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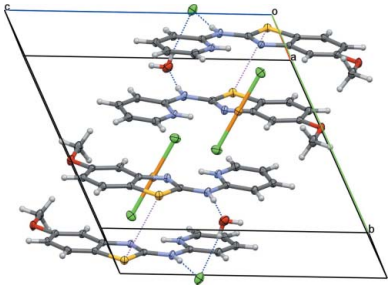
Benzothiazole derivatives are a class of privileged molecules due to their biological activity and pharmaceutical applications. One route to these molecules is *via* intramolecular cyclization of thioureas to form substituted 2-aminobenzothiazoles, but this often requires harsh conditions or employs expensive metal catalysts. Herein, the copper(II)- and gold(III)-mediated cyclizations of thioureas to substituted 2-aminobenzothiazoles are reported. The single-crystal X-ray structures of the thiourea *N*-(3-methoxyphenyl)-*N*′-(pyridin-2-yl)thiourea, $C_{13}H_{13}N_3OS$, and the intermediate metal complexes aquabis[5-methoxy-*N*-(pyridin-2-yl-κN)-1,3-benzothiazol-2-amine-κN^3]copper(II) dinitrate, $[Cu(C_{13}H_{11}N_3OS)_2(H_2O)](NO_3)_2$, and bis{2-[(5-methoxy-1,3-benzothiazol-2-yl)amino]pyridin-1-ium} dichloridogold(I) chloride monohydrate, $(C_{13}H_{12}N_3OS)_2[AuCl_2]Cl\cdot H_2O$, are reported. The copper complex exhibits a distorted trigonal–bipyramidal geometry, with direct metal-to-benzothiazole-ligand coordination, while the gold complex is a salt containing the protonated uncoordinated benzothiazole, and offers evidence that metal reduction (in this case, Au^{III} to Au^{I}) is required for the cyclization to proceed. As such, this study provides further mechanistic insight into the role of the metal cations in these transformations.

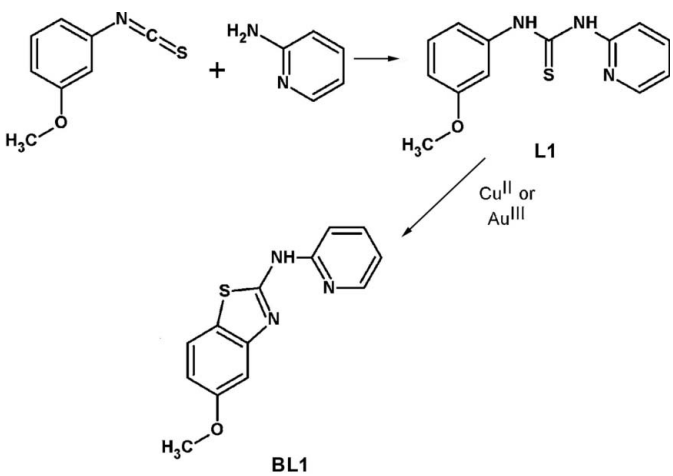
1. Introduction

Our research group has been exploring the supramolecular chemistry of a series of nonsymmetric pyridin-2-ylthiourea-based ligands, for example, *N*-(3-methoxyphenyl)-*N*′-(pyridin-2-yl)thiourea (**L1**) (see Scheme 1). This class of ligands can form six-membered chelate rings upon coordination with metal cations *via* the pyridyl N atom and the thiourea S atom (Mansour & Friedrich, 2017; Bharati *et al.*, 2013), or can bridge two metal centres *via* the thione functionality to form polymetallic clusters (Hollmann *et al.*, 2017; Saxena *et al.*, 2009; Lenthall *et al.*, 2007). Analogous to urea-based ligands, they can also serve as hydrogen-bond donors to anions *via* their amine groups, leading to larger supramolecular assemblies (Qureshi *et al.*, 2016; Akhuli *et al.*, 2013). Finally, in the interest of pursuing device applications and surface attachment, further functionality has been included on the terminal phenyl ring, with the future goal of having this moiety serve as a surface anchor.

Benzothiazole derivatives can be found in nature and are a class of privileged molecules due to their biological activity and pharmaceutical applications (Gill *et al.*, 2015). Thioureas are known to undergo intramolecular rearrangements under a variety of different conditions to form substituted 2-aminobenzothiazoles (Wang *et al.*, 2014). Synthetic routes to substituted benzothiazoles from thioureas often require relatively harsh conditions (for example, the Hugershoff reaction), employ expensive metal catalysts [palladium (Joyce & Batey,



2009) or ruthenium (Sharma *et al.*, 2016)] or require the incorporation of suitably positioned aryl halogen atoms, which are more easily removed for cyclization than more strongly bound hydrogens (Wang *et al.*, 2012; Evindar & Batey, 2006). Though copper is not used as commonly as other (catalytic) transition metals such as palladium and ruthenium, there have been a limited number of reports where this metal was successfully employed in the synthesis of 2-aminobenzothiazoles from thioureas (West *et al.*, 2003; Tadjarodi *et al.*, 2007).



Scheme 1

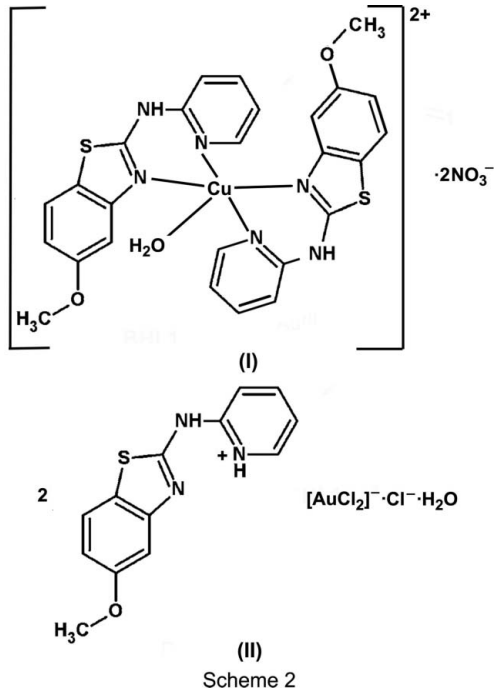
In this study, we report on the reaction of *N*-(3-methoxyphenyl)-*N*′-(pyridin-2-yl)thiourea (**L1**) with either copper(II) nitrate or gold(III) chloride, leading to the formation of 5-methoxy-*N*-(pyridin-2-yl)-1,3-benzothiazol-2-amine (**BL1**) (see Scheme 1). The redetermination of the single-crystal X-ray structure of **L1** is described, as well as the new crystal structures of aquabis[5-methoxy-*N*-(pyridin-2-yl-κN)-1,3-benzothiazol-2-amine-κN^3]copper(II) dinitrate, [Cu(**BL1**)$_2$(H$_2$O)](NO$_3$)$_2$, (I), and bis{2-[(5-methoxy-1,3-benzothiazol-2-yl)amino]pyridin-1-ium} dichloridogold(I) chloride monohydrate, (H**BL1**)$_2$[AuCl$_2$]Cl·H$_2$O, (II) (see Scheme 2).

2. Experimental

2.1. Synthesis and crystallization

2.1.1. *N*-(3-Methoxyphenyl)-*N*′-(pyridin-2-yl)thiourea (L1). The synthesis of **L1** has been reported previously (Giesen *et al.*, 2002). This procedure was modified slightly, with pyridine used as the reaction solvent, and crystals were grown from a 1:1 solution of methanol and acetonitrile. Characterization *via* IR spectroscopy, ^{1}H and ^{13}C NMR was consistent with the previous report.

2.1.2. Aquabis[5-methoxy-*N*-(pyridin-2-yl-κN)-1,3-benzothiazol-2-amine-κN^3]copper(II) dinitrate, (I). **L1** (49 mg, 0.19 mmol, 1 equiv.) and Cu(NO$_3$)$_2$·3H$_2$O (59 mg, 0.24 mmol, 1.3 equiv.) were dissolved separately in 1:1 (*v*/*v*) methanol/acetonitrile (5 ml). The solution of Cu(NO$_3$)$_2$ was added dropwise to the solution of **L1**. The resulting green reaction mixture was stirred vigorously with heating (∼333 K) for 20 min, after which time the solution became clear and yellow. This was filtered and left for slow evaporation. The solution turned green upon standing for less than one week. X-ray-quality crystals grew over the course of one month, providing complex (I) in 41% yield (29.2 mg, 0.0386 mmol). Analysis calculated for C$_{26}$H$_{24}$CuN$_8$O$_9$S$_2$: C 41.29, H 3.73, N 14.82%; found: C 41.11, H 3.46 N 15.28%.



Scheme 2

2.1.3. Bis{2-[(5-methoxy-1,3-benzothiazol-2-yl)amino]pyridin-1-ium} dichloridogold(I) chloride monohydrate, (II). **L1** (49 mg, 0.19 mmol, 1 equiv.) and AuCl$_3$ (62 mg, 0.20 mmol, 1 equiv.) were dissolved separately in 1:1 (*v*/*v*) methanol/acetonitrile (5 ml). The solution of AuCl$_3$ was added dropwise to the solution of **L1**, resulting in a light-yellow solution which was then stirred vigorously with heating (∼333 K) for 20 min, after which time a white solid formed. The solid was removed by suction filtration, while the filtrate was left for slow evaporation. X-ray-quality crystals were obtained from the filtrate providing the title complex in 15% yield (14.4 mg, 0.0165 mmol). Analysis calculated for C$_{26}$H$_{26}$AuCl$_3$N$_6$O$_3$S$_2$: C 35.73, H 3.46, N 9.62%; found: C 35.53, H 3.07, N 9.80%.

