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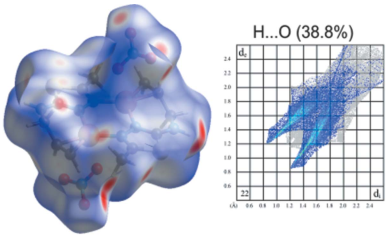
Ligand-forced dimerization of copper(I)–olefin complexes bearing a 1,3,4-thiadiazole core

Bohdan Ardan,[a] Vasyl Kinzhybalo,[b] Yurii Slyvka,[a] Olga Shyyka,[a] Mykhaylo Luk'yanov,[a] Tadeusz Lis[c] and Marian Mys'kiv[a]*

[a]Faculty of Chemistry, Ivan Franko National University, Kyryla i Mefodia Str. 6, 79005 L'viv, Ukraine, [b]Institute of Low Temperature and Structure Research, Okolna 2, 50-422 Wroclaw, Poland, and [c]Faculty of Chemistry, University of Wroclaw, Joliot-Curie 14, 50-383 Wroclaw, Poland. *Correspondence e-mail: myskiv@franko.lviv.ua

As an important class of heterocyclic compounds, 1,3,4-thiadiazoles have a broad range of potential applications in medicine, agriculture and materials chemistry, and were found to be excellent precursors for the crystal engineering of organometallic materials. The coordinating behaviour of allyl derivatives of 1,3,4-thiadiazoles with respect to transition metal ions has been little studied. Five new crystalline copper(I) π-complexes have been obtained by means of an alternating current electrochemical technique and have been characterized by single-crystal X-ray diffraction and IR spectroscopy. The compounds are bis[μ-5-methyl-*N*-(prop-2-en-1-yl)-1,3,4-thiadiazol-2-amine]bis[nitratocopper(I)], $[Cu_2(NO_3)_2(C_6H_9N_3S)_2]$, (1), bis[$\mu$-5-methyl-*N*-(prop-2-en-1-yl)-1,3,4-thiadiazol-2-amine]bis[(tetrafluoroborato)copper(I)], $[Cu_2(BF_4)_2(C_6H_9N_3S)_2]$, (2), μ-aqua-bis{μ-5-[(prop-2-en-1-yl)sulfanyl]-1,3,4-thiadiazol-2-amine}bis[nitratocopper(I)], $[Cu_2(NO_3)_2(C_5H_7N_3S_2)_2(H_2O)]$, (3), μ-aqua-(hexafluorosilicato)-bis{μ-5-[(prop-2-en-1-yl)sulfanyl]-1,3,4-thiadiazol-2-amine}dicopper(I)–acetonitrile–water (2/1/4), $[Cu_2(SiF_6)(C_5H_7N_3S_2)_2(H_2O)]\cdot 0.5CH_3CN\cdot 2H_2O$, (4), and μ-benzenesulfonato-bis{μ-5-[(prop-2-en-1-yl)sulfanyl]-1,3,4-thiadiazol-2-amine}-dicopper(I) benzenesulfonate–methanol–water (1/1/1), $[Cu_2(C_6H_5O_3S)(C_5H_7N_3S_2)_2](C_6H_5O_3S)\cdot CH_3OH\cdot H_2O$, (5). The structure of the ligand 5-methyl-*N*-(prop-2-en-1-yl)-1,3,4-thiadiazol-2-amine (*Mepeta*), $C_6H_9N_3S$, was also structurally characterized. Both *Mepeta* and 5-[(prop-2-en-1-yl)sulfanyl]-1,3,4-thiadiazol-2-amine (*Pesta*) (denoted *L*) reveal a strong tendency to form dimeric $\{Cu_2L_2\}^{2+}$ fragments, being attached to the metal atom in a chelating–bridging mode *via* two thiadiazole N atoms and an allylic C=C bond. Flexibility of the $\{Cu_2(Pesta)_2\}^{2+}$ unit allows the Cu^I atom site to be split into two positions with different metal-coordination environments, thus enabling the competitive participation of different molecules in bonding to the metal centre. The *Pesta* ligand in (4) allows the Cu^I atom to vary between water O-atom and hexafluorosilicate F-atom coordination, resulting in the rare case of a direct $Cu^I\cdots FSiF_5^{2-}$ interaction. Extensive three-dimensional hydrogen-bonding patterns are formed in the reported crystal structures. Complex (5) should be considered as the first known example of a $Cu^I(C_6H_5SO_3)$ coordination compound. To determine the hydrogen-bond interactions in the structures of (1) and (2), a Hirshfeld surface analysis has been performed.



1. Introduction

As an important class of heterocyclic compounds, 1,3,4-thiadiazoles have a broad range of potential applications in medicine as antibacterial, antioxidant, antidepressant, antidiabetic, antifungal, anti-inflammatory and antitumor agents (Khan *et al.*, 2010; Cressier *et al.*, 2009; Li *et al.*, 2014; Moshafi *et al.*, 2011; Pattn *et al.*, 2011; Lee *et al.*, 2010; Xu *et al.*, 2013; Zhang *et al.*, 2014). In agriculture, these compounds can be used as pesticides, insecticides and plant-growth-regulating agents (Gilden *et al.*, 2010; Alves *et al.*, 2012). They have applications in materials chemistry because of their interesting optical and electronic properties (Tao *et al.*, 2010; Granadino-Roldán *et al.*, 2011; He *et al.*, 2010). Due to their electron-deficient nature and good electron-accepting ability, 1,3,4-thiadiazoles were found to be excellent precursors for the crystal engineering of organometallic materials, possessing potential catalytic, luminescent, magnetic, nonlinear optic and other properties (Hu *et al.*, 2014; Trukhina *et al.*, 2010; Higashihara *et al.*, 2012). Among these, heterometallic coordination polymers based on 1,3,4-thiadiazole-2,5-dithiolates show optical transitions with gaps varying from 1.90 to 2.24 eV, indicating their semiconductor properties (Li *et al.*, 2008). A three-dimensional supramolecular network compound (*via* interlayer π–π stacking interactions and strong hydrogen bonding), based on the cadmium complex with 2-amino-5-mercapto-1,3,4-thiadiazole, shows a blue photoluminescence in the solid state at room temperature (Zhang *et al.*, 2007). The aromatic 1,3,4-thiadiazole ring allows good π-electron conjugation and the accompanying (in the case of amino or hydroxy substituents) proton-transfer and charge-transfer processes provide an excellent ability to promote the synthesis of heavy-metal clusters. For example, the first known tetranuclear Cu^{I} complex ($Cu\cdots Cu$ = 2.74 Å) of the azanide-type forms as a result of metal-induced deprotonation of 2-allylamino-5-phenyl-1,3,4-thiadiazole in acetonitrile under alternating current (ac) electrochemical conditions (Slyvka *et al.*, 2015). Similarly, cobalt-induced reductive nucleophilic addition of 2-amino-1,3,4-thiadiazole to acetonitrile also shows deprotonation of the same amine N atom, resulting in the *N*-(1,3,4-thiadiazol-2-yl)acetimidamide complex (Deng *et al.*, 2008).

In recent years, specific attention have been paid to the investigation of copper(I) π-complexes with allyl derivatives of heterocyclic compounds, since the simultaneous presence of a heterocyclic core and an allylic radical bonded to them plays an important role in the formation of unusual inorganic fragments (Slyvka *et al.*, 2013). The contribution from the π-dative ($Cu \rightarrow C{=}C$) π-component of a Cu^{I}–olefin bond to the tetrahedral ligand field leads to a splitting of the copper-ion *d* orbitals and brings about a considerable deformation of the initial tetrahedral copper(I) environment to trigonal pyramidal. Such a distortion of the copper(I) polyhedron is accompanied by an elongation of the $Cu-L_{ap}$ bond (ap is apical) compared to the $Cu-(C{=}C)$ and $Cu-L_{bas}$ bonds (where L_{bas} are heterocyclic donor N, O or S atoms). Therefore, the apical position of the Cu^{I} polyhedron becomes a selector of the coordinated inorganic anion, depending on the L_{bas} atom nature (*i.e.* the type of heterocyclic core), solvent type and other basal co-ligands. For instance, in the structure of the copper(I) hexafluorosilicate π-complex with 1-allylbenzotriazole, the first known example representing a direct $Cu^{I}\cdots FSiF_5^{2-}$ interaction was observed {the apical position of the copper(I) polyhedron is occupied by an F atom of the bridging SiF_6^{2-} anion [Cu—F = 2.439 (2) Å], while the basal positions are occupied by an allylic C=C bond, a triazole N atom and a solvent water molecule} (Goreshnik *et al.*, 2011).

Taking into account the mutual presence of two neighbouring nucleophilic N atoms in the 1,3,4-thiadiazole ring and the electron-deficient nature of the core, the appearance of an allyl substituent on this ring should significantly influence its unusual coordination abilities. This assertion is confirmed by the recently studied structure of $[Cu_2(\textit{Mepeta})_2]SiF_6 \cdot C_6H_6$ [*Mepeta* is 5-methyl-*N*-(prop-2-en-1-yl)-1,3,4-thiadiazol-2-amine], in which a $Cu^{I}\cdots FSiF_5^{2-}$ interaction was also observed. Despite the fact that allyl derivatives of 1,3,4-thiadiazoles were first obtained more than a century ago (Pulvermacher, 1894), their coordinating behaviour with respect to transition metal ions has been little studied. Overall, only a few copper(I) (CuCl, $CuCF_3SO_3$ and Cu_2SiF_6) π-complexes with *Mepeta* and *Phepeta* [5-phenyl-*N*-(prop-2-en-1-yl)-1,3,4-thiadiazol-2-amine] have been synthesized and structurally characterized by X-ray diffraction and Raman spectroscopy (Ardan *et al.*, 2013; Slyvka, 2015; Goreshnik *et al.*, 2016), and these only recently.

To fill the knowledge gap mentioned above and to explore the coordination behaviour of other allyl derivatives of thiadiazoles, such as *Pesta*, with respect to diverse copper(I) salts, we report the synthesis and structures of five new π-complexes, namely $[Cu(NO_3)(\textit{Mepeta})]_2$, (1), $[Cu(BF_4)(\textit{Mepeta})]_2$, (2), $[Cu_2(NO_3)_2(\textit{Pesta})_2(H_2O)]$, (3), $[Cu_2(SiF_6)(\textit{Pesta})_2(H_2O)]\cdot 0.5CH_3CN \cdot 2H_2O$, (4), and $[Cu_2(C_6H_5SO_3)(\textit{Pesta})_2](C_6H_5SO_3)\cdot CH_3OH \cdot H_2O$, (5), highlighting the influence of the ligand coordination mode in the rare case of $Cu^{I}\cdots FSiF_5^{2-}$ coordination.

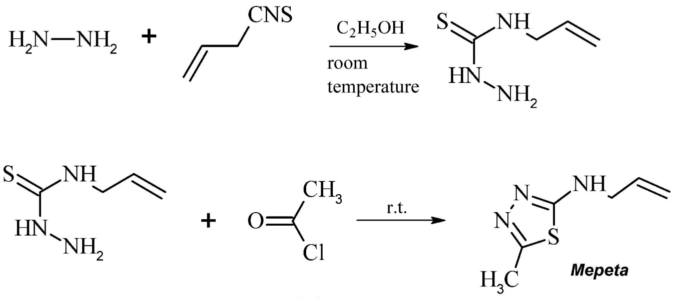
2. Experimental

2.1. General considerations

Unless mentioned otherwise, all chemicals were obtained from commercial sources and used without further purification. The ^1H NMR spectrum for *Mepeta* was measured on a Bruker Avance 400 MHz NMR spectrometer and the ^1H NMR spectrum of *Pesta* was measured on a Bruker Avance 500 MHz NMR instrument. The chemical shifts are reported in ppm relative to the residual peak of deuterated $CDCl_3$ or CD_3CN for the ^1H data. The IR spectra were recorded on Bruker Vertex 70 FT–IR and Bruker IFS-88 spectrometers as KBr pellets. Diffraction data for *Mepeta* were collected on a Kuma KM-4-CCD diffractometer with Mo $K\alpha$ radiation (λ = 0.71073 Å).

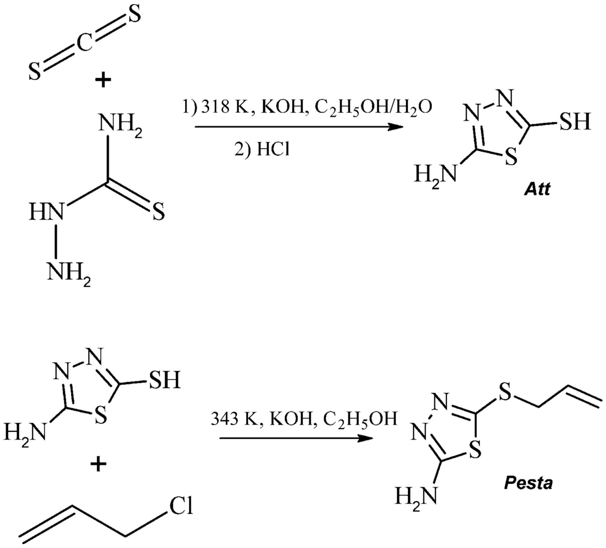
2.2. Preparation of the ligands *Mepeta* and *Pesta*

5-Methyl-*N*-(prop-2-en-1-yl)-1,3,4-thiadiazol-2-amine (*Mepeta*) was prepared according to the literature procedure of Ardan *et al.* (2013) (see Scheme 1). Recrystallization of *Mepeta* from water leads to lamellar crystals suitable for single-crystal X-ray study. The total yield was 63%. ^1H NMR (400 MHz, $CDCl_3$): δ 6.36 (*s*, 1H), 5.97–5.87 (*m*, 1H), 5.32 (*d*, *J* = 17.2 Hz, 1H), 5.22 (*d*, *J* = 10.4 Hz, 1H), 3.94 (*d*, *J* = 5.6 Hz, 2H), 2.57 (*s*, 3H). IR (KBr, cm^{-1}): 3179 (*vs*), 3076 (*m*), 2978 (*vs*), 2915 (*s*), 2855 (*m*), 2768 (*m*), 2357 (*m*), 2334 (*w*), 1643 (*m*), 1566 (*vs*), 1491 (*vs*), 1456 (*s*), 1435 (*m*), 1417 (*s*), 1336 (*m*), 1267 (*m*), 1214 (*s*), 1187 (*m*), 1145 (*w*), 1084 (*m*), 1008 (*w*), 992 (*m*), 960 (*m*), 925 (*s*), 814 (*w*), 756 (*m*), 650 (*m*), 617 (*w*), 522 (*w*).



Scheme 1

5-Amino-1,3,4-thiadiazole-2-thiol (*Att*) was prepared according to the literature procedure of Guha (1922) (see Scheme 2). 5-[(Prop-2-en-1-yl)sulfanyl]-1,3,4-thiadiazol-2-amine (*Pesta*) was synthesized in one step by stirring *Att* (20 mmol, 3.46 g) with 3-chloroprop-1-ene (23 mmol, 1.76 g) at 343 K in the presence of KOH (20 mmol, 1.12 g) in an ethanol solution for 8 h. The total yield was 92%. ^{1}H NMR (500 MHz, CD$_3$CN): δ 5.93 (*ddt*, J = 17.1, 10.0, 7.0 Hz, 1H), 5.80 (*s*, 2H), 5.21 (*dq*, J = 17.0, 1.4 Hz, 1H), 5.12 (*ddt*, J = 10.0, 1.6, 0.9 Hz, 1H), 3.72–3.65 (*m*, 2H). IR (KBr, cm^{-1}): 3279 (*vs*), 3093 (*vs*), 2959 (*vs*), 2923 (*vs*), 2785 (*m*), 2686 (*m*), 2337 (*w*), 1845 (*w*), 1643 (*s*), 1518 (*vs*), 1464 (*s*), 1424 (*s*), 1398 (*m*), 1376 (*m*), 1329 (*m*), 1233 (*m*), 1198 (*w*), 1141 (*m*), 1098 (*m*), 1062 (*s*), 1050 (*s*), 987 (*s*), 922 (*vs*), 867 (*m*), 779 (*w*), 729 (*m*), 686 (*m*), 617 (*m*), 580 (*m*), 545 (*w*).

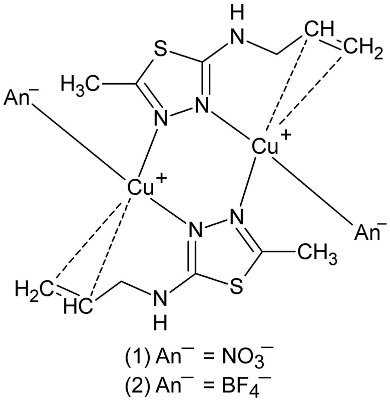


Scheme 2

2.3. Syntheses of complexes (1)–(5)

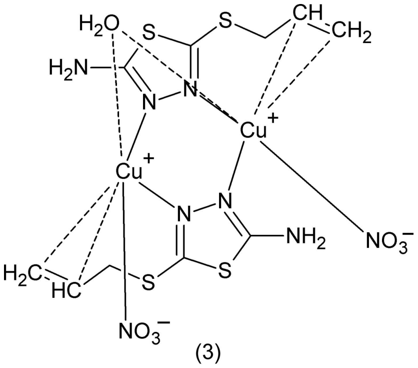
Crystals of complexes (1)–(5) were obtained under alternating current electrochemical synthesis conditions (Mykhalichko & Mys'kiv, 1998), starting with a water–acetonitrile or methanol–toluene solution of *Mepeta* or *Pesta* and the corresponding copper(II) salt.

2.3.1. Preparation of [Cu(NO$_3$)(*Mepeta*)]$_2$, (1). To an ethanol solution (2 ml) of *Mepeta* (1.1 mmol, 0.17 g), an ethanol solution (2.5 ml) of Cu(NO$_3$)$_2$·3H$_2$O (1.0 mmol, 0.24 g) was added. The resulting dark-green solution was placed in a small 5 ml test tube and a cork was added fitted with copper-wire electrodes. An alternating current (frequency 50 Hz) of 0.45 V was applied for 7 d, during which time good-quality colourless crystals of (1) appeared on the electrodes. IR (nujol, cm^{-1}): 3450 (*m*), 3215 (*m*), 2996 (*m*), 2392 (*w*), 1576 (*m*), 1509 (*w*), 1384 (*vs*), 1220 (*m*), 1043 (*w*), 976 (*w*), 942 (*w*), 898 (*w*), 826 (*w*), 785 (*w*), 717 (*w*), 676 (*w*), 620 (*w*), 544 (*w*), 514 (*w*).



Scheme 3

2.3.2. Preparation of [Cu(BF$_4$)(*Mepeta*)]$_2$, (2). To an ethanol solution (2 ml) of *Mepeta* (1.1 mmol, 0.17 g), an ethanol solution (2.5 ml) of Cu(BF$_4$)$_2$·6H$_2$O (1.0 mmol, 0.26 g) was added. The resulting dark-green solution was subjected to an alternating current (frequency 50 Hz) at 0.42 V and, after 1 d, good-quality colourless crystals of (2) appeared on the copper-wire electrodes. IR (KBr, cm^{-1}): 3338 (*s*), 3094 (*w*), 3036 (*m*), 2926 (*w*), 2367 (*m*), 2337 (*m*), 1565 (*vs*), 1522 (*s*), 1503 (*s*), 1445 (*s*), 1420 (*m*), 1387 (*m*), 1333 (*s*), 1284 (*s*), 1262 (*m*), 1246 (*w*), 1224 (*s*), 1068 (*vs*), 1012 (*vs*), 978 (*vs*), 946 (*s*), 903 (*m*), 786 (*m*), 703 (*w*), 683 (*w*), 599 (*w*), 546 (*m*), 519 (*m*).



(3)

Scheme 4

2.3.3. Preparation of [Cu$_2$(NO$_3$)$_2$(*Pesta*)$_2$(H$_2$O)], (3). *Pesta* (1.0 mmol, 0.17 g) was dissolved in an acetonitrile solution (4.5 ml) of Cu(NO$_3$)$_2$·3H$_2$O (1.0 mmol, 0.24 g). An alternating current (frequency 50 Hz) of 0.50 V was applied for 5 d, during which time good-quality colourless crystals of (3) appeared on the copper-wire electrodes. IR (KBr, cm^{-1}): 2955 (*vs*), 2922 (*vs*), 2852 (*vs*), 1463 (*s*), 1377 (*s*), 1342 (*m*), 1153 (*w*), 1044 (*w*), 723 (*m*), 511 (*w*).

2.3.4. Preparation of [Cu$_2$(SiF$_6$)(*Pesta*)$_2$(H$_2$O)]·0.5CH$_3$CN·2H$_2$O, (4). A solution of *Pesta* (1.0 mmol, 0.17 g) in acetonitrile (3.8 ml) was added to a saturated water solution

Table 1
Experimental details.

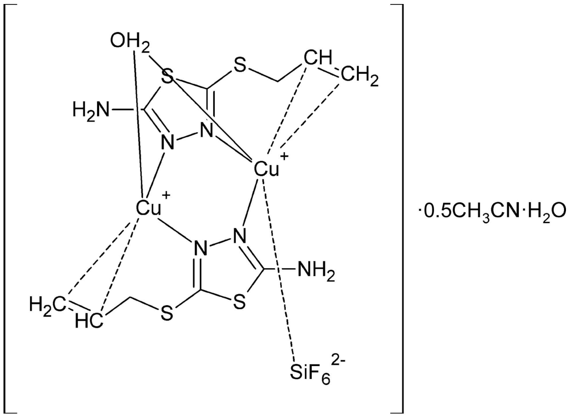
For all compounds, H atoms were treated by a mixture of independent and constrained refinement. *Mepeta* was refined as an inversion twin [absolute structure parameter = 0.27 (11)].

	Mepeta	(1)	(2)
Crystal data			
Chemical formula	$C_6H_9N_3S$	$[Cu_2(NO_3)_2(C_6H_9N_3S)_2]$	$[Cu_2(BF_4)_2(C_6H_9N_3S)_2]$
M_r	155.22	561.54	611.14
Crystal system, space group	Orthorhombic, $Pna2_1$	Triclinic, $P\overline{1}$	Triclinic, $P\overline{1}$
Temperature (K)	120	100	100
a, b, c (Å)	8.843 (3), 17.485 (5), 5.041 (3)	7.235 (3), 7.548 (3), 10.297 (4)	7.754 (3), 7.965 (3), 10.372 (4)
α, β, γ (°)	90, 90, 90	105.42 (3), 98.15 (3), 112.43 (3)	67.57 (3), 89.99 (3), 61.07 (3)
V (Å^3)	779.4 (6)	482.0 (4)	504.6 (4)
Z	4	1	1
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.34	2.47	2.40
Crystal size (mm)	0.98 × 0.42 × 0.11	0.43 × 0.21 × 0.14	0.44 × 0.23 × 0.18
Data collection			
Diffractometer	Kuma KM-4-CCD	Rigaku Xcalibur Onyx	Rigaku Xcalibur Onyx
Absorption correction	Analytical [*CrysAlis PRO* (Rigaku OD, 2015), based on expressions derived by Clark & Reid (1995)]	Analytical [*CrysAlis PRO* (Rigaku OD, 2015), based on expressions derived by Clark & Reid (1995)]	Analytical [*CrysAlis PRO* (Rigaku OD, 2015), based on expressions derived by Clark & Reid (1995)]
T_{min}, T_{max}	0.801, 0.964	0.542, 0.768	0.498, 0.711
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	11519, 3214, 2812	8459, 8459, 6900	8712, 4784, 4163
R_{int}	0.051	0.020	0.014
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.843	0.876	0.876
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.042, 0.105, 1.06	0.034, 0.096, 1.06	0.022, 0.061, 1.07
No. of reflections	3214	8459	4784
No. of parameters	124	141	149
No. of restraints	1	0	0
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.31, −0.31	0.88, −1.03	0.56, −0.51

	(3)	(4)	(5)
Crystal data			
Chemical formula	$[Cu_2(NO_3)_2(C_5H_7N_3S_2)_2(H_2O)]$	$[Cu_2(SiF_6)(C_5H_7N_3S_2)_2(H_2O)]\cdot 0.5C_2H_3N\cdot 2H_2O$	$[Cu_2(C_6H_5O_3S)(C_5H_7N_3S_2)_2](C_6H_5O_3S)\cdot CH_4O\cdot H_2O$
M_r	615.63	688.24	837.97
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/c$
Temperature (K)	100	260	110
a, b, c (Å)	7.379 (3), 18.780 (5), 14.702 (4)	11.899 (4), 11.442 (4), 17.678 (5)	14.944 (4), 16.587 (5), 14.658 (4)
α, β, γ (°)	90, 94.82 (3), 90	90, 102.04 (3), 90	90, 117.91 (3), 90
V (Å^3)	2030.2 (11)	2353.9 (13)	3210.7 (17)
Z	4	4	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Cu $K\alpha$
μ (mm^{-1})	2.56	2.29	5.77
Crystal size (mm)	0.3 × 0.18 × 0.13	0.52 × 0.17 × 0.09	0.45 × 0.32 × 0.17
Data collection			
Diffractometer	Rigaku Xcalibur Ruby	Rigaku Xcalibur Sapphire2 (large Be window)	Rigaku Xcalibur Onyx
Absorption correction	Analytical [*CrysAlis PRO* (Rigaku OD, 2015), based on expressions derived by Clark & Reid (1995)]	Analytical [*CrysAlis PRO* (Rigaku OD, 2015), based on expressions derived by Clark & Reid (1995)]	Analytical [*CrysAlis PRO* (Rigaku OD, 2015), based on expressions derived by Clark & Reid (1995)]
T_{min}, T_{max}	0.577, 0.776	0.452, 0.825	0.248, 0.540
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	11883, 6647, 4618	24572, 5649, 3717	16595, 6741, 6073
R_{int}	0.037	0.053	0.056
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.752	0.661	0.634
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.045, 0.115, 1.01	0.037, 0.087, 1.02	0.057, 0.166, 1.05
No. of reflections	6647	5649	6741
No. of parameters	346	412	487
No. of restraints	0	245	3
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.68, −0.70	0.47, −0.38	1.03, −1.49

Computer programs: *CrysAlis PRO* (Rigaku OD, 2015), *CrysAlis CCD* (Oxford Diffraction, 2010), *CrysAlis RED* (Oxford Diffraction, 2010), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*) and *OLEX2* (Dolomanov *et al.*, 2009).

