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The conformations of two copper(I) complexes of 1*H*-benzimidazole-2(3*H*)-thione and thiosaccharinate

Mariana Dennehy,[a] Oscar V. Quinzani,[a]‡ Ricardo Faccio,[b]* Eleonora Freire[c] and Álvaro W. Mombrú[b]

[a]INQUISUR, Departamento de Química, Universidad Nacional del Sur, Bahía Blanca B8000CPB, Argentina, [b]Cryssmat-Lab, Cátedra de Física, DETEMA, Facultad de Química, Universidad de la Reública, Montevideo, Uruguay, and [c]Departamento de Física, Centro Atómico Constituyentes (CAC), Comisión Nacional de Energía Atómica (CNEA), Provincia de Buenos Aires, Argentina
Correspondence e-mail: rfaccio@fq.edu.uy

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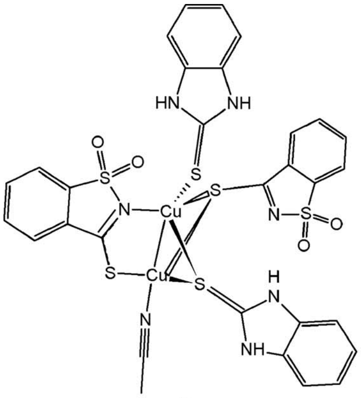
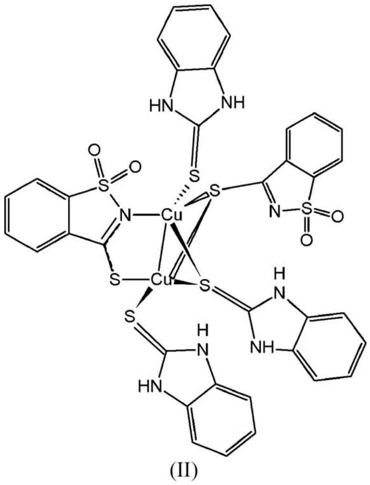
(Acetonitrile-1κN)[μ-1*H*-benzimidazole-2(3*H*)-thione-1:2-$\kappa^2 S$:*S*][1*H*-benzimidazole-2(3*H*)-thione-2κS]bis(μ-1,1-dioxo-1λ^6,2-benzothiazole-3-thiolato)-1:2$\kappa^2 S^3$:*N*;1:2$\kappa^2 S^3$:S^3-dicopper(I)(*Cu*—*Cu*), [$\mathrm{Cu_2(C_7H_4NO_2S_2)_2(C_7H_6N_2S)_2(CH_3CN)}$] or [$\mathrm{Cu_2(tsac)_2(Sbim)_2(CH_3CN)}$] [tsac is thiosaccharinate and Sbim is 1*H*-benzimidazole-2(3*H*)-thione], (I), is a new copper(I) compound that consists of a triply bridged dinuclear Cu—Cu unit. In the complex molecule, two tsac anions and one neutral Sbim ligand bind the metals. One anion bridges *via* the endocyclic N and exocyclic S atoms (μ-*S*:*N*). The other anion and one of the mercaptobenzimidazole molecules bridge the metals through their exocyclic S atoms (μ-*S*:*S*). The second Sbim ligand coordinates in a monodentate fashion (κS) to one Cu atom, while an acetonitrile molecule coordinates to the other Cu atom. The $\mathrm{Cu^I}$—$\mathrm{Cu^I}$ distance [2.6286 (6) Å] can be considered a strong 'cuprophilic' interaction. In the case of [μ-1*H*-benzimidazole-2(3*H*)-thione-1:2$\kappa^2 S$:*S*]bis[1*H*-benzimidazole-2(3*H*)-thione]-1κS;2κS-bis(μ-1,1-dioxo-1λ^6,2-benzothiazole-3-thiolato)-1:2$\kappa^2 S^3$:*N*;1:2$\kappa^2 S^3$:S^3-dicopper(I)(*Cu*—*Cu*), [$\mathrm{Cu_2(C_7H_4NO_2S_2)_2(C_7H_6N_2S)_3}$] or [$\mathrm{Cu_2(tsac)_2(Sbim)_3}$], (II), the acetonitrile molecule is substituted by an additional Sbim ligand, which binds one Cu atom *via* the exocylic S atom. In this case, the $\mathrm{Cu^I}$—$\mathrm{Cu^I}$ distance is 2.6068 (11) Å.