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. For all structures, H atoms bonded to O or N atoms were introduced in difference-map positions and refined isotropically with distance restraints and default standard uncertainties, while all other H atoms were introduced in calculated positions and refined as a riding model. For [Cu(**BL1**)$_2$(H$_2$O)](NO$_3$)$_2$, (I), the Cu—O(water) bond lies along a twofold rotation axis. The asymmetric unit contains both water protons at half-occupancy and so the symmetry-expanded model displays disorder in the H-atom positions.

Table 1
Experimental details.

	L1	(I)	(II)
Crystal data			
Chemical formula	$C_{13}H_{13}N_3OS$	$[Cu(C_{13}H_{11}N_3OS)_2(H_2O)](NO_3)_2$	$(C_{13}H_{12}N_3OS)_2[AuCl_2]Cl\cdot H_2O$
M_r	259.32	720.19	837.96
Crystal system, space group	Triclinic, $P\overline{1}$	Orthorhombic, *Pbcn*	Triclinic, $P\overline{1}$
Temperature (K)	173	110	110
a, *b*, *c* (Å)	8.4341 (2), 8.6991 (2), 10.1083 (2)	18.1534 (4), 7.1814 (1), 21.8523 (4)	10.0052 (1), 12.5940 (2), 12.9412 (1)
α, β, γ (°)	91.249 (2), 113.506 (2), 110.292 (2)	90, 90, 90	111.867 (1), 97.271 (1), 99.755 (1)
V (Å^3)	626.73 (3)	2848.81 (9)	1459.03 (3)
Z	2	4	2
Radiation type	Cu *K*α	Mo *K*α	Mo *K*α
μ (mm^{-1})	2.22	0.98	5.50
Crystal size (mm)	0.50 × 0.32 × 0.11	0.33 × 0.23 × 0.17	0.31 × 0.11 × 0.10
Data collection			
Diffractometer	Bruker APEXII CCD	Bruker APEXII CCD	Bruker APEXII CCD
Absorption correction	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2015)	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2015)	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2015)
T_{min}, T_{max}	0.668, 1.000	0.835, 1.000	0.473, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	12480, 2125, 2096	72311, 2703, 2703	85384, 5973, 5961
R_{int}	0.026	0.044	0.034
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.591	0.610	0.625
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.033, 0.084, 1.11	0.050, 0.105, 1.34	0.018, 0.041, 1.21
No. of reflections	2125	2703	5973
No. of parameters	172	215	396
No. of restraints	1	3	5
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.25, −0.26	0.79, −0.66	0.76, −0.85

Computer programs: *CrysAlis PRO* (Rigaku OD, 2015), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2016* (Sheldrick, 2015*b*) and *OLEX2* (Dolomanov *et al.*, 2009).

3. Results and discussion

3.1. Description of crystal structures

3.1.1. *N*-(3-Methoxyphenyl)-*N*′-(pyridin-2-yl)thiourea (L1). As reported previously (Giesen *et al.*, 2002), **L1** crystallized in the triclinic space group $P\overline{1}$. The structure was not reported in the standard reduced cell and data were collected at room temperature with Mo *K*α radiation. We report here the low-temperature structure, with reduced cell parameters, collected with Cu *K*α radiation. While this structure is in agreement with the previous report, we have included this result here to confirm the molecular structure of the starting material, which cyclized upon reaction with Cu^{II} and Au^{III} (*vide infra*).

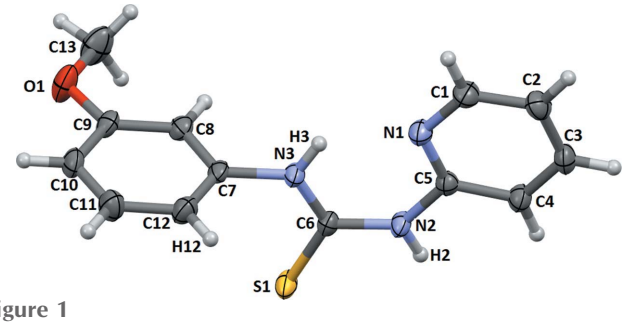


Figure 1
The asymmetric unit of *N*-(3-methoxyphenyl)-*N*′-(pyridin-2-yl)thiourea (**L1**), shown with 50% probability displacement ellipsoids.

The molecular structure of **L1** is nonplanar, with a dihedral angle of 88.70 (5)° between the planes of the pyridine and arene rings (Fig. 1). One amide group makes an intramolecular hydrogen bond with the pyridyl N atom (N3—H3···N1), while the other amide group leads to intermolecular association *via* hydrogen-bonded dimers [N2—H2···S1^{i}; symmetry code: (i) $-x+1, -y+2, -z+2$; Table 2]. Each dimer is further involved in supramolecular π–π interactions *via* the methoxyphenyl rings, with an intermolecular centroid-to-centroid distance of 3.9087 (13) Å and a plane-to-plane shift of 1.908 (3) Å (and, by symmetry, the dihedral angle between the planes is 0°; Fig. 2).

3.1.2. Aquabis[5-methoxy-*N*-(pyridin-2-yl-κN)-1,3-benzothiazol-2-amine-κN^3]copper(II) dinitrate, (I). $[Cu(\mathbf{BL1})_2(H_2O)](NO_3)_2$ crystallized in the orthorhombic space group

Table 2
Hydrogen-bond geometry (Å, °) for **L1**.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···S1^{i}	0.83 (2)	2.62 (2)	3.3882 (13)	154 (2)
N3—H3···N1	0.83 (2)	1.99 (2)	2.6624 (17)	138 (2)

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

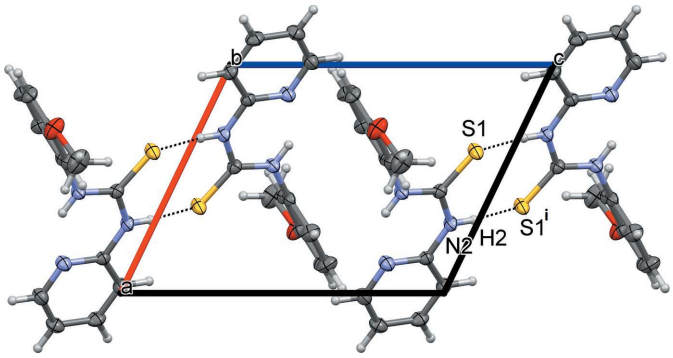


Figure 2
The packed unit cell for *N*-(3-methoxyphenyl)-*N*′-(pyridin-2-yl)thiourea (**L1**), shown with 50% probability displacement ellipsoids. Colour key: grey is carbon, red oxygen, blue nitrogen, yellow sulfur and white hydrogen. [Symmetry code: (i) $-x+1, -y+2, -z+2$.]

Pbcn. Each Cu^{II} ion is coordinated to a single water molecule and in a bidentate manner to two neutral molecules of 5-methoxy-*N*-(pyridin-2-yl)-1,3-benzothiazol-2-amine (**BL1**) *via* pyridyl and benzothiazole N atoms, forming six-membered chelate rings (Fig. 3). Charge balance is maintained by the presence of two nitrate ions per formula unit. The bidentate coordination holds the **BL1** ligand in a near planar geometry, with a dihedral angle of 16.44 (10)° between the pyridyl and benzothiazole ring planes. Half of the complex is contained in the asymmetric unit, with the copper–oxygen bond lying along a twofold rotation axis. The geometry about the Cu^{II} centre is distorted, and closer to trigonal bipyramidal, with a τ value of 0.77 (where $\tau = 0$ is ideal square pyramidal and $\tau = 1$ is ideal trigonal bipyramidal; Addison *et al.*, 1984). Metal–ligand bond lengths are similar (Table 3) but do exhibit a slight axial compression along the Cu1—N3 and Cu1—N3^{i} bonds [symmetry code: (i) $-x+1, y, -z+\frac{3}{2}$], consistent with a d_{z^2} electronic ground state (and consistent also with trigonal–bipyramidal geometry from crystal field theory). Three similar

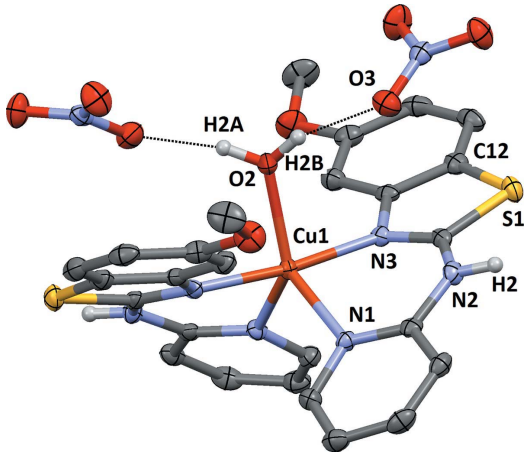


Figure 3
The molecular structure of $[Cu(\mathbf{BL1})_2(H_2O)](NO_3)_2$, (I), shown with 50% probability displacement ellipsoids. Colour key: grey is carbon, red oxygen, blue nitrogen, yellow sulfur and white hydrogen. H atoms not involved in hydrogen bonding (dashed lines) have been omitted for clarity.

Table 3
Selected geometric parameters (Å, °) for (I).