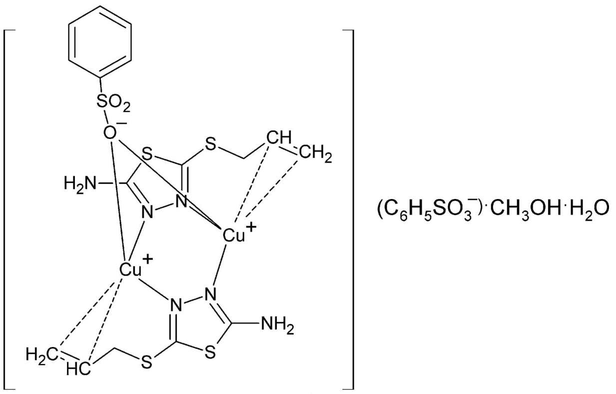
(0.9 ml) of $CuSiF_6{\cdot}4H_2O$ (in a 5 ml test tube). The mixture was stirred carefully. The resulting mixture consisted of an upper dark layer (acetonitrile) and a lower light-green layer (water). It was subjected to alternating current reduction (frequency 50 Hz, 0.5 V) (the acetonitrile layer became fully colourless and, after 4–5 d, only a few good-quality colourless crystals of (4) had appeared on the copper-wire electrodes.



(4)

Scheme 5

2.3.5. Preparation of $[Cu_2(C_6H_5SO_3)(\textit{Pesta})_2](C_6H_5SO_3){\cdot}CH_3OH{\cdot}H_2O$, (5). A solution of *Pesta* (1.0 mmol, 0.17 g) and $Cu(C_6H_5SO_3)_2{\cdot}6H_2O$ was prepared in a mixture of methanol (2.3 ml) and toluene (2.2 ml). The resulting green-coloured solution was subjected to alternating current (frequency 50 Hz, 0.45 V). After 1 d the solution became colourless and good-quality colourless crystals of (5) appeared on the copper electrodes. IR (KBr, cm^{-1}): 3498 (*m*), 3279 (*s*), 3122 (*s*), 2956 (*vs*), 2922 (*vs*), 2854 (*vs*), 1626 (*s*), 1540 (*s*), 1456 (*vs*), 1374 (*s*), 1346 (*w*), 1247 (*w*), 1220 (*s*), 1172 (*vs*), 1122 (*vs*), 1065 (*m*), 1035 (*s*), 1015 (*s*), 993 (*m*), 932 (*w*), 882 (*vw*), 753 (*m*), 727 (*s*), 692 (*m*), 609 (*s*), 563 (*m*).



(5)

Scheme 6

2.4. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. The *Mepeta* structure was refined as a racemic twin with a ratio of the components of 0.73 (11):0.27 (11). The amine H atom in *Mepeta* itself and the ligand amine H atoms in complexes (1)–(5) were derived from difference Fourier maps and refined with $U_{iso}(H) = 1.2U_{eq}(N)$. The water H atoms in (3)–(5) were derived from difference Fourier maps and refined with $U_{iso}(H) = 1.5U_{eq}(O)$. The other H atoms were refined in ideal positions (riding model), with C—H = 0.99 (methyl and methylene) or 0.95 Å (otherwise) and $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl H atoms or $1.2U_{eq}(C)$ otherwise. Some of the reflections, for which a considerable difference between the observed and calculated intensities were observed, were omitted from the final refinement cycles [4, 5, 1 and 3 reflections for (1)–(3) and (5), respectively]. In the *Mepeta* structure, the allyl group (atoms C7, C8 and C9) is disordered over two sites, with an occupancy ratio of 0.660 (6):0.340 (6). In (3), the allylsulfanyl group (atoms S12, C17, C18 and C19), together with Cu1, as well as the allyl group (atoms C27, C28 and C29), together with Cu2, are disordered over two sites, with occupancy ratios of 0.765 (6):0.235 (6) and 0.794 (7):0.206 (7), respectively. In (4), the allyl group (atoms C17, C18 and C19) is disordered over two sites, with an occupancy ratio of 0.616 (8):0.384 (8); the allyl group (atoms C27, C28 and C29), together with Cu2, is disordered over two sites, with a fixed occupancy ratio of 0.88:0.12 and the hexafluorosilicate F atoms (F3, F4, F5 and F6) are disordered over four sites, with an occupancy ratio of 0.426 (3):0.287 (3):0.172 (3):0.115 (3). In (4), the chemically equivalent bond lengths and angles involving the disordered C27, C28 and C29 atoms (as well as the disordered F3, F4, F5 and F6 atoms) were restrained to obtain similar geometries. In (5), two allyl groups (atoms C17/C18/C19 and C27/C28/C29) are disordered over two sites, with occupancy ratios of 0.80 (1):0.20 (1) and 0.66 (1):0.34 (1), respectively; one benzenesulfonate anion (atoms S3, O31, O32 and O33) is disordered over two sites, with an occupancy ratio of 0.644 (6):0.356 (6). The measured crystal of (1) appeared to be twinned by reticular merohedry, with two components rotated with respect to each other by ~180° around the direct-space *a* axis. 974 reflections were overlapped, whereas 3705 and 3735 reflections were isolated for components (1) and (2), respectively. Data reduction was conducted taking into account both twin domains and an HKLF 5 file was produced. The final refined twin ratio for (1) was 0.4489 (8):0.5511 (8).

2.5. Hirshfeld surface analysis and fingerprint plots

The three-dimensional Hirshfeld surfaces (HSs) and two-dimensional fingerprint plots for (1) and (2) were generated using *Crystal Explorer* (Wolff *et al.*, 2012; Spackman & Jayatilaka, 2009).

3. Results and discussion

Mepeta crystallizes in the noncentrosymmetric space group $Pna2_1$, with one molecule in the asymmetric unit (Fig. 1). The C2—N3 and C2—N1 bond lengths are consistent with delocalization of the electrons between the thiadiazole ring and the N atom of the amino group. The C2—N1 bond length of 1.338 (3) Å is slightly shorter than a nominal C_{ar}—N(sp^2)H bond length of 1.353 Å, while the C2—N3 bond length of 1.319 (2) Å is slightly longer than the neighbouring C5—N4

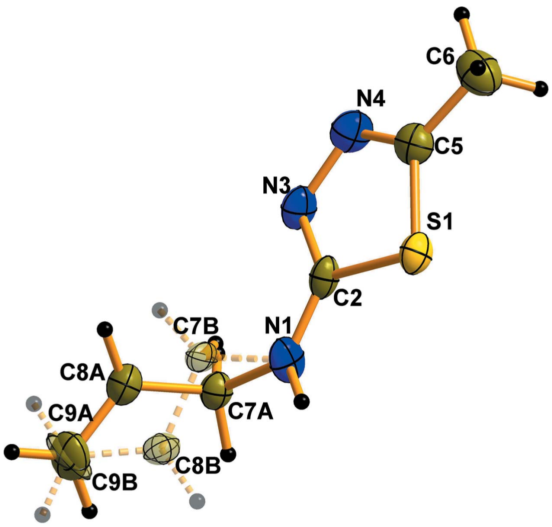


Figure 1
The independent part in the *Mepeta* crystal structure. Displacement ellipsoids are drawn at the 50% probability level.

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···N3^{i}	0.88 (3)	2.02 (3)	2.860 (2)	159 (3)
C7A—H7AA···S1^{ii}	0.99	2.97	3.462 (4)	112
C7B—H7BA···S1^{iii}	0.99	2.96	3.880 (8)	156
C8B—H8B···N4^{iv}	0.95	2.38	3.295 (5)	163

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

Table 3
Selected geometric parameters (Å, °) of (1) and (2).

m is the mid-point of the C═C bond.

Complex (1)			
Cu1—N3	1.9938 (17)	Cu1—m	1.940 (1)
Cu1—N4^{i}	1.9693 (19)	Cu1—O1	2.473 (3)
Cu1—C8	2.038 (2)	C8—C9	1.360 (3)
Cu1—C9	2.073 (2)		
N4^{i}—Cu1—N3	114.48 (7)	O1—Cu—m	97.76 (5)
C8—Cu1—C9	38.62 (8)	C9—C8—C7	122.8 (2)
Complex (2)			
Cu1—N3	2.0036 (15)	Cu1—m	1.9454 (9)
Cu1—N4^{i}	1.9646 (11)	Cu1 – F1	2.6670 (15)
Cu1—C8	2.0451 (12)	C8—C9	1.3706 (16)
Cu1—C9	2.0799 (15)		
N4^{i}—Cu1—N3	114.54 (5)	F1—Cu—m	95.51 (3)
C8—Cu1—C9	38.80 (5)	C9—C8—C7	123.77 (10)

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

bond [1.293 (3) Å] of the same thiadiazole ring. The H atom of the amino group participates in N—H···N hydrogen bonding (Table 2) with the thiadiazole N3 atom of the nearest molecule, forming an infinite hydrogen-bonded chain in the [100] direction (Fig. 2). Neighbouring *Mepeta* molecules within the chain are twisted relative to each other by 89.33 (3)°, thus enabling a larger allyl-group mobility in the space ($d \sim 6 \times 9$ Å) between the thiadiazole rings of the nearest chains. Therefore, the C atoms of the allyl groups are disordered over two sites [the site-occupation factors are 0.660 (6) for A and 0.340 (6) for B], so that the methene H atom (with a site-occupation factor of 0.340) from one $\{Mepeta\}_\infty$ chain is connected to the thiadiazole N4 atom of the nearest chain by a weak hydrogen bond (C8B—H8B···N4^{iv} = 2.38 Å; Table 2). The dihedral angles between the plane of the thiadiazole ring and the N1—C7A and N1—C7B bonds of the allylamino group are 4.2 (4) and −10.2 (4)°, respectively. The double-bond distances C8A═C9A and C8B═C9B are 1.325 (10) and 1.412 (19) Å, respectively.

Crystals of (1) and (2) (see Scheme 3) are similar to the previously studied $[Cu(CF_3SO_3)(Mepeta)]_2$ π-complex (Goreshnik *et al.*, 2016). The asymmetric unit contains one Cu^I centre, one *Mepeta* ligand and one nitrate ligand in (1) or one tetrafluoroborate ligand in (2) (donoted An). The *Mepeta* molecule is coordinated to the metal centre *via* the two N atoms of the thiadiazole ring and the allylic C═C bond in a chelating–bridging mode. The trigonal–pyramidal Cu^I environment in the basal plane includes the N3 atom and the C═C bond of one thiadiazole ligand and the N4 atom of another heterocyclic ring. The apical position of the metal coordination polyhedron is occupied by either weakly coordinating O or F atoms of NO_3^- or BF_4^- in (1) and (2), respectively. Therefore, two Cu^I atoms are bridged by two neighbouring *Mepeta* molecules, connecting them into centrosymmetrical $[Cu(NO_3)(Mepeta)]_2$, (1), and $[Cu(BF_4)(Mepeta)]_2$, (2), dimers (Fig. 3). The Cu···Cu distance of 3.472 (2) Å in (1) and of 3.488 (2) Å in (2) are too long for a cuprophilic interaction (Lake & Willans, 2013). Two thiadiazole rings from the same dimer are entirely coplanar. It is interesting to note that *S*-allyl derivatives of 1-aryl-substituted 1*H*-tetrazole-5-thiol have the same tridentate–chelate coordination mode, connecting two Cu^I atoms by means of an allylic C═C bond and two tetrazole N atoms into centrosymmetric $\{[Cu(L)(H_2O)]^+\}_2$ dimers (Slyvka *et al.*, 2009, 2010).

The strength of the Cu^I—(C═C) interaction is confirmed by the fact that the allylic C═C bonds are slightly elongated

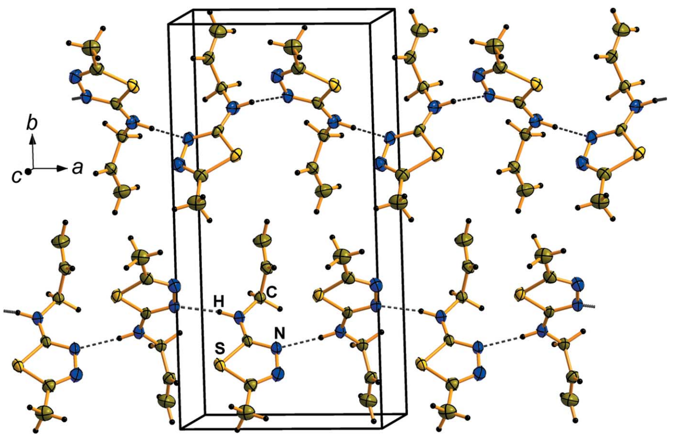
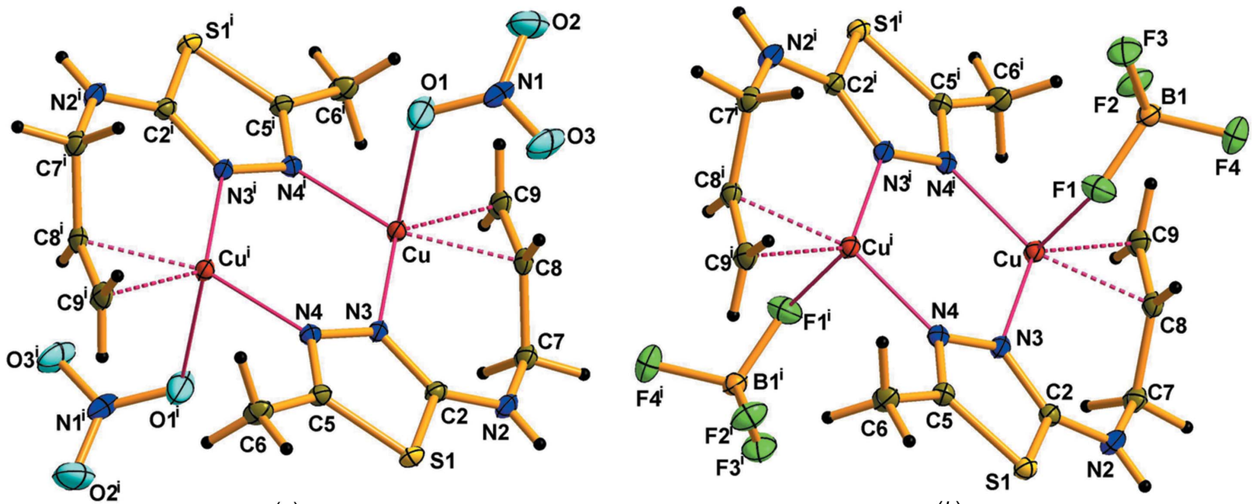


Figure 2
The hydrogen-bonded chains (dashed lines) in the *Mepeta* structure.



(*a*) (*b*)

Figure 3
Centrosymmetric $[Cu(An)(\mathit{Mepeta})]_2$ dimers in the structures of (*a*) (1) and (*b*) (2). Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (i) $-x + 1, -y + 1, -z + 1$.]

Table 4
Hydrogen-bond geometry (Å, °) for (1) and (2).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
Complex (1)				
N2—H2$\cdots$O1^{ii}	0.80 (3)	2.32 (3)	3.034 (3)	150 (2)
N2—H2$\cdots$O2^{ii}	0.80 (3)	2.24 (3)	2.970 (3)	153 (2)
Complex (2)				
N2—H2$\cdots$F2^{ii}	0.87 (2)	1.95 (2)	2.7874 (14)	160 (1)
N2—H2$\cdots$F3^{ii}	0.87 (2)	2.53 (2)	3.242 (2)	140 (1)
C7—H7$B\cdots$F4^{iii}	0.99	2.53	3.4900 (17)	163

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

to 1.360 (3) Å in (1) and 1.3706 (16) Å (2) [compared with a nominal value of 1.33 Å and a value of 1.340 (7) Å in *Mepeta*]. The Cu^I atom deviates from the base of the trigonal pyramid by Δ = 0.132 (3) Å in (1) and 0.062 (2) Å in (2), while the angle τ between the C=C bond and the basal plane is 11.3 (1)° in (1) and 12.5 (1)° in (2). This conclusion is also confirmed by the rather short Cu—m distances (m is the mid-point of C=C bond) and the rather large C—Cu—C angles (Table 3).

Through N—H$\cdots X$ [X = O in (1) or F in (2)] (Table 4) hydrogen bonds between the H atom of the ligand amino group and the X atoms of the NO_3^- ligand in (1) or the BF_4^- ligand in (2), neighbouring $[Cu(\mathit{Mepeta})(An)]_2$ fragments are linked into hydrogen-bonded stair-like chains extending in the [010] direction (Fig. 4). These chains are interpenetrated by a variety of C—H$\cdots X$ contacts to produce a three-dimensional framework.

The organic–inorganic hybrid π-complex (3) (see Scheme 4) crystallizes in the centrosymmetric space group $P2_1/c$. The asymmetric unit contains two Cu^I centres, two *Pesta* ligands, one bridging aqua ligand and two nitrate ligands. Similar to *Mepeta*, *Pesta* is coordinated to copper(I) *via* the thiadiazole N3 and N4 atoms and the allylic C=C bond in a chelating–bridging mode. In contrast to the $\{Cu_2(\mathit{Mepeta})_2\}^{2+}$ units in (1) and (2), two Cu^I atoms in (3) are connected by two *Pesta* ligands into a noncentrosymmetric $\{Cu_2(\mathit{Pesta})_2\}^{2+}$ unit (Fig. 5*a*). The planes of the thiadiazole rings from the same dimer form a dihedral angle of 31.2 (1)°. The conformational flexibility of the dimer allows the Cu^I atom site to be split over two positions with different coordination environments. The

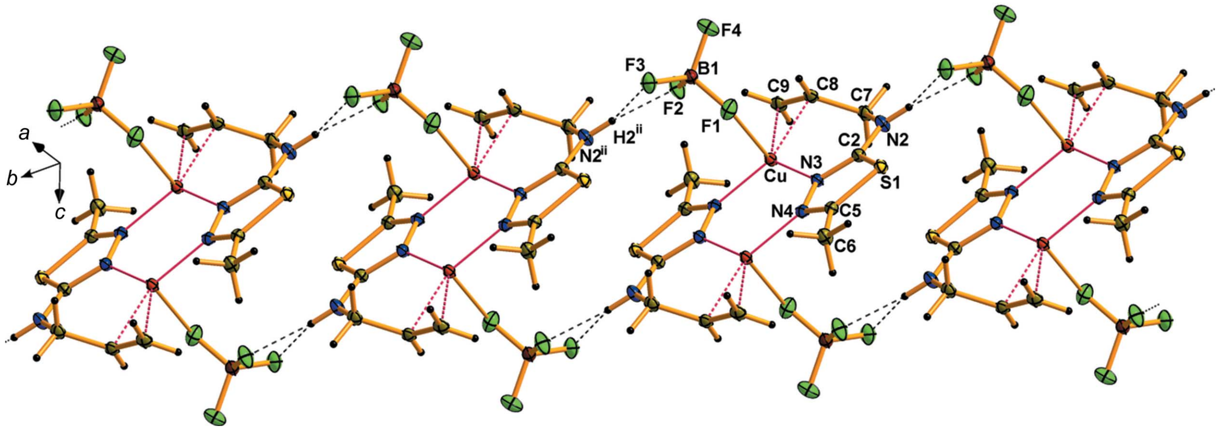


Figure 4
The hydrogen-bonded array in the structure of the $[Cu(BF_4)(\mathit{Mepeta})]_2$ π-complex, (2).

Table 5
Selected geometric parameters (Å, °) of (3).

m and *m*′ are the mid-points of the allylic C18*A*═C19*A* and C28*A*═C29*A* bonds, respectively.

Cu1*A*—N13	2.045 (3)	Cu2*A*—C28*A*	2.062 (4)
Cu1*A*—N24	1.962 (2)	Cu2*A*—C29*A*	2.052 (8)
Cu1*A*—C18*A*	2.054 (4)	Cu2*B*—O1	2.341 (7)
Cu1*A*—C19*A*	2.039 (6)	Cu1*A*—O11	2.4416 (29)
Cu1*B*—O1	2.363 (7)	Cu2*A*—O21	2.5391 (31)
Cu2*A*—N14	1.974 (3)	C18*A*—C19*A*	1.374 (9)
Cu2*A*—N23	1.998 (3)	C28*A*—C29*A*	1.369 (11)
Cu1*A*—*m*	1.928 (2)	Cu2*A*—*m*′	1.940 (2)
N24—Cu1*A*—N13	110.12 (11)	C19*A*—C18*A*—C17*A*	125.4 (5)
C19*A*—Cu1*A*—C18*A*	39.2 (2)	C29*A*—C28*A*—C27*A*	125.9 (5)
N14—Cu2*A*—N23	111.13 (12)	O11—Cu1*A*—*m*	98.77 (8)
C29*A*—Cu2*A*—C28*A*	38.9 (3)	O21—Cu2*A*—*m*′	101.25 (8)

Table 6
Hydrogen-bond geometry (Å, °) for (3).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*A*···O13^{i}	0.93 (5)	2.01 (5)	2.846 (4)	149 (4)
O1—H1*B*···O22^{ii}	0.99 (5)	2.29 (5)	3.142 (4)	143 (4)
O1—H1*B*···O23^{ii}	0.99 (5)	2.25 (5)	2.946 (3)	126 (3)
N12—H12*A*···O13^{iii}	0.93 (4)	2.16 (4)	3.053 (4)	161 (3)
N12—H12*B*···O22	0.84 (4)	2.09 (4)	2.918 (4)	166 (3)
N22—H22*A*···O12	0.85 (4)	2.07 (4)	2.895 (4)	163 (3)
N22—H22*B*···O23^{iv}	0.82 (3)	2.07 (3)	2.856 (3)	162 (3)

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

trigonal–pyramidal environments of atoms Cu1*A* and Cu2*A* [site-occupation factors = 0.765 (6) and 0.794 (7), respectively] in the basal plane include the C═C bond and two N atoms of neighbouring *Pesta* ligands, while the apical positions are occupied by weakly coordinated O atoms of NO_3^- ligands (Table 5). The common apical position of the two trigonal pyramids of the other Cu1*B* and Cu2*B* pair [site-occupation factors = 0.235 (7) and 0.206 (7)] is occupied by a bridging aqua molecule. The distances from Cu1*A* and Cu2*A* to the water O atom of 2.835 (7) and 2.767 (7) Å, respectively, are significantly longer than the formally limiting distance (2.63 Å; Slyvka *et al.*, 2013) of a Cu—O_{ap} interaction [in the case of copper(I) π-complexes with allyl derivatives of heterocycles], but at the same time it is slightly shorter than the sum of the van der Waals radii of 2.92 Å (Bondi, 1964).

The H atoms of the ligand amino group and the coordinated water molecule participate in *X*—H···*Y* (*X* and *Y* = N or O) hydrogen bonding with NO_3^- ligands, forming a three-dimensional hydrogen-bonded network (Table 6).

