluoridoborate), \([\{Cu_2(C_4H_8N_2S)_2(C_8H_14N_4S_3)\}(BF_4)_2\]\(_n\) or \([Cu_4(k^1:L^1—N—S—N—L^1)_2(k^1:L^1—NH)_2(k^2:L^1—NH)_2]^n−(BF_4)_{4n}\) \([L^1 = SC_3H_4(NMe)NH] with sulfur-bridged \{Cu\(^{1}\)\(_4\)S\(_{10}\}\)\(_n\) central cores. The in situ generated bis(1-methyl-1,3-imidazolidinyl-2-thione) sulfide [[SC\(_3\)H\(_4\)(NMe)NNS(NMe)C\(_3\)H\(_4\)S; abbrev. \(L^1—N—S—N—L^1\)] ligand, in combination with 1-methyl-1,3-imidazolidine-2-thione \((L^1—NH)\) ligands, construct this coordination polymer. Each Cu\(^{1}\) ion is bonded to four sulfur donor atoms in a distorted tetrahedral geometry and the formation of this polymer solely by sulfur donor atoms with \{Cu\(^{1}\)\(_4\)S\(_{10}\}\)\(_n\) central cores, is the first such example in copper–heterocyclic-2-thione chemistry.

1. Chemical context

The coordination chemistry of the coinage metals (Cu–Au) with heterocyclic-2-thione ligands (Fig. 1) is of considerable interest as these metals exhibit a wide range of coordination geometries, giving rise to coordination compounds of differing nuclearity, namely, mononuclear, homo- and hetero-bridged di-nuclear, clusters and coordination polymers (Lobana, 2021; Raper, 1994, 1996, 1997; García-Vázquez et al., 1999). It has been noted that coordination compounds of these metals have displayed promising bio-activity and, in addition, several copper-based reactions are involved in the activation of C=S (thione) bonds (Lobana, 2021).

As part of our ongoing studies in this area, we now describe the synthesis and structure of the title coordination polymer, 1.
2. Structural commentary

The analytical data of the colourless crystals (see Synthesis and crystallization) correspond to the empirical composition C_{16}H_{30}B_{2}Cu_{2}F_{8}N_{8}S_{5} and its crystal structure revealed the formation of an unusual coordination polymer, \( [\text{Cu}_{4}(\text{L}^1)_{2}(\text{L}^1)_{2}(\text{L}^1)]^{8}\) where \( \text{L}^1 = \text{SC}_{3}H_{4}(\text{NMe}) \). There is in situ generation of a new thio-ligand, namely, bis(1-methyl-1,3-imidazolidinyl-2-thione) sulfide \( [\text{SC}_{3}H_{4}(\text{NMe})] \) in which a sulfur atom connects two —NH groups of two imidazolidine rings. Fig. 2 shows the bonding patterns of \( \text{L}^1 — \text{NH} \), and the new thio-ligand, in the polymer 1.

The construction of the polymer 1 is believed to occur as represented in Fig. 3. Here the basic repeat unit is A, which is shown in a simplified way as unit B (omitting the imidazolidine rings). Two such B units combine to form a tetranuclear unit C, a basic building block, to construct the polymer 1. The building block C exhibits all three patterns of ligand bonding as represented in Fig. 2. The crystals of the polymer are

![Figure 1](image1.png)

Figure 1
A selected list of heterocyclic-2-thiones.

![Figure 2](image2.png)

Figure 2
Bonding pattern of 1-methyl-1,3-imidazodine-2-thione and its in situ generated bis(1-methyl-1,3-imidazolidinyl-2-thione)sulfide.

Table 1
Selected geometric parameters (Å, °).

| Bond | Distance/Angle | Cu1—S1 | 2.2590 (10) | Cu2—S5 | 2.2696 (11) |
|------|---------------|--------|-------------|--------|-------------|
| Cu1—S2 | 2.2997 (10) | Cu1—S3 | 2.3423 (10) | Cu2—S3\(^\ddagger\) | 2.4364 (11) |
| Cu1—S4 | 2.4162 (10) | Cu1—Cu2\(^\ddagger\) | 2.9074 (8) | S1—Cu1—S2 | 131.86 (4) |
| S1—Cu1—S3 | 105.12 (4) | S1—Cu2—S3\(^\ddagger\) | 109.15 (4) | S1—Cu2—S4 | 142.66 (4) |
| S2—Cu1—S3 | 102.79 (4) | S1—Cu2—S2\(^\ddagger\) | 105.31 (4) | S1—Cu2—S4 | 102.47 (4) |
| S3—Cu1—S4 | 89.72 (4) | S1—Cu2—S2\(^\ddagger\) | 114.68 (4) | S1—Cu1—S2 | 114.68 (4) |
| S4—Cu1—S1 | 131.86 (4) | S1—Cu2—S2\(^\ddagger\) | 100.47 (4) |

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

The contents of the asymmetric unit. N—H ⋅⋅⋅F hydrogen bonds are shown as dashed lines. Atomic displacement parameters are drawn at the 30% probability level.

![Figure 3](image3.png)

Figure 3
The basic repeating unit, A; the basic repeating unit with imidazolidine rings omitted, B; the tetranuclear unit, C; a part of the polymer, D.

![Figure 4](image4.png)

Figure 4
The tetranuclear repeating unit. H atoms and BF\(_4^−\) anions are omitted for clarity.
rise to a tetranuclear moiety as shown in Figs. 2 and 5. The chains of the polymer are hydrogen bonded to BF₄⁻ ions lying between the chains by multiple weak C–H⋯F interactions as shown in Fig. 6 and listed in Table 2.

CuI is bonded to four sulfur donor atoms (S1–S4) (Table 1). Here the thione (C=S) sulfur donor atoms are more strongly bonded relative to the sulfur atom of the –N–S–N– moiety. The Cu2–S2 and Cu2–S3 bond distances are the longest, while the other two Cu2–S1 and Cu2–S5 distances are short, and comparable to the Cu1–sulfur (S1–S3) bond distances, as noted above. The Cu⋯Cu separation of 2.9074 (8) Å, does not reveal any metal–metal interaction (the sum of the van der Waals radii of the Cu atoms is 2.80 Å; Huheey, 1993). Finally, the geometry about Cu1 is significantly distorted from a regular tetrahedron, as revealed by the S–Cu1–S bond angles, which fall in the range 89.72 (4) to 100.47 (4)°–122.65 (4)° (Okuniwski et al., 2015); in comparison, the geometry of Cu2 is less distorted, with S–Cu2–S bond angles in the range 91.53 (4)°–107.08 (4)°. The Cu–S bond distances fall in the range 2.31 (4)–2.59 (4) Å and this is illustrated by the r2 parameter of 0.725 (Okuniwski et al., 2015). Finally, the geometry about Cu1 is significantly distorted from a regular tetrahedron, as revealed by the S–Cu1–S bond angles, which fall in the range 89.72 (4) to 100.47 (4)°–122.65 (4)° (Okuniwski et al., 2015); in comparison, the geometry of Cu2 is less distorted, with S–Cu2–S bond angles in the range 91.53 (4)°–107.08 (4)°. The Cu–S bond distances fall in the range 2.31 (4)–2.59 (4) Å and this is illustrated by the r2 parameter of 0.725 (Okuniwski et al., 2015).