Comment

Thionates, anions produced by the deprotonation of heterocyclic thioamides, can coordinate to metals, producing mononuclear or complex polynuclear species. Like other thioamides, thiosaccharin [or 1,1-dioxo-1λ^6,2-benzothiazole-3(2*H*)-thione] is a versatile ligand with the ability to coordinate metal centres in many ways (Dennehy *et al.*, 2009). Particular attention has been devoted in recent decades to the synthesis of copper complexes in both the mono- and divalent oxidation states, due to the great variety and flexibility of their coordination environments (Rapper, 1994). Most of the chemistry of $\mathrm{Cu^I}$ with thionates has focused on the tetra- or hexanuclear binary complexes (García-Vázquez *et al.*, 2005; Ruan & Shi, 2007; López-Torres *et al.*, 2006). We have been working with binary and ternary copper thiosaccharinates, firstly synthesizing the Cu(tsac) complex (where tsac is the thiosaccharinate anion), which crystallized as the tetranuclear cluster [$\mathrm{Cu_4(tsac)_4(CH_3CN)_2}$]$\cdot$2$\mathrm{CH_3CN}$ from acetonitrile solution (Dennehy *et al.*, 2007), and then ternary phosphane complexes (Dennehy *et al.*, 2009). To study the competition between two different thiones bound to copper, we have synthesized two ternary thiosaccharinates with thiosaccharin and 1*H*-benzimidazole-2(3*H*)-thione (Sbim), *viz.* [$\mathrm{Cu_2(tsac)_2(Sbim)_2(CH_3CN)}$], (I), and [$\mathrm{Cu_2(tsac)_2(Sbim)_3}$], (II).



(I)



(II)

Compound (I) is a copper(I) thiosaccharinate and it crystallizes in the space group $P\bar{1}$. It is built of triply bridged dinuclear units (Fig. 1). Two tsac anions and one neutral Sbim ligand bind the metals. One anion bridges *via* the endocyclic N and exocyclic S atoms (μ-*S*:*N*), with Cu—N and Cu—S distances of 2.000 (2) and 2.2799 (9) Å, respectively. The other anion and one of the Sbim ligands bridge the metal centres through their exocyclic S atoms (μ-*S*:*S*), with Cu—S distances of 2.3743 (9) and 2.6711 (10) Å for tsac, and 2.3785 (10) and

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‡ Deceased.

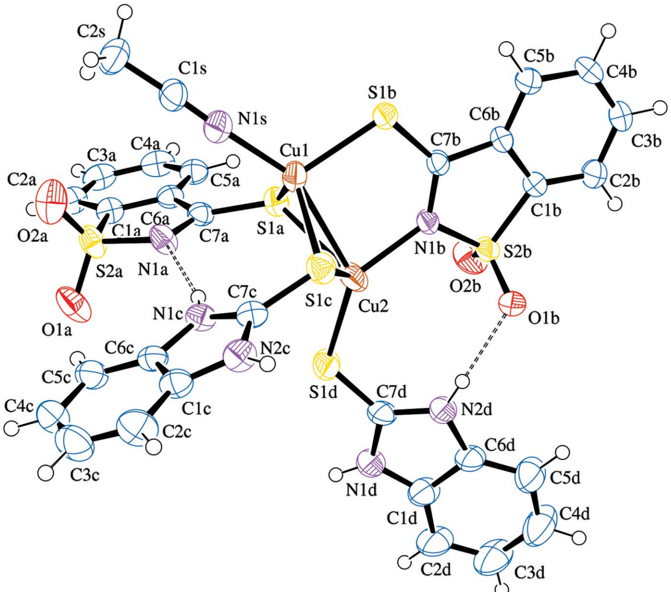

Figure 1
The molecular structure of $[Cu_2(tsac)_2(Sbim)_2(CH_3CN)]$, (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. Dashed lines indicate intramolecular hydrogen bonds.

