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{Dimethyl [2,2′-(ethane-1,2-diyldioxy)-bis(benzylidenehydrazono)]bis(dithioformato)-κ^4S,N,N',S'}copper(II)

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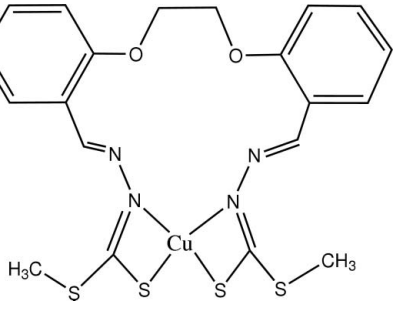
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.007 Å; R factor = 0.042; wR factor = 0.061; data-to-parameter ratio = 14.0.

The Cu atom in the title complex, $[Cu(C_{20}H_{20}N_4O_2S_4)]$, lies on a crystallographic twofold rotation axis and exists in a distorted square-planar coordination geometry. The geometry is distorted towards octahedral owing to the interactions of the ether O atoms.

Related literature

For related literature, see: Balamurugan *et al.* (2004); Knoblauch *et al.* (1999); Solomon *et al.* (1992).



Experimental

Crystal data

$[Cu(C_{20}H_{20}N_4O_2S_4)]$
M_r = 540.23
Orthorhombic, *Iba*2
a = 11.634 (2) Å
b = 12.983 (2) Å
c = 14.908 (3) Å
V = 2251.8 (7) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 1.37 mm^{-1}
T = 293 (2) K
0.2 × 0.15 × 0.1 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.782, T_{max} = 0.872
5393 measured reflections
1985 independent reflections
1557 reflections with $I > 2\sigma(I)$
R_{int} = 0.051

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.061
S = 0.99
1985 reflections
142 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.56 e Å^{-3}
$\Delta\rho_{min}$ = −0.59 e Å^{-3}
Absolute structure: Flack (1983), 942 Friedel pairs
Flack parameter: −0.03 (2)

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; 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: NG2251).

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supplementary materials

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{Dimethyl [2,2'-(ethane-1,2-diyldioxy)bis(benzylidenehydrazono)]bis(dithioformato)-κ^4S,N,N',S'}copper(II)

G.-Q. Mei and K.-L. Huang

Comment

Blue copper centers in Type I proteins are involved in electron transfer process such as photosynthesis, nitrogen fixation and lignin degradation (Solomon *et al.*,1992). Investigations of the coordination chemistry of $[CuN_2S_2]$ complexes revolve around the development of mimics for blue copper centers (Balamurugan *et al.*, 2004). Few $[CuN_2S_2]$ complexes and their crystal structures have been reported (Knoblauch *et al.*,1999). In (I), the ethane-1,2-bis((2-oxybenzylidene)hydrazono)(methylthio)methanethiolato dianion, like a pair of plipers, clamps the Cu atom through N and S atom to render a square-planar geometry at the metal. The two ether oxygen atoms are weakly involved [Cu···O 2.718 (2) Å] and their proximity distorts the geometry. The central ion deviates 0.363 (1) Å from the least-square plane.

Experimental

To a DMF solution (20 ml) of ethane-1,2-bis[(2-oxybenzylidene)hydrazono](methylthio)methanethiol (1 mmol), a methanolic solution (15 ml) of $Cu_2(ClO_4)\cdot 6H_2O$ (1 mmol) was added. Blue block-shaped crystals were obtained by diffusion of Et_2O into the mother liquour over one week.

Refinement

The carbon-bound H atoms were generated geometrically (C–H 0.93 to 0.97 Å) and were included in the refinement in the riding model approximation, with U(H) set to 1.2U_{eq}(C).

Figures

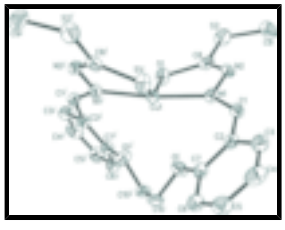

Fig. 1. **Figure 1**. Molecular structure of (I), with displacement ellipsoids drawn at the 30% probability level. H atoms have been omitted. [Symmetry codes: (i) 1 − x, 2 − y,z]

{Dimethyl [2,2'-(ethane-1,2-diyldioxy)bis(benzylidenehydrazono)]bis(dithioformato)- κ^4S,N,N',S'}copper(II)