Cu1—O2	2.020 (4)	Cu1—N3	1.962 (3)
Cu1—N1	2.089 (3)		
O2—Cu1—N1	127.91 (8)	N3—Cu1—N1	87.61 (11)
N1^{i}—Cu1—N1	104.18 (15)	N3—Cu1—N1^{i}	96.69 (11)
N3—Cu1—O2	86.51 (8)	N3—Cu1—N3^{i}	173.03 (16)

Symmetry code: (i) $-x+1, y, -z+\frac{3}{2}$.

Table 4
Hydrogen-bond geometry (Å, °) for (I).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2*B*···O3	0.86	1.92	2.715 (3)	151 (3)
O2—H2*A*···O3^{i}	0.86	1.89	2.715 (3)	160
N2—H2···O4^{ii}	0.86 (2)	1.95 (2)	2.781 (4)	162 (4)
C1—H1···O5^{iii}	0.95	2.34	3.268 (4)	165

Symmetry codes: (i) $-x+1, y, -z+\frac{3}{2}$; (ii) $-x+\frac{1}{2}, y+\frac{1}{2}, z$; (iii) $-x+1, y+1, -z+\frac{3}{2}$.

Table 5
Selected geometric parameters (Å, °) for (II).

Au1—Cl1	2.2592 (7)	Au1—Cl2	2.2560 (7)
S1···S2	3.7260 (8)		
Cl2—Au1—Cl1	179.62 (3)		

complexes have been reported previously (West *et al.*, 2003), *viz.* bis[2-(5-picolylamino)-*X*-methoxybenzothiazole]copper(II), where *X* = 2, 3 or 4. For all three, the Cu^{II} centre was four-coordinated involving only two benzothiazole ligands, each in a bidentate coordination mode. Unlike the current report, for those compounds the amine group was deprotonated, leading to a charge-balanced complex with no counter-ions.

Intermolecular interactions with free bridging nitrate counter-ions led to the formation of an infinite two-dimensional network in the (001) plane (Fig. 4), generated by hydrogen bonds with the coordinated water molecule [O2—H2*B*···O3 and O2—H2*A*···O3^{i}; symmetry code: (i) $-x+1, y, -z+\frac{3}{2}$; Table 4 and blue dashed lines in Fig. 4], with base vector [010], and with the ligand amine [N2—H2···O4^{ii}; symmetry code: (ii) $-x+\frac{1}{2}, y+\frac{1}{2}, z$; magenta dashed lines in Fig. 4], with base vector [100]. The S atoms appear to be involved in no significant supramolecular interactions (either to metal cations or *via* nontraditional hydrogen bonding or with other S atoms.)

3.1.3. Crystal structure of bis{2-[(5-methoxy-1,3-benzothiazol-2-yl)amino]pyridin-1-ium} dichloridogold(I) chloride monohydrate, (II). $(H\mathbf{BL1})_2[AuCl_2]Cl\cdot H_2O$ crystallized in the triclinic space group $P\overline{1}$. The asymmetric unit contains two pyridyl-protonated cations of **BL1**, denoted H**BL1**, one dichloridogold(I) anion (not bound to the benzothiazole molecule), an additional chloride ion (which maintains charge balance) and one lattice solvent molecule of water (Fig. 5; see §S2 of the supporting information for an NMR spectrum). In the asymmetric unit, the two cations associate directly through short intermolecular S···S contacts (Table 5) and π–π inter-

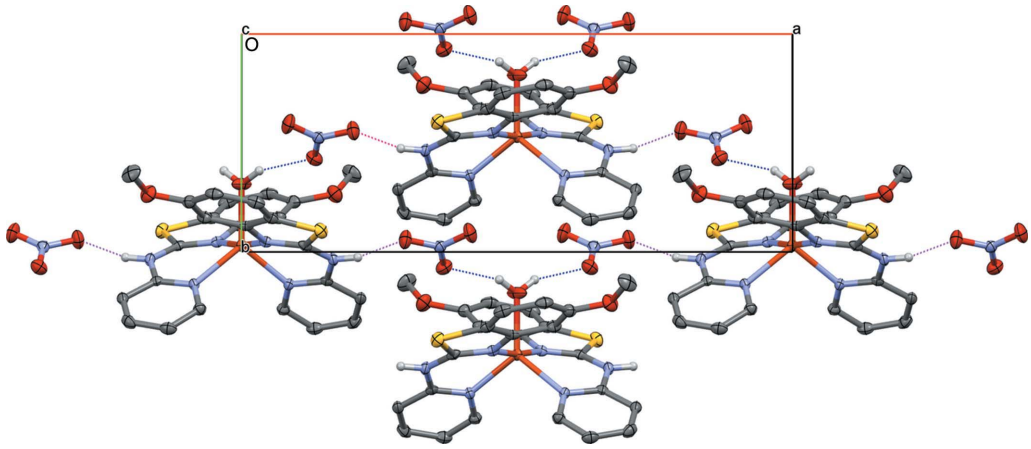


Figure 4
A packing view of [Cu(**BL1**)$_2$(H$_2$O)](NO$_3$)$_2$, (I), showing the two-dimensional hydrogen-bonded network in the (001) plane (viewed down the *c* axis) and 50% probability displacement ellipsoids. Colour key: orange is copper, grey carbon, red oxygen, blue nitrogen, yellow sulfur and white hydrogen. H atoms not involved in hydrogen bonding (dashed lines) have been omitted for clarity.

Table 6
Selected short intermolecular interactions for (H**BL1**)$_2$[AuCl$_2$]Cl·H$_2$O, (II).

*Cg*1 is the centroid of the N1/C1–C5 ring, *Cg*2 that of the C7–C12 ring, *Cg*3 that of the N4/C14–C18 ring and *Cg*4 that of the C20–C25 ring.

Centroids	*Cg*···*Cg* (Å)	Dihedral angle between planes (°)
*Cg*1···*Cg*3	3.8422 (14)	6.43 (8)
*Cg*2···*Cg*4	3.7491 (14)	3.38 (8)
*Cg*1···*Cg*2^{i}	3.8172 (14)	3.92 (8)
*Cg*3···*Cg*4^{ii}	3.7667 (14)	3.00 (8)

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

Table 7
Hydrogen-bond geometry (Å, °) for (II).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N5—H5···O3	0.85 (2)	1.91 (2)	2.758 (3)	173 (3)
N2—H2···Cl3	0.85 (2)	2.23 (2)	3.084 (2)	176 (4)
C3—H3···O1^{i}	0.95	2.46	3.284 (3)	145
O3—H3*A*···Cl3	0.78 (3)	2.39 (3)	3.155 (2)	171 (4)
O3—H3*B*···Cl3^{ii}	0.78 (3)	2.41 (3)	3.188 (2)	174 (4)

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

actions (Table 6), and indirectly through hydrogen bonding (Table 7 and Fig. 6). Molecules in the asymmetric unit are involved in further intermolecular π–π interactions with molecules in neighbouring units (Table 6).

3.2. Comment on reaction mechanism

Consistent with the two previous reports (West *et al.*, 2003; Tadjarodi *et al.*, 2007), where Cu^{II} was employed towards the intramolecular heterocyclic rearrangement of thioureas to benzothiazoles, the results of this study point to metal-cation reduction coupled with the oxidative cyclization process. In the reaction leading to the formation of [Cu(**BL1**)$_2$(H$_2$O)](NO$_3$)$_2$, (I), the initial observation upon addition of Cu(NO$_3$)$_2$ to **L1** was the formation of a colourless solution, consistent with the reduction of Cu^{II} to Cu^{I}. For this reaction, the solution was allowed to stand, exposed to regular atmo-

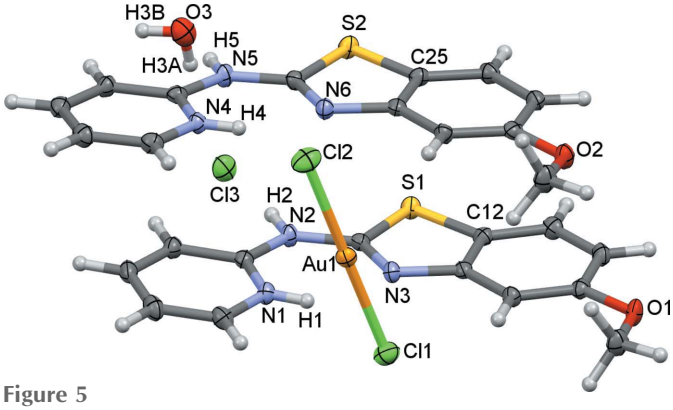


Figure 5
The asymmetric unit of (H**BL1**)$_2$[AuCl$_2$]Cl·H$_2$O, (II), shown with 50% probability displacement ellipsoids. Colour key: light orange is gold, grey carbon, red oxygen, blue nitrogen, yellow sulfur, white hydrogen and green chlorine.