2.3901 (10) Å for Sbim. The second Sbim ligand coordinates in a monodentate fashion (κS), with a Cu—S distance of 2.2091 (10) Å, and the coordination of Cu2 is completed by an acetonitrile molecule, with a Cu—N distance of 1.964 (3) Å. Each Cu^I atom has a nearly distorted tetrahedral coordination environment. Given the proximity of the two Cu^I atoms, with a $Cu^I—Cu^I$ distance of 2.6286 (6) Å, the two subunits form tetrahedra linked by edge-sharing. This short $Cu^I—Cu^I$ distance indicates a strong cuprophilic interaction.

Each $[Cu_2(tsac)_2(Sbim)_2(CH_3CN)]$ structural unit of (I) is stabilized by two intramolecular hydrogen bonds ($N1D—H2DA\cdots O1B$ and $N1C—H1C\cdots N1A$) and one intermolecular hydrogen bond [$N1D—H1DA\cdots O1A^i$; symmetry code: $-x + 1, -y + 1, -z$], establishing an interaction with another inversion-symmetry related $[Cu_2(tsac)_2(Sbim)_2(CH_3CN)]$ unit (Fig. 2 and Table 1). The $N2C—H2CA$ bond points towards a neighbouring Cu—Cu unit and away from acceptors. Therefore, it is blocked and unable to participate in any hydrogen bonds. Additionally, two Sbim and two tsac planar residues stack together through their six-membered planar rings in a four-layer group, with the negative tsac residues separated by the neutral Sbim ligands. There are also π–π interactions, with the rings arranged in the order $tsac^{iii}$/Sbim/$Sbim^{iv}$/$tsac^{v}$ [symmetry codes: (iii) $x + 1, y, z$; (iv) $-x + 2, -y + 1, -z$; (v) $x + 1, -y + 1, -z$]. The centroid–centroid distances are 3.588 (2) Å for $tsac^{iii}$–Sbim (rings $C1A$–$C6A$ and $C1C$–$C6C$, respectively) and equivalent $Sbim^{iv}$–$tsac^{v}$ interactions, and 3.616 (2) Å between parallel Sbim–$Sbim^{iv}$. The dihedral angle between adjacent tsac anions and nearby Sbim ligands is 12.53 (16)°.

Compound (II) crystallizes in the monoclinic space group $P2_1/c$. As mentioned before, this structure has important similarities with the structure of (I). In the case of (II) (Fig. 3), the acetonitrile molecule is substituted by an additional disordered Sbim ligand, which binds to Cu through the exocyclic S atom (κS), with a Cu—S distance of 2.2532 (18) Å. In this case, the tsac anion bridges *via* the endocyclic N and exocyclic S atoms (μ-S:N), with Cu—N and Cu—S distances of 2.047 (4) and 2.3057 (17) Å, respectively. Each Cu^I atom presents a distorted tetrahedral coordination environment and both tetrahedra are linked by edge-sharing. The other anion and one of the Sbim ligands bridge the metal centres through their exocyclic S atoms (μ-S:S), with Cu—S distances of 2.5470 (16) and 2.3261 (15) Å for tsac, and 2.4795 (15) and 2.3261 (15) Å for Sbim. The second Sbim ligand coordinates in a monodentate fashion (κS), with a Cu—S distance of 2.2748 (16) Å. An important difference between these two structures is the $Cu^I—Cu^I$ distance; in the case of (II), the distance is 2.6068 (11) Å, which is slightly shorter than that in (I). The weaker $Cu^I—Cu^I$ interaction in (I) is possibly a consequence of the considerably shorter Cu—N distance in (I) than that in (II).