Crystal data

$[Cu(C_{20}H_{20}N_4O_2S_4)]$	F_{000} = 1108
M_r = 540.23	D_x = 1.593 Mg m^{-3}

Orthorhombic, *Iba*2	Mo *K*α radiation λ = 0.71073 Å
Hall symbol: I 2 -2c	Cell parameters from 516 reflections
a = 11.634 (2) Å	θ = 3.1–19.6º
b = 12.983 (2) Å	μ = 1.37 mm^{-1}
c = 14.908 (3) Å	*T* = 293 (2) K
V = 2251.8 (7) $Å^3$	Block, blue
Z = 4	0.2 × 0.15 × 0.1 mm

Data collection

Bruker SMART CCD area-detector diffractometer	1985 independent reflections
Radiation source: fine-focus sealed tube	1557 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.051
T = 293(2) K	θ_{max} = 25.0º
φ and ω scans	θ_{min} = 2.4º
Absorption correction: multi-scan (SADABS; Bruker, 2000)	*h* = −12→13
T_{min} = 0.782, T_{max} = 0.872	*k* = −12→15
5393 measured reflections	*l* = −17→17

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)]$ = 0.042	$w = 1/[\sigma^2(F_o^2) + (0.005P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.061	$(\Delta/\sigma)_{max} < 0.001$
S = 0.99	$\Delta\rho_{max}$ = 0.56 e $Å^{-3}$
1985 reflections	$\Delta\rho_{min}$ = −0.59 e $Å^{-3}$
142 parameters	Extinction correction: none
1 restraint	Absolute structure: Flack (1983), from 942 Friedel pairs
Primary atom site location: structure-invariant direct methods	Flack parameter: −0.03 (2)
Secondary atom site location: difference Fourier map	

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}
Cu1	0.5000	1.0000	0.68635 (6)	0.0349 (2)
N1	0.5939 (3)	0.8681 (3)	0.6945 (3)	0.0355 (9)
N2	0.6911 (3)	0.8713 (3)	0.7513 (2)	0.0368 (10)
O1	0.4892 (3)	0.8974 (2)	0.5277 (2)	0.0491 (9)
C7	0.4388 (4)	0.8036 (4)	0.5383 (3)	0.0378 (12)
C6	0.3541 (4)	0.7662 (4)	0.4830 (3)	0.0476 (15)
H6	0.3259	0.8068	0.4366	0.057*
C5	0.3112 (5)	0.6691 (5)	0.4963 (4)	0.0570 (16)
H5	0.2510	0.6457	0.4606	0.068*
C4	0.3548 (5)	0.6071 (4)	0.5603 (4)	0.0600 (18)
H4	0.3261	0.5408	0.5676	0.072*
C3	0.4430 (5)	0.6425 (4)	0.6154 (4)	0.0531 (16)
H3	0.4745	0.5989	0.6584	0.064*
C2	0.4845 (5)	0.7431 (3)	0.6066 (3)	0.0392 (13)
C1	0.5741 (4)	0.7768 (3)	0.6668 (3)	0.0401 (13)
H1	0.6233	0.7258	0.6880	0.048*
C10	0.4623 (4)	0.9540 (3)	0.4493 (4)	0.0472 (15)
H10A	0.3821	0.9745	0.4498	0.057*
H10B	0.4762	0.9126	0.3962	0.057*
S1	0.66889 (11)	1.07741 (9)	0.72688 (11)	0.0513 (4)
S2	0.85065 (12)	0.97951 (11)	0.83033 (10)	0.0638 (5)
C8	0.7281 (4)	0.9633 (4)	0.7652 (3)	0.0441 (14)
C9	0.8979 (4)	0.8506 (4)	0.8538 (4)	0.0684 (19)
H9A	0.8364	0.8032	0.8422	0.103*
H9B	0.9205	0.8457	0.9156	0.103*
H9C	0.9623	0.8341	0.8161	0.103*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0355 (5)	0.0335 (4)	0.0357 (4)	−0.0002 (4)	0.000	0.000
N1	0.032 (2)	0.034 (2)	0.041 (3)	−0.0024 (16)	−0.001 (2)	−0.005 (2)
N2	0.032 (2)	0.044 (3)	0.034 (3)	0.0000 (19)	−0.0069 (19)	0.004 (2)
O1	0.066 (3)	0.035 (2)	0.047 (2)	−0.0108 (18)	−0.023 (2)	0.0052 (17)
C7	0.041 (3)	0.028 (3)	0.045 (3)	−0.004 (2)	0.002 (3)	−0.001 (3)
C6	0.053 (4)	0.037 (4)	0.053 (4)	−0.006 (3)	−0.008 (3)	−0.004 (3)
C5	0.052 (4)	0.059 (4)	0.060 (4)	−0.009 (3)	−0.010 (3)	−0.009 (3)
C4	0.070 (5)	0.050 (4)	0.060 (4)	−0.025 (3)	0.008 (4)	−0.013 (3)
C3	0.072 (4)	0.037 (3)	0.050 (4)	−0.006 (3)	0.005 (3)	0.002 (3)
C2	0.045 (3)	0.032 (3)	0.041 (3)	−0.002 (3)	0.004 (3)	−0.005 (2)
C1	0.041 (3)	0.042 (3)	0.038 (4)	0.005 (2)	0.003 (3)	0.005 (3)
C10	0.069 (4)	0.047 (3)	0.026 (3)	0.000 (2)	−0.007 (3)	−0.002 (3)