The in situ formation of the new thio-ligand appears in line with the metal-mediated variable chemical activity of N,S-donor thio-ligands, such as the activation of C=S (thione) bonds (Lobana, 2021; Lobana et al., 2010), as well as the activation of C–H and N–H bonds (Lobana et al., 2012, 2007, 2008). The oxidation of heterocyclic-2-thiones such as benzox-1,3-thiazoline-2-thione, pyridine-2-thione, pyrimidine-2-thione, 1,3-imidazolidine-2-thione, quinoline-2-thione, 1,3,4-thiadiazole-2,5-dithiazine and benzo-1,3-thiazoline-2-thione to their disulfides/trisulfides, followed by coordination to the metal ions, has been reported previously (Raper, 1994; Lobana, 2021). In the present case, in relation to the activation of C=S (thione) bonds, in situ generated thio-ligands, A–F, have been reported (Lobana, 2021; Raper, 1994; Ferrari et al., 1981; Kadooka et al., 1976; Simmons et al., 1979; Jeannin et al., 1979) (Fig. 7). In the E and F ligands, R is 2-pyridyl-, 2-pyrimidyl-, etc. and these have C=S (n = 2, 3) groups, connecting the heterocyclic rings. In the ligand G, there is one N–S–N connecting group, two thione groups, and thus it is a new and different ligand.

Figure 6
Packing viewed along the b-axis direction. N–H⋯F hydrogen bonds and C–H⋯F interactions shown as dashed lines.

Figure 7
In situ generated thio-ligands, A–G in heterocyclic-2-thione chemistry.
3. Supramolecular features

The BF₄⁻ ions lying between the chains are involved in interactions with various N—H and C—H hydrogen atoms of the thio-ligands (Figs. 4 and 6). Consider the dimeric unit shown in Fig. 4. Here the N11—H hydrogen atom interacts with the F12 and F12A fluorine atoms of one BF₄⁻ anion while the N51—H hydrogen atom interacts with the F23 fluorine atom of the second BF₄⁻ ion. Various other F atoms of both BF₄⁻ ions accept C—H···F interactions from the imidazolidine ring and the N-methyl group. The distances and angles involving hydrogen-bond interactions are shown in Table 2. In summary, the distances and angles are given as follows: N···F = 2.74 (2)—2.764 (11) Å, H···F = 2.12—2.15 Å, and N···H···F = 124—129°; C···F = 2.93 (2)—3.57 (2) Å; H···F = 2.09—2.64 Å; C···H···F = 111—170°. The N···F distances are less than the sum of van der Waals radii of N and F, namely, 3.05 to 3.15 Å, and likewise the C···F distances are either less than or comparable to the sum of van der Waals radii of C and F, namely, 3.15 to 3.30 Å (Huheey et al., 1983).

4. Database survey

In the light of the novelty of thio-ligands under discussion, a few examples of coordination compounds of pyridine-2-thione, pyrimidine-2-thione, dibenzothiophene, and 1,3-imidazolidine-2-thiones, are delineated here (Fig. 1). For example, pyridine-2-thione (pytH) in combination with copper(I) halides has formed a variety of coordination compounds: namely, mononuclear [CuX(k′S-pytH)(PPh₃)₂](X = Cl, Br, iodine), [Cu₂Br₂(μ-S-pytH)(PPh₃)₂], [Cu₂Br₂(μ-P, P-dpep)₃(k′S-pytH)₂](dppe = Ph₂P-CH₂-CH₂-PPh₂), [Cu₃(μ-S-pytH)(k′S-pytH)]₄(X = Br, Cl), [Cu₂I₂(μ-pytH)(k′S-pytH)]₃ and trinuclear, [Cu₃I₃(μ-P, P-dpep)₃(k′S-pytH)] (Lobana et al., 1989, 2002; Karagiannis et al., 1989; Cox et al., 2000; Stergioudis et al., 1987; Mentzafos et al., 1989; Davies et al., 1997; Lobana et al., 2003).

The examples of coordination polymers include a hexanuclear linear polymer, [Cu₆(μ₃-S-pytH)₆(μ₄-S-pytH)₂(L₄)(μ-I)₂]ₙ, 2nCH₃CN, pyrimidine-2-thione (pytH) and 2,4-dithiouracil (dtucH₂) based linear Cu(I) chain polymers, [Cu(μ-N,S-pytH)₄X₄](X = Cl, Br, I), imidazolinediene-2-thione (imidH₂) based polymers, [[Cu₄(μ₃-S-imdtH₂)₂(μ₄-S-imdtH₂)₄(X₄)(μ-X)₄]ₙ(X = Cl, Br, I, halogen bridged), [Cu₄(μ₃-S-imdtH₂)₄(μ₄-S-imdtH₂)₂(μ-I)₁]₄, (sulfur-bridged), and an octanuclear polymer, [Cu₈(μ₃-S-imdtH₂)₂(μ₄-S-imdtH₂)₄(k′-CH₃)₄], N-Phenyl-1,3-imidazoline-2-thione also forms a linear chain polymer, [Cu₄I₄(imdtH-PyH)₄]ₙ, with alternate CuI₂ and CuS₄ dimeric units forming the chains (Lobana et al., 2003, 2005, 2006, 2009; Li et al., 2005; Sultana et al., 2010; Aulakh et al., 2017).

In the literature, there are limited reports with complexes of ionic copper(I) salts, and the reported mono-, di-nuclear and trinuclear complexes have BF₄⁻, ClO₄⁻, PF₆⁻ etc., outside the metal coordination sphere (Lobana, 2021). The present study provides a basic background to develop a new class of polymers using copper(I) ionic salts with heterocyclic-2-thiones.

5. Synthesis and crystallization

All solvents were of HPLC grade and were stored over molecular sieves. The precursor, tetrakis(acetonitrile)copper(I) tetrafluoroborate, [Cu(CH₃CN)₄][BF₄]₂, was prepared by the slow addition of HBF₄ acid (from boric acid H₃BO₃ + HF acid in a plastic beaker) to a solution of CuO (0.200 g; 1.4 mmol) in dry acetonitrile (25 ml) in a round-bottom flask. The mixture slowly became colourless and a white salt settled in the flask. The mother liquor was removed and the salt was extracted with diethyl ether, followed by evaporation, which gave solid [Cu(CH₃CN)₄][BF₄].

**Synthesis of 1-methyl-1,3-imidazolidine-2-thione**

Carbon disulfide (4.1 ml, 76 mmol) was added to a cooled solution of 1-methyl-ethylenediamine (CH₃-NH-CH₂-CH₂-NH₂) (3 ml, 35 mmol) in dry acetonitrile (25 ml) in a round-bottom flask. The mixture was stirred for about half an hour, giving rise to the formation of a clear pale-yellow solution. It was further refluxed for one h, and placed for cooling, and precipitate formed was filtered and washed with cold acetone. Colour: white. Yield: 1.15 g, 50%; m.p. 351–354 K.

**Synthesis of 1**

To a solution of [Cu(CH₃CN)₄][BF₄]₂ (0.050 g, 0.15 mmol) in methanol (10 ml) was added a solution of the thio-ligand, SC₃H₇(NMe)NH (0.036 g, 0.31 mmol) in methanol. The mixture was stirred for about half an hour, giving rise to the formation of a clear pale-yellow solution. It was kept undisturbed for evaporation at room temperature. The colour of the solution turned green and a colourless crystalline compound was formed at the bottom, which was separated and dried at room temperature. Yield: 0.025 g; 40%; m.p. 450–452 K. Analysis found: C 24.14; H 3.77; N 14.08; S 20.50; C 24.52; H 3.69; N 13.87; S 20.50; Si 10.56; B 5.01; N 0.98; C 1686B₂Cu₂F₂N₄S₅ requires: C 24.14; H 3.77; N 14.08; S 20.11.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. All hydrogen atoms were placed geometrically and refined as riding atoms with Uiso(H) = 1.2Ueq(C) or 1.5Ueq(methyl C). Both BF₄ anions and one imidazoline ring are disordered over two sets of sites with occupancy ratios of 0.66 (2)/0.34 (2), 0.72 (2)/0.28 (2), and 0.622 (6)/0.378 (6), respectively.
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Table 3

| Crystal data | Chemical formula | 
|--------------|------------------|
| ***M***<sub>c</sub> | \([\text{Cu}_2(\text{C}_4\text{H}_8\text{N}_2\text{S})_2(\text{C}_8\text{H}_14\text{N}_4\text{S}_3)]^-\text{(BF}_4\text{)}_2\) |
| Crystal system, space group | Monoclinic, *P2_1/c* |
| Temperature (K) | 100 |
| *a*, *b*, *c* (Å) | 19.0636 (7), 13.6989 (3), 11.5770 (4) |
| β (°) | 101.734 (3) |
| V (Å<sup>3</sup>) | 2960.16 (17) |
| Z | 4 |
| Radiation type | *Mo Kα* |
| μ (mm<sup>-1</sup>) | 1.87 |
| Crystal size (mm<sup>2</super>) | 0.32 × 0.24 × 0.16 |

