

Crystal structure and Hirshfeld analysis of di- μ -bromido-bis[(1-[[dimethyl(phenylthiomethyl)silyl]methyl]piperidine- κ^2N,S)copper(I)] and di- μ -iodido-bis[(1-[[dimethyl(phenylthiomethyl)silyl]methyl]piperidine- κ^2N,S)copper(I)]

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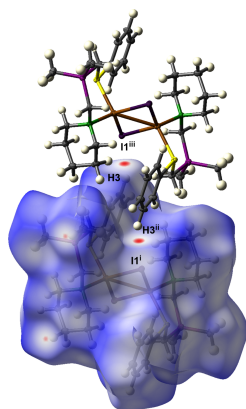
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The use of 1-[[dimethyl(phenylthiomethyl)silyl]methyl]piperidine as chelating ligand has been probed by complexation on CuI and CuBr in MeCN solution to afford the dinuclear *S,N*-chelate title complexes, [Cu₂I₂(C₁₅H₂₅NSSi)₂] and [Cu₂Br₂(C₁₅H₂₅NSSi)₂], which feature a halide-bridged rhomboid-shaped Cu(μ_2 -X)Cu (*X* = I, Br) core with Cu...Cu contacts of 2.8249 (5) and 2.7631 (6) Å, respectively. The two isostructural complexes crystallize in the triclinic space group *P* $\bar{1}$ with half molecule in the asymmetric unit. An analysis of the Hirshfeld surfaces shows that H...H (van der Waals) interactions dominate with a contact percentage of over 80% in both complexes.

1. Chemical context

In previous work, we have investigated the potential of the [(piperidinomethyl)silylmethyl] fragment for organic transformations and the preparation of cyclometallated Pd^{II} complexes (Schildbach *et al.*, 2004), (Colquhoun, *et al.*, 2012), (Koller *et al.*, 2017). In this context we have also synthesized 1-[[dimethyl(phenylthiomethyl)silyl]methyl]piperidine, **1**, by treatment of the organosulfur compound (chloromethyl)dimethyl[(phenylthio)methyl]silane with piperidine (Koller *et al.*, 2017). Based on our experience on the coordination of dytopic ligands possessing both a hard *N*-donor site and a soft *S*-donor site according to the hard and soft acids and bases (HSAB) concept (Pearson, 1963), such as thioether functionalized 2-azabutadienes (Jacquot-Rousseau *et al.*, 2005; Kinghat *et al.*, 2024; Kubicki *et al.*, 2025), we have chosen the soft copper(I) salts CuI and CuBr for the complexation studies. Cu^I is known to form mononuclear complexes with bidentate ligands (Kinghat *et al.*, 2016), but in most cases the dinuclear μ_2 -halide-bridged rhomboid dimer *L*₂Cu(μ_2 -X)CuL₂ or higher nuclear clusters such as the Cu₄X₄ cubane cluster are formed (Kim *et al.*, 2007; Bovin *et al.*, 2023). For example, we reported recently on the structure of the rhomboid-shaped dimer [L₂Cu(μ_2 -I)CuL₂] [*L*₂ = (iPrS)₂C=C(H)-N=CPh₂] (CSD refcode IYEVAN; Kinghat *et al.*, 2024), in which the two copper centers are additionally coordinated by the sulfur and nitrogen donor atoms in a chelating manner. This motif is also present in redox-active, tetradentate *S,N*-donor ligands that simultaneously coordinate both copper(I) centers (CSD refcode SAYJIO; Curcio *et al.*, 2017). The applications are not limited to redox chemistry; lumi-



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Table 1

Selected geometric parameters (Å, °) for **2a**.

I1—Cu1	2.5940 (3)	Cu1—S1	2.3533 (6)
I1—Cu1 ⁱ	2.6445 (3)	S1—C7	1.792 (2)
Cu1···Cu1 ⁱ	2.8249 (5)		
N1—Cu1—S1	97.68 (5)	C10—N1—Cu1	107.94 (12)
N1—Cu1—I1	122.78 (5)	C10—N1—C15	109.23 (15)
N1—Cu1—I1 ⁱ	103.18 (5)	C11—N1—Cu1	110.19 (12)
S1—Cu1—I1	108.475 (16)	C11—N1—C10	107.69 (16)
S1—Cu1—I1 ⁱ	108.077 (16)	C11—N1—C15	108.24 (16)
I1—Cu1—I1 ⁱ	114.743 (10)	C15—N1—Cu1	113.40 (13)
Cu1 ⁱ —I1—Cu1—I1 ⁱ	0	Cu1 ⁱ —I1 ⁱ —Cu1—I1	0

Symmetry code: (i) $-x, -y + 1, -z + 1$.

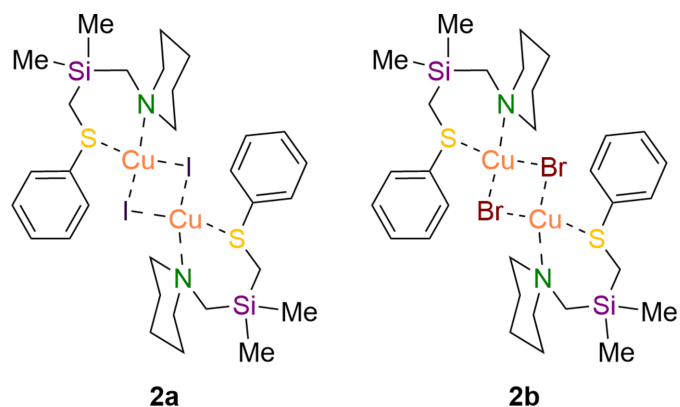
Table 2

Selected geometric parameters (Å, °) for **2b**.

Br1—Cu1	2.5197 (4)	Cu1—S1	2.3208 (6)
Br1—Cu1 ⁱ	2.4416 (4)	S1—C7	1.798 (2)
Cu1···Cu1 ⁱ	2.7631 (6)		
N1—Cu1—S1	98.95 (5)	C10—N1—Cu1	108.05 (13)
N1—Cu1—Br1	100.62 (5)	C11—N1—Cu1	110.20 (13)
N1—Cu1—Br1 ⁱ	123.97 (5)	C11—N1—C10	107.77 (16)
S1—Cu1—Br1	109.379 (19)	C15—N1—Cu1	112.46 (13)
S1—Cu1—Br1 ⁱ	110.223 (18)	C15—N1—C10	109.70 (17)
Br1 ⁱ —Cu1—Br1	112.332 (14)	C15—N1—C11	108.56 (17)
Cu1 ⁱⁱ —Br1—Cu1—I1 ⁱⁱ	0	Cu1 ⁱⁱ —Br1 ⁱⁱ —Cu1—I1	0

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

nescence properties have also been observed for rhomboid Cu···Cu dimers upon excitation by visible light (Zhang *et al.*, 2009; Kobayashi *et al.*, 2013; Shou *et al.*, 2017). This luminescence is also observed for species embedded in supramolecular assemblies, such as metallocages (Xu *et al.*, 2021).



A characteristic feature associated with the formation of Cu···Cu polynuclear clusters is the observation of Cu···Cu distance below the sum of the van der Waals radii (2.8 Å; Bondi, 1964). This interaction is referred to as ‘cuprophilicity’ and is indicative of an attractive interaction between the copper(I) centers (Che *et al.*, 2000). The shortened intermetallic distance can be enforced by bridging ligands such as μ_2 -halides, but can also occur in a ligand-unsupported fashion (Siemeling *et al.*, 1997; Cotton *et al.*, 1988). While most *S,N*-chelating ligands are based on thioether and pyridine or imine

functionalities (Curcio *et al.*, 2017; Cheon *et al.*, 2013; Zhang *et al.*, 2009; Kinghat *et al.*, 2024), we report here two examples of rhomboid copper(I) halide dimers coordinated by organosilicon-bridged *S,N*-donor ligands, utilizing amine moieties as *N*-donors. In the herein reported examples of silicon-bridged ligands, the silicon center enhances the coordination ability of the donor sites by increasing the electron density of their neighboring carbon centers (Schneider *et al.*, 2023; Chen *et al.*, 2013; Khatyr *et al.* 2026).