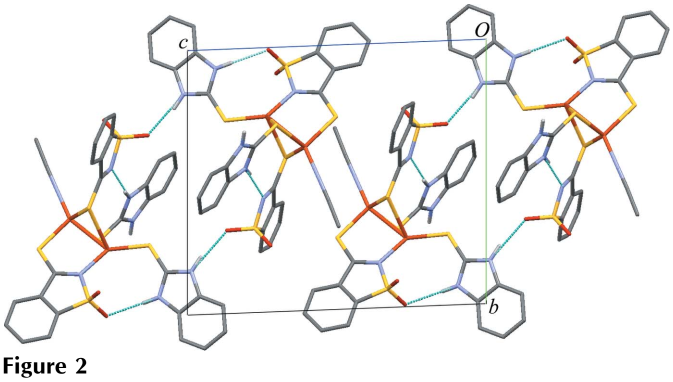

Figure 2
A view of the packing of (I), normal to the [100] direction, showing the intra- and intermolecular hydrogen bonds as dashed lines (cyan in the electronic version of the paper).

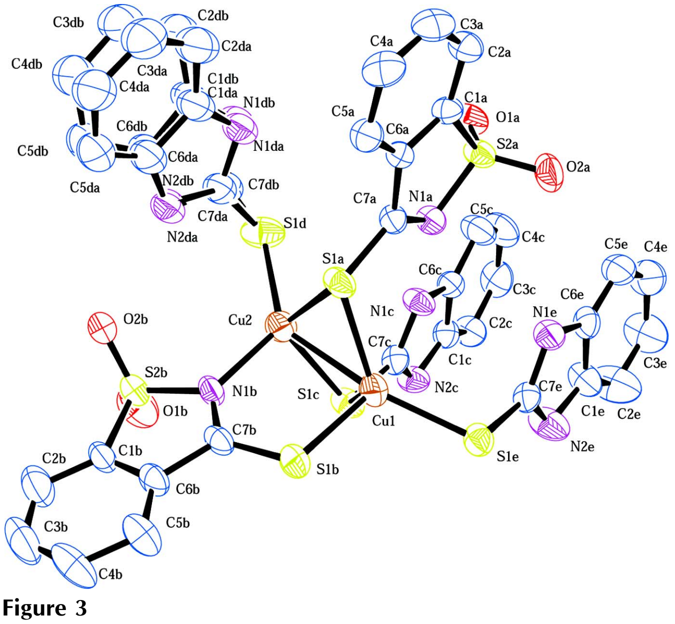

Figure 3
The molecular structure of $[Cu_2(tsac)_2(Sbim)_3)]$, (II), showing the atom-labelling scheme, indicating the two orientations of the disordered Sbim ligand. Displacement ellipsoids are drawn at the 30% probability level.

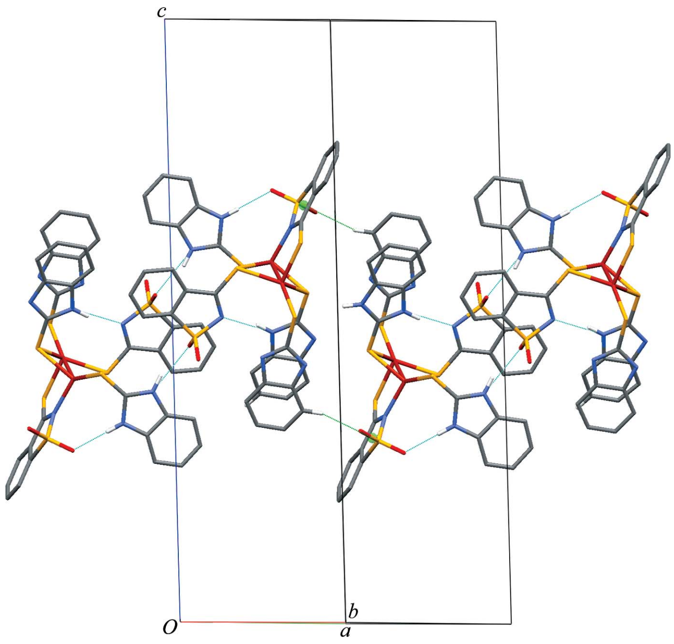

Figure 4
A partial view of the packing of (II), normal to the [110] direction. Dashed lines indicate the hydrogen-bonding interactions between $[Cu_2(tsac)_2(Sbim)_3]$ units (cyan in the electronic version of the paper) and the connections between them as a result of C—H$\cdots\pi$ interactions (green). One of the disordered Sbim ligands has been omitted for clarity.