A similar $\{Cu_2(\mathit{Pesta})_2\}^{2+}$ unit was found in the structure of (4) (see Scheme 5). The asymmetric unit contains two Cu^I centres, two *Pesta* ligands, one bridging aqua ligand and one anionic SiF_6^{2-} ligand (Fig. 6*a*). The planes of the thiadiazole rings from the same dimer form a dihedral angle of 28.3 (1)°. The π-complex $[Cu_2(SiF_6)(\mathit{Pesta})_2(H_2O)]\cdot0.5CH_3CN\cdot2H_2O$, (4), may be considered as a rare example of the direct Cu^I—$F(SiF_6^{2-})$ interaction. This interaction has been found previously in only two Cu_2SiF_6 π-complexes with 1-allylbenzotriazole, *Abtr* (Goreshnik *et al.*, 2011) and *Mepeta* (Goreshnik *et al.*, 2016). Despite the fact that the SiF_6^{2-} anions are not directly coordinated to the Cu^I atom, but form hydrogen bonds with the coordinated water molecules, the *Pesta* ligand allows the Cu^I ion to be divided between two positions with water O-atom or hexafluorosilicate F-atom coordination (Fig. 6*a*), resulting in the splitting of one Cu^I position of the $\{Cu_2(\mathit{Pesta})_2\}^{2+}$ unit into two sites, *i.e.* Cu2*A* and Cu2*B* (0.88:0.12). The Cu2*B*···F1 distance of 2.833 (16) Å in (4) is longer than the Cu^I···F distance of 2.44 Å in $[Cu_2(SiF_6)(\mathit{Abtr})_2(H_2O)_2]\cdot2H_2O$ (Goreshnik *et al.*, 2011), but is still shorter than the sum of the van der Waals radii (2.87 Å). The above interaction results in a lower U_{eq}(F1) value of 0.0531 (5) Å^2 compared with the U_{eq}(F2) value of 0.0641 (6) Å^2, while the other F atoms of the SiF_6^{2-} anion are disordered in a carousel-like mode. Thus, the two Cu^I atoms have different coordination environments: Cu1 and Cu2*A* have a trigonal–pyramidal surrounding, with a common apical

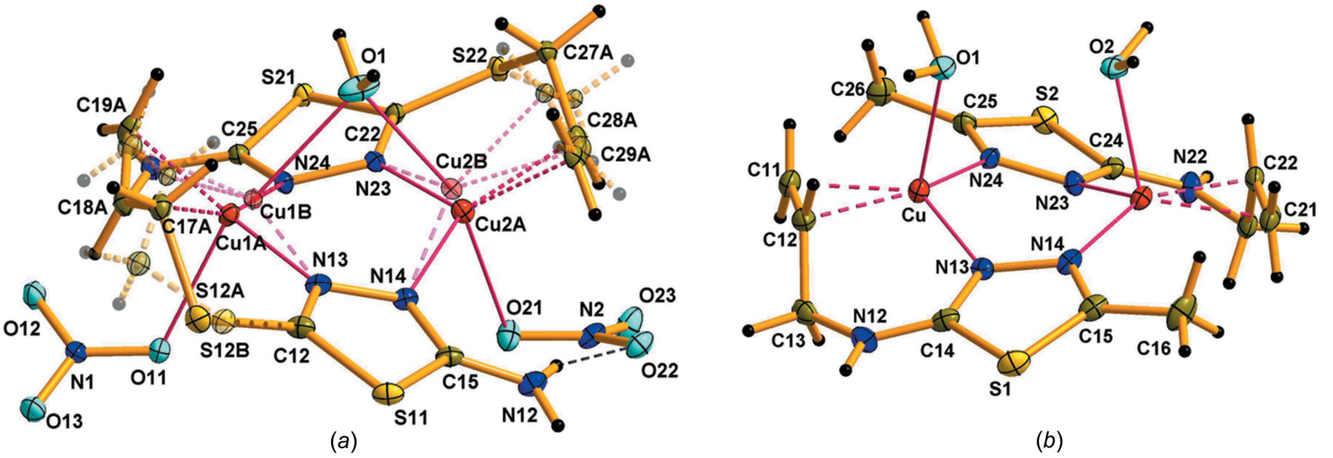


Figure 5
(*a*) The independent part of the structure of (3) and (*b*) the cationic $[Cu_2(\mathit{Mepeta})_2(H_2O)_2]^{2+}$ dimer in the $[Cu_2(\mathit{Mepeta})_2(H_2O)_2]SiF_6\cdot2.5H_2O$ complex (Ardan *et al.*, 2013). One of the two disordered positions of the allylsulfanyl group and the metal atom in (3), *i.e.* with the lower site-occupancy factor, are shown in semi-transparent mode. Displacement ellipsoids are drawn at the 20% probability level.

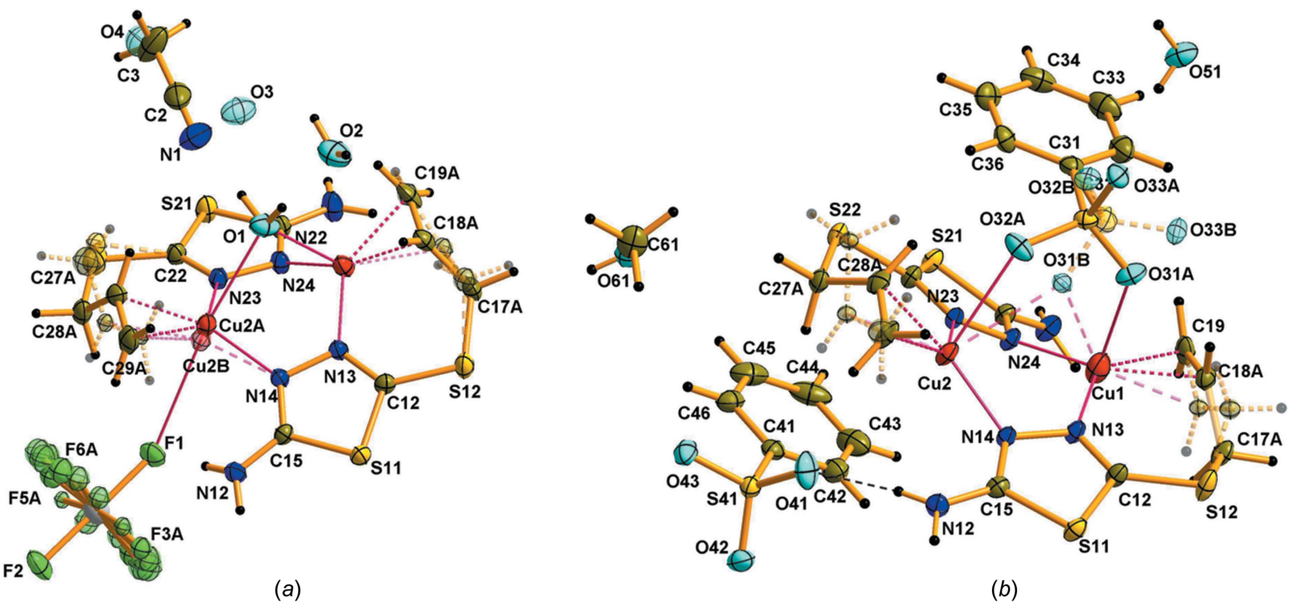


Figure 6

The structural arrangement in π-complexes (*a*) (4) and (*b*) (5). One of the two disordered positions of the Cu, C and F atoms in (4), and of the C, O and S atoms in (5), *i.e.* with the lower site-occupancy factor, is shown in semi-transparent mode. Displacement ellipsoids are drawn at the 30% probability level.

water molecule, while the apical position of the Cu2*B* polyhedron is occupied by a weakly coordinated F atom of the SiF_6^{2-} anion (Fig. 6). For comparison, in a previously studied π-complex of Cu_2SiF_6 with *Mepeta*, *viz.* [Cu_2(*Mepeta*)$_2$(-2(H_2O)$_2$]SiF_6·2.5H_2O, the noncentrosymmetric {Cu_2(*Me-Mepeta*)$_2$}$^{2+}$ unit was also found (Fig. 5*b*), but each Cu^I atom is linked with a different apical water molecule (Ardan *et al.*, 2013). Moreover, two coordinated water molecules in the last case are located on the same side of the dimer unit [as was found for the NO_3^- ligands in (3); Fig. 5*a*].

The H atoms of the ligand amino group in (4) are involved in N—H···F hydrogen bonding with the F1 and F2 atoms of two neighbouring SiF_6^{2-} anions, connecting {Cu_2(SiF_6)-(*Pesta*)$_2$(H_2O)} units into hydrogen-bonded layers. The latter, by means of O—H···O- and O—H···F-type hydrogen bonds involving atoms of the coordinated and constitutional water molecules, are interpenetrated into a supramolecular structure (Table 7).

Table 7

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N12—H12*A*···F1	0.86 (3)	2.14 (4)	2.973 (4)	163 (3)
N12—H12*B*···F2^{i}	0.86 (4)	2.04 (4)	2.827 (3)	152 (3)
N22—H22*A*···F2^{ii}	0.93 (4)	2.05 (4)	2.903 (4)	153 (3)
N22—H22*B*···F5*A*^{iii}	0.83 (4)	1.83 (4)	2.638 (5)	165 (4)
N22—H22*B*···F5*B*^{iii}	0.83 (4)	1.98 (4)	2.758 (9)	157 (4)
N22—H22*B*···F5*C*^{iii}	0.83 (4)	2.50 (4)	3.27 (2)	154 (4)
N22—H22*B*···F4*D*^{iii}	0.83 (4)	2.00 (4)	2.766 (15)	153 (4)
O1—H1*A*···N1	0.91	1.89	2.789 (10)	175
O1—H1*B*···O2	0.90	1.85	2.698 (4)	156
O2—H2*A*···F5*B*^{iv}	0.87	1.98	2.819 (11)	163
O2—H2*A*···F5*C*^{iv}	0.87	1.52	2.385 (12)	169
O2—H2*A*···F5*D*^{iv}	0.87	1.64	2.427 (15)	150
O2—H2*B*···F3*C*^{v}	0.87	1.59	2.383 (11)	149
O2—H2*B*···F3*D*^{v}	0.87	1.59	2.465 (18)	177
O2—H2*B*···F4*A*^{v}	0.87	2.09	2.952 (9)	169

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

The structure most similar to [Cu_2(*Mepeta*)$_2$(H_2O)$_2$]-SiF_6·2.5H_2O is the π-complex (5) (see Scheme 6) (Fig. 6*b*). Two O atoms of the benzenesulfonate ligand in (5) are bound to the two Cu^I atoms of the same {Cu_2(*Pesta*)$_2$}$^{2+}$ unit, while the other benzenesulfonate anion is involved in N—H···O hydrogen bonding with the ligand amine group. The tendency for the O atom to be bound simultaneously to the two metal atoms of the dimer appears to be common for dimeric {Cu_2(*Pesta*)$_2$}$^{2+}$ cations. Therefore, the sulfonate group of the anion in (5) is disordered over two sites (O31*A*/O32*A*/O33*A* and O31*B*/O32*B*/O33*B*), with an occupancy ratio of 0.644 (6):0.356 (6), and one O atom of the lower-occupancy unit plays the same role as the water molecule in (3), binding two metal centres. The planes of the thiadiazole rings from the same dimer in (5) form a dihedral angle of 34.4 (1)°. By means of a variety of N—H···O and O—H···O hydrogen bonds (Table 8), the above dimers are connected into a hydrogen-bonded framework (Fig. 7). To the best of our knowledge, complex (5) is the first known example of a $Cu^I(C_6H_5SO_3)$

Table 8

Hydrogen-bond geometry (Å, °) for (5).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N12—H12*A*···O51^{i}	0.91 (5)	1.94 (5)	2.765 (4)	150 (4)
N12—H12*B*···O41	0.87 (5)	2.00 (5)	2.867 (4)	174 (4)
N22—H22*A*···O42^{ii}	0.90 (5)	2.04 (5)	2.896 (4)	158 (4)
N22—H22*B*···O61^{iii}	0.86 (5)	1.96 (5)	2.758 (4)	154 (4)
O61—H61···O43^{iv}	0.75 (6)	1.98 (6)	2.726 (4)	174 (6)
O51—H51*A*···O43^{v}	0.82 (6)	2.00 (7)	2.790 (4)	164 (6)
O51—H51*B*···O32*B*	0.81 (7)	2.20 (7)	3.010 (11)	170 (6)
O51—H51*B*···O33*A*	0.81 (7)	1.84 (7)	2.641 (7)	168 (6)

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

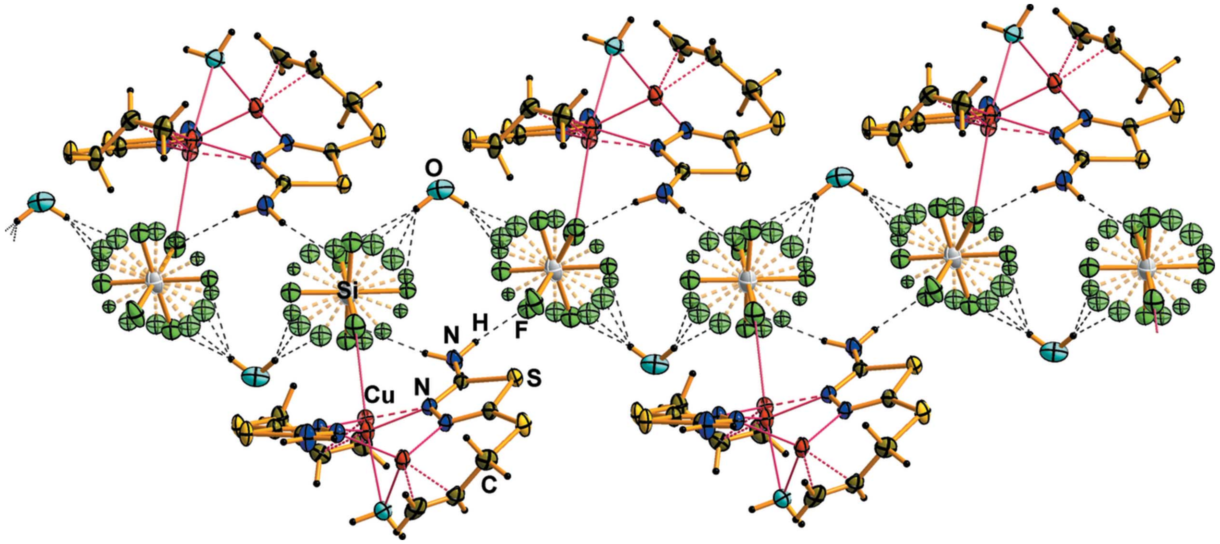


Figure 7
The hydrogen-bonded array in $[Cu_2(SiF_6)(\mathit{Pesta})_2(H_2O)]\cdot CH_3OH\cdot 2H_2O$, (4). Displacement ellipsoids are drawn at the 30% probability level.

coordination compound [for comparison, there are eight entries in the Cambridge Structural Database (Groom *et al.*, 2016) for $Cu^{II}(C_6H_5SO_3)$ coordination complexes].

3.1. Hirshfeld surface analysis

The Hirshfeld surfaces were built for $[Cu(NO_3)(\mathit{Mepeta})]_2$, (1), and $[Cu(BF_4)(\mathit{Mepeta})]_2$, (2), to analyze the interactions between the units. The most prominent interactions, between *Mepeta* H atoms and nitrate O atoms in (1), as well as between *Mepeta* H atoms and tetrafluoroborate F atoms, can be seen in the Hirshfeld surface plots as the bright and pale-pink areas (Fig. 8*a*). Fingerprint plots were produced to show the intermolecular surface bond lengths, with the regions highlighted for H···O, H···F and H···S interactions. The contribution to the surface area for H···H contacts is 27.7% in (1) and 24.4% in (2).

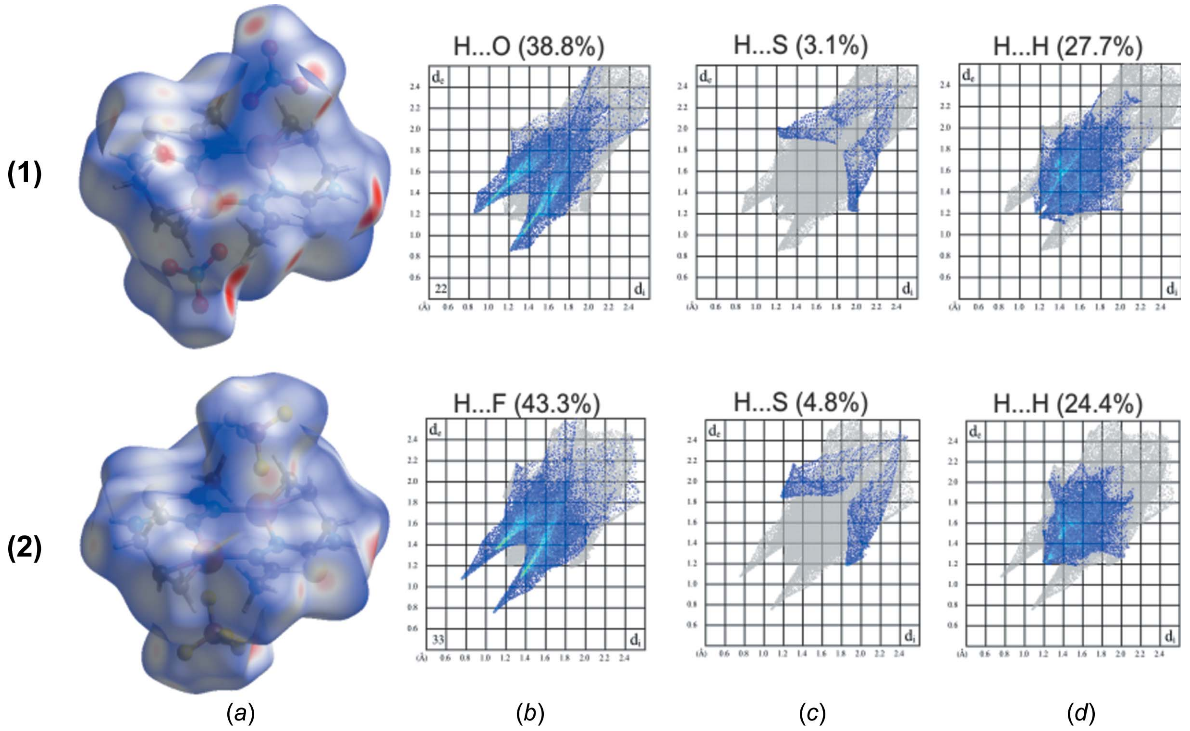


Figure 8
Hirshfeld surface analysis of the $[Cu(NO_3)(\mathit{Mepeta})]_2$, (1), and $[Cu(BF_4)(\mathit{Mepeta})]_2$, (2), dimers. (*a*) The Hirshfeld surfaces mapped with d_{norm}, which highlights both the donor and acceptor ability. (*b*) Fingerprint plots for the dimeric units resolved into (*L*)H···O(NO_3^-) or (*L*)H···F(BF_4^-) contacts. (*c*) Fingerprint plots for the dimeric units resolved into (*L*)H···S contacts. (*d*) Fingerprint plots for the dimeric units resolved into H···H contacts. The full fingerprint appears beneath each decomposed plot in grey.

4. Summary

The syntheses and crystal structures of 5-methyl-*N*-(prop-2-en-1-yl)-1,3,4-thiadiazol-2-amine (*Mepeta*) and five copper(I) π-complexes with *Mepeta* and 5-(prop-2-en-1-ylsulfanyl)-1,3,4-thiadiazol-2-amine (*Pesta*) have been described. *Mepeta* itself crystallizes in the noncentrosymmetric space group $Pna2_1$, with one molecule in the asymmetric unit. Both *Mepeta* and *Pesta* reveal a strong tendency towards the formation of dimeric $\{Cu_2L_2\}^{2+}$ fragments, being attached to the metal atom in a chelating–bridging mode *via* two thiadiazole N atoms and an allylic C=C bond. The symmetry of the $\{Cu_2(Mepeta)_2\}^{2+}$ unit depends on the charge of the anion; centrosymetric units were found in the presence of singly charged anions and a noncentrosymmetric dimer was found in the case of the doubly charged SiF_6^{2-} ion. The flexibility of the $\{Cu_2(Pesta)_2\}^{2+}$ unit allows the Cu^I atom site to be split over two positions with different coordination environments, thus enabling the competitive participation of different molecules in bonding to the metal centre. *Pesta* allows the Cu^I ion to be divided between two positions with water O-atom or hexafluorosilicate F-atom coordination, resulting in the rare case of a direct $Cu^I\cdots FSiF_5^{2-}$ interaction. The tendency of oxygen to be bound simultaneously to two metal atoms in the dimeric $\{Cu_2(Pesta)_2\}^{2+}$ cation is confirmed by the presence of disorder in the benzenesulfonate anion. By a variety of sufficiently strong hydrogen bonds, the dimeric $\{Cu_2(L)_2(An)_2\}$ (An = NO_3^-, BF_4^- and $\frac{1}{2}SiF_6^{2-}$) units participate in supramolecular structure formation. Structure (5) should be considered as the first known example of a $Cu^I(C_6H_5SO_3)$ coordination compound.

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Ligand-forced dimerization of copper(I)–olefin complexes bearing a 1,3,4-thiadiazole core

Bohdan Ardan, Vasyl Kinzhybalo, Yurii Slyvka, Olga Shyyka, Mykhaylo Luk`yanov, Tadeusz Lis and Marian Mys`kiv

Computing details

Data collection: *CrysAlis PRO* (Rigaku OD, 2015) for mepeta, (1), (3), (5); *CrysAlis CCD* (Oxford Diffraction, 2010) for (2), (4). Cell refinement: *CrysAlis PRO* (Rigaku OD, 2015) for mepeta, (1), (3), (5); *CrysAlis RED* (Oxford Diffraction, 2010) for (2), (4). Data reduction: *CrysAlis PRO* (Rigaku OD, 2015) for mepeta, (1), (3), (5); *CrysAlis RED* (Oxford Diffraction, 2010) for (2), (4). For all compounds, program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: OLEX2 (Dolomanov *et al.*, 2009); software used to prepare material for publication: OLEX2 (Dolomanov *et al.*, 2009).

(mepeta) 5-Methyl-*N*-(prop-2-en-1-yl)-1,3,4-thiadiazol-2-amine

Crystal data

$C_6H_9N_3S$
$M_r = 155.22$
Orthorhombic, $Pna2_1$
$a = 8.843$ (3) Å
$b = 17.485$ (5) Å
$c = 5.041$ (3) Å
$V = 779.4$ (6) Å^3
$Z = 4$
$F(000) = 328$
$D_x = 1.323$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 5973 reflections
$\theta = 3.3–36.3°$
$\mu = 0.34$ mm^{-1}
$T = 120$ K
Plate, clear light colourless
0.98 × 0.42 × 0.11 mm

Data collection

Kuma KM-4-CCD diffractometer
Radiation source: Kuma KM-4-CCD, Kuma KM-4-CCD
Graphite monochromator
Detector resolution: 8.3359 pixels mm^{-1}
ω scans
Absorption correction: analytical [CrysAlis PRO (Rigaku OD, 2015), based on expressions derived by Clark & Reid (1995)]
$T_{min} = 0.801$, $T_{max} = 0.964$
11519 measured reflections
3214 independent reflections
2812 reflections with $I > 2\sigma(I)$
$R_{int} = 0.051$
$\theta_{max} = 36.8°$, $\theta_{min} = 3.3°$
$h = -14\rightarrow11$
$k = -27\rightarrow26$
$l = -7\rightarrow8$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.105$
$S = 1.06$
3214 reflections
124 parameters
1 restraint

Primary atom site location: structure-invariant direct methods
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.061P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.31$ e Å^{-3}
$\Delta\rho_{min} = -0.31$ e Å^{-3}
Absolute structure: Refined as an inversion twin
Absolute structure parameter: 0.27 (11)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refined as a 2-component inversion twin

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	$U_{iso}*/U_{eq}$	Occ. (<1)
S1	0.77479 (4)	0.83578 (2)	0.66791 (14)	0.03107 (13)	
N1	0.71891 (16)	0.73279 (10)	0.2801 (4)	0.0345 (3)	
H1	0.814 (3)	0.7180 (15)	0.295 (6)	0.041*	
N3	0.51665 (15)	0.80284 (9)	0.4639 (4)	0.0335 (3)	
N4	0.48989 (16)	0.85941 (10)	0.6522 (5)	0.0387 (3)	
C2	0.66088 (16)	0.78417 (9)	0.4483 (4)	0.0279 (3)	
C5	0.6107 (2)	0.88210 (11)	0.7732 (4)	0.0346 (4)	
C6	0.6120 (3)	0.94181 (13)	0.9846 (5)	0.0469 (5)	
H6A	0.6634	0.9218	1.1422	0.070*	
H6B	0.5078	0.9556	1.0302	0.070*	
H6C	0.6656	0.9872	0.9200	0.070*	
C7A	0.6390 (4)	0.69117 (19)	0.0720 (8)	0.0276 (6)	0.660 (6)
H7AA	0.7062	0.6857	−0.0841	0.033*	0.660 (6)
H7AB	0.5492	0.7209	0.0164	0.033*	0.660 (6)
C7B	0.5939 (6)	0.6893 (4)	0.1468 (17)	0.0275 (12)	0.340 (6)
H7BA	0.5253	0.6662	0.2798	0.033*	0.340 (6)
H7BB	0.5343	0.7234	0.0298	0.033*	0.340 (6)
C8A	0.5898 (3)	0.61366 (15)	0.1627 (7)	0.0326 (6)	0.660 (6)
H8A	0.5342	0.6083	0.3229	0.039*	0.660 (6)
C8B	0.6714 (5)	0.6288 (3)	−0.0111 (11)	0.0296 (13)	0.340 (6)
H8B	0.7532	0.6415	−0.1250	0.035*	0.340 (6)
C9A	0.6238 (13)	0.5524 (6)	0.020 (3)	0.061 (4)	0.660 (6)
H9AA	0.6794	0.5578	−0.1404	0.073*	0.660 (6)
H9AB	0.5926	0.5032	0.0774	0.073*	0.660 (6)
C9B	0.621 (2)	0.5524 (9)	0.012 (3)	0.042 (6)	0.340 (6)
H9BA	0.5394	0.5403	0.1260	0.051*	0.340 (6)
H9BB	0.6694	0.5132	−0.0877	0.051*	0.340 (6)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.02516 (16)	0.0356 (2)	0.0324 (2)	−0.00651 (12)	−0.00796 (18)	0.0006 (2)

N1	0.0290 (6)	0.0327 (8)	0.0417 (8)	0.0004 (5)	−0.0151 (6)	−0.0023 (7)
N3	0.0227 (5)	0.0346 (8)	0.0430 (9)	−0.0016 (5)	−0.0083 (6)	0.0042 (7)
N4	0.0308 (6)	0.0407 (8)	0.0446 (9)	0.0035 (5)	−0.0044 (8)	0.0040 (9)
C2	0.0228 (5)	0.0278 (7)	0.0330 (9)	−0.0057 (5)	−0.0094 (6)	0.0072 (6)
C5	0.0360 (7)	0.0346 (9)	0.0332 (9)	0.0007 (6)	−0.0027 (7)	0.0042 (7)
C6	0.0613 (12)	0.0426 (11)	0.0368 (11)	0.0010 (10)	−0.0021 (10)	−0.0012 (9)
C7A	0.0245 (13)	0.0283 (13)	0.0302 (16)	−0.0014 (11)	−0.0038 (11)	0.0017 (12)
C7B	0.0136 (17)	0.037 (3)	0.032 (3)	−0.0037 (17)	−0.001 (2)	−0.012 (3)
C8A	0.0305 (10)	0.0327 (12)	0.0344 (13)	−0.0051 (8)	−0.0006 (13)	0.0042 (14)
C8B	0.0218 (17)	0.039 (3)	0.027 (3)	−0.0006 (16)	0.0011 (16)	−0.0031 (19)
C9A	0.056 (6)	0.035 (5)	0.092 (8)	0.005 (4)	−0.003 (5)	0.007 (4)
C9B	0.054 (10)	0.031 (8)	0.042 (8)	0.004 (6)	−0.012 (6)	−0.026 (6)