2. Structural commentary

The title compounds Cu₂I₂[PhSCH₂Si(Me)₂CH₂Pip]₂ (**2a**) and Cu₂Br₂[PhSCH₂Si(Me)₂CH₂Pip]₂ (**2b**) crystallize at room temperature from acetonitrile in the centrosymmetric space group *P* $\bar{1}$ with half a molecule in the asymmetric unit. The asymmetric units of the complexes are shown in Fig. 1, and characteristic bond parameters are listed in Tables 1 and 2. Both structures feature the same ligand, 1-[[dimethyl-(phenylthiomethyl)silyl]methyl]piperidine, which comprises an amine and a thioether Lewis donor moiety bridged *via* an SiMe₂ group as spacer. The S1—C7 bond length of 1.792 (2) Å and 1.798 (2) Å and the N1—C10 bond lengths of 1.483 (3) Å and 1.489 (3) Å for **2a** and **2b**, respectively, are consistent with typical values reported for such bond environments (Allen *et al.*, 1987). Slight deviations from the ideal tetrahedral angle (109.5°) are observed around the nitrogen atom. In compound **2a**, the bond angles around N1 range from 107.69 (16) to 113.40 (13)° while in compound **2b** they vary between 107.77 (16) and 112.46 (13)°. The N1—Cu1—S1 bite angles of 97.68 (5)° (**2a**) and 98.95 (5)° (**2b**) contribute to a slightly distorted tetrahedral geometry around the Cu^I centers. The *t*₄ parameters (Yang *et al.*, 2007) of 0.87 (**2a**) and 0.88 (**2b**) indicate a low degree of distortion in the tetrahedral coordination environment, in contrast to other reported examples of this structural motif. The maximum *t*₄ of 1.00 describes an ideal tetrahedral coordination environment, whereas a *t*₄ of 0 indicates an ideal square-planar coordination environment. A common coordination pattern in Cu^I halides is the formation of rhomboid dimers, which can exhibit a dissymmetric bridging by the halides (Kinghat *et al.*, 2014). However, in both reported compounds a torsion angle of 0°, enforced by inversion symmetry at the center of the dimer, prevents this

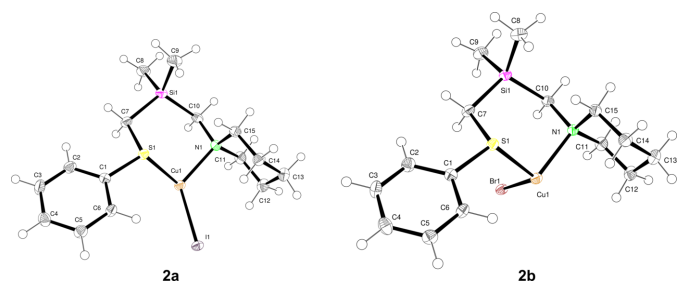


Figure 1

Asymmetric units of **2a** and **2b** with displacement ellipsoids drawn at the 50% probability level.

dissymmetry. A notable difference between the two structures lies in the $\text{Cu} \cdots \text{Cu}$ distances, which amounts to 2.8249 (5) Å for compound **2a**, while in compound **2b** it is slightly shorter at 2.7631 (6) Å. The latter value falls below the sum of the van der Waals radii of the two copper(I) centers (2.8 Å; Bondi, 1964), suggesting the presence of a weak $\text{Cu} \cdots \text{Cu}$ interaction.

3. Supramolecular features

For a detailed insight into the crystal packing, a Hirshfeld surface analysis was performed (Spackman & Jayatilaka, 2009). The Hirshfeld surface and the corresponding two-dimensional fingerprint plots were generated and analysed using *CrystalExplorer21* (Spackman *et al.* 2021). The Hirshfeld surface was mapped over d_{norm} in the range of -0.0729 to 1.4226 arbitrary units for compound **2a** and -0.0255 to 1.5298 arbitrary units for compound **2b**. While the Hirshfeld surfaces are shown in Fig. 2 (**2a**) and Fig. 4 (**2b**), the contribution of the different intermolecular interactions are depicted in the two-dimensional fingerprint plots Fig. 3 (**2a**) and Fig. 5 (**2b**). Intermolecular interactions are represented by the color coding on the surface: red spots indicate close contacts, whereas blue and white regions correspond to areas of no significant interaction. Both title compounds exhibit a close contact between the halide center and the hydrogen center H3

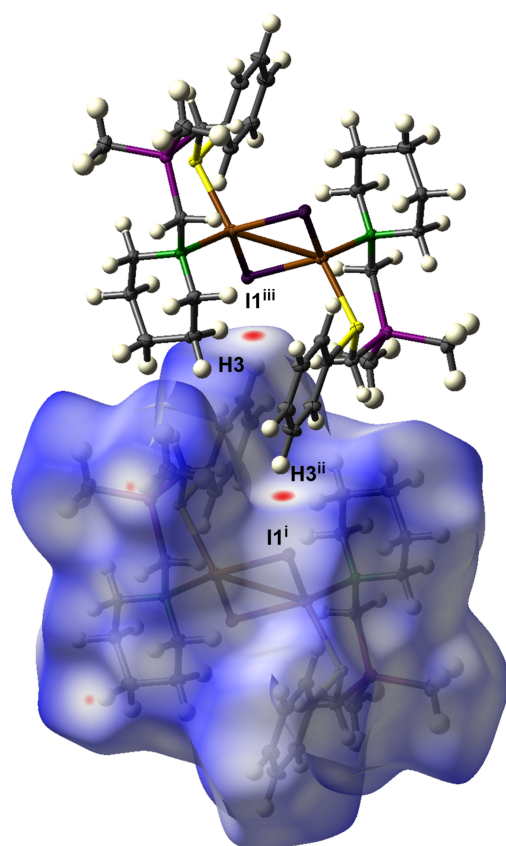


Figure 2
Hirshfeld surface analysis of **2a** showing close contacts in the crystal. The $\text{H3} \cdots \text{I1}^{\text{iii}}$ and $\text{I1}^{\text{i}} \cdots \text{H3}^{\text{ii}}$ contacts are indicated by the red spots [symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $-x, 2-y, 1-z$; (iii) $x, 1+y, z$].

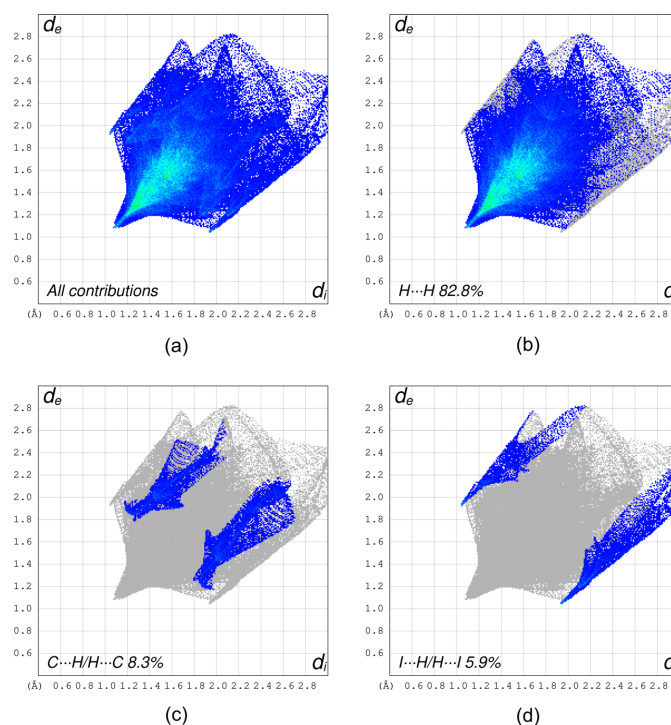


Figure 3
Two-dimensional fingerprint plots for compound **2a** showing (a) all contributions, and those delineated into (b) $\text{H} \cdots \text{H}$, (c) $\text{C} \cdots \text{H}/\text{H} \cdots \text{C}$ and (d) $\text{I} \cdots \text{H}/\text{H} \cdots \text{I}$ -interactions.