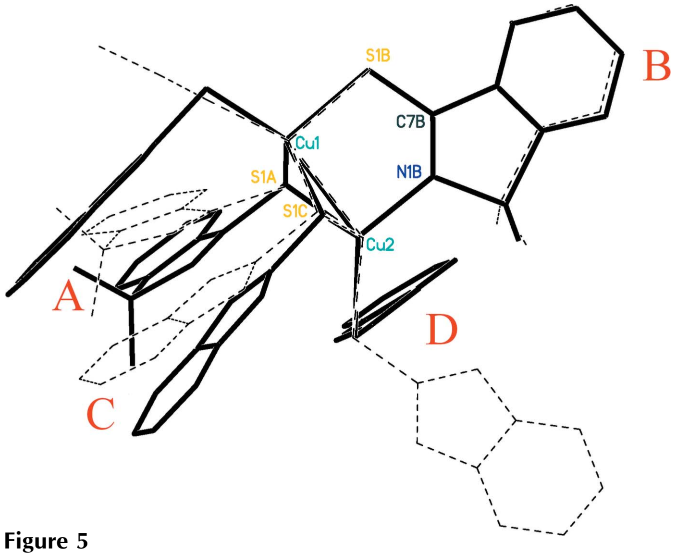

Figure 5
The overlap of $[Cu_2(tsac)_2(Sbim)_2(CH_3CN)]$ (dashed lines) and $[Cu_2(tsac)_2(Sbim)_3]$ (solid lines) units after a least-squares fit of atoms Cu1, Cu2, S1*A*, S1*B*, C7*B*, N1*B* and S1*C*. The letter **A** indicates the tsac(*A*) molecule, **B** the tsac(*B*) molecule, **C** the Sbim(*C*) molecule and **D** the Sbim(*D*) molecule.

The three-dimensional crystal structure of (II) is sustained by two intramolecular hydrogen bonds (N1*C*—H1*C*$\cdots$N1*A* and N2*DA*—H2*DA*$\cdots$O2*B*) and one intermolecular hydrogen bond (N1*DA*—H1*DA*$\cdots$O1*A*^{ii} [symmetry code: (ii) $-x, -y+1, -z$], which involves a molecule related by inversion symmetry (Table 3). The last two hydrogen bonds involve the interaction between the disordered Sbim(*D*) ligand and two tsac anions from two symmetry-related $[Cu_2(tsac)_2(Sbim)_3]$ units, as shown in Fig. 4. Finally, a possible intermolecular C—H$\cdots\pi$ interaction was identified as being responsible for the orientation of the Sbim(*B*) ligand, and responsible for the infinite two-dimensional networks lying parallel to the (001) plane. The C2*E*—H2*E*$\cdots$*Cg*^{vi} [*Cg* is the centroid of the S2*B*/N1*B*/C7*B*/C6*B*/C1*B* ring; symmetry code: (vi) $-x+1, -y, -z$] angle is 162° and the H2*E*$\cdots$*Cg*^{vi} distance is 2.77 Å.

In order to compare the conformational geometries of (I) and (II), we performed a least-squares plane fitting of all the Sbim and tsac molecules in the two compounds, and the results are presented in Tables 2 and 4. The planes are constituted by atoms S1/S2/N1/C1–C5 for Sbim ligands and S1/N1/N2/C1–C7 for tsac anions. According to the calculations, the r.m.s. deviations of the fitted atoms are all below the limit of 0.050 Å. A further comparison, assuming a common Cu1—Cu2 core, allows us to estimate the angles between the same kind of molecules in both conformations as 17.7, 14.2, 15.1 and 83.7° for molecules tsac(*A*), tsac(*B*), Sbim(*C*) and Sbim(*D*), respectively (see Fig. 5). In the case of Sbim(*D*), we included the conformation with the higher site-occupation factor, corresponding to Sbim(*DA*).