Data collection

| 
| Diffractometer |
|----------------|
| Xcalibur, Eos, Gemini Multi-scan (CrysAlis PRO) |

| 
| Absorption correction |
|-----------------------|
| Xcalibur, Eos, Gemini Multi-scan (CrysAlis PRO) |

| 
| No. of measured, independent and observed | *F* *σ*(*)*I* |
|------------------------------------------|------------------|
| reflections | 33195, 8277, 7139 |

| 
| R(int) | 0.032 |
| Δρ<sub>max</sub> | 1.91 |
| Δρ<sub>min</sub> | -1.29 |

| 
| H-atom treatment |
|-------------------|
| H-atom parameters constrained |

Computer programs: *CrysAlis PRO* and *CrysAlis RED* (Rigaku, 2019), *SHELXT* (Sheldrick, 2015a), *SHELXL2018/3* (Sheldrick, 2015b) and *SHELXTL* (Sheldrick, 2008).

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Incorporation of *in situ* generated 3,3′-(sulfanediyl)bis(1-methyl-1,3-imidazolidine-2-thione) into a one-dimensional Cu¹ coordination polymer with sulfur-bridged \{Cu¹S₁₀\}ₙ central cores

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Computing details

Data collection: *CrysAlis PRO* (Rigaku, 2019); cell refinement: *CrysAlis PRO* (Rigaku, 2019); data reduction: *CrysAlis RED* (Rigaku, 2019); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015b); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

catena-Poly[[[(1-methyl-1,3-imidazolidine-2-thione-κS)copper(I)]-μ-(1-methyl-1,3-imidazolidine-2-thione)-κ²S:S-copper(I)-μ-[3,3′-(sulfanediyl)bis(1-methyl-1,3-imidazolidine-2-thione)]-κ⁵S,S′,S″:S,S′′]bis(tetrafluoridoborate)]

Crystal data

[\(\text{Cu}_2(\text{C}_4\text{H}_8\text{N}_2\text{S})_2(\text{C}_8\text{H}_{14}\text{N}_4\text{S}_3)(\text{BF}_4)_2\)]

\(M_r = 795.48\)

Monoclinic, \(P2_1/c\)

\(a = 19.0636 (7)\) Å

\(b = 13.6989 (3)\) Å

\(c = 11.5770 (4)\) Å

\(β = 101.734 (3)^\circ\)

\(V = 2960.16 (17)\) Å³

\(Z = 4\)

\(F(000) = 1608\)

\(D_x = 1.785\) Mg m⁻³

Mo \(Kα\) radiation, \(λ = 0.71073\) Å

Cell parameters from 11503 reflections

\(θ = 3.1–32.3^\circ\)

\(μ = 1.87\) mm⁻¹

\(T = 100\) K

Chunk, colorless

0.32 × 0.24 × 0.16 mm

Data collection

Xcalibur, Eos, Gemini diffractometer

Detector resolution: 16.1500 pixels mm⁻¹

Absorption correction: multi-scan

(CrysAlisPro; Rigaku, 2019)

\(T_{\text{min}} = 0.673, T_{\text{max}} = 1.000\)

33195 measured reflections

8277 independent reflections

7139 reflections with \(I > 2σ(I)\)

\(R_{\text{int}} = 0.032\)

\(θ_{\text{max}} = 29.6^\circ, θ_{\text{min}} = 3.1^\circ\)

\(h = -26 → 26\)

\(k = -17 → 19\)

\(l = -16 → 16\)

Refinement

Refinement on \(F^2\)

Least-squares matrix: full

\(R[F^2 > 2σ(F^2)] = 0.055\)

\(wR(F^2) = 0.138\)

\(S = 1.09\)

8277 reflections

506 parameters

497 restraints

Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained

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 twin.

Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

| Atom | x     | y     | z     | Uiso*/Ueq | Occ. (<1) |
|------|-------|-------|-------|-----------|-----------|
| Cu1  | 0.17200 (3) | 0.29294 (3) | 0.41072 (4) | 0.02467 (12) |           |
| Cu2  | 0.19437 (3) | 0.17473 (4) | 0.67264 (5) | 0.03398 (14) |           |
| S1   | 0.10220 (5) | 0.21261 (7) | 0.51531 (8) | 0.02188 (18) |           |
| C11  | 0.05713 (19) | 0.2930 (3) | 0.5887 (3) | 0.0239 (7) |           |
| N11  | 0.0615 (2) | 0.3899 (3) | 0.5829 (4) | 0.0330 (8) |           |
| H11A | 0.083532 | 0.421452 | 0.534404 | 0.040* |           |
| C12  | 0.0247 (3) | 0.4373 (4) | 0.6680 (5) | 0.0490 (13) |           |
| H12A | −0.006637 | 0.491000 | 0.630846 | 0.059* |           |
| H12B | 0.059362 | 0.462956 | 0.736785 | 0.059* |           |
| C13  | −0.0185 (3) | 0.3537 (4) | 0.7028 (5) | 0.0476 (13) |           |
| H13A | −0.014559 | 0.351379 | 0.789336 | 0.057* |           |
| H13B | −0.069603 | 0.359160 | 0.663905 | 0.057* |           |
| C14  | −0.0110 (19) | 0.1701 (4) | 0.6768 (6) | 0.0540 (15) |           |
| H14A | 0.021727 | 0.121783 | 0.654344 | 0.081* |           |
| H14B | −0.058844 | 0.161726 | 0.627217 | 0.081* |           |
| H14C | −0.013555 | 0.160793 | 0.759755 | 0.081* |           |
| C21  | 0.16050 (5) | 0.44336 (7) | 0.32065 (8) | 0.02344 (18) |           |
| C22  | 0.2452 (2) | 0.4870 (3) | 0.3691 (3) | 0.0220 (7) |           |
| C23  | 0.30019 (17) | 0.4367 (2) | 0.4393 (3) | 0.0230 (6) |           |
| C24  | 0.3681 (2) | 0.4915 (3) | 0.4478 (4) | 0.0295 (8) |           |
| H22A | 0.396466 | 0.466287 | 0.391463 | 0.035* |           |
| H22B | 0.397611 | 0.489061 | 0.528730 | 0.035* |           |
| H23A | 0.339174 | 0.633096 | 0.486565 | 0.040* |           |
| H23B | 0.370330 | 0.627624 | 0.367087 | 0.040* |           |
| N22  | 0.26779 (19) | 0.5744 (2) | 0.3468 (3) | 0.0265 (7) |           |
| C24  | 0.2230 (3) | 0.6540 (3) | 0.2916 (4) | 0.0328 (9) |           |
| H24A | 0.183100 | 0.627598 | 0.232845 | 0.049* |           |
| H24B | 0.251451 | 0.698081 | 0.252849 | 0.049* |           |
| H24C | 0.204067 | 0.689934 | 0.351782 | 0.049* |           |
| S3   | 0.20669 (5) | 0.17479 (7) | 0.28720 (9) | 0.02339 (18) |           |
| C31  | 0.29663 (18) | 0.1774 (3) | 0.3396 (3) | 0.0196 (6) |           |
### Supporting Information