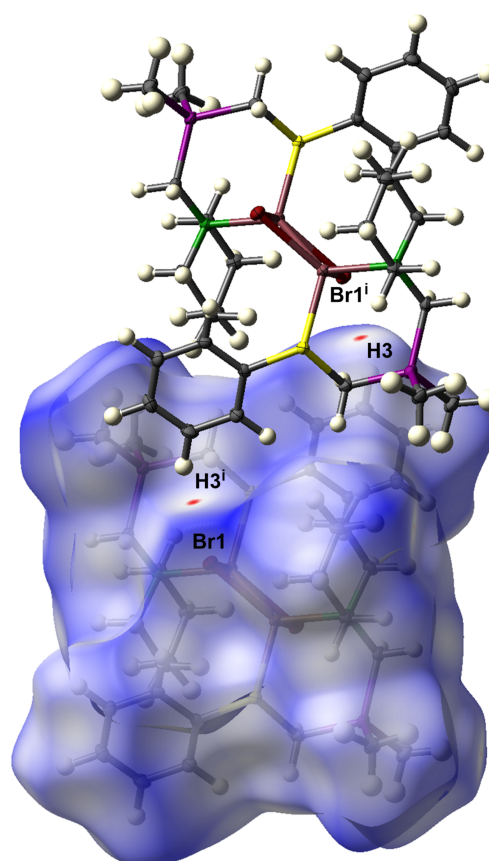


Figure 4
Hirshfeld surface analysis of **2b** showing close contacts in the crystal. The $\text{H3}^{\text{i}} \cdots \text{Br1}$ and $\text{Br1}^{\text{i}} \cdots \text{H3}$ contacts are indicated by the red spots [symmetry code: (i) $1-x, 1-y, 2-z$].

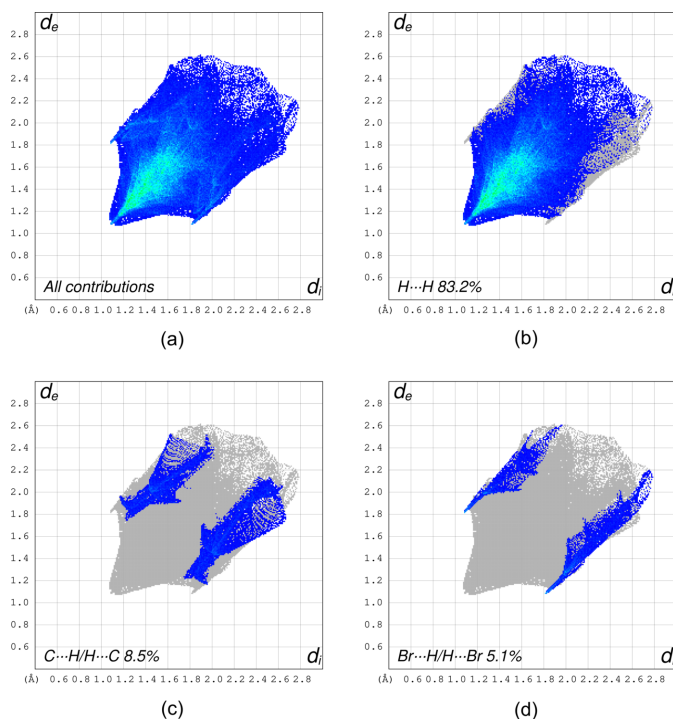


Figure 5
Two-dimensional fingerprint plots for compound **2b** showing (a) all contributions, and those delineated into (b) H...H, (c) C...H/H...C and (d) Br...H/H...Br interactions.

of a neighboring molecule $\text{H3} \cdots \text{I1/I1} \cdots \text{H3}$ within compound **2a** and $\text{H3} \cdots \text{Br1/Br1} \cdots \text{H3}$ within compound **2b** as can be seen from the Hirshfeld surfaces. Although these contacts are marked as close contacts on the surface, their contribution to the overall surface interactions is relatively small 5.1% for $\text{H} \cdots \text{Br/Br} \cdots \text{H}$ and 5.9% for $\text{H} \cdots \text{I/I} \cdots \text{H}$ making them comparable in magnitude. The largest contribution to the interactions in both compounds arises from weak van der Waals $\text{H} \cdots \text{H}$ contacts: 82.8% in compound **2a** and 83.2% in compound **2b**. This is followed by $\text{C} \cdots \text{H/H} \cdots \text{C}$ interactions, contributing to 8.3% and 8.5%, respectively. The smallest contribution comes from $\text{S} \cdots \text{H/H} \cdots \text{S}$ interactions at 3.1% in **2a** and 3.0% in **2b**. The crystal packing of both title compounds is illustrated in Fig. 6 and is characterized by propagation along the *b*-axis, which is promoted by the aforementioned close $\text{H} \cdots \text{I/I} \cdots \text{H}$ interactions.

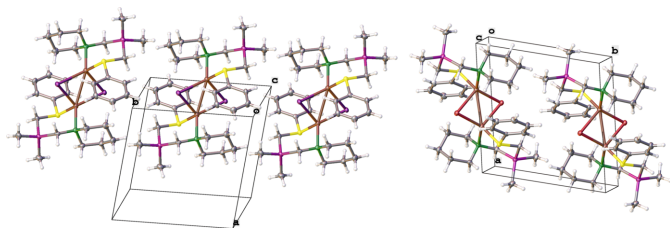


Figure 6
The packing of the solid state structures of **2a** (left) and **2b** (right) along the *b* axis.

4. Database survey

A search of the Cambridge Crystallographic Database (Groom *et al.*, 2016; WebCSD September 2025) revealed several structures of rhomboid-shaped dimeric CuI complexes, in which the metal centers are internally bridged by halide anions and additionally coordinated by *S,N*-donor ligands. The most common nitrogen donors in these complexes are imine moieties, as observed in structures such as (CSD AXEWIL, AXEWOR; Flörke *et al.*, 2016) and (CSD BURYOE; Flörke, 2015). Note that for dimer AXEWOR (bis[*N*-[2-(benzylsulfanyl)phenyl]-1,3-dimethylimidazolidin-2-imine]bis(μ -iodo)-dicopper) featuring a particular short $\text{Cu} \cdots \text{Cu}$ bond of only 2.5492 (4) Å, a deformation of the planar $\text{Cu}(\mu_2\text{-I})\text{Cu}$ core to a butterfly-shaped cluster is noticed, the $\mu_2\text{-I}$ atoms forming the wing tips (Flörke *et al.*, 2016). Aromatic pyridine-type and nitrile-based nitrogen donors have also been employed in similar coordination environments (CSD BARGARF; Lee *et al.*, 2017, CSD JIZZDE; Raghuvanshi *et al.*, 2019). Depending on the reaction conditions, CuI is reported to form with *t*-butylsulfanyl ethylpyridine the dinuclear species bis(μ_2 -iodo)bis[2-[2-(*t*-butylsulfanyl)ethyl]pyridine]dicopper or a heptanuclear pinwheel-shaped Cu_7I_7 cluster (CSD XENZIB; Cheon *et al.*, 2013). The entries are dominated by discrete dinuclear [(*S,N*)- $\text{Cu}(\mu_2\text{-I})\text{Cu}(\text{S},\text{N})$] species, but also some macrocyclic scaffolds such as tetrakis(μ_2 -iodo)-bis[μ_2 -4,6-bis[(pyrid-2-ylmethyl)sulfanylmethyl]dibenzo(*b,d*)furan]tetracopper are known (CSD EHOFE; Caradoc-Davies & Hanton, 2003). Using polydentate ligands such as 2,3-bis(*t*-butylthiomethyl)-quinoxaline also allows the assembly of supramolecular networks incorporating the $\text{Cu}(\mu_2\text{-I})\text{Cu}$ motif (CSD NUHQOX; Zhang *et al.*, 2009). According to the database survey, only one example exists in which a secondary amine-based *S,N*-donor ligand is coordinated to an iodine-bridged copper(I) dimer (CSD TOTQAU; Cran *et al.*, 1996). The $\text{Cu} \cdots \text{Cu}$ distances reported for the two independent molecules of bis(μ_2 -iodo)-bis[*N*-methyl-2-(*t*-butylthio)-1-phenylethylamine-*N,S*]dicopper [2.587 (1) and 2.650 (2) Å] are considerably shorter than those of **2a**. Likewise, no reports were identified involving organosilicon-bridged mixed *S,N*-donor ligands coordinating the mentioned copper(I) dimers. A variation of this structural motif, replacing a *N*-donor moiety with a second thioether, leads to the formation of another organosilicon-bridged ligand capable of chelating the targeted copper(I) dimer, as demonstrated by Yim *et al.* (CSD TAKWIM; Yim *et al.*, 2003). The coordination pattern of dithioethers is also present in copper halide coordination polymers. These types of organometallic polymers are of significant interest due to their intense luminescent properties (Harvey & Knorr, 2010). In particular, copper(I) halides coordinated to bis(arylthio)methane ligands (Knorr *et al.*, 2015). For bromide-bridged copper(I) complexes featuring a *S,N*-donor set, apart from two Cu^{II} species (Al-Noaimi *et al.*, 2024), just a single match was found, namely bis(μ -bromo)-bis[1,3-dimethyl-*N*-[2-(phenylsulfanyl)phenyl]imidazolidin-2-imine]dicopper with $d(\text{Cu} \cdots \text{Cu}) = 2.7545$ (5) Å (CSD