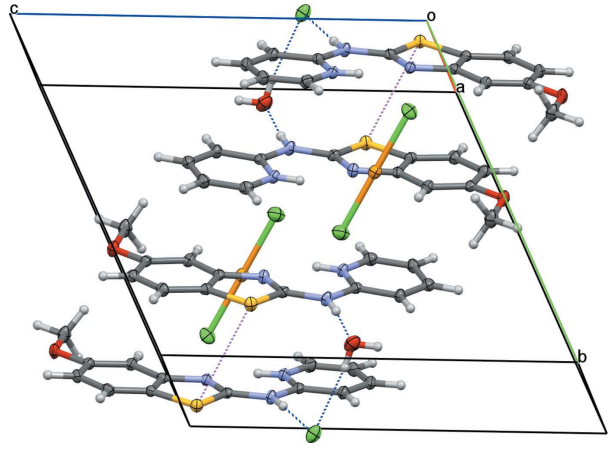


Figure 6
The packed unit cell for (H**BL1**)$_2$[AuCl$_2$]Cl·H$_2$O, (II), with 50% probability displacement ellipsoids. Colour key: light orange is gold, grey carbon, red oxygen, blue nitrogen, yellow sulfur, white hydrogen and green chlorine. Hydrogen-bond interactions are represented by blue dashed lines and short S···S interactions are represented by magenta dashed lines.

spheric conditions, and subsequently turned green, characteristic of oxidation of Cu^{I} back to Cu^{II}. Attempts to convert a variety of thioureas to benzothiazoles were undertaken (see supporting information), however, the presence of an electron-donating group appears to be required for cyclization (see Table S1 in the supporting information)

Interestingly, there is a previous report (Tadjarodi *et al.*, 2007) of the structure of 5-methoxy-*N*-(pyridin-2-yl)-1,3-benzothiazole, resulting from evaporation of the filtrate of the reaction of **L1** with copper acetate. The authors report a formula based on elemental analysis for their major product (an olive-green powder), which appears to correspond to (**L1**–H)$_2$Cu^{II}, analogous to the structures reported by West *et al.* (2003) (though this is not stated and no structure is included). The authors did not include any observations of a colour change upon reaction to indicate if the reduction to Cu^{I} was implicated in their reaction (though it could be speculated that the oxidation of Cu^{I} to Cu^{II} may have proceeded at a diffusion-limited rate with ample stirring under normal atmospheric onditions). The authors do state that the formation of the benzothiazole was the result of an oxidative cyclization.

Finally, the structure for (H**BL1**)$_2$[AuCl$_2$]Cl·H$_2$O, (II), supports the proposed metal reduction required for C—H bond activation. This structure resulted from the reaction of Au^{III} with **L1**, yet the crystal structure, NMR data and elemental analysis of the bulk product indicate the presence of only the protonated 2-aminobenzothiazole and Au^{I}.

4. Conclusion

Herein, we have reported on the facile metal-mediated transformation of *N*-(3-methoxyphenyl)-*N*′-(pyridin-2-yl)thiourea to 5-methoxy-*N*-(pyridin-2-yl)-1,3-benzothiazole. While not unprecedented, this report supports the requirement that an electron-donating group should be present for the cyclization and offers complimentary evidence from an Au^{I} structure that the role of the metal cation in the reaction is not catalytic, but rather involves a redox process between the thiourea substrate and the metal cation.

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supporting information

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Copper(II)- and gold(III)-mediated cyclization of a thiourea to a substituted 2-aminobenzothiazole

Zachary W. Schroeder, L. K. Hiscock and Louise Nicole Dawe

Computing details

For all structures, data collection: *CrysAlis PRO* (Rigaku OD, 2015); cell refinement: *CrysAlis PRO* (Rigaku OD, 2015); data reduction: *CrysAlis PRO* (Rigaku OD, 2015); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2016* (Sheldrick, 2015b); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

N-(3-Methoxyphenyl)-*N*′-(pyridin-2-yl)thiourea (n17037)

Crystal data

$C_{13}H_{13}N_3OS$
$M_r = 259.32$
Triclinic, $P\overline{1}$
$a = 8.4341$ (2) Å
$b = 8.6991$ (2) Å
$c = 10.1083$ (2) Å
$\alpha = 91.249$ (2)°
$\beta = 113.506$ (2)°
$\gamma = 110.292$ (2)°
$V = 626.73$ (3) Å^3
$Z = 2$
$F(000) = 272$
$D_x = 1.374$ Mg m^{-3}
Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å
Cell parameters from 11716 reflections
$\theta = 4.8$–$65.6°$
$\mu = 2.22$ mm^{-1}
$T = 173$ K
Prism, colorless
0.50 × 0.32 × 0.11 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed X-ray tube, Enhance (Cu) X-ray Source
Graphite monochromator
ω and φ scans
Absorption correction: multi-scan (CrysAlis PRO; Rigaku OD, 2015)
$T_{min} = 0.668$, $T_{max} = 1.000$
12480 measured reflections
2125 independent reflections
2096 reflections with $I > 2\sigma(I)$
$R_{int} = 0.026$
$\theta_{max} = 65.6°$, $\theta_{min} = 4.9°$
$h = -9 \rightarrow 9$
$k = -10 \rightarrow 9$
$l = -11 \rightarrow 11$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.084$
$S = 1.11$
2125 reflections
172 parameters
1 restraint
Primary atom site location: dual
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0415P)^2 + 0.2867P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.25$ e Å^{-3}
$\Delta\rho_{min} = -0.26$ 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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.37970 (5)	0.74874 (4)	0.88794 (4)	0.02876 (15)
O1	0.28022 (18)	0.16770 (13)	0.55060 (13)	0.0385 (3)
N1	0.87028 (18)	1.03625 (15)	0.77940 (14)	0.0266 (3)
N2	0.69580 (18)	0.98474 (15)	0.91734 (14)	0.0236 (3)
H2	0.680 (3)	1.026 (2)	0.9837 (19)	0.031 (5)*
N3	0.55882 (18)	0.76960 (15)	0.71919 (14)	0.0244 (3)
H3	0.648 (3)	0.821 (2)	0.701 (2)	0.040 (5)*
C1	1.0155 (2)	1.1378 (2)	0.75682 (18)	0.0305 (4)
H1	1.032837	1.102259	0.675841	0.037*
C2	1.1401 (2)	1.29027 (19)	0.84484 (18)	0.0303 (4)
H2A	1.240860	1.358462	0.825316	0.036*
C3	1.1143 (2)	1.34169 (19)	0.96316 (18)	0.0297 (4)
H3A	1.197544	1.446526	1.025915	0.036*
C4	0.9675 (2)	1.23997 (19)	0.98894 (17)	0.0268 (3)
H4	0.948182	1.272457	1.069814	0.032*
C5	0.84737 (19)	1.08752 (17)	0.89301 (15)	0.0215 (3)
C6	0.5532 (2)	0.83663 (17)	0.83584 (15)	0.0215 (3)
C7	0.4118 (2)	0.62124 (18)	0.61906 (16)	0.0225 (3)
C8	0.4249 (2)	0.46847 (18)	0.64025 (16)	0.0239 (3)
H8	0.528426	0.461636	0.721088	0.029*
C9	0.2840 (2)	0.32518 (18)	0.54118 (16)	0.0247 (3)
C10	0.1332 (2)	0.33607 (19)	0.42311 (17)	0.0297 (4)
H10	0.036818	0.238022	0.355995	0.036*
C11	0.1238 (2)	0.4893 (2)	0.40360 (18)	0.0349 (4)
H11	0.020819	0.496461	0.322431	0.042*
C12	0.2633 (2)	0.6337 (2)	0.50136 (18)	0.0313 (4)
H12	0.256619	0.739342	0.487419	0.038*
C13	0.4251 (3)	0.1471 (2)	0.6749 (2)	0.0457 (5)
H13A	0.402596	0.028361	0.670313	0.069*
H13B	0.425443	0.190958	0.765138	0.069*
H13C	0.546803	0.207955	0.674384	0.069*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0302 (2)	0.0208 (2)	0.0309 (2)	−0.00158 (16)	0.01936 (18)	−0.00503 (15)
O1	0.0508 (7)	0.0212 (6)	0.0308 (6)	0.0126 (5)	0.0071 (5)	−0.0007 (5)

N1	0.0268 (7)	0.0217 (6)	0.0297 (7)	0.0043 (5)	0.0155 (6)	−0.0001 (5)
N2	0.0258 (6)	0.0191 (6)	0.0226 (6)	0.0028 (5)	0.0126 (5)	−0.0036 (5)
N3	0.0230 (7)	0.0203 (6)	0.0260 (7)	0.0017 (5)	0.0131 (5)	−0.0042 (5)
C1	0.0311 (8)	0.0276 (8)	0.0350 (9)	0.0076 (7)	0.0198 (7)	0.0035 (7)
C2	0.0268 (8)	0.0248 (8)	0.0388 (9)	0.0057 (6)	0.0174 (7)	0.0077 (7)
C3	0.0252 (8)	0.0206 (7)	0.0316 (8)	0.0014 (6)	0.0076 (7)	−0.0001 (6)
C4	0.0270 (8)	0.0235 (8)	0.0246 (8)	0.0053 (6)	0.0100 (6)	−0.0012 (6)
C5	0.0210 (7)	0.0193 (7)	0.0220 (7)	0.0070 (6)	0.0082 (6)	0.0034 (6)
C6	0.0232 (7)	0.0165 (7)	0.0220 (7)	0.0063 (6)	0.0087 (6)	0.0005 (6)
C7	0.0224 (7)	0.0202 (7)	0.0232 (7)	0.0035 (6)	0.0127 (6)	−0.0041 (6)
C8	0.0257 (8)	0.0252 (8)	0.0198 (7)	0.0088 (6)	0.0101 (6)	0.0002 (6)
C9	0.0329 (8)	0.0196 (7)	0.0218 (7)	0.0076 (6)	0.0145 (6)	−0.0006 (6)
C10	0.0281 (8)	0.0245 (8)	0.0253 (8)	0.0037 (6)	0.0072 (6)	−0.0058 (6)
C11	0.0292 (8)	0.0332 (9)	0.0304 (9)	0.0116 (7)	0.0024 (7)	−0.0021 (7)
C12	0.0332 (9)	0.0240 (8)	0.0338 (9)	0.0126 (7)	0.0107 (7)	0.0002 (7)
C13	0.0624 (12)	0.0315 (9)	0.0382 (10)	0.0249 (9)	0.0114 (9)	0.0076 (8)