| Atom | U1     | U2     | U3     | U12    | U13    | U23   |
|------|--------|--------|--------|--------|--------|-------|
| N31  | 0.33350 (16) | 0.2506 (2) | 0.4087 (3) | 0.0208 (6) |
| C32  | 0.4110 (2)    | 0.2266 (4) | 0.4393 (4) | 0.0351 (9) |
| H32A | 0.427437      | 0.218752   | 0.525530   | 0.042*   |
| H32B | 0.440017      | 0.277800   | 0.410917   | 0.042*   |
| C33  | 0.4152 (2)    | 0.1304 (3) | 0.3749 (4) | 0.0353 (10) |
| H33A | 0.444575      | 0.137149   | 0.315261   | 0.042*   |
| H33B | 0.435200      | 0.078091   | 0.431056   | 0.042*   |
| N32  | 0.34084 (19)  | 0.1094 (3) | 0.3188 (3) | 0.0296 (7) |
| C34  | 0.3211 (3)    | 0.0212 (3) | 0.2520 (4) | 0.0391 (11) |
| H34A | 0.272500      | 0.027972   | 0.204794   | 0.059*   |
| H34B | 0.322777      | −0.034105  | 0.306143   | 0.059*   |
| C34C | 0.354725      | 0.009827   | 0.199567   | 0.059*   |
| S4   | 0.29655 (5)   | 0.32490 (6) | 0.49486 (8) | 0.02048 (17) |
| S5   | 0.30419 (5)   | 0.12584 (7) | 0.64829 (8) | 0.02327 (18) |
| C51  | 0.3161 (4)    | 0.0135 (4) | 0.5964 (6) | 0.0248 (12) | 0.622 (6) |
| N51  | 0.3829 (4)    | −0.0246 (5) | 0.6150 (7) | 0.0386 (14) | 0.622 (6) |
| H51A | 0.421277      | 0.005232   | 0.654537   | 0.046*   | 0.622 (6) |
| C52  | 0.3383 (4)    | −0.1209 (5) | 0.5618 (8) | 0.0435 (16) | 0.622 (6) |
| H52A | 0.406344      | −0.169866  | 0.620714   | 0.052*   | 0.622 (6) |
| H52B | 0.409746      | −0.119777  | 0.495817   | 0.052*   | 0.622 (6) |
| C53  | 0.3053 (6)    | −0.1418 (8) | 0.5183 (14)| 0.0364 (17) | 0.622 (6) |
| H53A | 0.295008      | −0.158421  | 0.433318   | 0.044*   | 0.622 (6) |
| H53B | 0.289407      | −0.196357  | 0.562912   | 0.044*   | 0.622 (6) |
| N52  | 0.2695 (3)    | −0.0493 (4) | 0.5398 (5) | 0.0325 (12) | 0.622 (6) |
| C54  | 0.1936 (4)    | −0.0347 (6) | 0.4976 (7) | 0.0364 (16) | 0.622 (6) |
| H54A | 0.181113      | 0.032894   | 0.512284   | 0.055*   | 0.622 (6) |
| H54B | 0.166873      | −0.079161  | 0.539145   | 0.055*   | 0.622 (6) |
| H54C | 0.181205      | −0.048104  | 0.412704   | 0.055*   | 0.622 (6) |
| C51A | 0.2840 (6)    | 0.0129 (8) | 0.5822 (11)| 0.0267 (18) | 0.378 (6) |
| N51A | 0.2168 (6)    | −0.0181 (7) | 0.5374 (10)| 0.0333 (19) | 0.378 (6) |
| H51B | 0.177838      | 0.012996   | 0.546084   | 0.040*   | 0.378 (6) |
| C52A | 0.2167 (7)    | −0.1106 (8) | 0.4719 (12)| 0.041 (2)  | 0.378 (6) |
| H52C | 0.200468      | −0.100562  | 0.385886   | 0.049*   | 0.378 (6) |
| H52D | 0.185884      | −0.160175  | 0.498967   | 0.049*   | 0.378 (6) |
| C53A | 0.2945 (9)    | −0.1396 (13)| 0.502 (3)  | 0.038 (2)   | 0.378 (6) |
| H53C | 0.301324      | −0.198020  | 0.553806   | 0.046*   | 0.378 (6) |
| H53D | 0.313059      | −0.153626  | 0.430208   | 0.046*   | 0.378 (6) |
| N52A | 0.3305 (5)    | −0.0534 (7) | 0.5651 (9) | 0.0344 (16) | 0.378 (6) |
| C54A | 0.4056 (6)    | −0.0555 (11)| 0.6164 (15)| 0.044 (3)   | 0.378 (6) |
| H54D | 0.423838      | 0.011507   | 0.627346   | 0.066*   | 0.378 (6) |
| H54E | 0.431180      | −0.090733  | 0.563981   | 0.066*   | 0.378 (6) |
| H54F | 0.413072      | −0.088521  | 0.693007   | 0.066*   | 0.378 (6) |
| B1   | 0.1527 (3)    | 0.6462 (4) | 0.6039 (5) | 0.0388 (12) | 0.662 (12) |
| B2   | 0.5451 (3)    | 0.1715 (4) | 0.7345 (5) | 0.0456 (14) | 0.662 (12) |
| F11  | 0.1661 (5)    | 0.6294 (6) | 0.7267 (5) | 0.0572 (16) | 0.662 (12) |
| F12  | 0.1231 (8)    | 0.5666 (8) | 0.5451 (12)| 0.094 (3)   | 0.662 (12) |
| F13  | 0.2172 (5)    | 0.6656 (7) | 0.5761 (9) | 0.0743 (18) | 0.662 (12) |
| F14  | 0.1088 (5)    | 0.7262 (5) | 0.5796 (7) | 0.0744 (18) | 0.662 (12) |
### Atomic displacement parameters (Å²)