Table 3
Experimental details.

	2a	2b
Crystal data		
Chemical formula	[Cu ₂ I ₂ (C ₁₅ H ₂₅ NSSi) ₂]	[Cu ₂ Br ₂ (C ₁₅ H ₂₅ NSSi) ₂]
<i>M_r</i>	939.90	845.92
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	173	173
<i>a</i> , <i>b</i> , <i>c</i> (Å)	9.9789 (4), 10.0149 (4), 10.1038 (5)	9.8697 (9), 9.9427 (6), 10.0331 (6)
α , β , γ (°)	74.788 (4), 74.367 (4), 73.590 (4)	73.450 (5), 73.529 (6), 73.946 (6)
<i>V</i> (Å ³)	913.64 (7)	884.28 (12)
<i>Z</i>	1	1
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α
μ (mm ⁻¹)	3.06	3.67
Crystal size (mm)	0.2 × 0.1 × 0.1	0.2 × 0.1 × 0.1
Data collection		
Diffractometer	Xcalibur, Sapphire3	Xcalibur, Sapphire3
Absorption correction	Multi-scan (<i>CrysAlis PRO</i> , Agilent, 2014)	Multi-scan (<i>CrysAlis PRO</i> , Agilent, 2014)
<i>T</i> _{min} , <i>T</i> _{max}	0.866, 1.000	0.815, 1.000
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	13850, 4322, 4000	11578, 3479, 3121
<i>R</i> _{int}	0.024	0.034
(sin θ /λ) _{max} (Å ⁻¹)	0.686	0.617
Refinement		
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.021, 0.046, 1.07	0.024, 0.056, 1.05
No. of reflections	4322	3479
No. of parameters	183	183
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.52, -0.37	0.39, -0.32

Computer programs: *CrysAlis PRO* (Agilent, 2014), *SHELXT* (Sheldrick, 2015a), *SHELXL* (Sheldrick, 2015b), *ORTEP-3 for Windows* (Farrugia, 2012), *OLEX2* (Dolomanov *et al.*, 2009), *CrystalExplorer21* (Spackman *et al.* 2021) and *publCIF* (Westrip, 2010).

HUWWIH0; Flörke *et al.*, 2016). For examples of rhomboid-shaped discrete Cu(μ_2 -I)Cu complexes featuring mixed *N,O* or *P,O* donors sets, see CSD refcodes POHKED (Rofouei & Hashempur 2008), BEMBAZ (Shou *et al.*, 2017) and XOVROR (Kinghat *et al.* 2014).

5. Synthesis and crystallization

Di- μ -iodido-bis[(1-[[dimethyl(phenylthiomethyl)silyl]methyl]piperidine-*k*²N¹,S¹)copper(I)] (**2a**) was synthesized by adding ligand **1** (614 mg, 2.2 mmol, 1.10 eq.) to CuI (380 mg, 2 mmol, 1.00 eq.) dissolved in acetonitrile (8 mL) at room temperature. For complete crystallization the sample was stored for one day at 278 K. Compound **2a** was isolated in the form of colorless blocks. Accordingly, di- μ -bromido-bis[(1-[[dimethyl(phenylthiomethyl)silyl]methyl]piperidine-*k*²N¹,S¹)copper(I)] (**2b**) was prepared by adding **1** (614 mg, 2.2 mmol, 1.10 eq.) to CuBr (286 mg, 2.0 mmol, 1.00 eq.) dissolved in 8 mL acetonitrile at room temperature. The sample was also stored at 278 K for one day, allowing the isolation of **2b** as colorless blocks.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. H atoms were positioned geometrically (C–H = 0.95–1.00 Å) and refined using a riding model, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for CH₂ and CH hydrogen

atoms and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for CH₃ hydrogen atoms. Idealized methyl groups were refined as rotating groups.

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supporting information

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Crystal structure and Hirshfeld analysis of di- μ -bromido-bis[(1-{[dimethyl(phenylthiomethyl)silyl]methyl}piperidine- κ^2N,S)copper(I)] and di- μ -iodido-bis-[(1-{[dimethyl(phenylthiomethyl)silyl]methyl}piperidine- κ^2N,S)copper(I)]

Kai Schäper, Michael Knorr and Carsten Strohmann

Computing details

Di- μ -bromido-bis[(1-{[dimethyl(phenylthiomethyl)silyl]methyl}piperidine- κ^2N,S)copper(I)] (2a)

Crystal data

[Cu₂I₂(C₁₅H₂₅NSSi)₂]

$M_r = 939.90$

Triclinic, $P\bar{1}$

$a = 9.9789$ (4) Å

$b = 10.0149$ (4) Å

$c = 10.1038$ (5) Å

$\alpha = 74.788$ (4)°

$\beta = 74.367$ (4)°

$\gamma = 73.590$ (4)°

$V = 913.64$ (7) Å³

$Z = 1$

$F(000) = 468$

$D_x = 1.708$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 4665 reflections

$\theta = 2.7$ – 29.0°

$\mu = 3.06$ mm⁻¹

$T = 173$ K

Block, colourless

$0.2 \times 0.1 \times 0.1$ mm

Data collection

Xcalibur, Sapphire3

diffractometer

Radiation source: Enhance (Mo) X-ray Source

Graphite monochromator

Detector resolution: 16.0560 pixels mm⁻¹

ω scans

Absorption correction: multi-scan

(CrysAlisPro, Agilent, 2014)

$T_{\min} = 0.866$, $T_{\max} = 1.000$

13850 measured reflections

4322 independent reflections

4000 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.024$

$\theta_{\max} = 29.2^\circ$, $\theta_{\min} = 2.2^\circ$

$h = -13 \rightarrow 13$

$k = -12 \rightarrow 12$

$l = -13 \rightarrow 13$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.021$