S1	0.0401 (7)	0.0390 (7)	0.0746 (10)	−0.0035 (6)	−0.0068 (8)	−0.0048 (8)
S2	0.0411 (9)	0.0754 (12)	0.0749 (11)	−0.0001 (7)	−0.0160 (8)	−0.0220 (9)
C8	0.038 (3)	0.055 (4)	0.039 (3)	−0.001 (3)	0.006 (3)	−0.011 (3)
C9	0.047 (4)	0.088 (5)	0.070 (5)	0.011 (3)	−0.010 (3)	0.014 (4)

Geometric parameters (Å, °)

Cu1—N1^{i}	2.035 (3)	C4—C3	1.392 (7)
Cu1—N1	2.035 (3)	C4—H4	0.9300
Cu1—S1^{i}	2.2882 (13)	C3—C2	1.398 (6)
Cu1—S1	2.2882 (13)	C3—H3	0.9300
N1—C1	1.276 (5)	C2—C1	1.444 (6)
N1—N2	1.413 (4)	C1—H1	0.9300
N2—C8	1.287 (5)	C10—C10^{i}	1.482 (8)
O1—C7	1.361 (5)	C10—H10A	0.9700
O1—C10	1.416 (5)	C10—H10B	0.9700
C7—C6	1.373 (6)	S1—C8	1.731 (5)
C7—C2	1.392 (6)	S2—C8	1.738 (5)
C6—C5	1.370 (7)	S2—C9	1.796 (5)
C6—H6	0.9300	C9—H9A	0.9600
C5—C4	1.348 (7)	C9—H9B	0.9600
C5—H5	0.9300	C9—H9C	0.9600
N1^{i}—Cu1—N1	173.2 (2)	C2—C3—H3	119.8
N1^{i}—Cu1—S1^{i}	83.85 (10)	C7—C2—C3	117.6 (5)
N1—Cu1—S1^{i}	94.34 (10)	C7—C2—C1	124.0 (4)
N1^{i}—Cu1—S1	94.34 (10)	C3—C2—C1	118.3 (5)
N1—Cu1—S1	83.85 (10)	N1—C1—C2	127.8 (4)
S1^{i}—Cu1—S1	149.38 (9)	N1—C1—H1	116.1
C1—N1—N2	111.4 (4)	C2—C1—H1	116.1
C1—N1—Cu1	131.7 (3)	O1—C10—C10^{i}	106.7 (3)
N2—N1—Cu1	116.1 (3)	O1—C10—H10A	110.4
C8—N2—N1	113.1 (4)	C10^{i}—C10—H10A	110.4
C7—O1—C10	117.8 (4)	O1—C10—H10B	110.4
O1—C7—C6	123.7 (5)	C10^{i}—C10—H10B	110.4
O1—C7—C2	115.2 (4)	H10A—C10—H10B	108.6
C6—C7—C2	120.9 (5)	C8—S1—Cu1	93.03 (17)
C5—C6—C7	120.0 (5)	C8—S2—C9	104.3 (2)
C5—C6—H6	120.0	N2—C8—S1	127.5 (4)
C7—C6—H6	120.0	N2—C8—S2	118.5 (4)
C4—C5—C6	121.0 (6)	S1—C8—S2	114.0 (3)
C4—C5—H5	119.5	S2—C9—H9A	109.5
C6—C5—H5	119.5	S2—C9—H9B	109.5
C5—C4—C3	119.9 (5)	H9A—C9—H9B	109.5
C5—C4—H4	120.0	S2—C9—H9C	109.5
C3—C4—H4	120.0	H9A—C9—H9C	109.5
C4—C3—C2	120.5 (5)	H9B—C9—H9C	109.5
C4—C3—H3	119.8		

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

Fig. 1