| Atom   | U₁₁   | U₂₂   | U₃₃   | U₁₂   | U₁₃   | U₂₃   |
|--------|-------|-------|-------|-------|-------|-------|
| Cu1    | 0.0257(2) | 0.0236(2) | 0.0267(2) | 0.00048(17) | 0.01001(18) | 0.00126(18) |
| Cu2    | 0.0295(3) | 0.0422(3) | 0.0289(3) | 0.0125(2) | 0.0030(2) | −0.0037(2) |
| S1     | 0.0228(4) | 0.0213(4) | 0.0222(4) | −0.0001(3) | 0.0059(3) | 0.0007(3) |
| C11    | 0.0178(16) | 0.0312(19) | 0.0220(17) | 0.0025(14) | 0.0022(13) | 0.0023(14) |
| N11    | 0.0318(18) | 0.0260(17) | 0.043(2) | 0.0039(14) | 0.0112(16) | −0.0041(15) |
| C12    | 0.044(3) | 0.052(3) | 0.048(3) | 0.014(2) | 0.005(2) | −0.02(3) |
| C13    | 0.043(3) | 0.068(4) | 0.037(2) | 0.025(3) | 0.019(2) | 0.004(2) |
| N12    | 0.0274(17) | 0.047(2) | 0.0311(18) | 0.0093(16) | 0.0150(14) | 0.0086(16) |
| C14    | 0.039(3) | 0.059(3) | 0.069(4) | 0.000(2) | 0.024(3) | 0.028(3) |
| S2     | 0.0247(4) | 0.0210(4) | 0.0253(4) | 0.0036(3) | 0.0067(3) | 0.0002(3) |
| C21    | 0.0309(19) | 0.0174(15) | 0.0181(15) | 0.0016(13) | 0.0066(13) | −0.0008(13) |
| N21    | 0.0261(15) | 0.0173(13) | 0.0251(15) | −0.0037(11) | 0.0043(12) | 0.0003(12) |
| C22    | 0.030(2) | 0.0273(19) | 0.030(2) | −0.0064(15) | 0.0027(16) | 0.0010(16) |
| C23    | 0.041(2) | 0.0226(18) | 0.035(2) | −0.0088(17) | 0.0040(18) | −0.0011(16) |
| N22    | 0.0377(19) | 0.0178(14) | 0.0245(16) | −0.0016(13) | 0.0071(14) | −0.0009(12) |
| C24    | 0.048(3) | 0.0207(18) | 0.031(2) | 0.0043(17) | 0.0121(19) | 0.0037(15) |
| S3     | 0.0260(4) | 0.0188(4) | 0.0248(4) | −0.0012(3) | 0.0036(3) | −0.0024(3) |
| C31    | 0.0221(16) | 0.0192(15) | 0.0183(15) | 0.0023(12) | 0.0059(13) | 0.0053(12) |
| N31    | 0.0217(14) | 0.0207(14) | 0.0205(14) | 0.0014(11) | 0.0053(11) | 0.0020(11) |
| C32    | 0.0212(19) | 0.044(2) | 0.040(2) | 0.0056(17) | 0.0049(17) | 0.001(2) |
| C33    | 0.031(2) | 0.034(2) | 0.044(2) | 0.0103(17) | 0.0145(19) | 0.0108(19) |
| N32    | 0.0371(19) | 0.0249(16) | 0.0289(17) | 0.0091(14) | 0.0119(14) | 0.0014(13) |
| C34    | 0.063(3) | 0.0231(19) | 0.035(2) | 0.0112(19) | 0.019(2) | −0.0022(17) |
| S4     | 0.0255(4) | 0.0190(4) | 0.0172(4) | −0.0005(3) | 0.0049(3) | 0.0012(3) |
| S5     | 0.0251(4) | 0.0208(4) | 0.0252(4) | −0.0006(3) | 0.0082(3) | −0.0019(3) |
| C51    | 0.037(3) | 0.018(2) | 0.024(3) | 0.002(2) | 0.018(3) | 0.003(2) |
| N51    | 0.039(3) | 0.027(3) | 0.054(3) | 0.008(2) | 0.018(3) | −0.004(3) |
| C52    | 0.055(3) | 0.030(3) | 0.048(3) | 0.013(3) | 0.017(3) | −0.003(3) |
| C53    | 0.059(4) | 0.020(3) | 0.034(4) | 0.003(3) | 0.020(3) | −0.003(3) |
| N52    | 0.048(3) | 0.019(2) | 0.032(2) | 0.005(2) | 0.011(2) | −0.0053(19) |
| C54    | 0.048(4) | 0.034(4) | 0.026(4) | −0.006(3) | 0.005(3) | −0.004(3) |
| C51A   | 0.039(4) | 0.019(3) | 0.026(3) | 0.001(3) | 0.016(4) | 0.004(3) |
### Geometric parameters (Å, °)

| Bond/Separation | Distance/Angle |
|-----------------|----------------|
| Cu1—S1          | 2.2590 (10)    |
| Cu1—S2          | 2.2997 (10)    |
| Cu1—S3          | 2.3423 (10)    |
| Cu1—S4          | 2.4162 (10)    |
| Cu1—Cu2         | 2.9074 (8)     |
| Cu2—S5          | 2.2696 (11)    |
| Cu2—S1          | 2.3179 (11)    |
| Cu2—S3          | 2.4364 (11)    |
| Cu2—S2          | 2.5338 (11)    |
| S1—C11          | 1.723 (4)      |
| C11—N12         | 1.319 (5)      |
| C11—N11         | 1.333 (5)      |
| N11—C12         | 1.471 (6)      |
| N11—H11A        | 0.8800         |
| C12—C13         | 1.512 (8)      |
| C12—H12A        | 0.9900         |
| C12—H12B        | 0.9900         |
| C13—N12         | 1.477 (6)      |
| C13—H13A        | 0.9900         |
| C13—H13B        | 0.9900         |
| N12—C14         | 1.442 (6)      |
| C14—H14A        | 0.9800         |