$wR(F^2) = 0.046$

$S = 1.07$

4322 reflections

183 parameters

0 restraints

Primary atom site location: dual

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0167P)^2 + 0.3459P]$

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

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.52$ e Å⁻³

$\Delta\rho_{\min} = -0.37$ 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 ($\text{\AA}^2$)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
I1	0.06780 (2)	0.31973 (2)	0.66613 (2)	0.01743 (5)
Cu1	0.14416 (3)	0.50933 (3)	0.44902 (3)	0.01735 (6)
S1	0.25677 (5)	0.64989 (5)	0.51718 (5)	0.01584 (11)
Si1	0.37208 (6)	0.74081 (6)	0.20604 (6)	0.01785 (13)
N1	0.30834 (17)	0.45600 (18)	0.27033 (18)	0.0158 (4)
C1	0.1595 (2)	0.7237 (2)	0.6666 (2)	0.0159 (4)
C2	0.1194 (2)	0.8681 (2)	0.6652 (2)	0.0215 (5)
H2	0.138647	0.934342	0.579854	0.026*
C3	0.0510 (2)	0.9157 (2)	0.7887 (2)	0.0259 (5)
H3	0.024847	1.014691	0.787903	0.031*
C4	0.0207 (2)	0.8207 (2)	0.9126 (2)	0.0243 (5)
H4	−0.026991	0.854107	0.996773	0.029*
C5	0.0600 (2)	0.6769 (2)	0.9138 (2)	0.0220 (5)
H5	0.039332	0.611119	0.999112	0.026*
C6	0.1292 (2)	0.6278 (2)	0.7914 (2)	0.0191 (4)
H6	0.155968	0.528652	0.792739	0.023*
C7	0.2573 (2)	0.7982 (2)	0.3721 (2)	0.0178 (4)
H7A	0.294285	0.870873	0.392614	0.021*
H7B	0.158342	0.841553	0.358996	0.021*
C8	0.3348 (3)	0.8914 (3)	0.0575 (2)	0.0280 (5)
H8A	0.349905	0.977373	0.074527	0.042*
H8B	0.235479	0.907385	0.049422	0.042*
H8C	0.399209	0.868585	−0.029822	0.042*
C9	0.5620 (2)	0.7058 (3)	0.2169 (3)	0.0288 (5)
H9A	0.623247	0.661353	0.139147	0.043*
H9B	0.576520	0.641839	0.306276	0.043*
H9C	0.586400	0.795547	0.211184	0.043*
C10	0.3219 (2)	0.5896 (2)	0.1665 (2)	0.0179 (4)
H10A	0.229140	0.629380	0.137285	0.022*
H10B	0.393116	0.562221	0.082991	0.022*
C11	0.2662 (2)	0.3637 (2)	0.2033 (2)	0.0222 (5)
H11A	0.336944	0.349938	0.115239	0.027*
H11B	0.172338	0.411965	0.178583	0.027*
C12	0.2562 (2)	0.2195 (2)	0.2968 (3)	0.0256 (5)
H12A	0.232010	0.160950	0.245354	0.031*
H12B	0.178821	0.232026	0.380775	0.031*
C13	0.3966 (2)	0.1432 (2)	0.3423 (3)	0.0278 (5)
H13A	0.383521	0.056052	0.413550	0.033*
H13B	0.470069	0.114689	0.260604	0.033*

C14	0.4464 (2)	0.2396 (2)	0.4035 (2)	0.0221 (5)
H14A	0.381405	0.253883	0.494406	0.026*
H14B	0.543355	0.193165	0.421308	0.026*
C15	0.4494 (2)	0.3824 (2)	0.3059 (2)	0.0199 (5)
H15A	0.479042	0.442933	0.350873	0.024*
H15B	0.521309	0.368636	0.218482	0.024*

Atomic displacement parameters ($\text{\AA}^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Il	0.01694 (7)	0.01668 (8)	0.01766 (8)	−0.00597 (5)	−0.00423 (5)	0.00114 (5)
Cu1	0.01938 (13)	0.01682 (13)	0.01575 (13)	−0.00612 (10)	−0.00242 (10)	−0.00227 (10)
S1	0.0175 (2)	0.0163 (3)	0.0149 (3)	−0.0056 (2)	−0.00332 (19)	−0.0033 (2)
Si1	0.0171 (3)	0.0197 (3)	0.0156 (3)	−0.0066 (2)	−0.0014 (2)	−0.0012 (2)
N1	0.0154 (8)	0.0190 (9)	0.0150 (9)	−0.0044 (7)	−0.0045 (7)	−0.0051 (7)
C1	0.0158 (10)	0.0211 (11)	0.0136 (10)	−0.0055 (8)	−0.0053 (8)	−0.0047 (8)
C2	0.0293 (12)	0.0163 (11)	0.0182 (11)	−0.0075 (9)	−0.0055 (9)	0.0007 (9)
C3	0.0352 (13)	0.0166 (11)	0.0256 (12)	−0.0024 (10)	−0.0065 (10)	−0.0073 (10)
C4	0.0305 (12)	0.0256 (12)	0.0179 (11)	−0.0049 (10)	−0.0052 (9)	−0.0079 (10)
C5	0.0293 (12)	0.0219 (12)	0.0168 (11)	−0.0097 (9)	−0.0062 (9)	−0.0013 (9)
C6	0.0242 (11)	0.0156 (10)	0.0191 (11)	−0.0057 (9)	−0.0079 (9)	−0.0012 (9)
C7	0.0217 (11)	0.0172 (10)	0.0154 (10)	−0.0091 (9)	−0.0034 (8)	−0.0003 (8)
C8	0.0324 (13)	0.0267 (13)	0.0203 (12)	−0.0077 (10)	−0.0002 (10)	−0.0013 (10)
C9	0.0217 (12)	0.0346 (14)	0.0306 (14)	−0.0100 (10)	−0.0038 (10)	−0.0050 (11)
C10	0.0160 (10)	0.0236 (11)	0.0136 (10)	−0.0041 (9)	−0.0026 (8)	−0.0036 (9)
C11	0.0246 (11)	0.0275 (12)	0.0187 (11)	−0.0076 (9)	−0.0044 (9)	−0.0100 (10)
C12	0.0310 (12)	0.0249 (12)	0.0273 (13)	−0.0110 (10)	−0.0061 (10)	−0.0111 (10)
C13	0.0323 (13)	0.0197 (12)	0.0328 (14)	−0.0062 (10)	−0.0064 (10)	−0.0078 (10)
C14	0.0191 (11)	0.0195 (11)	0.0267 (12)	−0.0018 (9)	−0.0075 (9)	−0.0033 (10)
C15	0.0151 (10)	0.0208 (11)	0.0249 (12)	−0.0038 (9)	−0.0055 (8)	−0.0052 (9)

Geometric parameters ($\text{\AA}$, $^\circ$)

Il—Cu1	2.5940 (3)	C7—H7A	0.9900
Il—Cu1 ⁱ	2.6445 (3)	C7—H7B	0.9900
Cu1—Cu1 ⁱ	2.8249 (5)	C8—H8A	0.9800
Cu1—S1	2.3533 (6)	C8—H8B	0.9800
Cu1—N1	2.1556 (17)	C8—H8C	0.9800
S1—C1	1.777 (2)	C9—H9A	0.9800
S1—C7	1.792 (2)	C9—H9B	0.9800
Si1—C7	1.886 (2)	C9—H9C	0.9800
Si1—C8	1.861 (2)	C10—H10A	0.9900
Si1—C9	1.855 (2)	C10—H10B	0.9900
Si1—C10	1.886 (2)	C11—H11A	0.9900
N1—C10	1.483 (3)	C11—H11B	0.9900
N1—C11	1.480 (3)	C11—C12	1.517 (3)
N1—C15	1.484 (3)	C12—H12A	0.9900
C1—C2	1.385 (3)	C12—H12B	0.9900