Experimental

$[Cu_4(tsac)_4(CH_3CN)_2]\cdot 2CH_3CN$ was synthesized as reported previously (Dennehy *et al.*, 2007). $[Cu_2(tsac)_2(Sbim)_2(CH_3CN)]$, (I), was synthesized by dropwise addition of a red solution of $[Cu_4(tsac)_4(CH_3CN)_2]\cdot 2CH_3CN$ (10 mg, 0.04 mmol of Cu^+) in CH_3CN (5 ml) to another solution of Sbim (6 mg, 0.04 mmol) in CH_3CN (4 ml) with mechanical stirring. The solution turned orange. After a day of slow evaporation of the solvent, red crystals of (I) suitable for X-ray diffraction studies were obtained. The crystals were washed with diethyl ether and were air stable.

$[Cu_2(tsac)_2(Sbim)_3]$, (II), was synthesized employing different molar ratios of (I) and Sbim (Cu:Sbim = 1:1, 1:4, 1:10) in CH_3CN solutions. When the molar ratio was 1:1 to 1:4, crystals of (I) were obtained as unique products. When the Cu:Sbim ratio was 1:10, a very few thin orange needles of (II) were obtained. Analysis calculated for $C_{30}H_{23}Cu_2N_7O_4S_6$: C 41.6, H 2.6, N 11.3%; found: C 41.6, H 2.3, N 11.3%. IR spectra were obtained in KBr dispersion and in Nujol mulls, and showed no differences in the vibrational bands. The IR spectrum of (I) confirm the presence of two different thiosaccharinate anions. Selected anion bands, KBr (cm^{-1}): 1394 (*w*)/1355 (*s*), 1258 (*s*), 1234/1222 (*w*), 1149 (*vs*), 1118 (*m*), 1022 (*vw*)/1008 (*m*), 837 (*m*)/822 (*m*), 622 (*w*). The UV–Vis spectrum of (I) presents broad bands (200/214/245 and 298/310 nm) that are assigned to transitions in the benzene rings and in the thiocarbonilic bonds within the ligands.

Compound (I)

Crystal data

$[Cu_2(C_7H_4NO_2S_2)_2(C_7H_6N_2S)_2$-
$(C_2H_3N)]$
$M_r = 865.01$
Triclinic, $P\bar{1}$
$a = 8.0466\ (1)$ Å
$b = 13.8150\ (2)$ Å
$c = 15.3621\ (2)$ Å
$\alpha = 87.739\ (1)°$
$\beta = 89.480\ (1)°$
$\gamma = 79.033\ (1)°$
$V = 1675.21\ (4)$ Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 1.69$ mm^{-1}
$T = 293$ K
$0.30 \times 0.20 \times 0.10$ mm

Table 1
Hydrogen-bond geometry (Å, °) for (I).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1D—H1$DA\cdots$O1$A^{\rm i}$	0.86	2.00	2.841 (4)	167
N1C—H1$C\cdots$N1A	0.86	2.10	2.918 (4)	160
N2D—H2$DA\cdots$O1B	0.86	2.05	2.893 (4)	166

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

Table 2
Least-squares planes, deviations and angles between the planes (Å, °) for $[Cu_2(tsac)_2(Sbim)_2(CH_3CN)]$, (I).