Geometric parameters (Å, º)

S1—C6	1.6910 (15)	C3—C4	1.375 (2)
O1—C9	1.3655 (19)	C4—H4	0.9500
O1—C13	1.428 (2)	C4—C5	1.398 (2)
N1—C1	1.347 (2)	C7—C8	1.386 (2)
N1—C5	1.3303 (19)	C7—C12	1.381 (2)
N2—H2	0.833 (17)	C8—H8	0.9500
N2—C5	1.4007 (19)	C8—C9	1.392 (2)
N2—C6	1.3689 (19)	C9—C10	1.389 (2)
N3—H3	0.828 (17)	C10—H10	0.9500
N3—C6	1.3290 (19)	C10—C11	1.377 (2)
N3—C7	1.4352 (18)	C11—H11	0.9500
C1—H1	0.9500	C11—C12	1.390 (2)
C1—C2	1.375 (2)	C12—H12	0.9500
C2—H2A	0.9500	C13—H13A	0.9800
C2—C3	1.389 (2)	C13—H13B	0.9800
C3—H3A	0.9500	C13—H13C	0.9800
C9—O1—C13	117.87 (13)	N3—C6—N2	117.86 (13)
C5—N1—C1	117.73 (13)	C8—C7—N3	119.07 (13)
C5—N2—H2	115.5 (13)	C12—C7—N3	119.58 (13)
C6—N2—H2	113.8 (13)	C12—C7—C8	121.32 (14)
C6—N2—C5	129.96 (13)	C7—C8—H8	120.5
C6—N3—H3	117.5 (14)	C7—C8—C9	118.93 (14)
C6—N3—C7	123.30 (13)	C9—C8—H8	120.5
C7—N3—H3	119.1 (14)	O1—C9—C8	124.51 (14)
N1—C1—H1	118.3	O1—C9—C10	115.24 (13)
N1—C1—C2	123.43 (15)	C10—C9—C8	120.24 (14)
C2—C1—H1	118.3	C9—C10—H10	120.1
C1—C2—H2A	121.0	C11—C10—C9	119.82 (14)

C1—C2—C3	118.07 (14)	C11—C10—H10	120.1
C3—C2—H2A	121.0	C10—C11—H11	119.6
C2—C3—H3A	120.2	C10—C11—C12	120.72 (15)
C4—C3—C2	119.63 (14)	C12—C11—H11	119.6
C4—C3—H3A	120.2	C7—C12—C11	118.96 (15)
C3—C4—H4	120.9	C7—C12—H12	120.5
C3—C4—C5	118.25 (14)	C11—C12—H12	120.5
C5—C4—H4	120.9	O1—C13—H13A	109.5
N1—C5—N2	118.64 (13)	O1—C13—H13B	109.5
N1—C5—C4	122.89 (13)	O1—C13—H13C	109.5
C4—C5—N2	118.47 (13)	H13A—C13—H13B	109.5
N2—C6—S1	118.69 (11)	H13A—C13—H13C	109.5
N3—C6—S1	123.46 (11)	H13B—C13—H13C	109.5

O1—C9—C10—C11	−179.94 (15)	C6—N2—C5—C4	175.50 (14)
N1—C1—C2—C3	0.0 (2)	C6—N3—C7—C8	−94.15 (17)
N3—C7—C8—C9	−178.66 (13)	C6—N3—C7—C12	87.82 (19)
N3—C7—C12—C11	178.71 (14)	C7—N3—C6—S1	4.4 (2)
C1—N1—C5—N2	179.20 (13)	C7—N3—C6—N2	−175.49 (13)
C1—N1—C5—C4	−0.5 (2)	C7—C8—C9—O1	−179.53 (14)
C1—C2—C3—C4	0.2 (2)	C7—C8—C9—C10	0.1 (2)
C2—C3—C4—C5	−0.6 (2)	C8—C7—C12—C11	0.7 (2)
C3—C4—C5—N1	0.7 (2)	C8—C9—C10—C11	0.4 (2)
C3—C4—C5—N2	−178.94 (13)	C9—C10—C11—C12	−0.3 (3)
C5—N1—C1—C2	0.1 (2)	C10—C11—C12—C7	−0.2 (3)
C5—N2—C6—S1	−175.35 (12)	C12—C7—C8—C9	−0.7 (2)
C5—N2—C6—N3	4.6 (2)	C13—O1—C9—C8	3.6 (2)
C6—N2—C5—N1	−4.2 (2)	C13—O1—C9—C10	−176.05 (15)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···S1^{i}	0.83 (2)	2.62 (2)	3.3882 (13)	154 (2)
N3—H3···N1	0.83 (2)	1.99 (2)	2.6624 (17)	138 (2)

Symmetry code: (i) −*x*+1, −*y*+2, −*z*+2.

Aquabis[5-methoxy-*N*-(pyridin-2-yl-κ*N*)benzothiazol-2-amine-κ*N*^{3}]copper(II) dinitrate (b17199)

Crystal data

$[Cu(C_{13}H_{11}N_3OS)_2(H_2O)](NO_3)_2$
M_r = 720.19
Orthorhombic, *Pbcn*
a = 18.1534 (4) Å
b = 7.1814 (1) Å
c = 21.8523 (4) Å
V = 2848.81 (9) Å^3
Z = 4
F(000) = 1476

D_x = 1.679 Mg m^{-3}
Mo *Kα* radiation, λ = 0.71073 Å
Cell parameters from 62086 reflections
θ = 2.2–39.5°
μ = 0.98 mm^{-1}
T = 110 K
Prism, green
0.33 × 0.23 × 0.17 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed X-ray tube, Enhance (Mo) X-ray Source
Graphite monochromator
ω and φ scans
Absorption correction: multi-scan (CrysAlis PRO; Rigaku OD, 2015)
T_{min} = 0.835, T_{max} = 1.000

72311 measured reflections
2703 independent reflections
2703 reflections with $I > 2\sigma(I)$
R_{int} = 0.044
θ_{max} = 25.7°, θ_{min} = 2.9°
h = −22→17
k = −8→8
l = −26→26

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.105
S = 1.34
2703 reflections
215 parameters
3 restraints
Primary atom site location: dual

Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0189P)^2 + 9.2626P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.79 e Å^{-3}
$\Delta\rho_{min}$ = −0.66 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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
Cu1	0.500000	0.47025 (8)	0.750000	0.01397 (16)	
S1	0.35592 (5)	0.40264 (13)	0.58540 (4)	0.0215 (2)	
O1	0.66894 (15)	0.2340 (4)	0.56003 (12)	0.0299 (6)	
O2	0.500000	0.1889 (5)	0.750000	0.0364 (10)	
H2A	0.5393 (11)	0.1272 (12)	0.759 (3)	0.055*	0.5
H2B	0.468 (2)	0.1274 (12)	0.729 (2)	0.055*	0.5
N1	0.41384 (14)	0.6490 (4)	0.77375 (12)	0.0149 (6)	
N2	0.33369 (15)	0.5337 (4)	0.69802 (13)	0.0179 (6)	
H2	0.2892 (12)	0.525 (6)	0.6845 (16)	0.021*	
N3	0.45591 (15)	0.4536 (4)	0.66819 (12)	0.0145 (6)	
C1	0.42390 (19)	0.7627 (5)	0.82261 (15)	0.0190 (7)	
H1	0.472590	0.782092	0.837217	0.023*	
C2	0.3669 (2)	0.8512 (5)	0.85188 (16)	0.0238 (8)	
H2C	0.375935	0.931356	0.885621	0.029*	
C3	0.2957 (2)	0.8207 (5)	0.83105 (16)	0.0245 (8)	
H3	0.255062	0.873649	0.852165	0.029*	
C4	0.28424 (18)	0.7144 (5)	0.78011 (16)	0.0204 (7)	
H4	0.236004	0.695842	0.764397	0.024*	
C5	0.34564 (18)	0.6334 (4)	0.75162 (15)	0.0166 (7)	
C6	0.38493 (18)	0.4711 (5)	0.65788 (14)	0.0159 (7)	