C1—C6	1.388 (3)	C12—C13	1.522 (3)
C2—H2	0.9500	C13—H13A	0.9900
C2—C3	1.385 (3)	C13—H13B	0.9900
C3—H3	0.9500	C13—C14	1.521 (3)
C3—C4	1.377 (3)	C14—H14A	0.9900
C4—H4	0.9500	C14—H14B	0.9900
C4—C5	1.380 (3)	C14—C15	1.512 (3)
C5—H5	0.9500	C15—H15A	0.9900
C5—C6	1.384 (3)	C15—H15B	0.9900
C6—H6	0.9500		
N1—Cu1—S1	97.68 (5)	H7A—C7—H7B	108.1
N1—Cu1—I1	122.78 (5)	Si1—C8—H8A	109.5
N1—Cu1—I1 ⁱ	103.18 (5)	Si1—C8—H8B	109.5
S1—Cu1—I1	108.475 (16)	Si1—C8—H8C	109.5
S1—Cu1—I1 ⁱ	108.077 (16)	H8A—C8—H8B	109.5
Cu1—I1—Cu1 ⁱ	65.257 (10)	H8A—C8—H8C	109.5
I1—Cu1—I1 ⁱ	114.743 (10)	H8B—C8—H8C	109.5
I1 ⁱ —Cu1—Cu1 ⁱ	56.508 (10)	Si1—C9—H9A	109.5
I1—Cu1—Cu1 ⁱ	58.234 (10)	Si1—C9—H9B	109.5
S1—Cu1—Cu1 ⁱ	125.555 (19)	Si1—C9—H9C	109.5
N1—Cu1—Cu1 ⁱ	135.29 (5)	H9A—C9—H9B	109.5
C1—S1—Cu1	115.60 (7)	H9A—C9—H9C	109.5
C1—S1—C7	105.22 (10)	H9B—C9—H9C	109.5
C7—S1—Cu1	101.58 (7)	Si1—C10—H10A	106.6
C8—Si1—C7	107.28 (10)	Si1—C10—H10B	106.6
C8—Si1—C10	104.34 (10)	N1—C10—Si1	122.89 (14)
C9—Si1—C7	107.99 (10)	N1—C10—H10A	106.6
C9—Si1—C8	109.50 (11)	N1—C10—H10B	106.6
C9—Si1—C10	114.44 (11)	H10A—C10—H10B	106.6
C10—Si1—C7	113.00 (9)	N1—C11—H11A	109.0
C10—N1—Cu1	107.94 (12)	N1—C11—H11B	109.0
C10—N1—C15	109.23 (15)	N1—C11—C12	112.88 (18)
C11—N1—Cu1	110.19 (12)	H11A—C11—H11B	107.8
C11—N1—C10	107.69 (16)	C12—C11—H11A	109.0
C11—N1—C15	108.24 (16)	C12—C11—H11B	109.0
C15—N1—Cu1	113.40 (13)	C11—C12—H12A	109.4
C2—C1—S1	123.74 (17)	C11—C12—H12B	109.4
C2—C1—C6	119.77 (19)	C11—C12—C13	111.07 (18)
C6—C1—S1	116.43 (16)	H12A—C12—H12B	108.0
C1—C2—H2	120.1	C13—C12—H12A	109.4
C1—C2—C3	119.7 (2)	C13—C12—H12B	109.4
C3—C2—H2	120.1	C12—C13—H13A	109.6
C2—C3—H3	119.7	C12—C13—H13B	109.6
C4—C3—C2	120.6 (2)	H13A—C13—H13B	108.1
C4—C3—H3	119.7	C14—C13—C12	110.35 (19)
C3—C4—H4	120.2	C14—C13—H13A	109.6
C3—C4—C5	119.6 (2)	C14—C13—H13B	109.6

C5—C4—H4	120.2	C13—C14—H14A	109.3
C4—C5—H5	119.8	C13—C14—H14B	109.3
C4—C5—C6	120.4 (2)	H14A—C14—H14B	107.9
C6—C5—H5	119.8	C15—C14—C13	111.69 (19)
C1—C6—H6	120.1	C15—C14—H14A	109.3
C5—C6—C1	119.9 (2)	C15—C14—H14B	109.3
C5—C6—H6	120.1	N1—C15—C14	112.25 (17)
S1—C7—Si1	110.86 (11)	N1—C15—H15A	109.2
S1—C7—H7A	109.5	N1—C15—H15B	109.2
S1—C7—H7B	109.5	C14—C15—H15A	109.2
Si1—C7—H7A	109.5	C14—C15—H15B	109.2
Si1—C7—H7B	109.5	H15A—C15—H15B	107.9
Cu1—S1—C1—C2	−121.35 (17)	C7—Si1—C10—N1	−51.87 (19)
Cu1—S1—C1—C6	61.48 (17)	C8—Si1—C7—S1	168.04 (11)
Cu1—S1—C7—Si1	−64.61 (10)	C8—Si1—C10—N1	−168.07 (16)
Cu1—N1—C10—Si1	60.38 (17)	C9—Si1—C7—S1	−74.02 (14)
Cu1—N1—C11—C12	−65.5 (2)	C9—Si1—C10—N1	72.28 (19)
Cu1—N1—C15—C14	63.7 (2)	C10—Si1—C7—S1	53.60 (14)
S1—C1—C2—C3	−176.20 (17)	C10—N1—C11—C12	176.99 (17)
S1—C1—C6—C5	176.87 (16)	C10—N1—C15—C14	−175.84 (17)
N1—C11—C12—C13	−56.6 (2)	C11—N1—C10—Si1	179.33 (14)
C1—S1—C7—Si1	174.54 (10)	C11—N1—C15—C14	−58.8 (2)
C1—C2—C3—C4	−1.0 (3)	C11—C12—C13—C14	51.3 (3)
C2—C1—C6—C5	−0.4 (3)	C12—C13—C14—C15	−51.8 (2)
C2—C3—C4—C5	0.6 (4)	C13—C14—C15—N1	56.9 (2)
C3—C4—C5—C6	−0.1 (3)	C15—N1—C10—Si1	−63.3 (2)
C4—C5—C6—C1	0.0 (3)	C15—N1—C11—C12	59.0 (2)
C6—C1—C2—C3	0.9 (3)	Cu1 ⁱ —I1—Cu1—I1 ⁱ	0
C7—S1—C1—C2	−10.2 (2)	Cu1 ⁱ —I1 ⁱ —Cu1—I1	0
C7—S1—C1—C6	172.64 (16)		

Symmetry code: (i) $-x, -y+1, -z+1$.

Di- μ -iodido-bis[(1-{[dimethyl(phenylthiomethyl)silyl]methyl}piperidine- κ^2N,S)copper(I)] (2b)

Crystal data

$[\text{Cu}_2\text{Br}_2(\text{C}_{15}\text{H}_{25}\text{NSSi})_2]$

$M_r = 845.92$

Triclinic, $P\bar{1}$

$a = 9.8697$ (9) Å

$b = 9.9427$ (6) Å

$c = 10.0331$ (6) Å

$\alpha = 73.450$ (5)°

$\beta = 73.529$ (6)°

$\gamma = 73.946$ (6)°

$V = 884.28$ (12) Å³

$Z = 1$

$F(000) = 432$

$D_x = 1.588$ Mg m^{−3}

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 5514 reflections

$\theta = 2.7\text{--}29.0^\circ$

$\mu = 3.67$ mm^{−1}

$T = 173$ K

Block, colourless

$0.2 \times 0.1 \times 0.1$ mm

Data collection

Xcalibur, Sapphire3
diffractometer
Radiation source: Enhance (Mo) X-ray Source
Graphite monochromator
Detector resolution: 16.0560 pixels mm⁻¹
 ω scans
Absorption correction: multi-scan
(CrysAlisPro, Agilent, 2014)
 $T_{\min} = 0.815$, $T_{\max} = 1.000$

11578 measured reflections
3479 independent reflections
3121 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.034$
 $\theta_{\max} = 26.0^\circ$, $\theta_{\min} = 2.2^\circ$
 $h = -12 \rightarrow 12$
 $k = -12 \rightarrow 12$
 $l = -12 \rightarrow 12$

Refinement

Refinement on F^2
Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.024$
 $wR(F^2) = 0.056$
 $S = 1.05$
3479 reflections
183 parameters
0 restraints
Primary atom site location: iterative

Hydrogen site location: inferred from
neighbouring sites
H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0217P)^2 + 0.1872P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.39 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.32 \text{ e } \text{\AA}^{-3}$

