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Dibromidobis(6-methyl-3-phenyl-*s*-triazolo[3,4-*b*][1,3,4]thiadiazole-κN^1)-copper(II)

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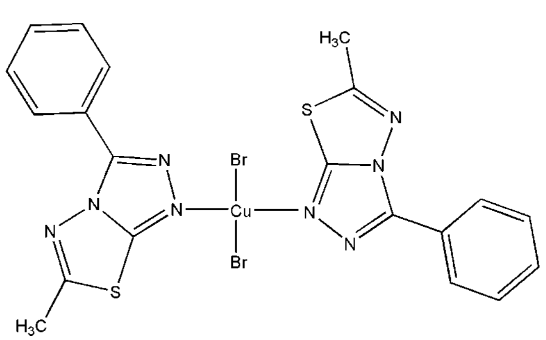
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.007 Å; R factor = 0.041; wR factor = 0.106; data-to-parameter ratio = 12.7.

In the title complex, $[CuBr_2(C_{10}H_8N_4S)_2]$, the Cu^{II} atom is located on an inversion centre and displays a distorted square-planar coordination geometry. The dihedral angle between the fused-ring system and its phenyl substituent is 2.1 (3)°. Intermolecular C—H···Br hydrogen bonds and π–π contacts [with an interplanar separation of 3.513 (3) Å] form a supramolecular network structure.

Related literature

For related literature, see: Fornies-Marquina *et al.* (1974); Molina *et al.* (1989); Huang *et al.* (2005); Naveen *et al.* (2006).



Experimental

Crystal data

$[CuBr_2(C_{10}H_8N_4S)_2]$
M_r = 655.89
Triclinic, $P\bar{1}$
a = 6.8286 (10) Å
b = 8.5231 (13) Å
c = 11.3654 (16) Å
α = 98.442 (2)°
β = 105.614 (2)°
γ = 108.859 (2)°
V = 582.69 (15) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 4.57 mm^{-1}
T = 298 (2) K
0.44 × 0.31 × 0.22 mm

Data collection

Bruker APEXII area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996) T_{min} = 0.196, T_{max} = 0.366
3511 measured reflections
1927 independent reflections
1430 reflections with $I > 2\sigma(I)$
R_{int} = 0.101

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.106
S = 0.89
1927 reflections
152 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.74 e Å^{-3}
$\Delta\rho_{min}$ = −0.82 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C10—H17*C*···Br1^{i}	0.96	2.90	3.769 (5)	151
C1—H1···N2	0.93	2.56	2.871 (5)	100
C5—H4···N4	0.93	2.45	3.122 (6)	129

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

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2004); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CF2132).

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supplementary materials

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Dibromidobis(6-methyl-3-phenyl-*s*-triazolo[3,4-*b*][1,3,4]thiadiazole-κN^1)copper(II)

H.-Q. Liu

Comment

The molecular structure of 2-methyl-5-phenyl-s-triazolo(3,4 − b)-1,3,4-thiadiazole (Fornies-Marquina *et al.*, 1974) and its substituted derivatives (Molina *et al.*, 1989; Huang *et al.*, 2005; Naveen *et al.*, 2006) have been reported; however, no metal complexes of the ligand have been reported. In this paper, we report the crystal structure of the title compound, (I), a Cu complex obtained by the reaction of 2-methyl-5-phenyl-s-triazolo(3,4 − b)-1,3,4-thiadiazole with copper(II) bromide in methanol solution.

As illustrated in Fig. 1, the Cu^{II} atom lies on an inversion centre and has a distorted square-planar geometry with two N atoms from two 2-methyl-5-phenyl-s-triazolo(3,4 − b)-1,3,4-thiadiazole ligands and two bromine atoms (Table 1). There are intramolecular C—H···N interactions. The molecules are connected through C—H···Br hydrogen bonding and π-π stacking interactions between the phenyl ring and triazolo ring, forming a supramolecular network structure (Table 2). The centroid-centroid distance of stacked rings is 3.513 (3) Å.

Experimental

The title complex was prepared by the addition of copper(II) bromide (0.0568 g, 0.25 mmol) to a hot methanol solution (10 ml) of 2-methyl-5-phenyl-s-triazolo(3,4 − b)-1,3,4-thiadiazole (0.085 g, 0.48 mmol). The resulting solution was filtered, and blue block crystals were obtained at room temperature on slow evaporation of the solvent over several days.

Refinement

H atoms were placed at calculated positions and were treated as riding on the parent C atoms with C—H = 0.93–0.97 and with $U_{iso}(H) = 1.2U_{eq}(C)$.

Figures

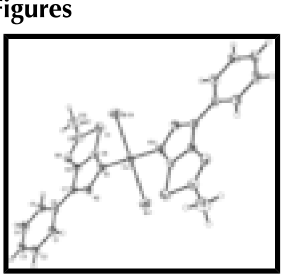

Fig. 1. The molecular structure of (I), showing the atom-numbering scheme and displacement ellipsoids drawn at the 50% probability level. Unlabelled atoms and atoms with the suffix A are related to the labelled atoms by the symmetry operator (1 − *x*, 1 − *y*, −*z*).