C7	0.49227 (19)	0.3806 (4)	0.61717 (15)	0.0179 (7)
C8	0.5671 (2)	0.3422 (5)	0.61330 (15)	0.0209 (7)
H8	0.598738	0.364950	0.647094	0.025*
C9	0.5946 (2)	0.2700 (5)	0.55917 (16)	0.0229 (8)
C10	0.5492 (2)	0.2336 (5)	0.50918 (16)	0.0248 (8)
H10	0.569235	0.183235	0.472601	0.030*
C11	0.4744 (2)	0.2715 (5)	0.51330 (16)	0.0246 (8)
H11	0.442796	0.248001	0.479545	0.030*
C12	0.44650 (19)	0.3441 (5)	0.56721 (15)	0.0199 (7)
C13	0.7001 (2)	0.1407 (6)	0.50876 (18)	0.0347 (10)
H13A	0.696266	0.220385	0.472504	0.052*
H13B	0.673452	0.024068	0.501516	0.052*
H13C	0.752063	0.113305	0.516961	0.052*
O3	0.36773 (14)	0.0698 (4)	0.70721 (12)	0.0281 (6)
O4	0.29737 (14)	−0.0570 (4)	0.63928 (12)	0.0302 (6)
O5	0.41492 (14)	−0.0873 (4)	0.63256 (13)	0.0340 (7)
N4	0.36037 (15)	−0.0238 (4)	0.65980 (13)	0.0197 (6)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0135 (3)	0.0163 (3)	0.0122 (3)	0.000	−0.0014 (2)	0.000
S1	0.0219 (4)	0.0260 (5)	0.0168 (4)	−0.0031 (4)	−0.0056 (3)	0.0002 (3)
O1	0.0295 (14)	0.0349 (15)	0.0252 (13)	0.0057 (12)	0.0083 (11)	−0.0043 (12)
O2	0.046 (3)	0.0155 (18)	0.048 (2)	0.000	−0.033 (2)	0.000
N1	0.0120 (13)	0.0151 (13)	0.0177 (13)	0.0017 (11)	0.0007 (10)	0.0004 (11)
N2	0.0121 (13)	0.0196 (15)	0.0218 (14)	−0.0023 (11)	−0.0011 (11)	0.0020 (12)
N3	0.0183 (14)	0.0141 (14)	0.0112 (12)	−0.0012 (11)	0.0000 (10)	0.0014 (11)
C1	0.0197 (17)	0.0173 (16)	0.0200 (16)	0.0001 (13)	−0.0019 (13)	−0.0021 (14)
C2	0.032 (2)	0.0183 (18)	0.0214 (17)	0.0021 (15)	0.0020 (15)	−0.0016 (14)
C3	0.0248 (18)	0.0224 (18)	0.0264 (18)	0.0071 (15)	0.0091 (15)	0.0028 (15)
C4	0.0143 (16)	0.0193 (17)	0.0276 (18)	0.0011 (13)	0.0016 (14)	0.0063 (15)
C5	0.0180 (16)	0.0117 (15)	0.0202 (16)	−0.0021 (12)	0.0008 (13)	0.0037 (13)
C6	0.0215 (16)	0.0136 (16)	0.0127 (15)	−0.0039 (13)	−0.0017 (13)	0.0024 (13)
C7	0.0266 (18)	0.0109 (15)	0.0162 (15)	−0.0008 (14)	0.0011 (13)	0.0016 (12)
C8	0.0248 (18)	0.0191 (17)	0.0189 (16)	−0.0013 (15)	0.0002 (14)	−0.0018 (14)
C9	0.0259 (18)	0.0180 (17)	0.0249 (18)	0.0003 (15)	0.0053 (15)	0.0007 (15)
C10	0.038 (2)	0.0168 (17)	0.0194 (18)	−0.0019 (16)	0.0061 (15)	−0.0022 (14)
C11	0.038 (2)	0.0204 (18)	0.0155 (17)	−0.0066 (16)	−0.0015 (15)	0.0000 (14)
C12	0.0251 (18)	0.0169 (16)	0.0178 (16)	−0.0037 (14)	0.0003 (14)	0.0029 (14)
C13	0.040 (2)	0.036 (2)	0.028 (2)	0.0104 (19)	0.0169 (17)	−0.0028 (18)
O3	0.0310 (14)	0.0261 (14)	0.0272 (13)	−0.0052 (11)	0.0005 (11)	−0.0018 (12)
O4	0.0180 (13)	0.0412 (17)	0.0314 (14)	−0.0043 (12)	−0.0017 (11)	−0.0054 (13)
O5	0.0202 (13)	0.0452 (17)	0.0367 (15)	0.0088 (13)	0.0059 (11)	0.0007 (14)
N4	0.0165 (14)	0.0191 (15)	0.0234 (15)	−0.0001 (12)	0.0011 (12)	0.0047 (12)

Geometric parameters (Å, º)

Cu1—O2	2.020 (4)	C2—H2C	0.9500
Cu1—N1^{i}	2.089 (3)	C2—C3	1.387 (5)
Cu1—N1	2.089 (3)	C3—H3	0.9500
Cu1—N3^{i}	1.962 (3)	C3—C4	1.366 (5)
Cu1—N3	1.962 (3)	C4—H4	0.9500
S1—C6	1.740 (3)	C4—C5	1.403 (5)
S1—C12	1.743 (4)	C7—C8	1.388 (5)
O1—C9	1.374 (4)	C7—C12	1.397 (5)
O1—C13	1.423 (4)	C8—H8	0.9500
O2—H2A^{i}	0.861 (7)	C8—C9	1.385 (5)
O2—H2A	0.861 (14)	C9—C10	1.393 (5)
O2—H2B^{i}	0.861 (7)	C10—H10	0.9500
O2—H2B	0.861 (14)	C10—C11	1.387 (5)
N1—C1	1.357 (4)	C11—H11	0.9500
N1—C5	1.334 (4)	C11—C12	1.384 (5)
N2—H2	0.861 (18)	C13—H13A	0.9800
N2—C5	1.390 (4)	C13—H13B	0.9800
N2—C6	1.355 (4)	C13—H13C	0.9800
N3—C6	1.314 (4)	O3—N4	1.242 (4)
N3—C7	1.398 (4)	O4—N4	1.251 (4)
C1—H1	0.9500	O5—N4	1.242 (4)
C1—C2	1.372 (5)		

O2—Cu1—N1	127.91 (8)	C4—C3—H3	120.1
O2—Cu1—N1^{i}	127.91 (7)	C3—C4—H4	120.9
N1^{i}—Cu1—N1	104.18 (15)	C3—C4—C5	118.2 (3)
N3—Cu1—O2	86.51 (8)	C5—C4—H4	120.9
N3^{i}—Cu1—O2	86.51 (8)	N1—C5—N2	119.6 (3)
N3—Cu1—N1	87.61 (11)	N1—C5—C4	122.8 (3)
N3—Cu1—N1^{i}	96.69 (11)	N2—C5—C4	117.6 (3)
N3^{i}—Cu1—N1^{i}	87.61 (11)	N2—C6—S1	118.4 (2)
N3^{i}—Cu1—N1	96.69 (11)	N3—C6—S1	115.2 (2)
N3—Cu1—N3^{i}	173.03 (16)	N3—C6—N2	126.4 (3)
C6—S1—C12	89.44 (16)	C8—C7—N3	125.8 (3)
C9—O1—C13	117.9 (3)	C8—C7—C12	119.8 (3)
Cu1—O2—H2A	121.0	C12—C7—N3	114.4 (3)
Cu1—O2—H2A^{i}	121.0 (8)	C7—C8—H8	120.7
Cu1—O2—H2B	120.9	C9—C8—C7	118.6 (3)
Cu1—O2—H2B^{i}	120.9 (8)	C9—C8—H8	120.7
H2A—O2—H2A^{i}	118.0	O1—C9—C8	114.4 (3)
H2A—O2—H2B	114.6	O1—C9—C10	123.8 (3)
H2A^{i}—O2—H2B^{i}	114.6	C8—C9—C10	121.8 (3)
H2B—O2—H2B^{i}	118.2	C9—C10—H10	120.3
C1—N1—Cu1	117.7 (2)	C11—C10—C9	119.4 (3)
C5—N1—Cu1	123.6 (2)	C11—C10—H10	120.3
C5—N1—C1	117.4 (3)	C10—C11—H11	120.4

C5—N2—H2	118 (3)	C12—C11—C10	119.2 (3)
C6—N2—H2	113 (3)	C12—C11—H11	120.4
C6—N2—C5	127.5 (3)	C7—C12—S1	109.7 (3)
C6—N3—Cu1	123.4 (2)	C11—C12—S1	129.1 (3)
C6—N3—C7	111.2 (3)	C11—C12—C7	121.2 (3)
C7—N3—Cu1	123.8 (2)	O1—C13—H13A	109.5
N1—C1—H1	118.5	O1—C13—H13B	109.5
N1—C1—C2	122.9 (3)	O1—C13—H13C	109.5
C2—C1—H1	118.5	H13A—C13—H13B	109.5
C1—C2—H2C	120.8	H13A—C13—H13C	109.5
C1—C2—C3	118.5 (3)	H13B—C13—H13C	109.5
C3—C2—H2C	120.8	O3—N4—O4	120.0 (3)
C2—C3—H3	120.1	O3—N4—O5	120.8 (3)
C4—C3—C2	119.9 (3)	O5—N4—O4	119.1 (3)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2*B*···O3	0.86	1.92	2.715 (3)	151 (3)
O2—H2*A*···O3^{i}	0.86	1.89	2.715 (3)	160
N2—H2···O4^{ii}	0.86 (2)	1.95 (2)	2.781 (4)	162 (4)
C1—H1···O5^{iii}	0.95	2.34	3.268 (4)	165

Symmetry codes: (i) $-x+1, y, -z+3/2$; (ii) $-x+1/2, y+1/2, z$; (iii) $-x+1, y+1, -z+3/2$.