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| Bond                  | Distance (Å) | Bond                  | Distance (Å) |
|-----------------------|--------------|-----------------------|--------------|
| C14—H14B              | 0.9800       | C52A—H52C             | 0.9900       |
| C14—H14C              | 0.9800       | C52A—H52D             | 0.9900       |
| S2—C21                | 1.706 (4)    | C53A—N52A             | 1.481 (12)   |
| C21—N22               | 1.317 (5)    | C53A—H53C             | 0.9900       |
| C21—N21               | 1.373 (5)    | C53A—H53D             | 0.9900       |
| N21—C22               | 1.482 (5)    | N52A—C54A             | 1.434 (12)   |
| N21—S4                | 1.669 (3)    | C54A—H54D             | 0.9800       |
| C22—C23               | 1.516 (6)    | C54A—H54E             | 0.9800       |
| C22—H22A              | 0.9900       | C54A—H54F             | 0.9800       |
| C22—H22B              | 0.9900       | B1—F11A               | 1.323 (12)   |
| C23—N22               | 1.475 (5)    | B1—F12                | 1.347 (9)    |
| C23—H23A              | 0.9900       | B1—F13                | 1.358 (9)    |
| C23—H23B              | 0.9900       | B1—F12A               | 1.365 (13)   |
| N22—C24               | 1.450 (5)    | B1—F14                | 1.374 (8)    |
| C24—H24A              | 0.9800       | B1—F13A               | 1.387 (13)   |
| C24—H24B              | 0.9800       | B1—F11                | 1.411 (8)    |
| C24—H24C              | 0.9800       | B1—F14A               | 1.419 (12)   |
| S3—C31                | 1.699 (4)    | B2—F21A               | 1.349 (13)   |
| C31—N32               | 1.312 (5)    | B2—F24                | 1.374 (8)    |
| C31—N31               | 1.381 (5)    | B2—F21                | 1.387 (8)    |
| N31—C32               | 1.484 (5)    | B2—F24A               | 1.388 (13)   |
| N31—S4                | 1.678 (3)    | B2—F22                | 1.390 (8)    |
| C32—C33               | 1.524 (6)    | B2—F23A               | 1.400 (13)   |
| C32—H32A              | 0.9900       | B2—F22A               | 1.400 (13)   |
| C32—H32B              | 0.9900       | B2—F23                | 1.403 (8)    |
| C33—N32               | 1.464 (6)    | F11—F11A              | 0.512 (15)   |
| C33—H33A              | 0.9900       | F13—F13A              | 0.514 (17)   |
| C33—H33B              | 0.9900       | F14—F14A              | 0.758 (14)   |
| N32—C34               | 1.442 (5)    | F22—F22A              | 0.554 (15)   |
| C34—H34A              | 0.9800       | F23—F23A              | 0.626 (15)   |
| C34—H34B              | 0.9800       | F24—F24A              | 0.571 (15)   |
| S1—Cu1—S2             | 131.86 (4)   | C51—N51—H51A          | 124.0        |
| S1—Cu1—S3             | 105.12 (4)   | C52—N51—H51A          | 124.0        |
| S2—Cu1—S3             | 110.79 (4)   | N51—C52—C53           | 102.5 (6)    |
| S1—Cu1—S4             | 120.66 (4)   | N51—C52—H52A          | 111.3        |
| S2—Cu1—S4             | 90.89 (4)    | C53—C52—H52A          | 111.3        |
| S3—Cu1—S4             | 89.72 (4)    | N51—C52—H52B          | 111.3        |
| S1—Cu1—Cu2$^a$        | 142.97 (3)   | C53—C52—H52B          | 111.3        |
| S2—Cu1—Cu2$^a$        | 56.80 (3)    | H52A—C52—H52B         | 109.2        |
| S3—Cu1—Cu2$^a$        | 54.01 (3)    | N52—C53—C52           | 103.9 (6)    |
| S4—Cu1—Cu2$^a$        | 91.89 (3)    | N52—C53—H53A          | 111.0        |
| S5—Cu2—S1             | 122.65 (4)   | C52—C53—H53A          | 111.0        |
| S5—Cu2—S3$^a$         | 109.15 (4)   | N52—C53—H53B          | 111.0        |
| S1—Cu2—S3$^a$         | 102.24 (4)   | C52—C53—H53B          | 111.0        |
| S5—Cu2—S2$^a$         | 105.31 (4)   | H53A—C53—H53B         | 109.0        |
| S1—Cu2—S2$^a$         | 114.68 (4)   | C51—N52—C54           | 127.5 (6)    |
| S3$^a$—Cu2—S2$^a$     | 100.47 (4)   | C51—N52—C53           | 110.9 (6)    |
S5—Cu2—Cu1\textsuperscript{ii} 118.66 (3)  
C54—N52—C53 121.6 (6)  
S1—Cu2—Cu1\textsuperscript{ii} 118.48 (3)  
N52—C54—H54A 109.5  
S3\textsuperscript{ii}—Cu2—Cu1\textsuperscript{ii} 51.07 (3)  
N52—C54—H54B 109.5  
S2\textsuperscript{ii}—Cu2—Cu1\textsuperscript{ii} 49.42 (3)  
H54A—C54—H54B 109.5  
C11—S1—Cu1 111.11 (13)  
C54—N52—C53 121.6 (6)  
C11—S1—Cu2i 97.47 (13)  
N52—C54—H54A 109.5  
C11—S1—Cu2i 95.46 (4)  
N52—C54—H54B 109.5  
N12—C11—N11 110.7 (4)  
N52A—C51A—N51A 110.0 (9)  
N12—C11—S1 124.6 (3)  
N52A—C51A—S5 126.0 (8)  
N11—C11—S1 124.7 (3)  
N51A—C51A—S5 124.0 (8)  
C11—N11—C12 111.3 (4)  
C51A—N51A—C52A 111.7 (9)  
C11—N11—H11A 124.4  
C51A—N51A—H51B 124.2  
C12—N11—H11A 124.4  
C52A—N51A—H51B 124.2  
N11—C12—C13 101.8 (4)  
N51A—C52A—C53A 102.0 (9)  
N11—C12—H12A 111.4  
N51A—C52A—H52C 111.4  
C13—C12—H12A 111.4  
C53A—C52A—H52C 111.4  
H12A—C12—H12B 109.3  
H52C—C52A—H52D 109.2  
N12—C13—C12 103.1 (4)  
N52A—C53A—C52A 103.9 (9)  
N12—C13—H13A 111.1  
N52A—C53A—H53C 111.0  
C12—C13—H13A 111.1  
C52A—C53A—H53C 111.0  
N12—C13—H13B 111.1  
C52A—C53A—H53D 111.0  
C12—C13—H13B 111.1  
H53C—C53A—H53D 109.0  
H13A—C13—H13B 109.1  
C51A—N52A—C54A 126.8 (10)  
C11—N12—C14 126.9 (4)  
C51A—N52A—C53A 111.4 (9)  
C11—N12—C13 110.5 (4)  
C54A—N52A—C53A 120.8 (10)  
C14—N12—C13 121.0 (4)  
C54A—N52A—C53A 120.8 (10)  
N12—C14—H14A 109.5  
N52A—C54A—H54C 109.5  
N12—C14—H14B 109.5  
N52A—C54A—H54E 109.5  
H14A—C14—H14B 109.5  
H54D—C54A—H54E 109.5  
N12—C14—H14C 109.5  
H54D—C54A—H54F 109.5  
H14A—C14—H14C 109.5  
H54E—C54A—H54F 109.5  
H14B—C14—H14C 109.5  
H54F—C54A—H54D 109.5  
C21—S2—Cu1 99.67 (12)  
F11A—B1—F12 118.7 (12)  
C21—S2—Cu2 95.24 (13)  
F11A—B1—F13 117.0 (11)  
Cu1—S2—Cu2 73.78 (3)  
F12—B1—F13 110.2 (8)  
N22—C21—N21 109.4 (3)  
F11A—B1—F12A 112.1 (13)  
N22—C21—S2 125.4 (3)  
F12—B1—F12A 13 (2)  
N21—C21—S2 125.2 (3)  
F13—B1—F12A 122.3 (16)  
C21—C21—C22 109.7 (3)  
F11A—B1—F14 87.1 (8)  
C21—N21—S4 127.0 (3)  
F12—B1—F14 111.5 (9)  
C22—N21—S4 122.9 (3)  
F13—B1—F14 109.8 (6)  
N21—C22—C23 101.3 (3)  
F12A—B1—F14 100.8 (15)  
N21—C22—H22A 111.5  
F11A—B1—F13A 113.2 (11)  
C23—C22—H22A 111.5  
F12—B1—F13A 97.0 (14)  
N21—C22—H22B 111.5  
F13—B1—F13A 21.6 (7)  
C23—C22—H22B 111.5  
F12A—B1—F13A 110.1 (13)
| Bond                  | Length  | Bond                  | Length  | Bond                  | Length  |
|----------------------|---------|----------------------|---------|----------------------|---------|
| H22A—C22—H22B       | 109.3   | F14—B1—F13A         | 131.3   |
| N22—C23—C22         | 102.1 (3) | F11A—B1—F11       | 21.3 (7)   |
| N22—C23—H23A        | 111.4   | F12—B1—F11         | 110.4 (8)   |
| C22—C23—H23A        | 111.4   | F13—B1—F11         | 106.5 (7)   |
| N22—C23—H23B        | 111.4   | F12A—B1—F11        | 108.5 (15)  |
| C22—C23—H23B        | 111.4   | F14—B1—F11         | 108.3 (5)    |
| H23A—C23—H23B       | 109.2   | F13A—B1—F11        | 96.6 (10)    |
| C21—N22—C24         | 125.7 (4) | F11A—B1—F14A      | 111.8 (9)    |
| C21—N22—C23         | 111.5 (3) | F12—B1—F14A       | 112.1 (11)   |
| C24—N22—C23         | 120.6 (3) | F13—B1—F14A       | 81.0 (8)     |
| N22—C24—H24A        | 109.5   | F12A—B1—F14A       | 107.1 (13)   |
| N22—C24—H24B        | 109.5   | F14—B1—F14A        | 31.4 (6)     |
| H24A—C24—H24B       | 109.5   | F13A—B1—F14A       | 101.9 (8)    |
| N22—C24—H24C        | 109.5   | F11—B1—F14A        | 130.7 (8)    |
| H24A—C24—H24C       | 109.5   | F21A—B2—F24        | 106.4 (15)   |
| H24B—C24—H24C       | 109.5   | F21A—B2—F21        | 5 (2)        |
| C31—S3—Cu1          | 99.03 (13) | F24—B2—F21        | 109.0 (7)    |
| C31—S3—Cu2'         | 98.92 (12) | F21A—B2—F24A      | 111.4 (14)   |
| Cu1—S3—Cu2'         | 74.92 (3)  | F24—B2—F24A       | 23.9 (6)     |
| N32—C31—N31         | 110.6 (3) | F21—B2—F24A       | 111.7 (12)   |
| N32—C31—S3          | 124.0 (3) | F21A—B2—F22       | 106.2 (16)   |
| N31—C31—S3          | 125.4 (3) | F24—B2—F22        | 109.4 (5)    |
| C31—N31—C32         | 110.0 (3) | F21—B2—F22        | 109.2 (8)    |
| C31—N31—S4          | 124.0 (3) | F24A—B2—F22       | 126.6 (8)    |
| C2—N31—S4           | 120.7 (3) | F21A—B2—F23A      | 111.6 (13)   |
| N31—C32—C33         | 103.0 (3) | F24—B2—F23A       | 131.2 (9)    |
| N31—C32—H32A        | 111.2   | F21—B2—F23A        | 106.9 (11)   |
| C33—C32—H32A        | 111.2   | F24A—B2—F23A       | 110.6 (9)    |
| N31—C32—H32B        | 111.2   | F22—B2—F23A        | 88.2 (8)     |
| C33—C32—H32B        | 111.2   | F21A—B2—F22A       | 111.1 (14)   |
| H32A—C32—H32B       | 109.1   | F24—B2—F22A        | 86.8 (8)     |
| N32—C33—C32         | 104.1 (3) | F21—B2—F22A       | 115.7 (12)   |
| N32—C33—H33A        | 110.9   | F24A—B2—F22A       | 105.7 (9)    |
| C32—C33—H33A        | 110.9   | F22—B2—F22A        | 22.9 (6)     |
| N32—C33—H33B        | 110.9   | F23A—B2—F22A       | 106.1 (9)    |
| C32—C33—H33B        | 110.9   | F21A—B2—F23        | 113.6 (15)   |
| H33A—C33—H33B       | 109.0   | F24—B2—F23        | 109.8 (6)    |
| C31—N32—C34         | 125.9 (4) | F21—B2—F23        | 108.1 (7)    |
| C31—N32—C33         | 112.3 (3) | F24A—B2—F23       | 86.9 (8)     |
| C34—N32—C33         | 121.8 (4) | F22—B2—F23        | 111.3 (5)    |
| N32—C34—H34A        | 109.5   | F23A—B2—F23       | 25.8 (6)     |
| N32—C34—H34B        | 109.5   | F22A—B2—F23       | 124.5 (9)    |
| H34A—C34—H34B       | 109.5   | F11A—F11—B1       | 69.6 (17)    |
| N32—C34—H34C        | 109.5   | F13A—F13—B1       | 82 (2)       |
| H34A—C34—H34C       | 109.5   | F14A—F14—B1       | 77.5 (11)    |
| H34B—C34—H34C       | 109.5   | F11—F11A—B1       | 89.1 (19)    |
| N21—S4—N31          | 105.82 (16) | F13—F13A—B1     | 76.0 (19)    |
| N21—S4—Cu1          | 97.21 (12) | F14—F14A—B1     | 71.0 (10)    |
N31—S4—Cu1 98.47 (11)  F22A—F22—B2  79.6 (16)
C51—S5—Cu2 120.6 (2)  F23A—F23—B2  76.8 (13)
C51A—S5—Cu2 101.0 (3)  F24A—F24—B2  79.4 (15)
N52—C51—N51 110.3 (6)  F22—F22A—B2  77.5 (16)
N52—C51—S5 130.6 (5)  F23—F23A—B2  77.3 (13)
N51—C51—S5 119.1 (5)  F24—F24A—B2  76.7 (16)
C51—N51—C52 112.0 (6)