Dibromidobis(6-methyl-3-phenyl-s-triazolo[3,4-*b*][1,3,4]thiadiazole-κN^1)\ copper(II)

Crystal data

$[CuBr_2(C_{10}H_8N_4S)_2]$	$Z = 1$
$M_r = 655.89$	$F_{000} = 323$
Triclinic, $P\overline{1}$	$D_x = 1.869$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 6.8286$ (10) Å	Cell parameters from 1927 reflections
$b = 8.5231$ (13) Å	$\theta = 1.9$–25.2°
$c = 11.3654$ (16) Å	$\mu = 4.57$ mm^{-1}
$\alpha = 98.442$ (2)°	$T = 298$ (2) K
$\beta = 105.614$ (2)°	Block, blue
$\gamma = 108.859$ (2)°	0.44 × 0.31 × 0.22 mm
$V = 582.69$ (15) Å^3	

Data collection

Bruker APEXII area-detector diffractometer	1927 independent reflections
Radiation source: fine-focus sealed tube	1430 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.101$
$T = 298(2)$ K	$\theta_{max} = 25.2$°
φ and ω scans	$\theta_{min} = 1.9$°
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$h = -8 \rightarrow 8$
$T_{min} = 0.196$, $T_{max} = 0.366$	$k = -10 \rightarrow 10$
3511 measured reflections	$l = -13 \rightarrow 13$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.041$	H-atom parameters constrained
$wR(F^2) = 0.106$	$w = 1/[\sigma^2(F_o^2) + (0.0555P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.89$	$(\Delta/\sigma)_{max} < 0.001$
1927 reflections	$\Delta\rho_{max} = 0.74$ e Å^{-3}
152 parameters	$\Delta\rho_{min} = -0.82$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

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

	x	y	z	U_{iso}*/U_{eq}
Br1	0.85241 (9)	0.72698 (7)	0.06813 (5)	0.0689 (3)
Cu1	0.5000	0.5000	0.0000	0.0354 (2)
S1	0.3985 (2)	0.08848 (13)	0.13106 (10)	0.0422 (3)
N1	0.5615 (6)	0.4521 (4)	0.1695 (3)	0.0372 (9)
N2	0.6696 (6)	0.5812 (4)	0.2825 (3)	0.0373 (8)
N3	0.6000 (6)	0.3339 (4)	0.3277 (3)	0.0313 (8)
N4	0.5775 (6)	0.1935 (4)	0.3769 (3)	0.0364 (8)
C1	0.8741 (8)	0.7801 (6)	0.5408 (4)	0.0427 (11)
H1	0.8617	0.8371	0.4771	0.051*
C2	0.9722 (8)	0.8728 (6)	0.6678 (4)	0.0488 (12)
H2	1.0251	0.9920	0.6893	0.059*
C3	0.9893 (8)	0.7859 (7)	0.7602 (4)	0.0482 (12)
H3	1.0539	0.8478	0.8445	0.058*
C5	0.8168 (8)	0.5183 (6)	0.6051 (4)	0.0412 (11)
H4	0.7661	0.3992	0.5848	0.049*
C6	0.7953 (7)	0.6014 (5)	0.5107 (4)	0.0321 (9)
C4	0.9144 (9)	0.6115 (6)	0.7317 (4)	0.0498 (12)
H6	0.9280	0.5551	0.7958	0.060*
C8	0.5198 (7)	0.3057 (5)	0.2006 (4)	0.0349 (10)
C9	0.4788 (8)	0.0574 (6)	0.2846 (4)	0.0410 (11)
C10	0.4271 (9)	−0.1187 (6)	0.3017 (5)	0.0628 (15)
H17A	0.4735	−0.1134	0.3902	0.094*
H17B	0.5029	−0.1739	0.2613	0.094*
H17C	0.2715	−0.1829	0.2645	0.094*
C7	0.6928 (7)	0.5087 (5)	0.3755 (4)	0.0321 (9)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0591 (4)	0.0724 (4)	0.0373 (3)	−0.0128 (3)	0.0003 (3)	0.0209 (3)
Cu1	0.0443 (5)	0.0328 (4)	0.0219 (4)	0.0077 (3)	0.0087 (3)	0.0071 (3)
S1	0.0511 (8)	0.0350 (6)	0.0336 (6)	0.0126 (5)	0.0102 (6)	0.0056 (5)