Geometric parameters (Å, º)

S1—C2	1.7478 (18)	C7A—H7AB	0.9900
S1—C5	1.744 (2)	C7A—C8A	1.495 (4)
N1—H1	0.88 (3)	C7B—H7BA	0.9900
N1—C2	1.338 (3)	C7B—H7BB	0.9900
N1—C7A	1.459 (4)	C7B—C8B	1.490 (9)
N1—C7B	1.501 (5)	C8A—H8A	0.9500
N3—N4	1.391 (3)	C8A—C9A	1.325 (10)
N3—C2	1.319 (2)	C8B—H8B	0.9500
N4—C5	1.293 (3)	C8B—C9B	1.412 (19)
C5—C6	1.492 (3)	C9A—H9AA	0.9500
C6—H6A	0.9800	C9A—H9AB	0.9500
C6—H6B	0.9800	C9B—H9BA	0.9500
C6—H6C	0.9800	C9B—H9BB	0.9500
C7A—H7AA	0.9900		

C5—S1—C2	87.31 (9)	N1—C7A—C8A	111.9 (3)
C2—N1—H1	120.7 (19)	H7AA—C7A—H7AB	107.9
C2—N1—C7A	127.2 (2)	C8A—C7A—H7AA	109.2
C2—N1—C7B	110.0 (3)	C8A—C7A—H7AB	109.2
C7A—N1—H1	112.0 (19)	N1—C7B—H7BA	110.7
C7B—N1—H1	126.2 (18)	N1—C7B—H7BB	110.7
C2—N3—N4	112.41 (14)	H7BA—C7B—H7BB	108.8
C5—N4—N3	113.55 (15)	C8B—C7B—N1	105.1 (4)
N1—C2—S1	121.81 (11)	C8B—C7B—H7BA	110.7
N3—C2—S1	113.06 (15)	C8B—C7B—H7BB	110.7
N3—C2—N1	125.11 (16)	C7A—C8A—H8A	120.0
N4—C5—S1	113.66 (16)	C9A—C8A—C7A	120.0 (6)
N4—C5—C6	123.92 (19)	C9A—C8A—H8A	120.0
C6—C5—S1	122.42 (15)	C7B—C8B—H8B	120.5
C5—C6—H6A	109.5	C9B—C8B—C7B	118.9 (8)
C5—C6—H6B	109.5	C9B—C8B—H8B	120.5
C5—C6—H6C	109.5	C8A—C9A—H9AA	120.0
H6A—C6—H6B	109.5	C8A—C9A—H9AB	120.0

H6A—C6—H6C	109.5	H9AA—C9A—H9AB	120.0
H6B—C6—H6C	109.5	C8B—C9B—H9BA	120.0
N1—C7A—H7AA	109.2	C8B—C9B—H9BB	120.0
N1—C7A—H7AB	109.2	H9BA—C9B—H9BB	120.0

N1—C7A—C8A—C9A	−128.3 (6)	C2—N1—C7B—C8B	−174.0 (4)
N1—C7B—C8B—C9B	130.5 (9)	C2—N3—N4—C5	−0.1 (2)
N3—N4—C5—S1	0.0 (2)	C5—S1—C2—N1	178.47 (17)
N3—N4—C5—C6	−179.6 (2)	C5—S1—C2—N3	−0.01 (15)
N4—N3—C2—S1	0.0 (2)	C7A—N1—C2—S1	−174.1 (2)
N4—N3—C2—N1	−178.39 (18)	C7A—N1—C2—N3	4.2 (4)
C2—S1—C5—N4	−0.02 (16)	C7B—N1—C2—S1	171.5 (4)
C2—S1—C5—C6	179.64 (18)	C7B—N1—C2—N3	−10.2 (4)
C2—N1—C7A—C8A	−96.0 (3)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···N3^{i}	0.88 (3)	2.02 (3)	2.860 (2)	159 (3)
C7*A*—H7*AA*···S1^{ii}	0.99	2.97	3.462 (4)	112
C7*B*—H7*BA*···S1^{iii}	0.99	2.96	3.880 (8)	156
C8*B*—H8*B*···N4^{iv}	0.95	2.38	3.295 (5)	163

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

(1) Bis[*μ*-5-methyl-*N*-(prop-2-en-1-yl)-1,3,4-thiadiazol-2-amine]bis[nitratocopper(I)]

Crystal data

$[Cu_2(NO_3)_2(C_6H_9N_3S)_2]$
M_r = 561.54
Triclinic, $P\bar{1}$
a = 7.235 (3) Å
b = 7.548 (3) Å
c = 10.297 (4) Å
α = 105.42 (3)°
β = 98.15 (3)°
γ = 112.43 (3)°
V = 482.0 (4) Å^3

Z = 1
$F(000)$ = 284
D_x = 1.934 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3143 reflections
θ = 3.1–38.5°
μ = 2.47 mm^{-1}
T = 100 K
Block, clear colourless
0.43 × 0.21 × 0.14 mm

Data collection

Rigaku Xcalibur Onyx diffractometer
Radiation source: fine-focus sealed X-ray tube, Enhance (Mo) X-ray Source
Graphite monochromator
Detector resolution: 8.1956 pixels mm^{-1}
ω and φ scans
Absorption correction: analytical [CrysAlis PRO (Rigaku OD, 2015), based on expressions derived by Clark & Reid (1995)]

T_{min} = 0.542, T_{max} = 0.768
8459 measured reflections
8459 independent reflections
6900 reflections with $I > 2\sigma(I)$
R_{int} = 0.020
θ_{max} = 38.5°, θ_{min} = 3.1°
$h = -7 \rightarrow 12$
$k = -13 \rightarrow 12$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.096$
$S = 1.06$
8459 reflections
141 parameters
0 restraints

Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.061P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.88$ e Å^{-3}
$\Delta\rho_{min} = -1.03$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refined as a 2-component twin.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cu1	0.57775 (3)	0.57834 (3)	0.68133 (2)	0.01261 (7)
S1	0.18975 (7)	−0.09982 (7)	0.47322 (5)	0.01402 (10)
O1	0.2950 (3)	0.6861 (3)	0.6800 (2)	0.0308 (4)
O2	0.2567 (3)	0.8531 (3)	0.8713 (2)	0.0348 (4)
O3	0.1088 (3)	0.5240 (3)	0.7949 (2)	0.0312 (4)
N1	0.2182 (3)	0.6865 (3)	0.7824 (2)	0.0193 (4)
N2	0.4533 (3)	0.1392 (3)	0.72781 (19)	0.0161 (3)
H2	0.411 (4)	0.037 (4)	0.746 (3)	0.019*
N3	0.4220 (2)	0.2864 (2)	0.55566 (17)	0.0122 (3)
N4	0.3167 (2)	0.2273 (2)	0.41582 (17)	0.0123 (3)
C2	0.3733 (3)	0.1302 (3)	0.6002 (2)	0.0127 (3)
C5	0.1895 (3)	0.0338 (3)	0.3607 (2)	0.0134 (3)
C6	0.0538 (3)	−0.0697 (3)	0.2141 (2)	0.0177 (4)
H6A	0.1375	−0.0900	0.1497	0.027*
H6B	−0.0103	0.0155	0.1914	0.027*
H6C	−0.0551	−0.2026	0.2048	0.027*
C7	0.6182 (3)	0.3254 (3)	0.8338 (2)	0.0161 (4)
H7A	0.7481	0.3591	0.8043	0.019*
H7B	0.6431	0.3010	0.9231	0.019*
C8	0.5662 (3)	0.5039 (3)	0.8573 (2)	0.0150 (4)
H8	0.4246	0.4786	0.8447	0.018*
C9	0.7131 (3)	0.7002 (3)	0.8957 (2)	0.0177 (4)
H9A	0.8556	0.7289	0.9089	0.021*
H9B	0.6733	0.8086	0.9095	0.021*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.01666 (12)	0.00964 (10)	0.00970 (11)	0.00374 (9)	0.00286 (9)	0.00403 (8)

S1	0.0159 (2)	0.00918 (18)	0.0168 (2)	0.00455 (16)	0.00471 (18)	0.00559 (17)
O1	0.0361 (10)	0.0419 (10)	0.0367 (10)	0.0264 (9)	0.0210 (8)	0.0279 (9)
O2	0.0434 (11)	0.0194 (8)	0.0398 (11)	0.0152 (7)	0.0100 (9)	0.0064 (8)
O3	0.0275 (9)	0.0200 (7)	0.0523 (12)	0.0074 (7)	0.0187 (8)	0.0224 (8)
N1	0.0164 (8)	0.0178 (8)	0.0296 (10)	0.0088 (7)	0.0069 (7)	0.0148 (8)
N2	0.0208 (8)	0.0123 (7)	0.0162 (8)	0.0057 (6)	0.0053 (6)	0.0087 (7)
N3	0.0162 (7)	0.0104 (6)	0.0098 (7)	0.0051 (6)	0.0036 (6)	0.0045 (6)
N4	0.0151 (7)	0.0098 (6)	0.0109 (7)	0.0042 (5)	0.0039 (6)	0.0036 (6)
C2	0.0136 (8)	0.0102 (7)	0.0153 (9)	0.0050 (6)	0.0054 (7)	0.0055 (7)
C5	0.0152 (8)	0.0103 (7)	0.0153 (9)	0.0057 (7)	0.0049 (7)	0.0050 (7)
C6	0.0184 (9)	0.0112 (7)	0.0168 (9)	0.0028 (7)	−0.0007 (7)	0.0029 (7)
C7	0.0198 (9)	0.0165 (8)	0.0134 (9)	0.0082 (7)	0.0034 (7)	0.0074 (7)
C8	0.0195 (9)	0.0174 (8)	0.0099 (8)	0.0083 (7)	0.0042 (7)	0.0070 (7)
C9	0.0238 (10)	0.0164 (8)	0.0098 (8)	0.0070 (7)	0.0009 (7)	0.0048 (7)

Geometric parameters (Å, º)

Cu1—N3	1.9940 (19)	N4—Cu1$^{\text{i}}$	1.9690 (18)
Cu1—N4$^{\text{i}}$	1.9690 (18)	N4—C5	1.299 (2)
Cu1—C8	2.038 (2)	C5—C6	1.491 (3)
Cu1—C9	2.073 (2)	C6—H6A	0.9800
S1—C2	1.741 (2)	C6—H6B	0.9800
S1—C5	1.727 (2)	C6—H6C	0.9800
O1—N1	1.259 (3)	C7—H7A	0.9900
O2—N1	1.243 (2)	C7—H7B	0.9900
O3—N1	1.233 (2)	C7—C8	1.502 (3)
N2—H2	0.80 (3)	C8—H8	0.9500
N2—C2	1.331 (3)	C8—C9	1.360 (3)
N2—C7	1.458 (3)	C9—H9A	0.9500
N3—N4	1.393 (2)	C9—H9B	0.9500
N3—C2	1.319 (3)		
N3—Cu1—C8	92.55 (8)	C5—C6—H6A	109.5
N3—Cu1—C9	129.43 (8)	C5—C6—H6B	109.5
N4$^{\text{i}}$—Cu1—N3	114.48 (7)	C5—C6—H6C	109.5
N4$^{\text{i}}$—Cu1—C8	152.33 (8)	H6A—C6—H6B	109.5
N4$^{\text{i}}$—Cu1—C9	113.75 (9)	H6A—C6—H6C	109.5
C8—Cu1—C9	38.62 (8)	H6B—C6—H6C	109.5
C5—S1—C2	87.58 (10)	N2—C7—H7A	109.1
O2—N1—O1	118.97 (19)	N2—C7—H7B	109.1
O3—N1—O1	120.4 (2)	N2—C7—C8	112.34 (17)
O3—N1—O2	120.6 (2)	H7A—C7—H7B	107.9
C2—N2—H2	118.5 (18)	C8—C7—H7A	109.1
C2—N2—C7	122.94 (18)	C8—C7—H7B	109.1
C7—N2—H2	118.6 (18)	Cu1—C8—H8	92.0
N4—N3—Cu1	122.79 (13)	C7—C8—Cu1	105.91 (14)
C2—N3—Cu1	123.96 (14)	C7—C8—H8	118.6
C2—N3—N4	112.03 (15)	C9—C8—Cu1	72.10 (13)

N3—N4—Cu1^{i}	117.17 (12)	C9—C8—C7	122.76 (19)
C5—N4—Cu1^{i}	127.96 (15)	C9—C8—H8	118.6
C5—N4—N3	113.16 (17)	Cu1—C9—H9A	106.6
N2—C2—S1	121.22 (15)	Cu1—C9—H9B	93.9
N3—C2—S1	113.25 (15)	C8—C9—Cu1	69.28 (13)
N3—C2—N2	125.52 (18)	C8—C9—H9A	120.0
N4—C5—S1	113.95 (16)	C8—C9—H9B	120.0
N4—C5—C6	124.60 (19)	H9A—C9—H9B	120.0
C6—C5—S1	121.45 (14)		

Cu1—N3—N4—Cu1^{i}	27.76 (18)	N4—N3—C2—N2	178.15 (18)
Cu1—N3—N4—C5	−165.92 (13)	C2—S1—C5—N4	0.82 (15)
Cu1—N3—C2—S1	166.41 (9)	C2—S1—C5—C6	−179.44 (17)
Cu1—N3—C2—N2	−14.2 (3)	C2—N2—C7—C8	52.9 (3)
Cu1^{i}—N4—C5—S1	162.81 (10)	C2—N3—N4—Cu1^{i}	−164.39 (13)
Cu1^{i}—N4—C5—C6	−16.9 (3)	C2—N3—N4—C5	1.9 (2)
N2—C7—C8—Cu1	−70.33 (19)	C5—S1—C2—N2	−179.15 (17)
N2—C7—C8—C9	−149.0 (2)	C5—S1—C2—N3	0.30 (15)
N3—N4—C5—S1	−1.7 (2)	C7—N2—C2—S1	175.35 (14)
N3—N4—C5—C6	178.57 (17)	C7—N2—C2—N3	−4.0 (3)
N4—N3—C2—S1	−1.3 (2)	C7—C8—C9—Cu1	97.74 (19)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···O1^{ii}	0.80 (3)	2.32 (3)	3.034 (3)	150 (2)
N2—H2···O2^{ii}	0.80 (3)	2.24 (3)	2.970 (3)	153 (2)
N2—H2···N1^{ii}	0.80 (3)	2.63 (3)	3.426 (3)	172 (2)
C6—H6*B*···O2^{iii}	0.98	2.44	3.391 (3)	164
C6—H6*C*···O3^{iv}	0.98	2.31	3.142 (3)	143
C7—H7*A*···O3^{v}	0.99	2.45	3.415 (3)	164
C8—H8···O3	0.95	2.44	3.350 (3)	160
C8—H8···N1	0.95	2.68	3.391 (3)	133

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

(2) Bis[*μ*-5-methyl-*N*-(prop-2-en-1-yl)-1,3,4-thiadiazol-2-amine]bis[(tetrafluoroborato)copper(I)]

Crystal data

$[Cu_2(BF_4)_2(C_6H_9N_3S)_2]$
$M_r = 611.14$
Triclinic, $P\overline{1}$
$a = 7.754$ (3) Å
$b = 7.965$ (3) Å
$c = 10.372$ (4) Å
$\alpha = 67.57$ (3)°
$\beta = 89.99$ (3)°
$\gamma = 61.07$ (3)°
$V = 504.6$ (4) Å^3

$Z = 1$
$F(000) = 304$
$D_x = 2.011$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 6709 reflections
$\theta = 3.0$–38.4°
$\mu = 2.40$ mm^{-1}
$T = 100$ K
Block, clear colourless
0.44 × 0.23 × 0.18 mm

Data collection

Rigaku Xcalibur Onyx
diffractometer
Radiation source: Enhance (Mo) X-ray Source
Graphite monochromator
Detector resolution: 8.1956 pixels mm^{-1}
ω and π scans
Absorption correction: analytical
[CrysAlis PRO (Rigaku OD, 2015), based on expressions derived by Clark & Reid (1995)]

$T_{\min} = 0.498$, $T_{\max} = 0.711$
8712 measured reflections
4784 independent reflections
4163 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.014$
$\theta_{\max} = 38.5°$, $\theta_{\min} = 3.0°$
$h = -12 \rightarrow 10$
$k = -13 \rightarrow 13$
$l = -16 \rightarrow 18$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.022$
$wR(F^2) = 0.061$
$S = 1.07$
4784 reflections
149 parameters
0 restraints

Primary atom site location: structure-invariant direct methods
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.037P)^2 + 0.007P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.56$ e Å^{-3}
$\Delta\rho_{\min} = -0.51$ 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}
Cu1	0.40020 (2)	0.60430 (2)	0.31778 (2)	0.01224 (4)
S1	0.81824 (4)	−0.10490 (3)	0.52116 (2)	0.01379 (5)
N2	0.52780 (14)	0.17402 (13)	0.27870 (9)	0.01616 (15)
H2	0.574 (2)	0.071 (2)	0.2533 (17)	0.019*
N3	0.56082 (13)	0.29189 (12)	0.44914 (8)	0.01262 (13)
N4	0.67773 (12)	0.20945 (12)	0.58491 (8)	0.01243 (13)
C2	0.61534 (15)	0.14328 (14)	0.40314 (10)	0.01299 (15)
C5	0.81566 (15)	0.00725 (14)	0.63542 (10)	0.01316 (15)
C6	0.96188 (16)	−0.12310 (15)	0.77723 (10)	0.01759 (18)
H6A	1.0653	−0.2615	0.7825	0.026*
H6B	0.8898	−0.1449	0.8537	0.026*
H6C	1.0266	−0.0486	0.7887	0.026*
C7	0.35674 (15)	0.37956 (15)	0.17735 (10)	0.01552 (16)
H7A	0.2370	0.4161	0.2201	0.019*
H7B	0.3234	0.3696	0.0894	0.019*
C8	0.40423 (15)	0.55286 (15)	0.13881 (10)	0.01463 (16)
H8	0.5411	0.5147	0.1408	0.018*
C9	0.26128 (16)	0.76235 (15)	0.10109 (10)	0.01708 (17)
H9A	0.1232	0.8052	0.0982	0.020*
H9B	0.3003	0.8647	0.0779	0.020*

F1	0.77274 (12)	0.53404 (11)	0.31378 (8)	0.02589 (15)
F2	0.58069 (11)	0.88916 (10)	0.16685 (8)	0.02546 (15)
F3	0.90363 (12)	0.74658 (12)	0.27778 (8)	0.02710 (15)
F4	0.84274 (12)	0.66901 (12)	0.09893 (8)	0.02720 (15)
B1	0.77701 (18)	0.70789 (18)	0.21457 (12)	0.01625 (19)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.01465 (6)	0.01181 (5)	0.00981 (5)	−0.00615 (4)	0.00179 (4)	−0.00534 (4)
S1	0.01564 (11)	0.01145 (9)	0.01421 (9)	−0.00626 (8)	0.00329 (8)	−0.00664 (7)
N2	0.0183 (4)	0.0156 (3)	0.0151 (3)	−0.0070 (3)	0.0018 (3)	−0.0096 (3)
N3	0.0145 (3)	0.0130 (3)	0.0110 (3)	−0.0068 (3)	0.0030 (3)	−0.0064 (2)
N4	0.0141 (3)	0.0123 (3)	0.0109 (3)	−0.0068 (3)	0.0027 (3)	−0.0052 (2)
C2	0.0140 (4)	0.0136 (3)	0.0136 (3)	−0.0077 (3)	0.0043 (3)	−0.0072 (3)
C5	0.0147 (4)	0.0131 (3)	0.0124 (3)	−0.0074 (3)	0.0037 (3)	−0.0060 (3)
C6	0.0192 (5)	0.0134 (4)	0.0152 (4)	−0.0057 (3)	−0.0005 (3)	−0.0053 (3)
C7	0.0170 (4)	0.0175 (4)	0.0135 (3)	−0.0095 (3)	0.0012 (3)	−0.0075 (3)
C8	0.0166 (4)	0.0180 (4)	0.0111 (3)	−0.0095 (3)	0.0035 (3)	−0.0075 (3)
C9	0.0207 (5)	0.0170 (4)	0.0116 (3)	−0.0092 (3)	0.0004 (3)	−0.0053 (3)
F1	0.0294 (4)	0.0217 (3)	0.0270 (3)	−0.0169 (3)	0.0054 (3)	−0.0063 (3)
F2	0.0218 (3)	0.0197 (3)	0.0337 (4)	−0.0066 (3)	0.0039 (3)	−0.0163 (3)
F3	0.0303 (4)	0.0363 (4)	0.0294 (4)	−0.0246 (3)	0.0069 (3)	−0.0183 (3)
F4	0.0300 (4)	0.0323 (4)	0.0234 (3)	−0.0140 (3)	0.0106 (3)	−0.0191 (3)
B1	0.0183 (5)	0.0171 (4)	0.0183 (4)	−0.0105 (4)	0.0054 (4)	−0.0106 (4)

Geometric parameters (Å, º)

Cu1—N3	2.0036 (15)	C6—H6A	0.9800
Cu1—N4$^{\text{i}}$	1.9646 (11)	C6—H6B	0.9800
Cu1—C8	2.0451 (12)	C6—H6C	0.9800
Cu1—C9	2.0799 (15)	C7—H7A	0.9900
S1—C2	1.7397 (16)	C7—H7B	0.9900
S1—C5	1.7301 (11)	C7—C8	1.5072 (15)
N2—H2	0.869 (15)	C8—H8	0.9500
N2—C2	1.3361 (13)	C8—C9	1.3706 (16)
N2—C7	1.4597 (16)	C9—H9A	0.9500
N3—N4	1.3983 (13)	C9—H9B	0.9500
N3—C2	1.3244 (13)	F1—B1	1.3908 (15)
N4—Cu1$^{\text{i}}$	1.9645 (11)	F2—B1	1.4055 (16)
N4—C5	1.3046 (14)	F3—B1	1.3914 (14)
C5—C6	1.4910 (16)	F4—B1	1.3873 (14)
N3—Cu1—C8	92.88 (5)	H6A—C6—H6C	109.5
N3—Cu1—C9	130.27 (5)	H6B—C6—H6C	109.5
N4$^{\text{i}}$—Cu1—N3	114.54 (5)	N2—C7—H7A	109.4
N4$^{\text{i}}$—Cu1—C8	152.58 (4)	N2—C7—H7B	109.4
N4$^{\text{i}}$—Cu1—C9	114.25 (5)	N2—C7—C8	111.16 (9)

C8—Cu1—C9	38.80 (5)	H7A—C7—H7B	108.0
C5—S1—C2	87.64 (6)	C8—C7—H7A	109.4
C2—N2—H2	120.4 (10)	C8—C7—H7B	109.4
C2—N2—C7	122.90 (9)	Cu1—C8—H8	93.4
C7—N2—H2	116.6 (10)	C7—C8—Cu1	104.65 (7)
N4—N3—Cu1	122.78 (7)	C7—C8—H8	118.1
C2—N3—Cu1	122.80 (7)	C9—C8—Cu1	71.97 (7)
C2—N3—N4	111.58 (9)	C9—C8—C7	123.77 (10)
N3—N4—Cu1^{i}	117.92 (7)	C9—C8—H8	118.1
C5—N4—Cu1^{i}	128.40 (7)	Cu1—C9—H9A	105.1
C5—N4—N3	113.33 (9)	Cu1—C9—H9B	95.4
N2—C2—S1	121.34 (8)	C8—C9—Cu1	69.23 (7)
N3—C2—S1	113.61 (8)	C8—C9—H9A	120.0
N3—C2—N2	125.05 (9)	C8—C9—H9B	120.0
N4—C5—S1	113.80 (8)	H9A—C9—H9B	120.0
N4—C5—C6	125.29 (9)	F1—B1—F2	108.91 (10)
C6—C5—S1	120.91 (8)	F1—B1—F3	110.33 (10)
C5—C6—H6A	109.5	F3—B1—F2	108.25 (9)
C5—C6—H6B	109.5	F4—B1—F1	109.58 (9)
C5—C6—H6C	109.5	F4—B1—F2	109.39 (10)
H6A—C6—H6B	109.5	F4—B1—F3	110.34 (10)

Cu1—N3—N4—Cu1^{i}	25.80 (10)	N4—N3—C2—N2	178.42 (9)
Cu1—N3—N4—C5	−160.39 (7)	C2—S1—C5—N4	−1.04 (8)
Cu1—N3—C2—S1	159.58 (5)	C2—S1—C5—C6	179.13 (9)
Cu1—N3—C2—N2	−20.20 (14)	C2—N2—C7—C8	54.40 (13)
Cu1^{i}—N4—C5—S1	173.28 (5)	C2—N3—N4—Cu1^{i}	−172.82 (7)
Cu1^{i}—N4—C5—C6	−6.89 (15)	C2—N3—N4—C5	1.00 (11)
N2—C7—C8—Cu1	−72.62 (9)	C5—S1—C2—N2	−178.59 (9)
N2—C7—C8—C9	−150.50 (9)	C5—S1—C2—N3	1.63 (8)
N3—N4—C5—S1	0.26 (11)	C7—N2—C2—S1	179.68 (8)
N3—N4—C5—C6	−179.91 (9)	C7—N2—C2—N3	−0.55 (16)
N4—N3—C2—S1	−1.80 (10)	C7—C8—C9—Cu1	95.87 (9)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···F2^{ii}	0.87 (2)	1.95 (2)	2.7874 (14)	160 (1)
N2—H2···F3^{ii}	0.87 (2)	2.53 (2)	3.242 (2)	140 (1)
C6—H6*A*···F1^{iii}	0.98	2.51	3.4175 (19)	154
C6—H6*B*···F4^{iv}	0.98	2.54	3.4628 (19)	157
C6—H6*C*···F3^{v}	0.98	2.56	3.4824 (18)	157
C7—H7*B*···F4^{vi}	0.99	2.53	3.4900 (17)	163
C8—H8···F1	0.95	2.64	3.2956 (18)	127

Symmetry codes: (ii) *x*, *y*−1, *z*; (iii) −*x*+2, −*y*, −*z*+1; (iv) *x*, *y*−1, *z*+1; (v) −*x*+2, −*y*+1, −*z*+1; (vi) −*x*+1, −*y*+1, −*z*.