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 ($\text{\AA}^2$)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.44330 (2)	0.16667 (2)	0.83511 (2)	0.01766 (7)
Cu1	0.64346 (3)	0.01004 (3)	0.95483 (3)	0.01744 (8)
S1	0.75500 (6)	0.15336 (6)	1.01668 (6)	0.01535 (13)
Si1	0.87510 (7)	0.24369 (7)	0.69886 (6)	0.01714 (15)
N1	0.80590 (19)	-0.04401 (19)	0.77416 (18)	0.0144 (4)
C1	0.6580 (2)	0.2289 (2)	1.1663 (2)	0.0149 (5)
C2	0.6241 (3)	0.3746 (2)	1.1623 (2)	0.0203 (5)
H2	0.646215	0.441359	1.074519	0.024*
C3	0.5580 (3)	0.4226 (3)	1.2866 (2)	0.0237 (6)
H3	0.536757	0.522468	1.283898	0.028*
C4	0.5225 (3)	0.3271 (3)	1.4146 (2)	0.0234 (6)
H4	0.476526	0.360868	1.499371	0.028*
C5	0.5546 (3)	0.1816 (3)	1.4181 (2)	0.0200 (5)
H5	0.530215	0.115342	1.505759	0.024*
C6	0.6222 (2)	0.1319 (2)	1.2946 (2)	0.0181 (5)
H6	0.643874	0.032017	1.297541	0.022*
C7	0.7568 (3)	0.3027 (2)	0.8650 (2)	0.0186 (5)
H7A	0.793498	0.377756	0.882548	0.022*
H7B	0.657043	0.344529	0.851143	0.022*
C8	1.0676 (3)	0.2078 (3)	0.7091 (3)	0.0259 (6)

H8A	1.129729	0.165515	0.629573	0.039*
H8B	1.081440	0.140825	0.799549	0.039*
H8C	1.093103	0.298004	0.703684	0.039*
C9	0.8400 (3)	0.3960 (3)	0.5453 (2)	0.0266 (6)
H9A	0.852695	0.483819	0.561937	0.040*
H9B	0.740823	0.409670	0.535477	0.040*
H9C	0.908085	0.374756	0.457758	0.040*
C10	0.8212 (2)	0.0911 (2)	0.6644 (2)	0.0167 (5)
H10A	0.727342	0.131098	0.635901	0.020*
H10B	0.892652	0.063205	0.579862	0.020*
C11	0.7603 (3)	−0.1381 (2)	0.7116 (2)	0.0199 (5)
H11A	0.832123	−0.154694	0.623141	0.024*
H11B	0.666236	−0.088987	0.685868	0.024*
C12	0.7457 (3)	−0.2822 (2)	0.8139 (3)	0.0225 (5)
H12A	0.667195	−0.266790	0.898499	0.027*
H12B	0.719428	−0.342937	0.766290	0.027*
C13	0.8855 (3)	−0.3588 (3)	0.8609 (3)	0.0246 (6)
H13A	0.959846	−0.389626	0.779328	0.030*
H13B	0.869890	−0.445559	0.936751	0.030*
C14	0.9384 (3)	−0.2601 (2)	0.9167 (2)	0.0207 (5)
H14A	0.871620	−0.242401	1.007412	0.025*
H14B	1.035159	−0.307698	0.936562	0.025*
C15	0.9471 (2)	−0.1180 (2)	0.8106 (2)	0.0179 (5)
H15A	0.979252	−0.055672	0.851440	0.021*
H15B	1.019779	−0.135032	0.722678	0.021*

Atomic displacement parameters ($\text{\AA}^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.01788 (13)	0.01598 (12)	0.01710 (13)	−0.00516 (10)	−0.00396 (10)	0.00099 (9)
Cu1	0.01935 (16)	0.01641 (15)	0.01617 (15)	−0.00650 (12)	−0.00149 (13)	−0.00287 (12)
S1	0.0178 (3)	0.0148 (3)	0.0142 (3)	−0.0049 (2)	−0.0034 (2)	−0.0031 (2)
Si1	0.0182 (3)	0.0174 (3)	0.0147 (3)	−0.0063 (3)	−0.0020 (3)	−0.0010 (3)
N1	0.0137 (10)	0.0153 (9)	0.0152 (9)	−0.0038 (8)	−0.0042 (8)	−0.0037 (8)
C1	0.0134 (11)	0.0194 (12)	0.0146 (11)	−0.0040 (10)	−0.0058 (10)	−0.0051 (9)
C2	0.0246 (13)	0.0180 (12)	0.0178 (12)	−0.0046 (10)	−0.0059 (11)	−0.0021 (10)
C3	0.0300 (14)	0.0147 (12)	0.0276 (13)	−0.0026 (11)	−0.0077 (12)	−0.0072 (10)
C4	0.0259 (14)	0.0270 (14)	0.0189 (12)	−0.0011 (11)	−0.0061 (11)	−0.0106 (11)
C5	0.0240 (13)	0.0222 (13)	0.0143 (11)	−0.0062 (11)	−0.0062 (10)	−0.0014 (10)
C6	0.0222 (13)	0.0154 (12)	0.0192 (12)	−0.0068 (10)	−0.0071 (10)	−0.0026 (9)
C7	0.0225 (13)	0.0171 (12)	0.0170 (12)	−0.0083 (10)	−0.0040 (10)	−0.0014 (9)
C8	0.0226 (13)	0.0297 (14)	0.0256 (13)	−0.0115 (11)	−0.0026 (11)	−0.0037 (11)
C9	0.0310 (15)	0.0231 (13)	0.0209 (13)	−0.0092 (12)	−0.0022 (12)	0.0023 (11)
C10	0.0175 (12)	0.0197 (12)	0.0122 (11)	−0.0047 (10)	−0.0019 (10)	−0.0030 (9)
C11	0.0228 (13)	0.0232 (13)	0.0190 (12)	−0.0059 (11)	−0.0073 (11)	−0.0092 (10)
C12	0.0279 (14)	0.0202 (13)	0.0255 (13)	−0.0084 (11)	−0.0070 (11)	−0.0101 (10)
C13	0.0285 (14)	0.0174 (12)	0.0291 (14)	−0.0067 (11)	−0.0058 (12)	−0.0057 (11)
C14	0.0172 (12)	0.0194 (12)	0.0253 (13)	−0.0031 (10)	−0.0080 (11)	−0.0019 (10)

C15 0.0138 (12) 0.0178 (12) 0.0228 (12) −0.0028 (10) −0.0051 (10) −0.0052 (10)

Geometric parameters (Å, °)