N1	0.045 (2)	0.0359 (19)	0.0236 (17)	0.0093 (17)	0.0078 (17)	0.0070 (15)
N2	0.045 (2)	0.0343 (19)	0.0250 (18)	0.0103 (17)	0.0083 (17)	0.0049 (15)
N3	0.038 (2)	0.0324 (19)	0.0257 (17)	0.0148 (16)	0.0108 (16)	0.0095 (15)
N4	0.041 (2)	0.039 (2)	0.0342 (19)	0.0186 (17)	0.0131 (18)	0.0151 (17)
C1	0.047 (3)	0.046 (3)	0.032 (2)	0.017 (2)	0.012 (2)	0.007 (2)
C2	0.046 (3)	0.050 (3)	0.036 (3)	0.011 (2)	0.008 (2)	−0.005 (2)
C3	0.042 (3)	0.070 (3)	0.027 (2)	0.019 (3)	0.011 (2)	0.000 (2)
C5	0.048 (3)	0.043 (2)	0.032 (2)	0.016 (2)	0.014 (2)	0.007 (2)
C6	0.034 (2)	0.040 (2)	0.025 (2)	0.016 (2)	0.013 (2)	0.0071 (18)
C4	0.057 (3)	0.066 (3)	0.028 (2)	0.023 (3)	0.016 (2)	0.015 (2)
C8	0.038 (3)	0.036 (2)	0.029 (2)	0.012 (2)	0.014 (2)	0.0072 (18)
C9	0.042 (3)	0.044 (3)	0.043 (3)	0.021 (2)	0.014 (2)	0.018 (2)
C10	0.073 (4)	0.046 (3)	0.063 (4)	0.025 (3)	0.006 (3)	0.021 (3)
C7	0.032 (2)	0.037 (2)	0.029 (2)	0.0130 (19)	0.0116 (19)	0.0100 (18)

Geometric parameters (Å, °)

Br1—Cu1	2.3834 (6)	C1—H1	0.930
Cu1—N1^{i}	1.990 (3)	C2—C3	1.372 (7)
Cu1—N1	1.990 (3)	C2—H2	0.930
Cu1—Br1^{i}	2.3834 (6)	C3—C4	1.362 (7)
S1—C8	1.722 (4)	C3—H3	0.930
S1—C9	1.770 (5)	C5—C6	1.372 (6)
N1—C8	1.311 (5)	C5—C4	1.397 (6)
N1—N2	1.398 (4)	C5—H4	0.930
N2—C7	1.300 (5)	C6—C7	1.477 (5)
N3—C8	1.353 (5)	C4—H6	0.930
N3—C7	1.372 (5)	C9—C10	1.482 (6)
N3—N4	1.376 (4)	C10—H17A	0.960
N4—C9	1.287 (6)	C10—H17B	0.960
C1—C6	1.394 (6)	C10—H17C	0.960
C1—C2	1.400 (6)		
N1^{i}—Cu1—N1	180	C6—C5—C4	120.4 (4)
N1^{i}—Cu1—Br1	89.18 (10)	C6—C5—H4	119.8
N1—Cu1—Br1	90.82 (10)	C4—C5—H4	119.8
N1^{i}—Cu1—Br1^{i}	90.82 (10)	C5—C6—C1	119.9 (4)
N1—Cu1—Br1^{i}	89.18 (10)	C5—C6—C7	122.5 (4)
Br1—Cu1—Br1^{i}	180	C1—C6—C7	117.6 (4)
C8—S1—C9	87.4 (2)	C3—C4—C5	119.2 (4)
C8—N1—N2	106.6 (3)	C3—C4—H6	120.4
C8—N1—Cu1	130.2 (3)	C5—C4—H6	120.4
N2—N1—Cu1	123.2 (2)	N1—C8—N3	110.1 (4)
C7—N2—N1	108.2 (3)	N1—C8—S1	140.1 (3)
C8—N3—C7	106.1 (3)	N3—C8—S1	109.8 (3)
C8—N3—N4	117.9 (3)	N4—C9—C10	123.5 (4)
C7—N3—N4	135.9 (3)	N4—C9—S1	116.5 (3)
C9—N4—N3	108.2 (3)	C10—C9—S1	119.9 (4)

C6—C1—C2	119.4 (4)	C9—C10—H17A	109.5
C6—C1—H1	120.3	C9—C10—H17B	109.5
C2—C1—H1	120.3	H17A—C10—H17B	109.5
C3—C2—C1	119.3 (4)	C9—C10—H17C	109.5
C3—C2—H2	120.3	H17A—C10—H17C	109.5
C1—C2—H2	120.3	H17B—C10—H17C	109.5
C4—C3—C2	121.7 (4)	N2—C7—N3	109.0 (3)
C4—C3—H3	119.1	N2—C7—C6	124.9 (4)
C2—C3—H3	119.1	N3—C7—C6	126.1 (4)

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

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C10—H17C···Br1^{ii}	0.96	2.90	3.769 (5)	151
C1—H1···N2	0.93	2.56	2.871 (5)	100
C5—H4···N4	0.93	2.45	3.122 (6)	129

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

Fig. 1