(3) *μ*-Aqua-bis{*μ*-5-[(prop-2-en-1-yl)sulfanyl]-1,3,4-thiadiazol-2-amine}bis[nitratocopper(I)]

Crystal data

$[Cu_2(NO_3)_2(C_5H_7N_3S_2)_2(H_2O)]$
$M_r = 615.63$
Monoclinic, $P2_1/c$
$a = 7.379\ (3)$ Å
$b = 18.780\ (5)$ Å
$c = 14.702\ (4)$ Å
$\beta = 94.82\ (3)°$
$V = 2030.2\ (11)$ Å^3
$Z = 4$

$F(000) = 1240$
$D_x = 2.014$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3740 reflections
$\theta = 2.8–32.2°$
$\mu = 2.56$ mm^{-1}
$T = 100$ K
Block, clear colourless
0.3 × 0.18 × 0.13 mm

Data collection

Rigaku Xcalibur Ruby diffractometer
Radiation source: Enhance (Mo) X-ray Source
Graphite monochromator
Detector resolution: 10.3456 pixels mm^{-1}
ω scans
Absorption correction: analytical [CrysAlis PRO (Rigaku OD, 2015), based on expressions derived by Clark & Reid (1995)]

$T_{min} = 0.577$, $T_{max} = 0.776$
11883 measured reflections
6647 independent reflections
4618 reflections with $I > 2\sigma(I)$
$R_{int} = 0.037$
$\theta_{max} = 32.3°$, $\theta_{min} = 2.8°$
$h = -7 \rightarrow 11$
$k = -28 \rightarrow 16$
$l = -21 \rightarrow 17$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.115$
$S = 1.01$
6647 reflections
346 parameters
0 restraints

Primary atom site location: structure-invariant direct methods
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.046P)^2 + 0.307P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.68$ e Å^{-3}
$\Delta\rho_{min} = -0.70$ 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)
Cu1A	0.6758 (2)	0.54841 (9)	0.28897 (8)	0.0254 (2)	0.765 (6)
Cu1B	0.6292 (7)	0.5656 (2)	0.2979 (3)	0.0226 (6)	0.235 (6)
Cu2A	0.4280 (2)	0.67847 (8)	0.15853 (14)	0.0280 (2)	0.794 (7)
Cu2B	0.4045 (8)	0.6712 (3)	0.1832 (4)	0.0222 (7)	0.206 (7)
S11	0.88194 (11)	0.77496 (4)	0.33415 (5)	0.03405 (17)	
S12A	0.9467 (2)	0.64460 (14)	0.45789 (9)	0.0351 (4)	0.765 (6)
S12B	0.9288 (9)	0.6667 (3)	0.4581 (4)	0.0348 (14)*	0.235 (6)
S21	0.32163 (10)	0.45394 (3)	0.06167 (5)	0.02596 (15)	

S22	0.09397 (10)	0.58465 (4)	0.02178 (5)	0.02980 (16)	
O1	0.3426 (4)	0.61593 (15)	0.31989 (18)	0.0561 (8)	
H1A	0.262 (7)	0.578 (3)	0.323 (3)	0.084*	
H1B	0.326 (6)	0.647 (2)	0.373 (3)	0.084*	
O21	0.5703 (3)	0.69954 (12)	0.00949 (15)	0.0405 (5)	
O22	0.4733 (3)	0.80878 (11)	0.00474 (15)	0.0381 (5)	
O23	0.4103 (4)	0.73874 (12)	−0.10980 (15)	0.0468 (6)	
N2	0.4863 (4)	0.74886 (13)	−0.03207 (16)	0.0321 (6)	
N12	0.6913 (4)	0.81795 (15)	0.17938 (18)	0.0358 (6)	
H12A	0.750 (5)	0.8612 (18)	0.189 (2)	0.043*	
H12B	0.624 (5)	0.8080 (19)	0.132 (2)	0.043*	
N13	0.7304 (3)	0.65507 (13)	0.29752 (15)	0.0280 (5)	
N14	0.6605 (3)	0.70080 (12)	0.22911 (15)	0.0264 (5)	
N22	0.6172 (4)	0.40718 (13)	0.16391 (18)	0.0301 (5)	
H22A	0.717 (5)	0.4157 (17)	0.196 (2)	0.036*	
H22B	0.585 (5)	0.3677 (17)	0.146 (2)	0.036*	
N23	0.4050 (3)	0.57409 (11)	0.13393 (15)	0.0231 (4)	
N24	0.5332 (3)	0.52684 (12)	0.17360 (14)	0.0238 (4)	
C12	0.8423 (4)	0.68604 (17)	0.35797 (19)	0.0318 (6)	
C15	0.7307 (4)	0.76500 (15)	0.23714 (19)	0.0287 (6)	
C17A	0.7803 (6)	0.5763 (2)	0.4787 (3)	0.0313 (10)	0.765 (6)
H17A	0.8043	0.5588	0.5421	0.038*	0.765 (6)
H17B	0.6575	0.5979	0.4732	0.038*	0.765 (6)
C17B	0.8942 (19)	0.5707 (7)	0.4540 (9)	0.033 (3)*	0.235 (6)
H17C	0.9706	0.5504	0.4082	0.040*	0.235 (6)
H17D	0.9375	0.5505	0.5141	0.040*	0.235 (6)
C18A	0.7815 (6)	0.5150 (2)	0.4155 (2)	0.0320 (10)	0.765 (6)
H18A	0.8945	0.5027	0.3932	0.038*	0.765 (6)
C18B	0.7029 (16)	0.5471 (6)	0.4311 (7)	0.019 (2)*	0.235 (6)
H18B	0.6054	0.5772	0.4447	0.023*	0.235 (6)
C19A	0.6328 (11)	0.4744 (4)	0.3864 (4)	0.0318 (13)	0.765 (6)
H19A	0.5172	0.4850	0.4071	0.038*	0.765 (6)
H19B	0.6456	0.4359	0.3456	0.038*	0.765 (6)
C19B	0.669 (4)	0.4866 (14)	0.3933 (19)	0.038 (7)*	0.235 (6)
H19C	0.7658	0.4562	0.3796	0.045*	0.235 (6)
H19D	0.5463	0.4720	0.3791	0.045*	0.235 (6)
C22	0.2827 (4)	0.54435 (13)	0.07774 (17)	0.0227 (5)	
C25	0.5102 (4)	0.46214 (14)	0.14025 (18)	0.0247 (5)	
C27A	0.0483 (5)	0.65593 (18)	0.1045 (3)	0.0288 (9)	0.794 (7)
H27A	−0.0763	0.6745	0.0898	0.035*	0.794 (7)
H27B	0.0539	0.6353	0.1667	0.035*	0.794 (7)
C27B	0.0940 (17)	0.6732 (6)	0.0521 (8)	0.020 (3)*	0.206 (7)
H27C	0.1816	0.6983	0.0159	0.024*	0.206 (7)
H27D	−0.0281	0.6927	0.0336	0.024*	0.206 (7)
C28A	0.1794 (5)	0.71578 (19)	0.1038 (3)	0.0298 (9)	0.794 (7)
H28A	0.2256	0.7269	0.0471	0.036*	0.794 (7)
C28B	0.1379 (17)	0.6907 (7)	0.1468 (9)	0.021 (3)*	0.206 (7)
H28B	0.1072	0.6591	0.1936	0.025*	0.206 (7)

C29A	0.2400 (13)	0.7564 (4)	0.1775 (7)	0.0273 (14)	0.794 (7)
H29A	0.1975	0.7472	0.2356	0.033*	0.794 (7)
H29B	0.3244	0.7938	0.1705	0.033*	0.794 (7)
C29B	0.220 (6)	0.750 (2)	0.167 (3)	0.047 (13)*	0.206 (7)
H29C	0.2503	0.7817	0.1197	0.057*	0.206 (7)
H29D	0.2501	0.7629	0.2291	0.057*	0.206 (7)
O11	0.9655 (3)	0.52030 (11)	0.22839 (16)	0.0409 (5)	
O12	0.9797 (3)	0.40739 (11)	0.25601 (18)	0.0424 (6)	
O13	1.2039 (3)	0.47483 (12)	0.30109 (17)	0.0440 (6)	
N1	1.0495 (3)	0.46788 (13)	0.26096 (17)	0.0291 (5)	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1A	0.0284 (5)	0.0246 (5)	0.0226 (3)	−0.0032 (3)	−0.0014 (3)	0.0019 (3)
Cu1B	0.0236 (14)	0.0197 (12)	0.0243 (10)	0.0019 (9)	0.0010 (9)	0.0013 (8)
Cu2A	0.0269 (4)	0.0242 (4)	0.0322 (6)	−0.0001 (3)	−0.0019 (4)	−0.0069 (4)
Cu2B	0.0211 (14)	0.0241 (13)	0.0210 (17)	0.0010 (10)	0.0004 (11)	−0.0033 (12)
S11	0.0330 (4)	0.0402 (4)	0.0290 (3)	−0.0121 (3)	0.0033 (3)	−0.0092 (3)
S12A	0.0342 (7)	0.0434 (10)	0.0260 (5)	−0.0039 (7)	−0.0083 (4)	0.0001 (6)
S21	0.0265 (3)	0.0213 (3)	0.0293 (3)	0.0002 (3)	−0.0021 (3)	−0.0018 (2)
S22	0.0271 (4)	0.0277 (3)	0.0331 (4)	0.0004 (3)	−0.0067 (3)	−0.0001 (3)
O1	0.0697 (19)	0.0507 (15)	0.0515 (15)	−0.0236 (14)	0.0268 (14)	−0.0185 (12)
O21	0.0516 (15)	0.0365 (12)	0.0335 (11)	0.0071 (11)	0.0034 (10)	0.0053 (9)
O22	0.0520 (14)	0.0264 (10)	0.0363 (11)	−0.0083 (10)	0.0056 (10)	−0.0030 (9)
O23	0.0761 (19)	0.0342 (12)	0.0280 (11)	−0.0094 (12)	−0.0078 (11)	0.0015 (9)
N2	0.0456 (16)	0.0268 (12)	0.0243 (11)	−0.0089 (11)	0.0054 (10)	0.0010 (9)
N12	0.0432 (16)	0.0323 (13)	0.0317 (13)	−0.0092 (12)	0.0027 (11)	−0.0041 (11)
N13	0.0279 (12)	0.0348 (12)	0.0213 (10)	−0.0054 (10)	0.0026 (9)	−0.0019 (9)
N14	0.0284 (12)	0.0280 (11)	0.0230 (10)	−0.0042 (10)	0.0036 (9)	−0.0031 (9)
N22	0.0272 (13)	0.0253 (12)	0.0369 (13)	0.0026 (10)	−0.0036 (10)	−0.0005 (10)
N23	0.0221 (11)	0.0249 (11)	0.0222 (10)	0.0015 (9)	0.0009 (8)	−0.0007 (8)
N24	0.0241 (11)	0.0251 (11)	0.0217 (10)	0.0017 (9)	−0.0002 (8)	−0.0004 (8)
C12	0.0288 (14)	0.0427 (17)	0.0242 (13)	−0.0068 (13)	0.0035 (11)	−0.0044 (12)
C15	0.0289 (14)	0.0322 (14)	0.0261 (13)	−0.0061 (12)	0.0075 (11)	−0.0064 (11)
C17A	0.035 (2)	0.034 (2)	0.0250 (18)	0.0057 (17)	0.0033 (15)	0.0022 (15)
C18A	0.037 (2)	0.036 (2)	0.0227 (17)	0.0091 (19)	0.0003 (15)	0.0018 (15)
C19A	0.048 (4)	0.024 (2)	0.022 (2)	−0.003 (3)	−0.001 (2)	0.0059 (17)
C22	0.0237 (13)	0.0209 (11)	0.0233 (12)	−0.0004 (10)	0.0005 (9)	−0.0007 (9)
C25	0.0242 (13)	0.0254 (12)	0.0249 (12)	0.0006 (11)	0.0037 (10)	0.0017 (10)
C27A	0.0245 (17)	0.0233 (16)	0.039 (2)	0.0042 (14)	0.0035 (15)	0.0003 (14)
C28A	0.0298 (19)	0.0235 (17)	0.037 (2)	0.0039 (15)	0.0055 (15)	0.0001 (15)
C29A	0.027 (3)	0.019 (2)	0.036 (3)	0.0021 (18)	0.003 (2)	−0.008 (2)
O11	0.0340 (12)	0.0339 (11)	0.0556 (14)	0.0059 (10)	0.0085 (10)	0.0185 (10)
O12	0.0344 (12)	0.0255 (10)	0.0654 (16)	0.0004 (9)	−0.0067 (11)	0.0016 (10)
O13	0.0293 (12)	0.0375 (12)	0.0633 (16)	−0.0031 (10)	−0.0071 (11)	0.0079 (11)
N1	0.0244 (12)	0.0280 (12)	0.0355 (13)	0.0025 (10)	0.0068 (10)	0.0038 (10)

Geometric parameters (Å, º)

Cu1A—N13	2.045 (3)	N13—C12	1.299 (4)
Cu1A—N24	1.962 (2)	N14—C15	1.314 (4)
Cu1A—C18A	2.054 (4)	N22—H22A	0.85 (4)
Cu1A—C19A	2.039 (6)	N22—H22B	0.82 (3)
Cu1B—Cu2B	3.009 (7)	N22—C25	1.328 (4)
Cu1B—O1	2.363 (7)	N23—N24	1.389 (3)
Cu1B—N13	1.838 (4)	N23—C22	1.297 (3)
Cu1B—N24	2.038 (4)	N24—C25	1.316 (3)
Cu1B—C18B	2.019 (11)	C17A—H17A	0.9900
Cu1B—C19B	2.05 (3)	C17A—H17B	0.9900
Cu2A—N14	1.974 (3)	C17A—C18A	1.480 (6)
Cu2A—N23	1.998 (3)	C17B—H17C	0.9900
Cu2A—C28A	2.062 (4)	C17B—H17D	0.9900
Cu2A—C29A	2.052 (8)	C17B—C18B	1.490 (17)
Cu2B—O1	2.341 (7)	C18A—H18A	0.9500
Cu2B—N14	2.029 (6)	C18A—C19A	1.374 (9)
Cu2B—N23	1.962 (6)	C18B—H18B	0.9500
Cu2B—C28B	2.028 (13)	C18B—C19B	1.28 (3)
Cu2B—C29B	2.02 (5)	C19A—H19A	0.9500
S11—C12	1.736 (3)	C19A—H19B	0.9500
S11—C15	1.746 (3)	C19B—H19C	0.9500
S12A—C12	1.779 (3)	C19B—H19D	0.9500
S12A—C17A	1.819 (4)	C27A—H27A	0.9900
S12B—C12	1.596 (7)	C27A—H27B	0.9900
S12B—C17B	1.823 (14)	C27A—C28A	1.484 (5)
S21—C22	1.741 (3)	C27B—H27C	0.9900
S21—C25	1.739 (3)	C27B—H27D	0.9900
S22—C22	1.731 (3)	C27B—C28B	1.441 (17)
S22—C27A	1.859 (4)	C28A—H28A	0.9500
S22—C27B	1.721 (12)	C28A—C29A	1.369 (11)
O1—H1A	0.93 (5)	C28B—H28B	0.9500
O1—H1B	0.99 (5)	C28B—C29B	1.30 (4)
O21—N2	1.246 (3)	C29A—H29A	0.9500
O22—N2	1.256 (3)	C29A—H29B	0.9500
O23—N2	1.244 (3)	C29B—H29C	0.9500
N12—H12A	0.93 (4)	C29B—H29D	0.9500
N12—H12B	0.84 (4)	O11—N1	1.238 (3)
N12—C15	1.324 (4)	O12—N1	1.247 (3)
N13—N14	1.389 (3)	O13—N1	1.245 (3)

N13—Cu1A—C18A	100.70 (14)	N13—C12—S12A	125.1 (2)
N24—Cu1A—N13	110.12 (11)	N13—C12—S12B	135.4 (3)
N24—Cu1A—C18A	148.79 (15)	N12—C15—S11	122.3 (2)
N24—Cu1A—C19A	111.3 (2)	N14—C15—S11	113.1 (2)
C19A—Cu1A—N13	131.7 (2)	N14—C15—N12	124.6 (3)
C19A—Cu1A—C18A	39.2 (2)	S12A—C17A—H17A	108.8

O1—Cu1B—Cu2B	49.91 (17)	S12A—C17A—H17B	108.8
N13—Cu1B—Cu2B	66.50 (19)	H17A—C17A—H17B	107.7
N13—Cu1B—O1	90.2 (2)	C18A—C17A—S12A	113.8 (3)
N13—Cu1B—N24	115.78 (19)	C18A—C17A—H17A	108.8
N13—Cu1B—C18B	94.8 (3)	C18A—C17A—H17B	108.8
N13—Cu1B—C19B	129.1 (7)	S12B—C17B—H17C	108.4
N24—Cu1B—Cu2B	66.39 (16)	S12B—C17B—H17D	108.4
N24—Cu1B—O1	91.02 (19)	H17C—C17B—H17D	107.5
N24—Cu1B—C19B	112.0 (7)	C18B—C17B—S12B	115.4 (10)
C18B—Cu1B—Cu2B	138.4 (4)	C18B—C17B—H17C	108.4
C18B—Cu1B—O1	96.1 (4)	C18B—C17B—H17D	108.4
C18B—Cu1B—N24	148.6 (4)	Cu1A—C18A—H18A	92.3
C18B—Cu1B—C19B	36.7 (7)	C17A—C18A—Cu1A	108.0 (3)
C19B—Cu1B—Cu2B	154.4 (8)	C17A—C18A—H18A	117.3
C19B—Cu1B—O1	105.9 (8)	C19A—C18A—Cu1A	69.8 (3)
N14—Cu2A—N23	111.13 (12)	C19A—C18A—C17A	125.4 (5)
N14—Cu2A—C28A	146.92 (15)	C19A—C18A—H18A	117.3
N14—Cu2A—C29A	110.2 (3)	Cu1B—C18B—H18B	87.4
N23—Cu2A—C28A	101.74 (14)	C17B—C18B—Cu1B	109.9 (8)
N23—Cu2A—C29A	132.6 (3)	C17B—C18B—H18B	119.7
C29A—Cu2A—C28A	38.9 (3)	C19B—C18B—Cu1B	72.8 (14)
O1—Cu2B—Cu1B	50.57 (17)	C19B—C18B—C17B	120.6 (17)
N14—Cu2B—Cu1B	62.64 (17)	C19B—C18B—H18B	119.7
N14—Cu2B—O1	94.6 (2)	Cu1A—C19A—H19A	106.2
N23—Cu2B—Cu1B	64.95 (19)	Cu1A—C19A—H19B	92.7
N23—Cu2B—O1	84.9 (3)	C18A—C19A—Cu1A	71.0 (3)
N23—Cu2B—N14	110.3 (3)	C18A—C19A—H19A	120.0
N23—Cu2B—C28B	95.9 (4)	C18A—C19A—H19B	120.0
N23—Cu2B—C29B	131.6 (13)	H19A—C19A—H19B	120.0
C28B—Cu2B—Cu1B	138.0 (5)	Cu1B—C19B—H19C	110.8
C28B—Cu2B—O1	93.0 (4)	Cu1B—C19B—H19D	88.8
C28B—Cu2B—N14	153.3 (5)	C18B—C19B—Cu1B	70.4 (13)
C29B—Cu2B—Cu1B	152.5 (15)	C18B—C19B—H19C	120.0
C29B—Cu2B—O1	104.5 (15)	C18B—C19B—H19D	120.0
C29B—Cu2B—N14	115.9 (13)	H19C—C19B—H19D	120.0
C29B—Cu2B—C28B	37.4 (13)	S22—C22—S21	119.80 (15)
C12—S11—C15	87.41 (14)	N23—C22—S21	113.1 (2)
C12—S12A—C17A	101.29 (17)	N23—C22—S22	127.1 (2)
C12—S12B—C17B	98.6 (5)	N22—C25—S21	122.0 (2)
C25—S21—C22	87.44 (13)	N24—C25—S21	113.6 (2)
C22—S22—C27A	100.77 (15)	N24—C25—N22	124.4 (3)
C27B—S22—C22	108.4 (4)	S22—C27A—H27A	109.0
Cu1B—O1—H1A	107 (3)	S22—C27A—H27B	109.0
Cu1B—O1—H1B	121 (3)	H27A—C27A—H27B	107.8
Cu2B—O1—Cu1B	79.52 (18)	C28A—C27A—S22	112.7 (3)
Cu2B—O1—H1A	124 (3)	C28A—C27A—H27A	109.0
Cu2B—O1—H1B	118 (3)	C28A—C27A—H27B	109.0
H1A—O1—H1B	106 (4)	S22—C27B—H27C	107.9

O21—N2—O22	120.5 (2)	S22—C27B—H27D	107.9
O23—N2—O21	120.3 (2)	H27C—C27B—H27D	107.2
O23—N2—O22	119.2 (3)	C28B—C27B—S22	117.8 (10)
H12A—N12—H12B	124 (3)	C28B—C27B—H27C	107.9
C15—N12—H12A	119 (2)	C28B—C27B—H27D	107.9
C15—N12—H12B	116 (2)	Cu2A—C28A—H28A	92.5
N14—N13—Cu1A	120.13 (17)	C27A—C28A—Cu2A	107.4 (2)
N14—N13—Cu1B	116.2 (2)	C27A—C28A—H28A	117.0
C12—N13—Cu1A	126.3 (2)	C29A—C28A—Cu2A	70.2 (4)
C12—N13—Cu1B	130.0 (2)	C29A—C28A—C27A	125.9 (5)
C12—N13—N14	113.3 (2)	C29A—C28A—H28A	117.0
N13—N14—Cu2A	120.19 (18)	Cu2B—C28B—H28B	88.9
N13—N14—Cu2B	110.5 (2)	C27B—C28B—Cu2B	110.3 (9)
C15—N14—Cu2A	124.1 (2)	C27B—C28B—H28B	120.6
C15—N14—Cu2B	129.1 (3)	C29B—C28B—Cu2B	71 (2)
C15—N14—N13	112.5 (2)	C29B—C28B—C27B	119 (3)
H22A—N22—H22B	124 (3)	C29B—C28B—H28B	120.6
C25—N22—H22A	118 (2)	Cu2A—C29A—H29A	105.7
C25—N22—H22B	118 (2)	Cu2A—C29A—H29B	93.2
N24—N23—Cu2A	120.41 (17)	C28A—C29A—Cu2A	71.0 (4)
N24—N23—Cu2B	117.4 (2)	C28A—C29A—H29A	120.0
C22—N23—Cu2A	125.57 (19)	C28A—C29A—H29B	120.0
C22—N23—Cu2B	127.8 (2)	H29A—C29A—H29B	120.0
C22—N23—N24	113.9 (2)	Cu2B—C29B—H29C	110.2
N23—N24—Cu1A	121.87 (17)	Cu2B—C29B—H29D	88.2
N23—N24—Cu1B	108.7 (2)	C28B—C29B—Cu2B	72 (2)
C25—N24—Cu1A	123.76 (19)	C28B—C29B—H29C	120.0
C25—N24—Cu1B	133.5 (2)	C28B—C29B—H29D	120.0
C25—N24—N23	111.8 (2)	H29C—C29B—H29D	120.0
S11—C12—S12A	121.24 (18)	O11—N1—O12	120.7 (3)
S12B—C12—S11	110.1 (3)	O11—N1—O13	120.6 (3)
N13—C12—S11	113.6 (2)	O13—N1—O12	118.7 (2)

Cu1A—N13—N14—Cu2A	29.4 (3)	N23—N24—C25—S21	−3.1 (3)
Cu1A—N13—N14—C15	−169.9 (2)	N23—N24—C25—N22	177.7 (3)
Cu1A—N13—C12—S11	170.37 (15)	N24—Cu1B—N13—N14	30.0 (4)
Cu1A—N13—C12—S12A	−10.5 (4)	N24—Cu1B—N13—C12	−159.7 (3)
Cu1A—N24—C25—S21	159.03 (15)	N24—N23—C22—S21	−4.0 (3)
Cu1A—N24—C25—N22	−20.2 (4)	N24—N23—C22—S22	175.27 (19)
Cu1B—N13—N14—Cu2B	23.5 (3)	C12—S11—C15—N12	−179.7 (3)
Cu1B—N13—N14—C15	175.6 (3)	C12—S11—C15—N14	1.2 (2)
Cu1B—N13—C12—S11	−173.2 (3)	C12—S12A—C17A—C18A	75.0 (3)
Cu1B—N13—C12—S12B	−5.7 (6)	C12—S12B—C17B—C18B	−55.7 (10)
Cu1B—N24—C25—S21	145.9 (3)	C12—N13—N14—Cu2A	−157.0 (2)
Cu1B—N24—C25—N22	−33.3 (5)	C12—N13—N14—Cu2B	−148.3 (3)
Cu2A—N14—C15—S11	156.82 (16)	C12—N13—N14—C15	3.7 (3)
Cu2A—N14—C15—N12	−22.3 (4)	C15—S11—C12—S12A	−178.2 (2)
Cu2A—N23—N24—Cu1A	26.1 (3)	C15—S11—C12—S12B	−169.8 (3)