Br1—Cu1	2.5197 (4)	C7—H7A	0.9900
Br1—Cu1 ⁱ	2.4416 (4)	C7—H7B	0.9900
Cu1—Cu1 ⁱ	2.7631 (6)	C8—H8A	0.9800
Cu1—S1	2.3208 (6)	C8—H8B	0.9800
Cu1—N1	2.1391 (18)	C8—H8C	0.9800
S1—C1	1.778 (2)	C9—H9A	0.9800
S1—C7	1.798 (2)	C9—H9B	0.9800
Si1—C7	1.887 (2)	C9—H9C	0.9800
Si1—C8	1.861 (2)	C10—H10A	0.9900
Si1—C9	1.863 (2)	C10—H10B	0.9900
Si1—C10	1.885 (2)	C11—H11A	0.9900
N1—C10	1.489 (3)	C11—H11B	0.9900
N1—C11	1.483 (3)	C11—C12	1.523 (3)
N1—C15	1.478 (3)	C12—H12A	0.9900
C1—C2	1.385 (3)	C12—H12B	0.9900
C1—C6	1.391 (3)	C12—C13	1.514 (3)
C2—H2	0.9500	C13—H13A	0.9900
C2—C3	1.384 (3)	C13—H13B	0.9900
C3—H3	0.9500	C13—C14	1.520 (3)
C3—C4	1.381 (3)	C14—H14A	0.9900
C4—H4	0.9500	C14—H14B	0.9900
C4—C5	1.385 (3)	C14—C15	1.515 (3)
C5—H5	0.9500	C15—H15A	0.9900
C5—C6	1.386 (3)	C15—H15B	0.9900
C6—H6	0.9500		
N1—Cu1—S1	98.95 (5)	H7A—C7—H7B	108.1
N1—Cu1—Br1	100.62 (5)	Si1—C8—H8A	109.5
N1—Cu1—Br1 ⁱ	123.97 (5)	Si1—C8—H8B	109.5
S1—Cu1—Br1	109.379 (19)	Si1—C8—H8C	109.5
S1—Cu1—Br1 ⁱ	110.223 (18)	H8A—C8—H8B	109.5
Br1 ⁱ —Cu1—Br1	112.332 (14)	H8A—C8—H8C	109.5
Cu1 ⁱ —Br1—Cu1	67.668 (13)	H8B—C8—H8C	109.5
Br1 ⁱ —Cu1—Cu1 ⁱ	57.513 (12)	Si1—C9—H9A	109.5
Br1—Cu1—Cu1 ⁱ	54.819 (12)	Si1—C9—H9B	109.5
S1—Cu1—Cu1 ⁱ	127.45 (2)	Si1—C9—H9C	109.5
N1—Cu1—Cu1 ⁱ	131.44 (5)	H9A—C9—H9B	109.5
C1—S1—Cu1	116.49 (7)	H9A—C9—H9C	109.5
C1—S1—C7	105.35 (10)	H9B—C9—H9C	109.5
C7—S1—Cu1	101.37 (8)	Si1—C10—H10A	106.7
C8—Si1—C7	108.62 (11)	Si1—C10—H10B	106.7
C8—Si1—C9	109.66 (12)	N1—C10—Si1	122.41 (15)
C8—Si1—C10	114.59 (11)	N1—C10—H10A	106.7
C9—Si1—C7	106.74 (11)	N1—C10—H10B	106.7

C9—Si1—C10	104.44 (11)	H10A—C10—H10B	106.6
C10—Si1—C7	112.43 (10)	N1—C11—H11A	109.2
C10—N1—Cu1	108.05 (13)	N1—C11—H11B	109.2
C11—N1—Cu1	110.20 (13)	N1—C11—C12	112.25 (18)
C11—N1—C10	107.77 (16)	H11A—C11—H11B	107.9
C15—N1—Cu1	112.46 (13)	C12—C11—H11A	109.2
C15—N1—C10	109.70 (17)	C12—C11—H11B	109.2
C15—N1—C11	108.56 (17)	C11—C12—H12A	109.4
C2—C1—S1	123.93 (17)	C11—C12—H12B	109.4
C2—C1—C6	119.8 (2)	H12A—C12—H12B	108.0
C6—C1—S1	116.20 (17)	C13—C12—C11	111.02 (19)
C1—C2—H2	120.1	C13—C12—H12A	109.4
C3—C2—C1	119.8 (2)	C13—C12—H12B	109.4
C3—C2—H2	120.1	C12—C13—H13A	109.6
C2—C3—H3	119.6	C12—C13—H13B	109.6
C4—C3—C2	120.7 (2)	C12—C13—C14	110.39 (19)
C4—C3—H3	119.6	H13A—C13—H13B	108.1
C3—C4—H4	120.3	C14—C13—H13A	109.6
C3—C4—C5	119.4 (2)	C14—C13—H13B	109.6
C5—C4—H4	120.3	C13—C14—H14A	109.3
C4—C5—H5	119.8	C13—C14—H14B	109.3
C4—C5—C6	120.4 (2)	H14A—C14—H14B	108.0
C6—C5—H5	119.8	C15—C14—C13	111.55 (19)
C1—C6—H6	120.1	C15—C14—H14A	109.3
C5—C6—C1	119.8 (2)	C15—C14—H14B	109.3
C5—C6—H6	120.1	N1—C15—C14	111.56 (18)
S1—C7—Si1	110.73 (12)	N1—C15—H15A	109.3
S1—C7—H7A	109.5	N1—C15—H15B	109.3
S1—C7—H7B	109.5	C14—C15—H15A	109.3
Si1—C7—H7A	109.5	C14—C15—H15B	109.3
Si1—C7—H7B	109.5	H15A—C15—H15B	108.0
Cu1—S1—C1—C2	−124.41 (19)	C7—Si1—C10—N1	−53.0 (2)
Cu1—S1—C1—C6	58.85 (19)	C8—Si1—C7—S1	−72.86 (14)
Cu1—S1—C7—Si1	−64.89 (12)	C8—Si1—C10—N1	71.6 (2)
Cu1—N1—C10—Si1	60.00 (19)	C9—Si1—C7—S1	168.97 (12)
Cu1—N1—C11—C12	−64.1 (2)	C9—Si1—C10—N1	−168.38 (18)
Cu1—N1—C15—C14	62.6 (2)	C10—Si1—C7—S1	55.03 (15)
S1—C1—C2—C3	−175.05 (18)	C10—N1—C11—C12	178.24 (19)
S1—C1—C6—C5	175.94 (17)	C10—N1—C15—C14	−177.15 (17)
N1—C11—C12—C13	−56.6 (3)	C11—N1—C10—Si1	179.07 (16)
C1—S1—C7—Si1	173.31 (11)	C11—N1—C15—C14	−59.6 (2)
C1—C2—C3—C4	−1.3 (4)	C11—C12—C13—C14	51.7 (3)
C2—C1—C6—C5	−0.9 (3)	C12—C13—C14—C15	−52.5 (3)
C2—C3—C4—C5	0.4 (4)	C13—C14—C15—N1	57.5 (3)
C3—C4—C5—C6	0.2 (4)	C15—N1—C10—Si1	−62.9 (2)
C4—C5—C6—C1	0.1 (4)	C15—N1—C11—C12	59.5 (2)
C6—C1—C2—C3	1.6 (4)	Cu1 ⁱⁱ —Br1—Cu1—I1 ⁱⁱ	0

C7—S1—C1—C2	−13.0 (2)	Cu1 ⁱⁱ —Br1 ⁱⁱ —Cu1—I1	0
C7—S1—C1—C6	170.27 (17)		

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

Selected geometric parameters (Å, °) for 2a

I1—Cu1	2.5940 (3)
I1—Cu1i	2.6445 (3)
Cu1⋯Cu1i	2.8249 (5)
Cu1—S1	2.3533 (6)
S1—C7	1.792 (2)
N1—Cu1—S1	97.68 (5)
N1—Cu1—I1	122.78 (5)
N1—Cu1—I1i	103.18 (5)
S1—Cu1—I1	108.475 (16)
S1—Cu1—I1i	108.077 (16)
I1—Cu1—I1i	114.743 (10)
C10—N1—Cu1	107.94 (12)
C10—N1—C15	109.23 (15)
C11—N1—Cu1	110.19 (12)
C11—N1—C10	107.69 (16)
C11—N1—C15	108.24 (16)
C15—N1—Cu1	113.40 (13)
Cu1i—I1—Cu1—I1i	0.000
Cu1i—I1i—Cu1—I1	0.000

Symmetry code: (i) $-x, 1-y, 1-z$.

Selected geometric parameters (Å, °) for 2b.

Br1—Cu1	2.5197 (4)
Br1—Cu1i	2.4416 (4)
Cu1⋯Cu1i	2.7631 (6)
Cu1—S1	2.3208 (6)
S1—C7	1.798 (2)
N1—Cu1—S1	98.95 (5)
N1—Cu1—Br1	100.62 (5)
N1—Cu1—Br1i	123.97 (5)
S1—Cu1—Br1	109.379 (19)
S1—Cu1—Br1i	110.223 (18)
Br1—Cu1—Br1i	112.332 (14)
C10—N1—Cu1	108.05 (13)
C11—N1—Cu1	110.20 (13)
C11—N1—C10	107.77 (16)
C15—N1—Cu1	112.46 (13)
C15—N1—C10	109.70 (17)
C15—N1—C11	108.56 (17)

Cu1i—Br1—Cu1—Br1i	0.000
Cu1i—Br1i—Cu1—Br1	0.000

Symmetry code: (i) 1-x, -y, 2-z