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Bis(μ-thiophene-2-carbaldehyde thiosemicarbazonato)bis[acetonitrilecopper(**I**)] bis(tetrafluoroborate)

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The title compound, $[Cu_2(C_6H_7N_3S_2)_2(C_2H_3N)_2](BF_4)_2$, is a dimer with a central Cu_2S_2 core resulting from thiosemicarbazone sulfur bridging. Both Cu–TCT units (TCT is the thiophene-2-carboxaldehyde thiosemicarbazone anion) are roughly planar and are parallel to one another and perpendicular to the Cu_2S_2 plane.

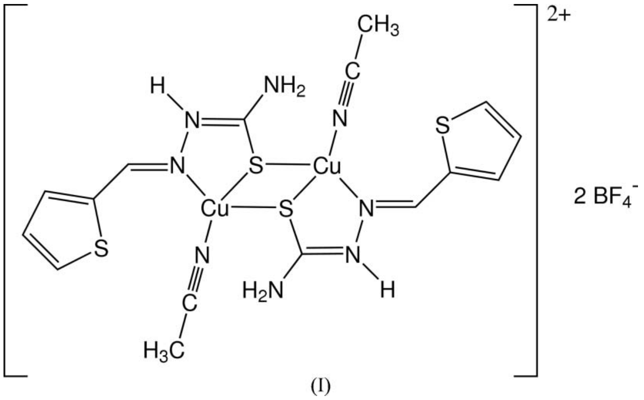
Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.011 Å
R factor = 0.045
wR factor = 0.111
Data-to-parameter ratio = 13.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

As part of a study of thioamide complexes of copper(I), the title compound, $[Cu_2(TCT)_2(NCMe)_2](BF_4)_2$, (I), was prepared and its crystal structure is presented here.



(I)

Compound (I) crystallizes in the orthorhombic space group $Pca2_1$. Each Cu^I center is chelated by a TCT ligand (TCT is the thiophene-2-carboxaldehyde thiosemicarbazone anion) in a similar fashion to that of the previously known TCT complexes *trans*-Ni(TCT)$_2$ (Garcia-Tojal *et al.*, 2001), *trans*-Cu(TCT)$_2$ (Garcia-Tojal *et al.*, 1999), PhHg(TCT) (Lobana *et al.*, 2001) and *cis*-Fe(CO)$_2$(TCT)$_2$ (Hong *et al.*, 2004). In contrast with these species, but in keeping with typical Cu^I behavior, the two Cu^I centers are bridged by the thiosemicarbazone S atoms to form a rhomboid dimer. As is the case with the previously known complexes, the thiophene S atoms fail to coordinate, with Cu1···S3 = 3.190 (2) Å. Instead, acetonitrile ligands complete the distorted tetrahedral coordination of each Cu^I.

An analysis of the bond angles reveals that most of the angles about the Cu^I atoms are near the nominal tetrahedral value. However, the angles within the Cu–TCT metallocyclic ring, *e.g.* N3—Cu1—S1, are acute, and the angles between the acetonitrile and the chelating TCT, *e.g.* N7—Cu1—N3 and N7—Cu1—S1, are large (>120°). Thus, the acetonitrile associated with each Cu^I center is angled away from the chelating TCT ligand and slightly towards the bridging TCT ligand. The S—Cu—S angles are near the nominal tetrahedral value, but

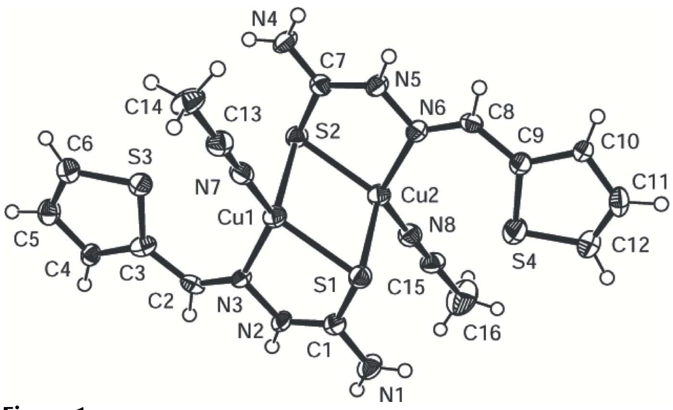


Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids. The anions have been omitted for clarity.

the Cu—S—Cu values are <75°. The chelating (*e.g.* N3—Cu1—S1) and non-chelating (*e.g.* N3—Cu1—S2) angles in the current structure are relaxed by about 2–7° in comparison with the analogous angles in the literature structures cited above. This effect is due to the preference of Cu$^{\rm I}$ for quasi-tetrahedral, rather than square-planar or octahedral, geometry.

The Cu1···Cu2 distance of 2.8094 (15) Å indicates a long-range metal–metal interaction. The Cu—S and Cu—N distances within the chelate rings, *e.g.* Cu1—S1 and Cu1—N3, are within the range found for other M–TCT complexes. The fact that the non-chelate Cu—S distances (*e.g.* Cu1—S2) are significantly longer than the chelate distances suggests that dimer formation is the weaker effect. Comparison of the chelate Cu—S and Cu—N bonds with those in the Cu$^{\rm II}$–TCT structure (Garcia-Tojal *et al.*, 1999) reveals that those in the current structure are longer by about 0.06 Å, a fact that is consistent with the lesser charge on Cu$^{\rm I}$.