Cu2A—N23—N24—C25	−171.39 (19)	C15—S11—C12—N13	0.9 (2)
Cu2A—N23—C22—S21	171.75 (15)	C17A—S12A—C12—S11	151.7 (2)
Cu2A—N23—C22—S22	−9.0 (4)	C17A—S12A—C12—N13	−27.3 (3)
Cu2B—Cu1B—N13—N14	−16.0 (2)	C17A—C18A—C19A—Cu1A	98.2 (4)
Cu2B—Cu1B—N13—C12	154.3 (3)	C17B—S12B—C12—S11	−172.0 (5)
Cu2B—N14—C15—S11	142.6 (3)	C17B—S12B—C12—N13	20.1 (8)
Cu2B—N14—C15—N12	−36.5 (5)	C17B—C18B—C19B—Cu1B	−103.3 (13)
Cu2B—N23—N24—Cu1B	17.8 (3)	C18B—Cu1B—N13—N14	−157.4 (4)
Cu2B—N23—N24—C25	174.6 (3)	C18B—Cu1B—N13—C12	12.8 (5)
Cu2B—N23—C22—S21	−172.7 (3)	C19B—Cu1B—N13—N14	−172.0 (11)
Cu2B—N23—C22—S22	6.5 (4)	C19B—Cu1B—N13—C12	−1.8 (12)
S12A—C17A—C18A—Cu1A	−71.1 (3)	C22—S21—C25—N22	−180.0 (3)
S12A—C17A—C18A—C19A	−148.7 (4)	C22—S21—C25—N24	0.8 (2)
S12B—C17B—C18B—Cu1B	72.2 (11)	C22—S22—C27A—C28A	74.8 (3)
S12B—C17B—C18B—C19B	153.6 (17)	C22—S22—C27B—C28B	−43.0 (11)
S22—C27A—C28A—Cu2A	−69.4 (3)	C22—N23—N24—Cu1A	−157.90 (19)
S22—C27A—C28A—C29A	−147.2 (5)	C22—N23—N24—Cu1B	−152.1 (2)
S22—C27B—C28B—Cu2B	69.6 (12)	C22—N23—N24—C25	4.6 (3)
S22—C27B—C28B—C29B	148 (3)	C25—S21—C22—S22	−177.47 (18)
O1—Cu1B—N13—N14	−61.2 (2)	C25—S21—C22—N23	1.9 (2)
O1—Cu1B—N13—C12	109.0 (3)	C27A—S22—C22—S21	150.13 (18)
N13—N14—C15—S11	−3.0 (3)	C27A—S22—C22—N23	−29.1 (3)
N13—N14—C15—N12	177.9 (3)	C27A—C28A—C29A—Cu2A	97.5 (4)
N14—N13—C12—S11	−2.8 (3)	C27B—S22—C22—S21	179.8 (5)
N14—N13—C12—S12A	176.3 (2)	C27B—S22—C22—N23	0.5 (5)
N14—N13—C12—S12B	164.8 (4)	C27B—C28B—C29B—Cu2B	−103.2 (17)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*A*···O13^{i}	0.93 (5)	2.01 (5)	2.846 (4)	149 (4)
O1—H1*B*···O22^{ii}	0.99 (5)	2.29 (5)	3.142 (4)	143 (4)
O1—H1*B*···O23^{ii}	0.99 (5)	2.25 (5)	2.946 (3)	126 (3)
O1—H1*B*···N2^{ii}	0.99 (5)	2.63 (5)	3.453 (4)	140 (4)
N12—H12*A*···O12^{iii}	0.93 (4)	2.26 (4)	3.038 (4)	141 (3)
N12—H12*A*···O13^{iii}	0.93 (4)	2.16 (4)	3.053 (4)	161 (3)
N12—H12*A*···N1^{iii}	0.93 (4)	2.56 (4)	3.475 (4)	169 (3)
N12—H12*B*···O22	0.84 (4)	2.09 (4)	2.918 (4)	166 (3)
N22—H22*A*···O12	0.85 (4)	2.07 (4)	2.895 (4)	163 (3)
N22—H22*B*···O23^{iv}	0.82 (3)	2.07 (3)	2.856 (3)	162 (3)
C17*A*—H17*A*···O13^{v}	0.99	2.40	3.369 (5)	167
C17*A*—H17*B*···O22^{ii}	0.99	2.29	3.175 (5)	149
C18*A*—H18*A*···O11	0.95	2.54	3.170 (5)	124
C18*A*—H18*A*···N1	0.95	2.43	3.258 (5)	146
C18*B*—H18*B*···O1	0.95	2.66	3.268 (12)	123
C18*B*—H18*B*···O22^{ii}	0.95	2.54	3.417 (12)	154
C27*A*—H27*B*···O11^{i}	0.99	2.45	3.219 (4)	134
C27*B*—H27*C*···N2	0.99	2.59	3.540 (13)	160

C27*B*—H27*D*···S11^{vi}	0.99	3.01	3.581 (12)	118
C27*B*—H27*D*···S12*B*^{vi}	0.99	2.87	3.487 (14)	121
C28*A*—H28*A*···O22	0.95	2.51	3.226 (5)	133
C28*A*—H28*A*···N2	0.95	2.37	3.204 (5)	147
C28*B*—H28*B*···O1	0.95	2.57	3.175 (13)	122

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

(4) *μ*-Aqua-(hexafluorosilicato)bis{*μ*-5-[(prop-2-en-1-yl)sulfanyl]-1,3,4-thiadiazol-2-amine}dicopper(I) acetonitrile hemisolvate dihydrate

Crystal data

$[Cu_2(SiF_6)(C_5H_7N_3S_2)_2(H_2O)]\cdot0.5C_2H_3N\cdot2H_2O$
$M_r = 688.24$
Monoclinic, $P2_1/n$
$a = 11.899$ (4) Å
$b = 11.442$ (4) Å
$c = 17.678$ (5) Å
$\beta = 102.04$ (3)°
$V = 2353.9$ (13) Å^3
$Z = 4$
$F(000) = 1380$
$D_x = 1.942$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 9071 reflections
$\theta = 2.9–36.8°$
$\mu = 2.29$ mm^{-1}
$T = 260$ K
Prism, clear colourless
0.52 × 0.17 × 0.09 mm

Data collection

Rigaku Xcalibur Sapphire2 (large Be window) diffractometer
Radiation source: Enhance (Mo) X-ray Source
Graphite monochromator
Detector resolution: 8.3359 pixels mm^{-1}
ω scans
Absorption correction: analytical [CrysAlis PRO (Rigaku OD, 2015), based on expressions derived by Clark & Reid (1995)]
$T_{min} = 0.452$, $T_{max} = 0.825$
24572 measured reflections
5649 independent reflections
3717 reflections with $I > 2\sigma(I)$
$R_{int} = 0.053$
$\theta_{max} = 28.0°$, $\theta_{min} = 2.9°$
$h = -15\rightarrow15$
$k = -15\rightarrow12$
$l = -23\rightarrow23$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.087$
$S = 1.02$
5649 reflections
412 parameters
245 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.042P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.47$ e Å^{-3}
$\Delta\rho_{min} = -0.38$ 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)
C12	−0.3873 (2)	−1.0688 (2)	0.07294 (15)	0.0321 (6)	
C15	−0.4799 (2)	−0.9721 (2)	0.16465 (16)	0.0305 (6)	
C22	−0.3561 (3)	−0.5332 (2)	0.05978 (17)	0.0357 (7)	
C25	−0.3182 (3)	−0.6313 (2)	−0.05172 (16)	0.0353 (7)	
Cu1	−0.26289 (3)	−0.86456 (3)	0.02532 (2)	0.03965 (12)	
N12	−0.5426 (2)	−0.9414 (3)	0.21542 (17)	0.0434 (7)	
H12A	−0.562 (3)	−0.869 (3)	0.211 (2)	0.052*	
H12B	−0.590 (3)	−0.987 (3)	0.230 (2)	0.052*	
N13	−0.36247 (19)	−0.9572 (2)	0.08057 (13)	0.0312 (5)	
N14	−0.4136 (2)	−0.9013 (2)	0.13454 (13)	0.0320 (5)	
N22	−0.2988 (3)	−0.6624 (3)	−0.12019 (16)	0.0537 (8)	
H22A	−0.288 (3)	−0.737 (3)	−0.139 (2)	0.064*	
H22B	−0.288 (3)	−0.609 (3)	−0.150 (2)	0.064*	
N23	−0.3555 (2)	−0.6453 (2)	0.06740 (13)	0.0327 (5)	
N24	−0.3312 (2)	−0.7043 (2)	0.00340 (12)	0.0338 (5)	
O1	−0.1575 (2)	−0.7886 (2)	0.14329 (14)	0.0535 (6)	
H1A	−0.1317	−0.7155	0.1371	0.080*	
H1B	−0.0955	−0.8336	0.1620	0.080*	
O2	0.0394 (2)	−0.9116 (3)	0.15841 (17)	0.0727 (8)	
H2A	0.0713	−0.9607	0.1940	0.109*	
H2B	0.0844	−0.8516	0.1583	0.109*	
S11	−0.47951 (7)	−1.11532 (6)	0.13071 (4)	0.03665 (18)	
S12	−0.33947 (8)	−1.16900 (7)	0.01339 (5)	0.0477 (2)	
S21	−0.33098 (8)	−0.48476 (7)	−0.02800 (5)	0.0456 (2)	
C17A	−0.2451 (6)	−1.0907 (5)	−0.0365 (4)	0.0449 (17)	0.617 (10)
H17A	−0.1995	−1.1480	−0.0572	0.054*	0.617 (10)
H17B	−0.2926	−1.0510	−0.0802	0.054*	0.617 (10)
C18A	−0.1651 (5)	−1.0035 (4)	0.0071 (4)	0.0404 (17)	0.617 (10)
H18A	−0.1392	−1.0130	0.0601	0.048*	0.617 (10)
C19A	−0.1303 (15)	−0.9146 (16)	−0.0265 (11)	0.054 (5)	0.617 (10)
H19A	−0.1555	−0.9041	−0.0795	0.065*	0.617 (10)
H19B	−0.0800	−0.8611	0.0022	0.065*	0.617 (10)
C27A	−0.4091 (3)	−0.5095 (3)	0.2051 (2)	0.0449 (9)	0.88
H27A	−0.4137	−0.4558	0.2468	0.054*	0.88
H27B	−0.4841	−0.5453	0.1888	0.054*	0.88
C28A	−0.3229 (4)	−0.6045 (3)	0.2367 (2)	0.0415 (9)	0.88
H28A	−0.2485	−0.5999	0.2282	0.050*	0.88
C29A	−0.3530 (8)	−0.6966 (5)	0.2773 (4)	0.0501 (19)	0.88
H29A	−0.4272	−0.7019	0.2860	0.060*	0.88
H29B	−0.2993	−0.7542	0.2962	0.060*	0.88
Cu2A	−0.36197 (18)	−0.7398 (3)	0.1618 (2)	0.0345 (4)	0.88
S22A	−0.37812 (15)	−0.42713 (12)	0.12585 (9)	0.0447 (3)	0.88
C17B	−0.2026 (9)	−1.1074 (8)	0.0012 (7)	0.042 (3)*	0.383 (10)
H17C	−0.1555	−1.0932	0.0521	0.051*	0.383 (10)
H17D	−0.1635	−1.1657	−0.0237	0.051*	0.383 (10)

C18B	−0.2086 (7)	−0.9980 (7)	−0.0438 (6)	0.034 (2)*	0.383 (10)
H18B	−0.2687	−0.9927	−0.0867	0.041*	0.383 (10)
C19B	−0.135 (2)	−0.902 (3)	−0.0297 (15)	0.034 (5)*	0.383 (10)
H19C	−0.0738	−0.9021	0.0124	0.041*	0.383 (10)
H19D	−0.1482	−0.8375	−0.0625	0.041*	0.383 (10)
C27B	−0.298 (3)	−0.510 (3)	0.2236 (19)	0.065 (9)*	0.12
H27C	−0.2242	−0.5457	0.2237	0.078*	0.12
H27D	−0.2866	−0.4536	0.2655	0.078*	0.12
C28B	−0.376 (2)	−0.603 (2)	0.2419 (15)	0.027 (6)*	0.12
H28B	−0.4533	−0.5838	0.2353	0.032*	0.12
C29B	−0.345 (4)	−0.712 (2)	0.267 (3)	0.018 (8)*	0.12
H29C	−0.2684	−0.7356	0.2748	0.022*	0.12
H29D	−0.4001	−0.7645	0.2772	0.022*	0.12
Cu2B	−0.3927 (13)	−0.736 (2)	0.1605 (14)	0.033 (3)	0.12
S22B	−0.3398 (9)	−0.4323 (12)	0.1362 (7)	0.035 (3)*	0.12
F1	−0.62718 (17)	−0.70348 (17)	0.16507 (10)	0.0531 (5)	
F2	−0.81507 (19)	−0.63711 (17)	0.27744 (12)	0.0641 (6)	
Si1	−0.72257 (8)	−0.67000 (7)	0.21978 (5)	0.0384 (2)	
F3A	−0.7269 (6)	−0.8125 (4)	0.2448 (4)	0.0351 (13)*	0.428 (3)
F5A	−0.7214 (8)	−0.5319 (4)	0.1966 (4)	0.0492 (14)*	0.428 (3)
F6A	−0.6161 (5)	−0.6498 (7)	0.2977 (3)	0.0509 (17)*	0.428 (3)
F3B	−0.7584 (8)	−0.8120 (5)	0.2227 (6)	0.0309 (19)*	0.288 (3)
F4B	−0.8174 (7)	−0.6539 (12)	0.1374 (4)	0.055 (3)*	0.288 (3)
F5B	−0.6735 (9)	−0.5315 (5)	0.2150 (6)	0.0382 (18)*	0.288 (3)
F6B	−0.6144 (7)	−0.6912 (11)	0.2998 (4)	0.047 (2)*	0.288 (3)
F3C	−0.7978 (15)	−0.7868 (13)	0.1936 (11)	0.069 (4)*	0.168 (3)
F4C	−0.8099 (11)	−0.5889 (17)	0.1521 (8)	0.052 (3)*	0.168 (3)
F5C	−0.6468 (12)	−0.5443 (11)	0.2502 (12)	0.060 (4)*	0.168 (3)
F6C	−0.6360 (12)	−0.7418 (14)	0.2924 (6)	0.038 (3)*	0.168 (3)
F3D	−0.8290 (15)	−0.7443 (19)	0.1626 (12)	0.065 (6)*	0.116 (3)
F4D	−0.7765 (17)	−0.5445 (12)	0.1737 (9)	0.023 (3)*	0.116 (3)
F5D	−0.6264 (15)	−0.590 (2)	0.2817 (12)	0.063 (6)*	0.116 (3)
F6D	−0.6817 (17)	−0.7901 (13)	0.2728 (10)	0.026 (3)*	0.116 (3)
C2	−0.0535 (7)	−0.4794 (9)	0.0952 (6)	0.075 (3)	0.5
C3	−0.001 (3)	−0.379 (2)	0.0769 (18)	0.100 (11)	0.5
H3A	0.0722	−0.3702	0.1111	0.150*	0.5
H3B	−0.0487	−0.3127	0.0821	0.150*	0.5
H3C	0.0088	−0.3837	0.0245	0.150*	0.5
N1	−0.0887 (8)	−0.5623 (9)	0.1155 (6)	0.089 (3)	0.5
F4A	−0.8329 (5)	−0.6949 (7)	0.1425 (4)	0.0542 (16)*	0.428 (3)
O4	−0.011 (2)	−0.3481 (18)	0.0721 (15)	0.097 (5)	0.5
O3	−0.0385 (6)	−0.6046 (6)	0.0816 (4)	0.0777 (18)	0.5

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C12	0.0349 (16)	0.0308 (15)	0.0307 (14)	0.0005 (13)	0.0069 (13)	0.0024 (12)
C15	0.0343 (15)	0.0247 (14)	0.0316 (14)	−0.0003 (12)	0.0047 (12)	0.0031 (11)

C22	0.0451 (17)	0.0271 (15)	0.0377 (15)	−0.0006 (13)	0.0149 (14)	0.0005 (12)
C25	0.0465 (18)	0.0282 (15)	0.0332 (15)	0.0027 (13)	0.0129 (13)	0.0012 (12)
Cu1	0.0469 (2)	0.0295 (2)	0.0491 (2)	0.00365 (17)	0.02508 (18)	0.00394 (16)
N12	0.0483 (17)	0.0327 (15)	0.0571 (17)	−0.0018 (13)	0.0290 (14)	−0.0010 (13)
N13	0.0350 (13)	0.0281 (12)	0.0327 (12)	0.0019 (10)	0.0120 (10)	0.0006 (10)
N14	0.0357 (13)	0.0273 (12)	0.0361 (13)	0.0011 (10)	0.0148 (11)	−0.0008 (10)
N22	0.089 (2)	0.0409 (17)	0.0393 (15)	0.0028 (17)	0.0326 (16)	0.0034 (13)
N23	0.0425 (14)	0.0260 (12)	0.0313 (12)	−0.0015 (11)	0.0114 (11)	−0.0010 (10)
N24	0.0448 (15)	0.0319 (13)	0.0266 (11)	0.0006 (11)	0.0118 (11)	0.0003 (10)
O1	0.0438 (13)	0.0496 (14)	0.0677 (15)	0.0009 (11)	0.0130 (12)	0.0152 (12)
O2	0.0505 (16)	0.098 (2)	0.0692 (18)	0.0040 (15)	0.0127 (14)	0.0034 (17)
S11	0.0417 (4)	0.0286 (4)	0.0427 (4)	−0.0049 (3)	0.0160 (3)	−0.0023 (3)
S12	0.0672 (6)	0.0310 (4)	0.0514 (5)	−0.0026 (4)	0.0274 (4)	−0.0090 (3)
S21	0.0727 (6)	0.0275 (4)	0.0417 (4)	0.0013 (4)	0.0237 (4)	0.0058 (3)
C17A	0.047 (4)	0.053 (4)	0.040 (3)	0.004 (3)	0.020 (3)	−0.010 (3)
C18A	0.040 (3)	0.042 (3)	0.045 (4)	0.011 (2)	0.019 (3)	0.004 (2)
C19A	0.056 (6)	0.055 (8)	0.063 (7)	0.024 (4)	0.041 (4)	0.008 (4)
C27A	0.066 (3)	0.0340 (19)	0.0399 (19)	−0.0042 (18)	0.0238 (19)	−0.0056 (15)
C28A	0.044 (3)	0.048 (2)	0.0343 (19)	−0.010 (2)	0.0116 (19)	−0.0099 (16)
C29A	0.070 (4)	0.052 (3)	0.031 (3)	−0.004 (3)	0.018 (2)	−0.009 (2)
Cu2A	0.0476 (11)	0.0274 (4)	0.0305 (4)	−0.0023 (8)	0.0126 (8)	0.0006 (3)
S22A	0.0631 (11)	0.0244 (6)	0.0524 (8)	−0.0018 (7)	0.0253 (8)	−0.0050 (5)
Cu2B	0.041 (7)	0.032 (3)	0.027 (2)	−0.002 (5)	0.007 (5)	−0.0004 (19)
F1	0.0664 (13)	0.0538 (12)	0.0482 (10)	−0.0033 (10)	0.0328 (10)	0.0035 (9)
F2	0.0802 (15)	0.0500 (12)	0.0762 (14)	0.0223 (11)	0.0487 (12)	0.0078 (10)
Si1	0.0500 (5)	0.0294 (4)	0.0402 (4)	0.0016 (4)	0.0193 (4)	0.0037 (3)
C2	0.048 (5)	0.087 (7)	0.087 (6)	−0.002 (5)	0.007 (4)	−0.034 (6)
C3	0.15 (2)	0.070 (16)	0.084 (12)	−0.057 (16)	0.034 (12)	−0.023 (11)
N1	0.074 (6)	0.075 (6)	0.119 (8)	−0.029 (5)	0.021 (5)	−0.012 (6)
O4	0.115 (10)	0.059 (8)	0.127 (9)	0.003 (7)	0.051 (7)	0.013 (6)
O3	0.070 (4)	0.067 (4)	0.093 (5)	−0.008 (3)	0.011 (4)	0.013 (4)

Geometric parameters (Å, º)

C12—N13	1.311 (4)	C28A—H28A	0.9300
C12—S11	1.731 (3)	C28A—C29A	1.364 (6)
C12—S12	1.731 (3)	C28A—Cu2A	2.027 (5)
C15—N12	1.328 (4)	C29A—H29A	0.9300
C15—N14	1.319 (3)	C29A—H29B	0.9300
C15—S11	1.745 (3)	C29A—Cu2A	2.082 (7)
C22—N23	1.289 (4)	C17B—H17C	0.9700
C22—S21	1.732 (3)	C17B—H17D	0.9700
C22—S22A	1.742 (3)	C17B—C18B	1.476 (15)
C22—S22B	1.757 (13)	C18B—H18B	0.9300
C25—N22	1.328 (4)	C18B—C19B	1.39 (3)
C25—N24	1.317 (3)	C19B—H19C	0.9300
C25—S21	1.742 (3)	C19B—H19D	0.9300
Cu1—N13	1.991 (2)	C27B—H27C	0.9700

Cu1—N24	2.010 (2)	C27B—H27D	0.9700
Cu1—O1	2.364 (3)	C27B—C28B	1.487 (18)
Cu1—C18A	2.035 (5)	C27B—S22B	1.76 (3)
Cu1—C19A	2.064 (18)	C28B—H28B	0.9300
Cu1—C18B	2.138 (8)	C28B—C29B	1.358 (18)
Cu1—C19B	2.01 (3)	C28B—Cu2B	2.08 (4)
N12—H12A	0.86 (3)	C29B—H29C	0.9300
N12—H12B	0.86 (4)	C29B—H29D	0.9300
N13—N14	1.389 (3)	C29B—Cu2B	1.87 (5)
N14—Cu2A	1.975 (4)	F1—Si1	1.682 (2)
N14—Cu2B	1.95 (3)	F2—Si1	1.691 (2)
N22—H22A	0.93 (4)	Si1—F3A	1.693 (4)
N22—H22B	0.83 (4)	Si1—F5A	1.633 (4)
N23—N24	1.399 (3)	Si1—F6A	1.682 (5)
N23—Cu2A	2.003 (4)	Si1—F3B	1.683 (6)
N23—Cu2B	2.07 (3)	Si1—F4B	1.656 (7)
O1—H1A	0.9054	Si1—F5B	1.697 (6)
O1—H1B	0.9041	Si1—F6B	1.719 (7)
O2—H2A	0.8695	Si1—F3C	1.621 (9)
O2—H2B	0.8712	Si1—F4C	1.689 (9)
S12—C17A	1.804 (6)	Si1—F5C	1.723 (9)
S12—C17B	1.828 (10)	Si1—F6C	1.682 (8)
C17A—H17A	0.9700	Si1—F3D	1.678 (11)
C17A—H17B	0.9700	Si1—F4D	1.709 (9)
C17A—C18A	1.480 (9)	Si1—F5D	1.681 (10)
C18A—H18A	0.9300	Si1—F6D	1.677 (9)
C18A—C19A	1.29 (2)	Si1—F4A	1.710 (5)
C19A—H19A	0.9300	C2—C3	1.38 (3)
C19A—H19B	0.9300	C2—N1	1.126 (12)
C27A—H27A	0.9700	C3—H3A	0.9600
C27A—H27B	0.9700	C3—H3B	0.9600
C27A—C28A	1.519 (5)	C3—H3C	0.9600
C27A—S22A	1.790 (4)		

N13—C12—S11	113.3 (2)	H17C—C17B—H17D	107.3
N13—C12—S12	127.7 (2)	C18B—C17B—S12	116.5 (8)
S12—C12—S11	118.98 (17)	C18B—C17B—H17C	108.2
N12—C15—S11	121.6 (2)	C18B—C17B—H17D	108.2
N14—C15—N12	125.3 (3)	Cu1—C18B—H18B	98.5
N14—C15—S11	113.1 (2)	C17B—C18B—Cu1	106.5 (6)
N23—C22—S21	114.4 (2)	C17B—C18B—H18B	116.0
N23—C22—S22A	128.4 (2)	C19B—C18B—Cu1	65.6 (12)
N23—C22—S22B	125.2 (5)	C19B—C18B—C17B	128.0 (14)
S21—C22—S22A	117.13 (17)	C19B—C18B—H18B	116.0
S21—C22—S22B	117.8 (5)	Cu1—C19B—H19C	99.3
N22—C25—S21	121.2 (2)	Cu1—C19B—H19D	95.2
N24—C25—N22	125.0 (3)	C18B—C19B—Cu1	75.4 (13)
N24—C25—S21	113.8 (2)	C18B—C19B—H19C	120.0