Bis{2-[(5-methoxy-1,3-benzothiazol-2-yl)amino]pyridin-1-ium} dichloridogold(I) chloride monohydrate (b18056)

Crystal data

$(C_{13}H_{12}N_3OS)_2[AuCl_2]Cl\cdot H_2O$
$M_r = 837.96$
Triclinic, $P\overline{1}$
$a = 10.0052$ (1) Å
$b = 12.5940$ (2) Å
$c = 12.9412$ (1) Å
$\alpha = 111.867$ (1)°
$\beta = 97.271$ (1)°
$\gamma = 99.755$ (1)°
$V = 1459.03$ (3) Å^3
$Z = 2$
$F(000) = 820$
$D_x = 1.907$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 104589 reflections
$\theta = 2.0$–50.4°
$\mu = 5.50$ mm^{-1}
$T = 110$ K
Prism, colorless
0.31 × 0.11 × 0.10 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed X-ray tube, Enhance (Mo) X-ray Source
Graphite monochromator
ω and φ scans
Absorption correction: multi-scan (CrysAlis PRO; Rigaku OD, 2015)
$T_{min} = 0.473$, $T_{max} = 1.000$
85384 measured reflections
5973 independent reflections
5961 reflections with $I > 2\sigma(I)$
$R_{int} = 0.034$
$\theta_{max} = 26.4°$, $\theta_{min} = 2.1°$
$h = -12\rightarrow12$
$k = -15\rightarrow15$
$l = -16\rightarrow16$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.018$
$wR(F^2) = 0.041$
$S = 1.21$
5973 reflections
396 parameters
5 restraints
Primary atom site location: dual
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0122P)^2 + 2.4258P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.004$
$\Delta\rho_{max} = 0.76$ e Å^{-3}
$\Delta\rho_{min} = -0.85$ 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}
S2	0.41939 (6)	0.75769 (5)	0.72552 (5)	0.01731 (12)
O2	0.69431 (19)	0.54362 (16)	0.99756 (15)	0.0200 (4)
N4	0.6790 (2)	0.59876 (18)	0.46614 (18)	0.0151 (4)
H4	0.685 (3)	0.588 (3)	0.524 (2)	0.026 (9)*
N5	0.5244 (2)	0.71619 (19)	0.53596 (18)	0.0166 (4)
H5	0.475 (3)	0.762 (2)	0.527 (3)	0.030 (9)*
N6	0.6055 (2)	0.63748 (18)	0.66463 (17)	0.0162 (4)
C14	0.7519 (3)	0.5493 (2)	0.3865 (2)	0.0188 (5)
H14	0.809858	0.500715	0.398392	0.023*
C15	0.7421 (3)	0.5692 (2)	0.2899 (2)	0.0203 (5)
H15	0.792297	0.534357	0.233677	0.024*
C16	0.6570 (3)	0.6418 (2)	0.2745 (2)	0.0192 (5)
H16	0.650252	0.657322	0.207853	0.023*
C17	0.5831 (3)	0.6909 (2)	0.3550 (2)	0.0176 (5)
H17	0.524868	0.739685	0.344054	0.021*
C18	0.5944 (2)	0.6682 (2)	0.4532 (2)	0.0147 (5)
C19	0.5267 (2)	0.6976 (2)	0.6343 (2)	0.0151 (5)
C20	0.5867 (2)	0.6376 (2)	0.7700 (2)	0.0154 (5)
C21	0.6560 (2)	0.5815 (2)	0.8265 (2)	0.0158 (5)
H21	0.719188	0.537189	0.793601	0.019*
C22	0.6301 (2)	0.5923 (2)	0.9322 (2)	0.0162 (5)
C23	0.5347 (3)	0.6558 (2)	0.9798 (2)	0.0169 (5)
H23	0.518375	0.661493	1.052217	0.020*
C24	0.4644 (3)	0.7100 (2)	0.9233 (2)	0.0180 (5)
H24	0.399545	0.752526	0.955570	0.022*
C25	0.4912 (2)	0.7005 (2)	0.8175 (2)	0.0149 (5)
C26	0.7772 (3)	0.4653 (3)	0.9462 (2)	0.0249 (6)
H26A	0.721112	0.401457	0.875988	0.037*
H26B	0.811827	0.432201	0.998916	0.037*
H26C	0.855757	0.508348	0.928260	0.037*

S1	0.67232 (6)	1.00715 (5)	0.96345 (5)	0.01600 (12)
O1	0.93392 (19)	0.79817 (16)	1.24720 (14)	0.0197 (4)
N1	0.9505 (2)	0.85301 (18)	0.71852 (18)	0.0162 (4)
H1	0.960 (3)	0.849 (3)	0.779 (2)	0.025 (8)*
N2	0.7788 (2)	0.95630 (18)	0.77372 (17)	0.0158 (4)
H2	0.723 (3)	0.993 (3)	0.755 (3)	0.041 (10)*
N3	0.8627 (2)	0.88981 (18)	0.91125 (17)	0.0149 (4)
C1	1.0317 (3)	0.8078 (2)	0.6446 (2)	0.0195 (5)
H1A	1.097152	0.768019	0.663529	0.023*
C2	1.0195 (3)	0.8194 (2)	0.5435 (2)	0.0219 (5)
H2A	1.075907	0.787838	0.491432	0.026*
C3	0.9224 (3)	0.8786 (2)	0.5176 (2)	0.0204 (5)
H3	0.911822	0.886335	0.446918	0.024*
C4	0.8424 (3)	0.9256 (2)	0.5936 (2)	0.0182 (5)
H4A	0.777686	0.966903	0.576547	0.022*
C5	0.8574 (2)	0.9118 (2)	0.6971 (2)	0.0155 (5)
C6	0.7823 (2)	0.9451 (2)	0.8760 (2)	0.0140 (5)
C7	0.8413 (2)	0.8923 (2)	1.0163 (2)	0.0143 (5)
C8	0.9101 (2)	0.8387 (2)	1.0766 (2)	0.0148 (5)
H8	0.978627	0.798434	1.048471	0.018*
C9	0.8748 (3)	0.8464 (2)	1.1788 (2)	0.0161 (5)
C10	0.7728 (3)	0.9049 (2)	1.2202 (2)	0.0177 (5)
H10	0.750185	0.907910	1.290212	0.021*
C11	0.7047 (3)	0.9584 (2)	1.1609 (2)	0.0179 (5)
H11	0.635812	0.998071	1.189050	0.021*
C12	0.7408 (2)	0.9520 (2)	1.0584 (2)	0.0146 (5)
C13	1.0300 (3)	0.7290 (2)	1.2054 (2)	0.0228 (5)
H13A	0.984946	0.664647	1.131747	0.034*
H13B	1.060746	0.696365	1.259637	0.034*
H13C	1.110250	0.778632	1.196026	0.034*
Au1	0.95986 (2)	0.55935 (2)	0.71308 (2)	0.01682 (3)
Cl1	1.11166 (7)	0.70866 (6)	0.86031 (6)	0.02465 (13)
Cl2	0.80710 (7)	0.41058 (6)	0.56663 (6)	0.02767 (14)
O3	0.3768 (2)	0.87843 (19)	0.5227 (2)	0.0272 (4)
H3A	0.425 (4)	0.938 (3)	0.566 (3)	0.037 (11)*
H3B	0.380 (4)	0.885 (4)	0.465 (3)	0.053 (13)*
Cl3	0.58921 (7)	1.10213 (6)	0.71166 (6)	0.02530 (14)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S2	0.0189 (3)	0.0197 (3)	0.0165 (3)	0.0097 (2)	0.0050 (2)	0.0082 (2)
O2	0.0229 (9)	0.0241 (9)	0.0196 (9)	0.0095 (8)	0.0066 (7)	0.0135 (8)
N4	0.0166 (10)	0.0163 (10)	0.0163 (10)	0.0052 (8)	0.0042 (8)	0.0099 (8)
N5	0.0184 (10)	0.0189 (10)	0.0182 (10)	0.0090 (8)	0.0051 (8)	0.0113 (9)
N6	0.0172 (10)	0.0193 (10)	0.0150 (10)	0.0059 (8)	0.0044 (8)	0.0091 (8)
C14	0.0179 (12)	0.0181 (12)	0.0214 (13)	0.0056 (10)	0.0050 (10)	0.0080 (10)
C15	0.0219 (13)	0.0198 (12)	0.0187 (12)	0.0054 (10)	0.0069 (10)	0.0061 (10)