Least-squares planes were calculated for Cu1/S1/N2/N3/C1 (plane *A*, maximum deviation 0.053 Å for atom N3), Cu1/S1/Cu2/S2 (plane *B*, maximum deviation 0.007 Å for all atoms), Cu2/S2/N5/N6/C7 (plane *C*, maximum deviation 0.061 Å for atom S2), C3/C4/C5/C6/S3 (plane *D*, maximum deviation 0.004 Å for atoms C5 and C6) and C9/C10/C11/C12/S4 (plane *E*, maximum deviation 0.001 Å for atoms C9, C10 and C11). The chelate ring planes (*A* and *C*) are nearly parallel [dihedral angle 0.7 (3)°] and are canted by 7.0 (3) and 8.0 (3)° with respect to the associated thiophene planes (*D* and *E*). This result differs from that of the Cu$^{\rm II}$–TCT complex, for which the chelate and thiophene planes lie at a dihedral angle of 17.85° (Garcia-Tojal *et al.*, 1999). The Cu$_2$S$_2$ plane *B* is nearly perpendicular to the Cu–TCT chelate planes *A* and *C* (*A*/*B* and *B*/*C* dihedral angles are 81.66 (9) and 81.44 (9)°, respectively), resulting in a zigzag tri-fold arrangement of the fused rings.

Experimental

The TCT ligand was prepared according to the literature method of Hong *et al.* (2004). The metal complex was prepared through the reaction of [Cu(NCMe)$_4$]BF$_4$ (4.36 g, 13.9 mmol) and TCT (2.57 g, 13.9 mmol) in acetonitrile (80 ml). The resulting yellow solution was stirred for 30 min at room temperature. The yellow product was precipitated from the solution with the addition of diethyl ether (yield 74.3%). Analysis, calculated for C$_8$H$_{10}$BCuF$_4$N$_4$S$_2$: Cu 16.87, C 25.51, H 2.68, N 14.87%; found: Cu 16.92, C 24.04, H 2.68, N 14.03%. X-ray quality crystals of (I) were grown by layering an acetonitrile solution with diethyl ether.

Crystal data

[Cu$_2$(C$_6$H$_7$N$_3$S$_2$)$_2$(C$_2$H$_3$N)$_2$](BF$_4$)$_2$
M_r = 753.34
Orthorhombic, $Pca2_1$
a = 13.3357 (3) Å
b = 9.1867 (2) Å
c = 22.7980 (5) Å
V = 2793.01 (11) Å^3
Z = 4
D_x = 1.792 Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 470 reflections
θ = 3.9–69.5°
μ = 5.40 mm^{-1}
T = 100 (2) K
Block, yellow
0.12 × 0.10 × 0.10 mm

Data collection

Bruker SMART APEX-II CCD area-detector diffractometer
ω and φ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2004)
$T_{\rm min}$ = 0.534, $T_{\rm max}$ = 0.583
30209 measured reflections
4947 independent reflections
3981 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.088
$\theta_{\rm max}$ = 69.5°
$h = -15 \rightarrow 14$
$k = -10 \rightarrow 10$
$l = -27 \rightarrow 26$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.111$
S = 1.07
4947 reflections
363 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0722P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max}$ = 1.22 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.36 e Å^{-3}
Absolute structure: Flack (1983), with 2291 Friedel pairs
Flack parameter: 0.13 (4)

Table 1
Selected geometric parameters (Å, °).

Cu1—N7	1.944 (7)	Cu2—S1	2.472 (2)
Cu1—N3	2.031 (6)	S1—C1	1.705 (8)
Cu1—S1	2.327 (2)	S2—C7	1.723 (8)
Cu1—S2	2.463 (2)	N2—C1	1.327 (9)
Cu1—Cu2	2.8094 (15)	N2—N3	1.384 (8)
Cu2—N8	1.929 (7)	N5—C7	1.350 (10)
Cu2—N6	2.051 (6)	N5—N6	1.385 (8)
Cu2—S2	2.313 (2)		
N7—Cu1—N3	133.4 (2)	N6—Cu2—S1	101.33 (18)
N7—Cu1—S1	120.6 (2)	S2—Cu2—S1	108.27 (7)
N3—Cu1—S1	87.43 (18)	Cu1—S1—Cu2	71.59 (6)
N7—Cu1—S2	103.00 (19)	Cu2—S2—Cu1	71.98 (6)
N3—Cu1—S2	101.75 (18)	C1—N2—N3	122.3 (6)
S1—Cu1—S2	108.15 (7)	N2—N3—Cu1	112.5 (4)
N8—Cu2—N6	130.2 (3)	C7—N5—N6	121.9 (6)
N8—Cu2—S2	124.0 (2)	N5—N6—Cu2	113.0 (4)
N6—Cu2—S2	87.36 (18)	N2—C1—S1	123.5 (6)
N8—Cu2—S1	102.9 (2)	C2—C3—S3	124.4 (6)

H atoms were treated as riding, with C—H = 0.96 and 0.93 Å for methyl and vinyl groups, and N—H = 0.86 Å, and with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C,N) for all H atoms. The largest peak in the final difference map lies near the centroid of the Cu2/N6/C8/C9/S4 arc.

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT-Plus* (Bruker, 2004); data reduction: *SAINT-Plus*; program(s) used to

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solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *XSHELL* (Bruker, 2004); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97* (Sheldrick, 1997).

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