Cu1—S1—C11—N12 −177.0 (3)  N51A—C51A—N52A—C53A 0 (2)
Cu2—S1—C11—N12 −78.2 (4)  S5—C51A—N52A—C53A −177.9 (16)
Cu1—S1—C11—N11 1.3 (4)  C52A—C53A—N52A—C51A 6 (2)
Cu2—S1—C11—N11 100.1 (4)  C52A—C53A—N52A—C54A 175.4 (15)
N12—C11—N11—C12 6.4 (5)  F12—B1—F11—F11A −117 (3)
S1—C11—N11—C12 −172.1 (3)  F13—B1—F11—F11A 123 (3)
C11—N11—C12—C13 −14.2 (5)  F12A—B1—F11—F11A −104 (3)
N11—C12—C13—N12 170.6 (5)  F14—B1—F11—F11A 5 (3)
N11—C12—C13—N12 10.9 (7)  F13A—B1—F11—F11A 143 (3)
N11—C11—N12—C14 4.8 (5)  F14—B1—F11—F11A 31 (4)
S1—C11—N12—C14 −10.9 (7)  F11A—B1—F13—F13A 85 (4)
C12—C13—N12—C13 −176.6 (3)  F12B—B1—F13—F13A −60 (4)
C12—C13—N12—C11 15.6 (5)  F12B—B1—F13—F13A −178 (3)
C12—C13—N12—C14 179.9 (5)  F13B—B1—F14—F14A 65 (4)
C12—C13—N12—C13 177.5 (3)  F14B—B1—F14—F14A 31 (4)
C12—C13—N12—C14 164.1 (3)  F12B—B1—F13—F13A −165 (4)