C16	0.0213 (13)	0.0181 (12)	0.0168 (12)	0.0013 (10)	0.0019 (10)	0.0074 (10)
C17	0.0189 (12)	0.0182 (12)	0.0170 (12)	0.0045 (10)	0.0012 (10)	0.0093 (10)
C18	0.0133 (11)	0.0129 (11)	0.0173 (12)	0.0018 (9)	0.0022 (9)	0.0064 (9)
C19	0.0142 (11)	0.0149 (11)	0.0175 (12)	0.0036 (9)	0.0033 (9)	0.0080 (10)
C20	0.0142 (11)	0.0154 (11)	0.0151 (11)	0.0001 (9)	0.0018 (9)	0.0063 (9)
C21	0.0146 (11)	0.0182 (12)	0.0180 (12)	0.0049 (9)	0.0047 (9)	0.0104 (10)
C22	0.0153 (11)	0.0149 (11)	0.0187 (12)	0.0005 (9)	0.0016 (9)	0.0089 (10)
C23	0.0167 (12)	0.0183 (12)	0.0150 (11)	0.0018 (9)	0.0043 (9)	0.0066 (10)
C24	0.0172 (12)	0.0188 (12)	0.0178 (12)	0.0046 (10)	0.0054 (10)	0.0064 (10)
C25	0.0137 (11)	0.0140 (11)	0.0173 (12)	0.0035 (9)	0.0024 (9)	0.0068 (9)
C26	0.0271 (14)	0.0308 (15)	0.0249 (14)	0.0147 (12)	0.0070 (11)	0.0162 (12)
S1	0.0184 (3)	0.0168 (3)	0.0156 (3)	0.0082 (2)	0.0054 (2)	0.0073 (2)
O1	0.0275 (10)	0.0230 (9)	0.0139 (8)	0.0104 (8)	0.0053 (7)	0.0108 (7)
N1	0.0191 (10)	0.0169 (10)	0.0148 (10)	0.0046 (8)	0.0040 (8)	0.0086 (9)
N2	0.0180 (10)	0.0185 (10)	0.0160 (10)	0.0078 (8)	0.0051 (8)	0.0104 (8)
N3	0.0169 (10)	0.0155 (10)	0.0144 (10)	0.0039 (8)	0.0041 (8)	0.0081 (8)
C1	0.0207 (13)	0.0183 (12)	0.0217 (13)	0.0058 (10)	0.0083 (10)	0.0088 (10)
C2	0.0269 (14)	0.0206 (13)	0.0181 (12)	0.0048 (11)	0.0099 (11)	0.0065 (10)
C3	0.0241 (13)	0.0212 (13)	0.0149 (12)	−0.0002 (10)	0.0039 (10)	0.0087 (10)
C4	0.0195 (12)	0.0189 (12)	0.0172 (12)	0.0030 (10)	0.0019 (10)	0.0095 (10)
C5	0.0159 (11)	0.0140 (11)	0.0153 (11)	0.0004 (9)	0.0017 (9)	0.0061 (9)
C6	0.0124 (11)	0.0136 (11)	0.0154 (11)	0.0016 (9)	0.0030 (9)	0.0060 (9)
C7	0.0150 (11)	0.0135 (11)	0.0122 (11)	0.0005 (9)	0.0021 (9)	0.0040 (9)
C8	0.0158 (11)	0.0154 (11)	0.0153 (11)	0.0048 (9)	0.0046 (9)	0.0076 (9)
C9	0.0182 (12)	0.0146 (11)	0.0147 (11)	0.0021 (9)	0.0015 (9)	0.0063 (9)
C10	0.0218 (13)	0.0179 (12)	0.0130 (11)	0.0036 (10)	0.0066 (10)	0.0053 (10)
C11	0.0197 (12)	0.0161 (12)	0.0167 (12)	0.0053 (10)	0.0059 (10)	0.0043 (10)
C12	0.0156 (11)	0.0122 (11)	0.0145 (11)	0.0025 (9)	0.0017 (9)	0.0044 (9)
C13	0.0249 (13)	0.0271 (14)	0.0240 (13)	0.0124 (11)	0.0062 (11)	0.0158 (11)
Au1	0.01572 (5)	0.01910 (5)	0.01926 (5)	0.00721 (4)	0.00532 (4)	0.00985 (4)
Cl1	0.0202 (3)	0.0280 (3)	0.0226 (3)	0.0066 (3)	0.0017 (2)	0.0073 (3)
Cl2	0.0290 (3)	0.0211 (3)	0.0284 (3)	0.0057 (3)	−0.0016 (3)	0.0074 (3)
O3	0.0301 (11)	0.0249 (11)	0.0333 (12)	0.0103 (9)	0.0100 (10)	0.0163 (10)
Cl3	0.0242 (3)	0.0298 (3)	0.0319 (3)	0.0131 (3)	0.0070 (3)	0.0202 (3)

Geometric parameters (Å, º)

S2—C19	1.747 (2)	O1—C9	1.376 (3)
S2—C25	1.746 (2)	O1—C13	1.428 (3)
O2—C22	1.373 (3)	N1—H1	0.80 (3)
O2—C26	1.426 (3)	N1—C1	1.359 (3)
N4—H4	0.81 (3)	N1—C5	1.347 (3)
N4—C14	1.360 (3)	N2—H2	0.852 (15)
N4—C18	1.354 (3)	N2—C5	1.360 (3)
N5—H5	0.851 (15)	N2—C6	1.379 (3)
N5—C18	1.361 (3)	N3—C6	1.294 (3)
N5—C19	1.375 (3)	N3—C7	1.393 (3)
N6—C19	1.301 (3)	C1—H1A	0.9500

N6—C20	1.400 (3)	C1—C2	1.363 (4)
C14—H14	0.9500	C2—H2A	0.9500
C14—C15	1.358 (4)	C2—C3	1.401 (4)
C15—H15	0.9500	C3—H3	0.9500
C15—C16	1.400 (4)	C3—C4	1.373 (4)
C16—H16	0.9500	C4—H4A	0.9500
C16—C17	1.372 (4)	C4—C5	1.406 (3)
C17—H17	0.9500	C7—C8	1.397 (3)
C17—C18	1.398 (3)	C7—C12	1.401 (3)
C20—C21	1.392 (3)	C8—H8	0.9500
C20—C25	1.400 (3)	C8—C9	1.385 (3)
C21—H21	0.9500	C9—C10	1.404 (3)
C21—C22	1.386 (3)	C10—H10	0.9500
C22—C23	1.403 (3)	C10—C11	1.383 (4)
C23—H23	0.9500	C11—H11	0.9500
C23—C24	1.378 (4)	C11—C12	1.396 (3)
C24—H24	0.9500	C13—H13A	0.9800
C24—C25	1.394 (3)	C13—H13B	0.9800
C26—H26A	0.9800	C13—H13C	0.9800
C26—H26B	0.9800	Au1—Cl1	2.2592 (7)
C26—H26C	0.9800	Au1—Cl2	2.2560 (7)
S1—C6	1.747 (2)	O3—H3A	0.78 (3)
S1—C12	1.745 (2)	O3—H3B	0.78 (3)

C25—S2—C19	88.15 (11)	C9—O1—C13	117.33 (19)
C22—O2—C26	117.14 (19)	C1—N1—H1	120 (2)
C14—N4—H4	121 (2)	C5—N1—H1	117 (2)
C18—N4—H4	117 (2)	C5—N1—C1	122.5 (2)
C18—N4—C14	122.3 (2)	C5—N2—H2	115 (2)
C18—N5—H5	118 (2)	C5—N2—C6	125.4 (2)
C18—N5—C19	125.7 (2)	C6—N2—H2	119 (2)
C19—N5—H5	117 (2)	C6—N3—C7	110.1 (2)
C19—N6—C20	109.9 (2)	N1—C1—H1A	119.9
N4—C14—H14	119.9	N1—C1—C2	120.3 (2)
C15—C14—N4	120.2 (2)	C2—C1—H1A	119.9
C15—C14—H14	119.9	C1—C2—H2A	120.6
C14—C15—H15	120.6	C1—C2—C3	118.8 (2)
C14—C15—C16	118.9 (2)	C3—C2—H2A	120.6
C16—C15—H15	120.6	C2—C3—H3	119.8
C15—C16—H16	119.7	C4—C3—C2	120.5 (2)
C17—C16—C15	120.6 (2)	C4—C3—H3	119.8
C17—C16—H16	119.7	C3—C4—H4A	120.4
C16—C17—H17	120.4	C3—C4—C5	119.2 (2)
C16—C17—C18	119.3 (2)	C5—C4—H4A	120.4
C18—C17—H17	120.4	N1—C5—N2	120.6 (2)
N4—C18—N5	119.9 (2)	N1—C5—C4	118.7 (2)
N4—C18—C17	118.7 (2)	N2—C5—C4	120.6 (2)
N5—C18—C17	121.3 (2)	N2—C6—S1	119.11 (18)

N5—C19—S2	119.11 (18)	N3—C6—S1	117.41 (18)
N6—C19—S2	117.11 (18)	N3—C6—N2	123.5 (2)
N6—C19—N5	123.8 (2)	N3—C7—C8	124.4 (2)
N6—C20—C25	114.7 (2)	N3—C7—C12	114.6 (2)
C21—C20—N6	124.3 (2)	C8—C7—C12	121.0 (2)
C21—C20—C25	120.9 (2)	C7—C8—H8	121.2
C20—C21—H21	121.0	C9—C8—C7	117.5 (2)
C22—C21—C20	117.9 (2)	C9—C8—H8	121.2
C22—C21—H21	121.0	O1—C9—C8	124.0 (2)
O2—C22—C21	123.5 (2)	O1—C9—C10	114.6 (2)
O2—C22—C23	115.5 (2)	C8—C9—C10	121.5 (2)
C21—C22—C23	121.0 (2)	C9—C10—H10	119.4
C22—C23—H23	119.4	C11—C10—C9	121.2 (2)
C24—C23—C22	121.2 (2)	C11—C10—H10	119.4
C24—C23—H23	119.4	C10—C11—H11	121.1
C23—C24—H24	121.0	C10—C11—C12	117.7 (2)
C23—C24—C25	118.1 (2)	C12—C11—H11	121.1
C25—C24—H24	121.0	C7—C12—S1	110.12 (17)
C20—C25—S2	110.04 (18)	C11—C12—S1	128.73 (19)
C24—C25—S2	129.11 (19)	C11—C12—C7	121.1 (2)
C24—C25—C20	120.9 (2)	O1—C13—H13A	109.5
O2—C26—H26A	109.5	O1—C13—H13B	109.5
O2—C26—H26B	109.5	O1—C13—H13C	109.5
O2—C26—H26C	109.5	H13A—C13—H13B	109.5
H26A—C26—H26B	109.5	H13A—C13—H13C	109.5
H26A—C26—H26C	109.5	H13B—C13—H13C	109.5
H26B—C26—H26C	109.5	Cl2—Au1—Cl1	179.62 (3)
C12—S1—C6	87.80 (11)	H3A—O3—H3B	102 (4)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N5—H5···O3	0.85 (2)	1.91 (2)	2.758 (3)	173 (3)
N2—H2···Cl3	0.85 (2)	2.23 (2)	3.084 (2)	176 (4)
C3—H3···O1^{i}	0.95	2.46	3.284 (3)	145
O3—H3*A*···Cl3	0.78 (3)	2.39 (3)	3.155 (2)	171 (4)
O3—H3*B*···Cl3^{ii}	0.78 (3)	2.41 (3)	3.188 (2)	174 (4)

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