N13—Cu1—N24	108.81 (10)
N13—Cu1—O1	91.35 (9)
N13—Cu1—C18A	94.59 (16)
N13—Cu1—C19A	131.2 (5)
N13—Cu1—C18B	100.4 (2)
N13—Cu1—C19B	135.2 (9)
N24—Cu1—O1	87.32 (9)
N24—Cu1—C18A	154.62 (17)
N24—Cu1—C19A	118.9 (5)
N24—Cu1—C18B	134.4 (3)
N24—Cu1—C19B	114.6 (9)
C18A—Cu1—O1	102.20 (19)
C18A—Cu1—C19A	36.6 (6)
C19A—Cu1—O1	100.4 (5)
C18B—Cu1—O1	126.8 (3)
C19B—Cu1—O1	101.0 (6)
C19B—Cu1—C18B	39.1 (8)
C15—N12—H12A	112 (2)
C15—N12—H12B	123 (2)
H12A—N12—H12B	116 (3)
C12—N13—Cu1	127.76 (19)
C12—N13—N14	113.4 (2)
N14—N13—Cu1	118.83 (17)
C15—N14—N13	112.3 (2)
C15—N14—Cu2A	131.2 (2)
C15—N14—Cu2B	124.0 (6)
N13—N14—Cu2A	116.08 (19)
N13—N14—Cu2B	123.8 (6)
C25—N22—H22A	129 (2)
C25—N22—H22B	117 (3)
H22A—N22—H22B	114 (3)
C22—N23—N24	113.2 (2)
C22—N23—Cu2A	128.6 (2)
C22—N23—Cu2B	125.7 (7)
N24—N23—Cu2A	117.60 (19)
N24—N23—Cu2B	121.1 (7)
C25—N24—Cu1	128.1 (2)
C25—N24—N23	111.6 (2)
N23—N24—Cu1	115.34 (16)
Cu1—O1—H1A	111.4
Cu1—O1—H1B	110.8
H1A—O1—H1B	107.4
H2A—O2—H2B	109.5
C12—S11—C15	87.83 (14)
C12—S12—C17A	106.6 (2)
C12—S12—C17B	103.3 (3)
C22—S21—C25	87.00 (14)
S12—C17A—H17A	107.7
C18B—C19B—H19D	120.0
H19C—C19B—H19D	120.0
H27C—C27B—H27D	107.1
C28B—C27B—H27C	107.7
C28B—C27B—H27D	107.7
C28B—C27B—S22B	118 (2)
S22B—C27B—H27C	107.7
S22B—C27B—H27D	107.7
C27B—C28B—H28B	116.8
C27B—C28B—Cu2B	110 (2)
C29B—C28B—C27B	126 (3)
C29B—C28B—H28B	116.8
C29B—C28B—Cu2B	62 (2)
Cu2B—C28B—H28B	97.7
C28B—C29B—H29C	120.0
C28B—C29B—H29D	120.0
C28B—C29B—Cu2B	78 (2)
H29C—C29B—H29D	120.0
Cu2B—C29B—H29C	100.7
Cu2B—C29B—H29D	91.1
N14—Cu2B—N23	109.7 (12)
N14—Cu2B—C28B	149.8 (15)
N23—Cu2B—C28B	100.2 (13)
C29B—Cu2B—N14	111.9 (15)
C29B—Cu2B—N23	131.2 (17)
C29B—Cu2B—C28B	39.8 (9)
C22—S22B—C27B	108.0 (13)
F1—Si1—F2	178.11 (12)
F1—Si1—F3A	89.52 (17)
F1—Si1—F6A	91.1 (2)
F1—Si1—F3B	90.2 (2)
F1—Si1—F5B	84.4 (2)
F1—Si1—F6B	87.8 (3)
F1—Si1—F4C	96.1 (5)
F1—Si1—F5C	89.9 (5)
F1—Si1—F6C	87.0 (4)
F1—Si1—F4D	98.5 (4)
F1—Si1—F4A	90.0 (2)
F2—Si1—F3A	89.89 (17)
F2—Si1—F5B	95.5 (2)
F2—Si1—F6B	90.3 (3)
F2—Si1—F5C	89.4 (5)
F2—Si1—F4D	82.7 (4)
F2—Si1—F4A	91.8 (2)
F3A—Si1—F4A	89.3 (3)
F5A—Si1—F1	92.0 (2)
F5A—Si1—F2	88.7 (2)
F5A—Si1—F3A	178.5 (3)

S12—C17A—H17B	107.7	F5A—Si1—F6A	91.6 (3)
H17A—C17A—H17B	107.1	F5A—Si1—F4A	90.3 (3)
C18A—C17A—S12	118.6 (5)	F6A—Si1—F2	87.1 (2)
C18A—C17A—H17A	107.7	F6A—Si1—F3A	88.7 (3)
C18A—C17A—H17B	107.7	F6A—Si1—F4A	177.7 (3)
Cu1—C18A—H18A	90.7	F3B—Si1—F2	89.7 (2)
C17A—C18A—Cu1	106.4 (4)	F3B—Si1—F5B	174.2 (4)
C17A—C18A—H18A	119.1	F3B—Si1—F6B	89.4 (4)
C19A—C18A—Cu1	72.9 (7)	F4B—Si1—F1	86.4 (3)
C19A—C18A—C17A	121.7 (10)	F4B—Si1—F2	95.5 (3)
C19A—C18A—H18A	119.1	F4B—Si1—F3B	90.2 (4)
Cu1—C19A—H19A	107.2	F4B—Si1—F5B	91.8 (4)
Cu1—C19A—H19B	92.2	F4B—Si1—F6B	174.2 (5)
C18A—C19A—Cu1	70.5 (9)	F5B—Si1—F6B	88.1 (4)
C18A—C19A—H19A	120.0	F3C—Si1—F1	92.7 (6)
C18A—C19A—H19B	120.0	F3C—Si1—F2	88.0 (6)
H19A—C19A—H19B	120.0	F3C—Si1—F4C	91.7 (5)
H27A—C27A—H27B	107.5	F3C—Si1—F5C	177.4 (8)
C28A—C27A—H27A	108.4	F3C—Si1—F6C	91.7 (5)
C28A—C27A—H27B	108.4	F4C—Si1—F2	85.6 (5)
C28A—C27A—S22A	115.5 (3)	F4C—Si1—F5C	88.1 (5)
S22A—C27A—H27A	108.4	F6C—Si1—F2	91.2 (4)
S22A—C27A—H27B	108.4	F6C—Si1—F4C	175.3 (6)
C27A—C28A—H28A	119.5	F6C—Si1—F5C	88.4 (5)
C27A—C28A—Cu2A	105.2 (3)	F3D—Si1—F1	93.0 (8)
C29A—C28A—C27A	121.0 (5)	F3D—Si1—F2	88.4 (8)
C29A—C28A—H28A	119.5	F3D—Si1—F4D	88.7 (6)
C29A—C28A—Cu2A	72.8 (3)	F3D—Si1—F5D	174.0 (11)
Cu2A—C28A—H28A	92.0	F5D—Si1—F1	92.8 (7)
C28A—C29A—H29A	120.0	F5D—Si1—F2	85.8 (7)
C28A—C29A—H29B	120.0	F5D—Si1—F4D	89.3 (6)
C28A—C29A—Cu2A	68.4 (3)	F6D—Si1—F1	89.0 (5)
H29A—C29A—H29B	120.0	F6D—Si1—F2	89.7 (5)
Cu2A—C29A—H29A	106.9	F6D—Si1—F3D	90.9 (6)
Cu2A—C29A—H29B	94.4	F6D—Si1—F4D	172.4 (6)
N14—Cu2A—N23	111.49 (19)	F6D—Si1—F5D	90.3 (6)
N14—Cu2A—C28A	153.0 (2)	N1—C2—C3	174.2 (17)
N14—Cu2A—C29A	114.2 (2)	C2—C3—H3A	109.5
N23—Cu2A—C28A	95.1 (2)	C2—C3—H3B	109.5
N23—Cu2A—C29A	133.3 (2)	C2—C3—H3C	109.5
C28A—Cu2A—C29A	38.75 (19)	H3A—C3—H3B	109.5
C22—S22A—C27A	104.05 (16)	H3A—C3—H3C	109.5
S12—C17B—H17C	108.2	H3B—C3—H3C	109.5
S12—C17B—H17D	108.2		

C12—N13—N14—C15	−2.4 (3)	S12—C12—S11—C15	−179.84 (18)
C12—N13—N14—Cu2A	170.8 (2)	S12—C17A—C18A—Cu1	−72.0 (6)
C12—N13—N14—Cu2B	179.3 (7)	S12—C17A—C18A—C19A	−151.8 (9)

C12—S12—C17A—C18A	40.2 (6)	S12—C17B—C18B—Cu1	69.4 (9)
C12—S12—C17B—C18B	−68.3 (8)	S12—C17B—C18B—C19B	141.0 (17)
C22—N23—N24—C25	−2.2 (3)	S21—C22—N23—N24	1.7 (3)
C22—N23—N24—Cu1	154.9 (2)	S21—C22—N23—Cu2A	172.19 (16)
Cu1—N13—N14—C15	177.89 (18)	S21—C22—N23—Cu2B	−175.7 (6)
Cu1—N13—N14—Cu2A	−9.0 (3)	S21—C22—S22A—C27A	176.71 (19)
Cu1—N13—N14—Cu2B	−0.5 (8)	S21—C22—S22B—C27B	−150.7 (11)
N12—C15—N14—N13	−177.4 (3)	S21—C25—N24—Cu1	−151.74 (16)
N12—C15—N14—Cu2A	10.8 (4)	S21—C25—N24—N23	1.7 (3)
N12—C15—N14—Cu2B	1.0 (8)	C17A—C18A—C19A—Cu1	99.0 (7)
N12—C15—S11—C12	178.4 (3)	C27A—C28A—C29A—Cu2A	97.7 (4)
N13—C12—S11—C15	0.0 (2)	C28A—C27A—S22A—C22	51.8 (3)
N13—C12—S12—C17A	0.9 (4)	Cu2A—N23—N24—C25	−173.8 (2)
N13—C12—S12—C17B	26.1 (5)	Cu2A—N23—N24—Cu1	−16.7 (3)
N14—C15—S11—C12	−1.3 (2)	S22A—C22—N23—N24	−178.0 (2)
N22—C25—N24—Cu1	29.1 (5)	S22A—C22—N23—Cu2A	−7.5 (4)
N22—C25—N24—N23	−177.4 (3)	S22A—C22—S21—C25	179.1 (2)
N22—C25—S21—C22	178.5 (3)	S22A—C27A—C28A—C29A	−157.8 (4)
N23—C22—S21—C25	−0.6 (2)	S22A—C27A—C28A—Cu2A	−79.0 (3)
N23—C22—S22A—C27A	−3.6 (4)	C17B—C18B—C19B—Cu1	−92.4 (13)
N23—C22—S22B—C27B	10.0 (13)	C27B—C28B—C29B—Cu2B	−96 (3)
N24—C25—S21—C22	−0.7 (2)	C28B—C27B—S22B—C22	−60 (3)
S11—C12—N13—Cu1	−178.94 (13)	C28B—C29B—Cu2B—N14	−166.5 (17)
S11—C12—N13—N14	1.3 (3)	C28B—C29B—Cu2B—N23	47 (3)
S11—C12—S12—C17A	−179.3 (3)	Cu2B—N23—N24—C25	175.3 (6)
S11—C12—S12—C17B	−154.2 (4)	Cu2B—N23—N24—Cu1	−27.6 (6)
S11—C15—N14—N13	2.3 (3)	S22B—C22—N23—N24	−159.6 (5)
S11—C15—N14—Cu2A	−169.48 (18)	S22B—C22—N23—Cu2B	23.0 (8)
S11—C15—N14—Cu2B	−179.3 (7)	S22B—C22—S21—C25	162.2 (4)
S12—C12—N13—Cu1	0.8 (4)	S22B—C27B—C28B—C29B	133 (3)
S12—C12—N13—N14	−178.9 (2)	S22B—C27B—C28B—Cu2B	63 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N12—H12*A*···F1	0.86 (3)	2.14 (4)	2.973 (4)	163 (3)
N12—H12*A*···F3*A*	0.86 (3)	2.26 (4)	2.780 (6)	119 (3)
N12—H12*A*···F3*B*	0.86 (3)	2.48 (4)	2.990 (9)	119 (3)
N12—H12*A*···F6*C*	0.86 (3)	2.35 (4)	2.989 (14)	132 (3)
N12—H12*A*···F6*D*	0.86 (3)	2.17 (4)	2.733 (13)	123 (3)
N12—H12*B*···F2^{i}	0.86 (4)	2.04 (4)	2.827 (3)	152 (3)
N22—H22*A*···F2^{ii}	0.93 (4)	2.05 (4)	2.903 (4)	153 (3)
N22—H22*A*···F6*C*^{ii}	0.93 (4)	2.40 (4)	2.931 (15)	117 (3)
N22—H22*B*···F5*A*^{iii}	0.83 (4)	1.83 (4)	2.638 (5)	165 (4)
N22—H22*B*···F3*B*^{ii}	0.83 (4)	2.52 (4)	2.931 (9)	112 (3)
N22—H22*B*···F5*B*^{iii}	0.83 (4)	1.98 (4)	2.758 (9)	157 (4)
N22—H22*B*···F4*C*^{iii}	0.83 (4)	2.55 (4)	3.250 (19)	142 (3)
N22—H22*B*···F5*C*^{iii}	0.83 (4)	2.50 (4)	3.27 (2)	154 (4)

N22—H22*B*···F4*D*$^{\text{iii}}$	0.83 (4)	2.00 (4)	2.766 (15)	153 (4)
O1—H1*A*···N1	0.91	1.89	2.789 (10)	175
O1—H1*A*···O3	0.91	2.06	2.875 (7)	149
O1—H1*B*···O2	0.90	1.85	2.698 (4)	156
O2—H2*A*···F5*A*$^{\text{iv}}$	0.87	2.48	3.293 (9)	156
O2—H2*A*···F6*A*$^{\text{iv}}$	0.87	2.23	2.926 (8)	138
O2—H2*A*···F5*B*$^{\text{iv}}$	0.87	1.98	2.819 (11)	163
O2—H2*A*···F6*B*$^{\text{iv}}$	0.87	2.68	3.361 (13)	136
O2—H2*A*···F5*C*$^{\text{iv}}$	0.87	1.52	2.385 (12)	169
O2—H2*A*···F5*D*$^{\text{iv}}$	0.87	1.64	2.427 (15)	150
O2—H2*B*···F3*A*$^{\text{v}}$	0.87	2.48	3.095 (9)	128
O2—H2*B*···F3*B*$^{\text{v}}$	0.87	2.03	2.691 (9)	132
O2—H2*B*···F4*B*$^{\text{v}}$	0.87	2.61	3.464 (13)	168
O2—H2*B*···F3*C*$^{\text{v}}$	0.87	1.59	2.383 (11)	149
O2—H2*B*···F3*D*$^{\text{v}}$	0.87	1.59	2.465 (18)	177
O2—H2*B*···F4*A*$^{\text{v}}$	0.87	2.09	2.952 (9)	169
C17*A*—H17*A*···F4*A*$^{\text{vi}}$	0.97	2.43	3.333 (8)	155
C27*A*—H27*A*···O2$^{\text{vii}}$	0.97	2.52	3.322 (5)	140
C27*A*—H27*B*···F1	0.97	2.46	3.376 (4)	157
C27*B*—H27*D*···O1$^{\text{vii}}$	0.97	2.66	3.57 (4)	157
C28*B*—H28*B*···F1	0.93	2.57	3.23 (3)	128

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

(5) *μ*-Benzenesulfonato-bis{*μ*-5-[(prop-2-en-1-yl)sulfanyl]-1,3,4-thiadiazol-2-amine}dicopper(I) benzenesulfonate methanol monosolvate monohydrate

Crystal data

$[Cu_2(C_6H_5O_3S)(C_5H_7N_3S_2)_2](C_6H_5O_3S)\cdot CH_4O\cdot H_2O$
$M_r = 837.97$
Monoclinic, $P2_1/c$
$a = 14.944$ (4) Å
$b = 16.587$ (5) Å
$c = 14.658$ (4) Å
$\beta = 117.91$ (3)°
$V = 3210.7$ (17) Å^3
$Z = 4$
$F(000) = 1712$
$D_x = 1.734$ Mg m^{-3}
Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å
Cell parameters from 10457 reflections
$\theta = 3.4$–77.6°
$\mu = 5.77$ mm^{-1}
$T = 110$ K
Block, clear colourless
0.45 × 0.32 × 0.17 mm

Data collection

Rigaku Xcalibur Onyx diffractometer
Radiation source: fine-focus sealed X-ray tube, Enhance (Cu) X-ray Source
Graphite monochromator
Detector resolution: 8.1956 pixels mm^{-1}
ω scans
Absorption correction: analytical [CrysAlis PRO (Rigaku OD, 2015), based on expressions derived by Clark & Reid (1995)]
$T_{\min} = 0.248$, $T_{\max} = 0.540$
16595 measured reflections
6741 independent reflections
6073 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.056$
$\theta_{\max} = 78.0°$, $\theta_{\min} = 3.4°$
$h = -16\rightarrow18$
$k = -20\rightarrow17$
$l = -18\rightarrow16$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.057$
$wR(F^2) = 0.166$
$S = 1.05$
6741 reflections
487 parameters
3 restraints

Primary atom site location: structure-invariant direct methods
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.108P)^2 + 2.144P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 1.03$ e Å^{-3}
$\Delta\rho_{\min} = -1.49$ 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	$U_{\rm iso}$*/$U_{\rm eq}$	Occ. (<1)
Cu1	0.71463 (4)	0.46102 (3)	0.25333 (4)	0.03132 (15)	
Cu2	0.70615 (4)	0.53623 (3)	0.46302 (4)	0.03199 (15)	
S11	0.74240 (6)	0.73187 (5)	0.27560 (6)	0.03241 (18)	
S12	0.68469 (9)	0.63190 (6)	0.08869 (7)	0.0451 (2)	
S21	0.80874 (6)	0.27825 (5)	0.50610 (6)	0.03168 (18)	
S22	0.73084 (6)	0.36872 (5)	0.62865 (5)	0.03159 (18)	
S31A	0.4810 (3)	0.4424 (3)	0.2480 (3)	0.0304 (6)	0.644 (6)
S31B	0.4816 (6)	0.4310 (5)	0.2230 (5)	0.0296 (11)	0.356 (6)
O31A	0.5331 (3)	0.4589 (3)	0.1884 (4)	0.0449 (11)	0.644 (6)
O31B	0.5736 (4)	0.4754 (4)	0.2891 (5)	0.0310 (16)	0.356 (6)
O32A	0.5256 (3)	0.4869 (3)	0.3451 (3)	0.0448 (11)	0.644 (6)
O32B	0.3953 (7)	0.4564 (6)	0.2366 (9)	0.037 (2)	0.356 (6)
O33A	0.3728 (4)	0.4551 (4)	0.1911 (4)	0.0383 (12)	0.644 (6)
O33B	0.4610 (5)	0.4282 (5)	0.1179 (5)	0.0378 (18)	0.356 (6)
N12	0.7894 (2)	0.72597 (17)	0.4762 (2)	0.0345 (6)	
H12A	0.797 (3)	0.781 (3)	0.478 (4)	0.041*	
H12B	0.814 (4)	0.700 (3)	0.535 (4)	0.041*	
N13	0.7226 (2)	0.57953 (16)	0.2809 (2)	0.0289 (5)	
N14	0.74612 (19)	0.60649 (16)	0.37976 (18)	0.0262 (5)	
N22	0.8476 (2)	0.28718 (18)	0.3451 (2)	0.0360 (6)	
H22A	0.871 (4)	0.315 (3)	0.308 (4)	0.043*	
H22B	0.871 (4)	0.239 (3)	0.362 (4)	0.043*	
N23	0.75070 (18)	0.42421 (16)	0.46223 (18)	0.0257 (5)	
N24	0.7777 (2)	0.40025 (16)	0.38683 (19)	0.0276 (5)	
C12	0.7161 (3)	0.63734 (19)	0.2188 (3)	0.0320 (6)	
C15	0.7616 (2)	0.68478 (19)	0.3896 (2)	0.0295 (6)	
C17A	0.7197 (3)	0.5307 (3)	0.0744 (3)	0.0357 (11)	0.801 (10)
H17A	0.7098	0.5241	0.0032	0.043*	0.801 (10)
H17B	0.7927	0.5233	0.1221	0.043*	0.801 (10)

C17B	0.6409 (11)	0.5277 (9)	0.0557 (11)	0.027 (4)*	0.199 (10)
H17C	0.5832	0.5191	0.0701	0.033*	0.199 (10)
H17D	0.6157	0.5200	−0.0193	0.033*	0.199 (10)
C18A	0.6618 (3)	0.4659 (3)	0.0951 (3)	0.0333 (10)	0.801 (10)
H18A	0.5946	0.4772	0.0821	0.040*	0.801 (10)
C18B	0.7173 (13)	0.4671 (8)	0.1108 (11)	0.022 (4)*	0.199 (10)
H18B	0.7859	0.4825	0.1345	0.026*	0.199 (10)
C19	0.7008 (3)	0.3910 (2)	0.1317 (2)	0.0388 (7)	
H19A	0.7679	0.3781	0.1453	0.047*	0.801 (10)
H19B	0.6608	0.3520	0.1435	0.047*	0.801 (10)
H19C	0.6336	0.3727	0.1097	0.047*	0.199 (10)
H19D	0.7564	0.3558	0.1685	0.047*	0.199 (10)
C22	0.7610 (2)	0.36726 (18)	0.5270 (2)	0.0274 (6)	
C25	0.8116 (2)	0.32546 (19)	0.4009 (2)	0.0289 (6)	
C27A	0.7145 (4)	0.4774 (3)	0.6479 (4)	0.0346 (13)	0.664 (10)
H27A	0.6940	0.4827	0.7028	0.042*	0.664 (10)
H27B	0.7806	0.5049	0.6722	0.042*	0.664 (10)
C28A	0.6385 (4)	0.5191 (4)	0.5539 (4)	0.0368 (14)	0.664 (10)
H28A	0.5841	0.4891	0.5025	0.044*	0.664 (10)
C29A	0.6456 (12)	0.6009 (6)	0.5396 (12)	0.035 (4)	0.664 (10)
H29A	0.6999	0.6313	0.5905	0.042*	0.664 (10)
H29B	0.5963	0.6266	0.4789	0.042*	0.664 (10)
C27B	0.6490 (6)	0.4546 (5)	0.6003 (6)	0.023 (2)*	0.336 (10)
H27C	0.5910	0.4487	0.5304	0.027*	0.336 (10)
H27D	0.6221	0.4573	0.6504	0.027*	0.336 (10)
C28B	0.7036 (6)	0.5298 (5)	0.6054 (6)	0.022 (2)*	0.336 (10)
H28B	0.7748	0.5334	0.6477	0.026*	0.336 (10)
C29B	0.648 (3)	0.5963 (14)	0.546 (3)	0.049 (11)*	0.336 (10)
H29C	0.5769	0.5921	0.5042	0.058*	0.336 (10)
H29D	0.6819	0.6454	0.5484	0.058*	0.336 (10)
C31	0.5023 (2)	0.3352 (2)	0.2756 (3)	0.0331 (6)	
C32	0.5006 (3)	0.2774 (3)	0.2070 (3)	0.0487 (9)	
H32	0.4892	0.2926	0.1399	0.058*	
C33	0.5157 (3)	0.1973 (3)	0.2365 (4)	0.0594 (12)	
H33	0.5148	0.1577	0.1893	0.071*	
C34	0.5320 (3)	0.1741 (3)	0.3333 (4)	0.0549 (11)	
H34	0.5425	0.1190	0.3531	0.066*	
C35	0.5329 (3)	0.2328 (3)	0.4021 (3)	0.0480 (9)	
H35	0.5434	0.2178	0.4690	0.058*	
C36	0.5186 (2)	0.3121 (2)	0.3729 (3)	0.0403 (7)	
H36	0.5200	0.3519	0.4201	0.048*	
S41	0.97251 (6)	0.62170 (5)	0.76431 (6)	0.03256 (19)	
O41	0.8831 (2)	0.6489 (2)	0.6743 (2)	0.0575 (8)	
O42	1.0634 (2)	0.66597 (18)	0.7849 (2)	0.0463 (6)	
O43	0.95553 (18)	0.61808 (18)	0.85462 (19)	0.0414 (6)	
C41	0.9942 (2)	0.5208 (2)	0.7391 (3)	0.0338 (6)	
C42	1.0076 (3)	0.5059 (3)	0.6531 (3)	0.0448 (8)	
H42	1.0049	0.5489	0.6090	0.054*	