Cu2l—S2—C21—N22 108.5 (3)  F12B—B1—F13—F13A −142.8 (17)
Cu1—S2—C21—N21 1.6 (3)  F14B—B1—F14—F14A 141.0 (15)
Cu2l—S2—C21—N21 −72.8 (3)  F12B—B1—F13—F13A −55 (4)
N22—C21—N21—C22 −9.8 (4)  F14B—B1—F14—F14A −97.4 (17)
S2—C21—N21—C22 171.3 (3)  F13B—B1—F14—F14A −105.2 (19)
N22—C21—N21—S4 177.5 (3)  F13B—B1—F14—F14A −141 (15)
S2—C21—N21—S4 −1.5 (5)  F13B—B1—F14—F14A 72 (3)
C21—C22—C22—C23 21.3 (4)  F12B—B1—F11A—F11 −64 (3)
S4—N22—C21—N22 −165.6 (3)  F12B—B1—F11A—F11 84 (3)
N21—C22—C22—C23 −23.3 (4)  F12B—B1—F11A—F11 −175 (3)
N21—C22—C22—C24 −169.8 (4)  F14B—B1—F11A—F11 −41 (3)
S2—C22—N22—C24 9.2 (6)  F13B—B1—F11A—F11 −155 (3)
N21—C22—C22—C23 −7.0 (5)  F11A—B1—F13A—F13 −105 (4)
S2—C22—C22—C23 171.9 (3)  F11A—B1—F13A—F13 129 (4)
C22—C23—N22—C21 20.0 (5)  F12B—B1—F13A—F13 128 (4)
C22—C23—N22—C24 −176.3 (4)  F12B—B1—F13A—F13 3 (4)
Cu1—S3—C31—N32 164.1 (3)  F14B—B1—F13A—F13 −119 (3)
Cu2l—S3—C31—N32 −119.9 (3)  F14B—B1—F13A—F13 15 (4)
Cu1—S3—C31—N31 164.1 (3)  F11A—B1—F14A—F14 −40.6 (18)
Cu2l—S3—C31—N31 −119.9 (3)  F12B—B1—F14A—F14 95.5 (16)
N32—C31—N31—C32 −1.5 (4)  F13B—B1—F14A—F14 −156.2 (16)
S3—C31—N31—C32 178.9 (3)  F12B—B1—F14A—F14 83 (2)
N32—C31—N31—S4 −155.7 (3)  F13B—B1—F14A—F14 −161.8 (16)
S3—C31—N31—S4 24.7 (4)  F11A—B1—F14A—F14 −52.1 (19)
C31—N31—C32—C33 1.9 (4)
S4—N31—C32—C33 157.0 (3) F21A—B2—F22—F22A 106 (3)
N31—C32—C33—N32 −1.5 (4) F24—B2—F22—F22A −8 (3)
N31—C31—N32—C34 178.6 (4) F21—B2—F22—F22A 111 (3)
S3—C31—N32—C34 −1.8 (6) F24A—B2—F22—F22A 27 (3)
N31—C31—N32—C33 0.5 (5) F23A—B2—F22—F22A −142 (2)
S3—C31—N32—C33 −180.0 (3) F23—B2—F22—F22A 1 (2)
C32—C33—N32—C31 0.8 (5) F21A—B2—F23—F23A 91 (2)
C32—C33—N32—C34 −177.5 (4) F24—B2—F23—F23A 149.7 (19)
C21—N21—S4—N31 101.3 (3) F21—B2—F23—F23A 91 (2)
C22—N21—S4—N31 −70.6 (3) F24A—B2—F23—F23A 156.7 (19)
C21—N21—S4—Cu1 0.3 (3) F22—B2—F23—F23A −28 (2)
C22—N21—S4—Cu1 −171.6 (3) F22A—B2—F23—F23A −50 (2)
N31—C31—N32—C34 −115.8 (3) F21A—B2—F24—F24A 106 (3)
N31—C31—N32—C33 167.3 (3) F21—B2—F24—F24A 106 (3)
C31—N31—S4—N21 −115.8 (3) F22—B2—F24—F24A −143 (2)
C31—N31—S4—Cu1 −167.3 (3) F22A—B2—F24—F24A 1 (2)
N52—C51—N51—C52 3.0 (10) F23A—B2—F24—F24A 60 (3)
S5—C51—N51—C52 178.5 (6) F24—B2—F24A—F24A 157 (2)
C51—N51—C52—C53 −6.1 (11) F24—B2—F24A—F24A 157 (2)
N51—C52—C53—N52 6.5 (12) F23A—B2—F24—F24A 143 (2)
N51—C51—N52—C54 176.3 (7) F23A—B2—F24—F24A 143 (2)
S5—C51—N51—C52 −178.5 (6) F24—B2—F24A—F24A 157 (2)
C51—N51—C52—C53 6.5 (12) F23A—B2—F24—F24A 143 (2)
N51—C51—N52—C54 176.3 (7) F23A—B2—F24—F24A 143 (2)
S5—C51—N51—C52 −178.5 (6) F24—B2—F24A—F24A 157 (2)
C51—N51—C52—C53 6.5 (12) F23A—B2—F24—F24A 143 (2)
N51—C51—N52—C54 176.3 (7) F23A—B2—F24—F24A 143 (2)
S5—C51—N51—C52 −178.5 (6) F24—B2—F24A—F24A 157 (2)
C51—N51—C52—C53 6.5 (12) F23A—B2—F24—F24A 143 (2)
N51—C51—N52—C54 176.3 (7) F23A—B2—F24—F24A 143 (2)
C52—C53—N52—C51 0.98 (2) F23A—B2—F24—F24A 143 (2)
N51—C51—N52—C54 176.3 (7) F23A—B2—F24—F24A 143 (2)
S5—C51—N51—C52 −178.5 (6) F24—B2—F24A—F24A 157 (2)
C51—N51—C52—C53 6.5 (12) F23A—B2—F24—F24A 143 (2)
N51—C51—N52—C54 176.3 (7) F23A—B2—F24—F24A 143 (2)
C52—C53—N52—C51 0.98 (2) F23A—B2—F24—F24A 143 (2)
Cu2—S5—C51A—N52A −169.1 (11) F22—B2—F23A—F23 143 (2)
Cu2—S5—C51A—N51A 13.0 (12) F22A—B2—F23A—F23 153.6 (18)
N52A—C51A—N51A—C52A −6.4 (15) F21A—B2—F24A—F24 139.1 (19)
S5—C51A—N51A—C52A 171.7 (9) F21—B2—F24A—F24 159 (2)
C51A—N51A—C52A—C53A 9.5 (19) F22—B2—F24A—F24 159 (2)
N51A—C52A—C53A—N52A −9 (2) F23A—B2—F24A—F24 159 (2)
N51A—C51A—N52A—C54A 169.8 (13) F22A—B2—F24A—F24 159 (2)
S5—C51A—N52A—C54A 13 (2) F23—B2—F24A—F24 164 (2)

Symmetry codes: (i) x, −y+1/2, z−1/2; (ii) x, −y+1/2, z+1/2.

Hydrogen-bond geometry (Å, °)

| D—H···A | D—H | H···A | D···A | D—H···A |
|--------|-----|------|-------|---------|
| N11—H11A···F12 | 0.88 | 2.12 | 2.764 (11) | 129 |
| N11—H11A···F12A | 0.88 | 2.15 | 2.74 (2) | 124 |
| N51—H51A···F23 | 0.88 | 2.20 | 2.995 (12) | 150 |
| C13—H13B···F12 | 0.99 | 2.63 | 3.329 (17) | 128 |
| C13—H13B···F12A | 0.99 | 2.59 | 3.22 (3) | 122 |
| C14—H14B···F14A | 0.98 | 2.59 | 3.331 (14) | 133 |

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### Supporting Information

| Bond        | d (Å) | r (Å) | ϕ (deg) | Symmetry Code |
|-------------|-------|-------|---------|---------------|
| C14—H14C···F11A<sup>iv</sup> | 0.98  | 2.64  | 3.119 (17) | 111 |
| C22—H22B···F24<sup>vi</sup> | 0.99  | 2.63  | 3.293 (8)  | 125 |
| C22—H22B···F24<sup>iv</sup> | 0.99  | 2.61  | 3.395 (17) | 136 |
| C23—H23A···F24<sup>i</sup>  | 0.99  | 2.56  | 3.164 (8)  | 119 |
| C23—H23A···F24<sup>vi</sup> | 0.99  | 2.63  | 3.453 (8)  | 140 |
| C24—H24C···F13    | 0.98  | 2.58  | 3.321 (11) | 133 |
| C32—H32A···F21    | 0.99  | 2.33  | 3.259 (15) | 155 |
| C32—H32A···F21A   | 0.99  | 2.46  | 3.38 (3)   | 155 |
| C32—H32A···F23A   | 0.99  | 2.61  | 3.287 (16) | 126 |
| C32—H32B···F24<sup>i</sup> | 0.99  | 2.56  | 3.499 (9)  | 158 |
| C32—H32B···F24A<sup>v</sup> | 0.99  | 2.59  | 3.569 (18) | 170 |
| C33—H33A···F21<sup>i</sup> | 0.99  | 2.33  | 3.182 (12) | 144 |
| C33—H33A···F21A   | 0.99  | 2.31  | 3.16 (3)   | 145 |
| C34—H34A···F13A<sup>iv</sup> | 0.98  | 2.62  | 3.154 (18) | 114 |
| C34—H34A···F13<sup>vi</sup> | 0.98  | 2.60  | 3.247 (8)  | 123 |
| C53—H53A···F13<sup>vii</sup> | 0.99  | 2.36  | 3.269 (16) | 152 |
| C54—H54A···S1     | 0.98  | 2.89  | 3.835 (8)  | 162 |
| C54—H54A···F11<sup>i</sup> | 0.98  | 2.39  | 3.335 (10) | 162 |
| C53A—H53A···F22<sup>vii</sup> | 0.99  | 2.52  | 3.49 (3)   | 167 |
| C54A—H54A···F23    | 0.98  | 2.09  | 2.933 (16) | 144 |
| C54A—H54A···F23A  | 0.98  | 2.60  | 3.43 (2)   | 143 |
| C54A—H54A···F23A<sup>iii</sup> | 0.98  | 2.47  | 3.36 (2)   | 152 |

Symmetry codes: (i) x, −y+1/2, z+1/2; (iii) −x, −y+1, −z+1; (iv) −x, y−1/2, −z+3/2; (v) −x+1, y+1/2, −z+3/2; (vi) −x+1, −y+1, −z+1; (vii) −x+1, −y, −z+1; (viii) x, −y, z.