Plane	R.m.s. deviation	tsac(A)	tsac(B)	Sbim(C)
tsac(A)	0.0159			
tsac(B)	0.0171	86.89 (5)		
Sbim(C)	0.0414	14.68 (8)	89.73 (7)	
Sbim(D)	0.0138	84.99 (8)	23.30 (8)	86.27 (9)

Data collection

Oxford Xcalibur Eos Gemini diffractometer
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2009)
$T_{\min} = 0.716$, $T_{\max} = 0.801$
97442 measured reflections
8285 independent reflections
5570 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.046$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.118$
$S = 1.10$
8285 reflections
443 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 0.50$ e Å^{-3}
$\Delta\rho_{\min} = -0.65$ e Å^{-3}

Compound (II)

Crystal data

$[Cu_2(C_7H_4NO_2S_2)_2(C_7H_6N_2S)_3]$
$M_r = 974.14$
Monoclinic, $P2_1/c$
$a = 13.2395$ (12) Å
$b = 10.2731$ (10) Å
$c = 29.536$ (15) Å
$\beta = 93.135$ (16)°
$V = 4011$ (2) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 1.48$ mm^{-1}
$T = 293$ K
0.25 × 0.15 × 0.10 mm

Data collection

Oxford Xcalibur Eos Gemini diffractometer
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2009)
$T_{\min} = 0.814$, $T_{\max} = 0.867$
18885 measured reflections
8812 independent reflections
4863 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.066$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.067$
$wR(F^2) = 0.154$
$S = 1.01$
8812 reflections
587 parameters
317 restraints
H-atom parameters constrained
$\Delta\rho_{\max} = 0.78$ e Å^{-3}
$\Delta\rho_{\min} = -0.39$ e Å^{-3}

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1DA—H1$DA\cdots$O1$A^{\rm ii}$	0.86	2.13	2.957 (14)	161
N1C—H1$C\cdots$N1A	0.86	2.17	3.014 (6)	166
N2DA—H2$DA\cdots$O2B	0.86	1.90	2.756 (19)	174
N2DB—H2$DB\cdots$O2B	0.86	1.97	2.827 (12)	173

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

Table 4
Least-squares planes, deviations and angles between the planes (Å, °) for $[Cu_2(tsac)_2(Sbim)_3]$, (II).

Plane	R.m.s. deviation	tsac(A)	tsac(B)	Sbim(C)	Sbim(DA)
tsac(A)	0.0317				
tsac(B)	0.0362	84.40 (8)			
Sbim(C)	0.0448	11.33 (17)	81.95 (11)		
Sbim(DA)	0.0495	6.9 (5)	88.6 (3)	17.8 (5)	
Sbim(E)	0.0097	10.6 (2)	88.89 (12)	9.6 (2)	13.9 (5)

For (I), the H atoms were positioned geometrically and treated as riding, with C—H = 0.93 (aromatic) or 0.96 Å (methyl) and N—H = 0.86 Å. H atoms bonded to aromatic C atoms and N atoms were refined with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C,N})$, while for the methyl group, $U_{\rm iso}({\rm H}) = 1.5U_{\rm eq}({\rm C})$. The anisotropic displacement ellipsoid of atom S1D displays a marked elongation in the normal direction to both the S—C and S—Cu bonds. This can be related to the motion of the corresponding Sbim ligand, which coordinates to Cu *via* only atom S1D. The highest residual electron-density peak is located 0.79 Å from atom S1D.

In the case of (II), refinement proceeded in a similar manner. The Sbim(D) molecule is disordered and two positions were defined for all atoms of this ligand, except for atom S1D. Similarity restraints, with an effective s.u. value of 0.001 Å, were applied to the corresponding bond lengths and angles of the two orientations, while neighbouring atoms within and between the two orientations were restrained, with an effective s.u. value of 0.01 Å^2, to have similar anisotropic displacement parameters. The site-occupation factor of the major orientation refined to 0.510 (11). The highest residual electron-density peak is located 2.39 Å from atom H4DA.

For both compounds, data collection: *CrysAlis PRO* (Oxford Diffraction, 2009); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *Mercury* [Version 1.4.2 (Build 2); Macrae *et al.*, 2008]; software used to prepare material for publication: *PLATON* (Spek, 2009).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FN3087). Services for accessing these data are described at the back of the journal.

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