C43	1.0252 (3)	0.4279 (3)	0.6323 (4)	0.0608 (12)
H43	1.0348	0.4171	0.5739	0.073*
C44	1.0287 (3)	0.3646 (3)	0.6973 (5)	0.0641 (14)
H44	1.0403	0.3110	0.6827	0.077*
C45	1.0155 (3)	0.3804 (3)	0.7818 (4)	0.0577 (12)
H45	1.0188	0.3375	0.8262	0.069*
C46	0.9975 (3)	0.4584 (2)	0.8035 (3)	0.0429 (8)
H46	0.9874	0.4688	0.8618	0.052*
O61	0.9016 (2)	0.35933 (15)	0.9454 (2)	0.0377 (5)
H61	0.944 (4)	0.366 (3)	0.999 (4)	0.057*
C61	0.8226 (4)	0.4136 (3)	0.9263 (4)	0.0536 (10)
H61A	0.7620	0.3975	0.8633	0.080*
H61B	0.8430	0.4680	0.9176	0.080*
H61C	0.8078	0.4131	0.9847	0.080*
O51	0.1975 (3)	0.38050 (17)	0.0872 (3)	0.0481 (7)
H51A	0.162 (5)	0.379 (4)	0.116 (5)	0.072*
H51B	0.248 (5)	0.407 (4)	0.124 (5)	0.072*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0483 (3)	0.0242 (3)	0.0271 (2)	0.00226 (17)	0.0224 (2)	0.00268 (16)
Cu2	0.0501 (3)	0.0251 (3)	0.0337 (3)	0.00360 (18)	0.0305 (2)	0.00246 (17)
S11	0.0443 (4)	0.0243 (4)	0.0373 (4)	0.0033 (3)	0.0263 (3)	0.0055 (3)
S12	0.0792 (6)	0.0346 (4)	0.0339 (4)	0.0096 (4)	0.0367 (4)	0.0095 (3)
S21	0.0415 (4)	0.0272 (4)	0.0332 (4)	0.0057 (3)	0.0232 (3)	0.0079 (3)
S22	0.0376 (4)	0.0373 (4)	0.0247 (3)	0.0021 (3)	0.0186 (3)	0.0059 (3)
S31A	0.0278 (7)	0.0293 (11)	0.0368 (17)	−0.0016 (6)	0.0175 (11)	−0.0018 (10)
S31B	0.0242 (12)	0.037 (3)	0.026 (2)	0.0010 (14)	0.0107 (16)	0.0011 (17)
O31A	0.047 (2)	0.045 (2)	0.058 (3)	−0.0005 (17)	0.037 (2)	0.0055 (19)
O31B	0.027 (3)	0.031 (3)	0.027 (3)	−0.006 (2)	0.006 (2)	0.003 (2)
O32A	0.0359 (18)	0.040 (2)	0.048 (2)	0.0005 (15)	0.0107 (16)	−0.0140 (18)
O32B	0.027 (4)	0.044 (4)	0.044 (5)	0.006 (3)	0.021 (4)	0.001 (5)
O33A	0.029 (2)	0.046 (2)	0.033 (3)	0.0025 (18)	0.010 (2)	0.005 (3)
O33B	0.037 (3)	0.050 (4)	0.026 (3)	0.008 (3)	0.014 (3)	0.007 (3)
N12	0.0449 (14)	0.0252 (13)	0.0334 (13)	−0.0004 (11)	0.0183 (12)	−0.0012 (11)
N13	0.0416 (13)	0.0260 (12)	0.0270 (12)	0.0024 (10)	0.0226 (10)	0.0005 (10)
N14	0.0341 (11)	0.0251 (12)	0.0238 (11)	0.0009 (9)	0.0172 (9)	0.0004 (9)
N22	0.0517 (16)	0.0263 (13)	0.0432 (15)	0.0076 (11)	0.0333 (13)	0.0047 (11)
N23	0.0310 (11)	0.0282 (12)	0.0217 (10)	0.0011 (9)	0.0155 (9)	0.0005 (9)
N24	0.0382 (12)	0.0256 (12)	0.0279 (11)	0.0031 (9)	0.0229 (10)	0.0011 (9)
C12	0.0454 (16)	0.0265 (15)	0.0326 (15)	0.0027 (12)	0.0253 (13)	0.0030 (12)
C15	0.0285 (12)	0.0292 (15)	0.0335 (14)	0.0039 (11)	0.0170 (11)	0.0030 (12)
C17A	0.046 (2)	0.036 (2)	0.036 (2)	0.0079 (16)	0.0287 (18)	0.0045 (16)
C18A	0.031 (2)	0.041 (2)	0.0251 (18)	0.0033 (15)	0.0113 (15)	0.0050 (15)
C19	0.0546 (19)	0.0335 (17)	0.0251 (14)	0.0007 (14)	0.0160 (13)	−0.0073 (12)
C22	0.0316 (13)	0.0283 (14)	0.0259 (13)	0.0035 (11)	0.0164 (11)	0.0049 (11)
C25	0.0323 (13)	0.0265 (14)	0.0306 (13)	−0.0002 (11)	0.0171 (11)	0.0025 (11)

C27A	0.044 (3)	0.038 (3)	0.026 (2)	0.000 (2)	0.020 (2)	0.0006 (19)
C28A	0.034 (3)	0.050 (3)	0.039 (3)	0.005 (2)	0.027 (2)	0.004 (2)
C29A	0.058 (7)	0.029 (4)	0.043 (6)	0.012 (2)	0.044 (5)	0.002 (2)
C31	0.0235 (12)	0.0339 (16)	0.0368 (15)	−0.0038 (11)	0.0099 (11)	0.0002 (13)
C32	0.0465 (19)	0.060 (3)	0.046 (2)	−0.0038 (17)	0.0271 (16)	−0.0105 (18)
C33	0.050 (2)	0.054 (3)	0.075 (3)	−0.0051 (18)	0.030 (2)	−0.026 (2)
C34	0.0360 (16)	0.036 (2)	0.077 (3)	−0.0033 (14)	0.0136 (18)	0.0017 (19)
C35	0.0403 (17)	0.050 (2)	0.0416 (18)	0.0047 (16)	0.0091 (14)	0.0146 (16)
C36	0.0332 (14)	0.045 (2)	0.0309 (15)	0.0037 (13)	0.0054 (12)	0.0004 (14)
S41	0.0324 (3)	0.0379 (4)	0.0270 (3)	0.0006 (3)	0.0136 (3)	0.0044 (3)
O41	0.0610 (17)	0.0601 (19)	0.0351 (13)	0.0229 (15)	0.0089 (12)	0.0111 (13)
O42	0.0559 (15)	0.0435 (15)	0.0536 (15)	−0.0159 (12)	0.0374 (13)	−0.0107 (12)
O43	0.0360 (11)	0.0578 (16)	0.0362 (12)	0.0015 (10)	0.0216 (10)	0.0022 (11)
C41	0.0238 (12)	0.0399 (17)	0.0347 (15)	−0.0034 (12)	0.0113 (11)	0.0019 (13)
C42	0.0428 (17)	0.050 (2)	0.0473 (19)	−0.0056 (15)	0.0257 (15)	−0.0039 (17)
C43	0.050 (2)	0.064 (3)	0.076 (3)	−0.009 (2)	0.036 (2)	−0.024 (2)
C44	0.0369 (18)	0.043 (2)	0.112 (4)	−0.0040 (15)	0.034 (2)	−0.013 (2)
C45	0.0361 (17)	0.041 (2)	0.088 (3)	−0.0022 (15)	0.023 (2)	0.012 (2)
C46	0.0321 (15)	0.044 (2)	0.051 (2)	−0.0039 (13)	0.0174 (14)	0.0094 (16)
O61	0.0455 (12)	0.0322 (12)	0.0347 (12)	−0.0001 (10)	0.0183 (10)	−0.0046 (10)
C61	0.067 (3)	0.037 (2)	0.058 (2)	0.0139 (18)	0.031 (2)	0.0029 (18)
O51	0.0623 (17)	0.0329 (13)	0.0722 (19)	0.0012 (12)	0.0506 (16)	−0.0025 (13)

Geometric parameters (Å, º)

Cu1—O31A	2.418 (4)	C18B—C19	1.348 (14)
Cu1—O31B	2.409 (7)	C19—H19A	0.9500
Cu1—N13	1.999 (3)	C19—H19B	0.9500
Cu1—N24	2.002 (3)	C19—H19C	0.9500
Cu1—C18A	2.072 (4)	C19—H19D	0.9500
Cu1—C18B	2.111 (14)	C27A—H27A	0.9900
Cu1—C19	2.055 (3)	C27A—H27B	0.9900
Cu2—N14	1.972 (2)	C27A—C28A	1.484 (7)
Cu2—N23	1.976 (3)	C28A—H28A	0.9500
Cu2—C28A	2.033 (4)	C28A—C29A	1.384 (11)
Cu2—C29A	2.044 (11)	C29A—H29A	0.9500
Cu2—C28B	2.107 (8)	C29A—H29B	0.9500
Cu2—C29B	2.06 (4)	C27B—H27C	0.9900
S11—C12	1.732 (3)	C27B—H27D	0.9900
S11—C15	1.743 (3)	C27B—C28B	1.473 (10)
S12—C12	1.740 (3)	C28B—H28B	0.9500
S12—C17A	1.799 (4)	C28B—C29B	1.408 (17)
S12—C17B	1.830 (15)	C29B—H29C	0.9500
S21—C22	1.728 (3)	C29B—H29D	0.9500
S21—C25	1.748 (3)	C31—C32	1.380 (5)
S22—C22	1.747 (3)	C31—C36	1.384 (5)
S22—C27A	1.858 (6)	C32—H32	0.9500
S22—C27B	1.795 (8)	C32—C33	1.383 (7)

S31A—O31A	1.444 (5)	C33—H33	0.9500
S31A—O32A	1.458 (5)	C33—C34	1.378 (7)
S31A—O33A	1.447 (7)	C34—H34	0.9500
S31A—C31	1.819 (6)	C34—C35	1.398 (7)
S31B—O31B	1.458 (9)	C35—H35	0.9500
S31B—O32B	1.457 (11)	C35—C36	1.369 (6)
S31B—O33B	1.424 (8)	C36—H36	0.9500
S31B—C31	1.729 (9)	S41—O41	1.442 (3)
N12—H12A	0.91 (5)	S41—O42	1.446 (3)
N12—H12B	0.87 (5)	S41—O43	1.461 (2)
N12—C15	1.326 (4)	S41—C41	1.775 (4)
N13—N14	1.395 (3)	C41—C42	1.389 (5)
N13—C12	1.294 (4)	C41—C46	1.386 (5)
N14—C15	1.315 (4)	C42—H42	0.9500
N22—H22A	0.90 (5)	C42—C43	1.383 (7)
N22—H22B	0.86 (5)	C43—H43	0.9500
N22—C25	1.331 (4)	C43—C44	1.402 (8)
N23—N24	1.400 (3)	C44—H44	0.9500
N23—C22	1.296 (4)	C44—C45	1.367 (8)
N24—C25	1.319 (4)	C45—H45	0.9500
C17A—H17A	0.9900	C45—C46	1.388 (6)
C17A—H17B	0.9900	C46—H46	0.9500
C17A—C18A	1.498 (6)	O61—H61	0.75 (6)
C17B—H17C	0.9900	O61—C61	1.404 (5)
C17B—H17D	0.9900	C61—H61A	0.9800
C17B—C18B	1.45 (2)	C61—H61B	0.9800
C18A—H18A	0.9500	C61—H61C	0.9800
C18A—C19	1.369 (6)	O51—H51A	0.82 (6)
C18B—H18B	0.9500	O51—H51B	0.81 (7)

N13—Cu1—O31A	92.50 (13)	C18A—C19—H19A	120.0
N13—Cu1—O31B	80.46 (17)	C18A—C19—H19B	120.0
N13—Cu1—N24	109.96 (11)	C18B—C19—Cu1	73.4 (6)
N13—Cu1—C18A	98.26 (15)	C18B—C19—H19C	120.0
N13—Cu1—C18B	97.3 (4)	C18B—C19—H19D	120.0
N13—Cu1—C19	134.67 (13)	H19A—C19—H19B	120.0
N24—Cu1—O31A	107.80 (13)	H19C—C19—H19D	120.0
N24—Cu1—O31B	84.07 (16)	S21—C22—S22	117.10 (17)
N24—Cu1—C18A	150.68 (15)	N23—C22—S21	114.2 (2)
N24—Cu1—C18B	140.6 (4)	N23—C22—S22	128.7 (2)
N24—Cu1—C19	111.94 (13)	N22—C25—S21	120.8 (2)
C18A—Cu1—O31A	77.89 (17)	N24—C25—S21	113.1 (2)
C18B—Cu1—O31B	129.4 (5)	N24—C25—N22	126.1 (3)
C19—Cu1—O31A	90.65 (16)	S22—C27A—H27A	108.7
C19—Cu1—O31B	120.10 (19)	S22—C27A—H27B	108.7
C19—Cu1—C18A	38.75 (16)	H27A—C27A—H27B	107.6
C19—Cu1—C18B	37.7 (4)	C28A—C27A—S22	114.1 (4)
N14—Cu2—N23	110.59 (10)	C28A—C27A—H27A	108.7

N14—Cu2—C28A	151.09 (18)	C28A—C27A—H27B	108.7
N14—Cu2—C29A	111.7 (3)	Cu2—C28A—H28A	93.4
N14—Cu2—C28B	142.6 (2)	C27A—C28A—Cu2	105.9 (3)
N14—Cu2—C29B	114.5 (6)	C27A—C28A—H28A	119.4
N23—Cu2—C28A	98.32 (18)	C29A—C28A—Cu2	70.6 (5)
N23—Cu2—C29A	137.2 (3)	C29A—C28A—C27A	121.2 (8)
N23—Cu2—C28B	96.9 (2)	C29A—C28A—H28A	119.4
N23—Cu2—C29B	134.1 (5)	Cu2—C29A—H29A	106.0
C28A—Cu2—C29A	39.7 (3)	Cu2—C29A—H29B	94.0
C29B—Cu2—C28B	39.5 (6)	C28A—C29A—Cu2	69.7 (4)
C12—S11—C15	87.34 (15)	C28A—C29A—H29A	120.0
C12—S12—C17A	103.40 (18)	C28A—C29A—H29B	120.0
C12—S12—C17B	102.6 (5)	H29A—C29A—H29B	120.0
C22—S21—C25	87.48 (14)	S22—C27B—H27C	109.4
C22—S22—C27A	104.32 (18)	S22—C27B—H27D	109.4
C22—S22—C27B	103.5 (3)	H27C—C27B—H27D	108.0
O31A—S31A—O32A	111.4 (4)	C28B—C27B—S22	111.1 (6)
O31A—S31A—O33A	113.5 (4)	C28B—C27B—H27C	109.4
O31A—S31A—C31	103.4 (3)	C28B—C27B—H27D	109.4
O32A—S31A—C31	109.0 (3)	Cu2—C28B—H28B	96.3
O33A—S31A—O32A	111.4 (4)	C27B—C28B—Cu2	105.0 (5)
O33A—S31A—C31	107.7 (4)	C27B—C28B—H28B	120.7
O31B—S31B—C31	104.6 (5)	C29B—C28B—Cu2	68.2 (15)
O32B—S31B—O31B	112.5 (7)	C29B—C28B—C27B	118.7 (17)
O32B—S31B—C31	101.0 (6)	C29B—C28B—H28B	120.7
O33B—S31B—O31B	113.2 (6)	Cu2—C29B—H29C	103.6
O33B—S31B—O32B	113.6 (7)	Cu2—C29B—H29D	94.0
O33B—S31B—C31	110.8 (5)	C28B—C29B—Cu2	72.3 (13)
S31A—O31A—Cu1	126.0 (3)	C28B—C29B—H29C	120.0
S31B—O31B—Cu1	117.0 (4)	C28B—C29B—H29D	120.0
H12A—N12—H12B	118 (4)	H29C—C29B—H29D	120.0
C15—N12—H12A	122 (3)	C32—C31—S31A	125.1 (3)
C15—N12—H12B	119 (3)	C32—C31—S31B	112.0 (3)
N14—N13—Cu1	119.16 (19)	C32—C31—C36	119.6 (4)
C12—N13—Cu1	127.5 (2)	C36—C31—S31A	115.3 (3)
C12—N13—N14	113.1 (3)	C36—C31—S31B	128.4 (3)
N13—N14—Cu2	116.85 (19)	C31—C32—H32	120.2
C15—N14—Cu2	127.2 (2)	C31—C32—C33	119.6 (4)
C15—N14—N13	112.1 (2)	C33—C32—H32	120.2
H22A—N22—H22B	116 (4)	C32—C33—H33	119.5
C25—N22—H22A	121 (3)	C34—C33—C32	121.0 (4)
C25—N22—H22B	119 (3)	C34—C33—H33	119.5
N24—N23—Cu2	119.61 (18)	C33—C34—H34	120.5
C22—N23—Cu2	127.3 (2)	C33—C34—C35	119.1 (4)
C22—N23—N24	113.1 (3)	C35—C34—H34	120.5
N23—N24—Cu1	116.81 (18)	C34—C35—H35	120.1
C25—N24—Cu1	126.6 (2)	C36—C35—C34	119.8 (4)
C25—N24—N23	112.0 (2)	C36—C35—H35	120.1

S11—C12—S12	117.25 (18)	C31—C36—H36	119.5
N13—C12—S11	114.0 (2)	C35—C36—C31	120.9 (4)
N13—C12—S12	128.7 (3)	C35—C36—H36	119.5
N12—C15—S11	121.6 (3)	O41—S41—O42	114.2 (2)
N14—C15—S11	113.3 (2)	O41—S41—O43	111.24 (18)
N14—C15—N12	125.1 (3)	O41—S41—C41	106.60 (18)
S12—C17A—H17A	108.6	O42—S41—O43	112.07 (16)
S12—C17A—H17B	108.6	O42—S41—C41	106.11 (16)
H17A—C17A—H17B	107.5	O43—S41—C41	105.98 (17)
C18A—C17A—S12	114.8 (3)	C42—C41—S41	118.3 (3)
C18A—C17A—H17A	108.6	C46—C41—S41	121.0 (3)
C18A—C17A—H17B	108.6	C46—C41—C42	120.7 (4)
S12—C17B—H17C	108.6	C41—C42—H42	120.3
S12—C17B—H17D	108.6	C43—C42—C41	119.3 (4)
H17C—C17B—H17D	107.6	C43—C42—H42	120.3
C18B—C17B—S12	114.6 (11)	C42—C43—H43	119.9
C18B—C17B—H17C	108.6	C42—C43—C44	120.1 (4)
C18B—C17B—H17D	108.6	C44—C43—H43	119.9
Cu1—C18A—H18A	92.6	C43—C44—H44	120.1
C17A—C18A—Cu1	107.5 (3)	C45—C44—C43	119.8 (4)
C17A—C18A—H18A	118.3	C45—C44—H44	120.1
C19—C18A—Cu1	69.9 (2)	C44—C45—H45	119.6
C19—C18A—C17A	123.4 (4)	C44—C45—C46	120.8 (4)
C19—C18A—H18A	118.3	C46—C45—H45	119.6
Cu1—C18B—H18B	99.7	C41—C46—C45	119.3 (4)
C17B—C18B—Cu1	102.1 (10)	C41—C46—H46	120.3
C17B—C18B—H18B	116.7	C45—C46—H46	120.3
C19—C18B—Cu1	68.9 (6)	C61—O61—H61	109 (4)
C19—C18B—C17B	126.6 (14)	O61—C61—H61A	109.5
C19—C18B—H18B	116.7	O61—C61—H61B	109.5
Cu1—C19—H19A	106.1	O61—C61—H61C	109.5
Cu1—C19—H19B	92.5	H61A—C61—H61B	109.5
Cu1—C19—H19C	97.9	H61A—C61—H61C	109.5
Cu1—C19—H19D	98.6	H61B—C61—H61C	109.5
C18A—C19—Cu1	71.3 (2)	H51A—O51—H51B	107 (6)

Cu1—N13—N14—Cu2	−28.8 (3)	C12—S11—C15—N14	−1.4 (2)
Cu1—N13—N14—C15	171.7 (2)	C12—S12—C17A—C18A	63.3 (4)
Cu1—N13—C12—S11	−172.29 (16)	C12—S12—C17B—C18B	−63.0 (11)
Cu1—N13—C12—S12	7.9 (5)	C12—N13—N14—Cu2	156.3 (2)
Cu1—N24—C25—S21	−153.25 (16)	C12—N13—N14—C15	−3.2 (4)
Cu1—N24—C25—N22	28.4 (5)	C15—S11—C12—S12	179.4 (2)
Cu2—N14—C15—S11	−154.08 (16)	C15—S11—C12—N13	−0.5 (3)
Cu2—N14—C15—N12	26.2 (4)	C17A—S12—C12—S11	154.6 (2)
Cu2—N23—N24—Cu1	−26.2 (3)	C17A—S12—C12—N13	−25.5 (4)
Cu2—N23—N24—C25	176.0 (2)	C17A—C18A—C19—Cu1	98.2 (4)
Cu2—N23—C22—S21	−176.45 (14)	C17B—S12—C12—S11	−169.9 (5)
Cu2—N23—C22—S22	5.0 (4)	C17B—S12—C12—N13	9.9 (6)

S12—C17A—C18A—Cu1	−73.8 (3)	C17B—C18B—C19—Cu1	−89.6 (14)
S12—C17A—C18A—C19	−151.0 (3)	C22—S21—C25—N22	177.7 (3)
S12—C17B—C18B—Cu1	81.3 (11)	C22—S21—C25—N24	−0.8 (2)
S12—C17B—C18B—C19	153.9 (10)	C22—S22—C27A—C28A	55.9 (4)
S22—C27A—C28A—Cu2	−75.7 (4)	C22—S22—C27B—C28B	−64.8 (6)
S22—C27A—C28A—C29A	−152.3 (6)	C22—N23—N24—Cu1	155.4 (2)
S22—C27B—C28B—Cu2	80.4 (6)	C22—N23—N24—C25	−2.4 (4)
S22—C27B—C28B—C29B	153.5 (18)	C25—S21—C22—S22	178.01 (19)
S31A—C31—C32—C33	−178.5 (3)	C25—S21—C22—N23	−0.7 (2)
S31A—C31—C36—C35	178.2 (3)	C27A—S22—C22—S21	166.1 (2)
S31B—C31—C32—C33	−179.9 (4)	C27A—S22—C22—N23	−15.4 (3)
S31B—C31—C36—C35	179.4 (4)	C27A—C28A—C29A—Cu2	97.3 (5)
O31A—S31A—C31—C32	−39.7 (5)	C27B—S22—C22—S21	−162.1 (3)
O31A—S31A—C31—C36	142.0 (3)	C27B—S22—C22—N23	16.4 (4)
O31B—S31B—C31—C32	−118.6 (4)	C27B—C28B—C29B—Cu2	−95.7 (12)
O31B—S31B—C31—C36	61.8 (6)	C31—S31A—O31A—Cu1	−70.9 (4)
O32A—S31A—O31A—Cu1	46.0 (5)	C31—S31B—O31B—Cu1	83.3 (5)
O32A—S31A—C31—C32	−158.4 (3)	C31—C32—C33—C34	0.3 (6)
O32A—S31A—C31—C36	23.3 (4)	C32—C31—C36—C35	−0.2 (5)
O32B—S31B—O31B—Cu1	−168.0 (6)	C32—C33—C34—C35	0.2 (6)
O32B—S31B—C31—C32	124.4 (6)	C33—C34—C35—C36	−0.6 (6)
O32B—S31B—C31—C36	−55.2 (7)	C34—C35—C36—C31	0.6 (6)
O33A—S31A—O31A—Cu1	172.8 (4)	C36—C31—C32—C33	−0.3 (5)
O33A—S31A—C31—C32	80.6 (5)	S41—C41—C42—C43	179.6 (3)
O33A—S31A—C31—C36	−97.7 (4)	S41—C41—C46—C45	−179.4 (3)
O33B—S31B—O31B—Cu1	−37.5 (8)	O41—S41—C41—C42	58.2 (3)
O33B—S31B—C31—C32	3.7 (7)	O41—S41—C41—C46	−121.7 (3)
O33B—S31B—C31—C36	−175.9 (4)	O42—S41—C41—C42	−63.9 (3)
N13—N14—C15—S11	2.8 (3)	O42—S41—C41—C46	116.2 (3)
N13—N14—C15—N12	−176.9 (3)	O43—S41—C41—C42	176.8 (3)
N14—N13—C12—S11	2.1 (3)	O43—S41—C41—C46	−3.1 (3)
N14—N13—C12—S12	−177.7 (2)	C41—C42—C43—C44	0.3 (6)
N23—N24—C25—S21	1.9 (3)	C42—C41—C46—C45	0.7 (5)
N23—N24—C25—N22	−176.5 (3)	C42—C43—C44—C45	−0.5 (6)
N24—N23—C22—S21	1.9 (3)	C43—C44—C45—C46	0.7 (6)
N24—N23—C22—S22	−176.6 (2)	C44—C45—C46—C41	−0.9 (6)
C12—S11—C15—N12	178.3 (3)	C46—C41—C42—C43	−0.4 (5)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N12—H12*A*···O51^{i}	0.91 (5)	1.94 (5)	2.765 (4)	150 (4)
N12—H12*B*···O41	0.87 (5)	2.00 (5)	2.867 (4)	174 (4)
N22—H22*A*···O42^{ii}	0.90 (5)	2.04 (5)	2.896 (4)	158 (4)
N22—H22*B*···O61^{iii}	0.86 (5)	1.96 (5)	2.758 (4)	154 (4)
C17*A*—H17*A*···O33*A*^{iv}	0.99	2.54	3.476 (7)	157
C17*B*—H17*D*···S31*B*^{iv}	0.99	2.76	3.676 (16)	154
C17*B*—H17*D*···O33*B*^{iv}	0.99	1.61	2.387 (16)	132

C18*A*—H18*A*···O31*A*	0.95	2.17	2.835 (6)	126
C27*A*—H27*A*···O33*A*$^{\text{v}}$	0.99	2.44	3.377 (8)	159
C28*A*—H28*A*···O32*A*	0.95	2.05	2.769 (7)	131
C27*B*—H27*D*···O32*B*$^{\text{v}}$	0.99	2.29	3.133 (13)	142
C28*B*—H28*B*···S41	0.95	3.01	3.891 (8)	155
C28*B*—H28*B*···O41	0.95	2.42	3.096 (9)	128
O61—H61···O43$^{\text{vi}}$	0.75 (6)	1.98 (6)	2.726 (4)	174 (6)
C61—H61*B*···O51$^{\text{v}}$	0.98	2.58	3.426 (5)	145
O51—H51*A*···O43$^{\text{v}}$	0.82 (6)	2.00 (7)	2.790 (4)	164 (6)
O51—H51*B*···O32*B*	0.81 (7)	2.20 (7)	3.010 (11)	170 (6)
O51—H51*B*···O33*A*	0.81 (7)	1.84 (7)	2.641 (7)	168 (6)

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