Er2‡	0.44011 (2)	−0.05904 (2)	0.426368 (14)	0.03443 (8)
Ti1	1/2	0	0.28555 (6)	0.0378 (3)
O1	0.5086 (3)	0.1354 (3)	0.3826 (2)	0.0437 (14)
O2	0.3642 (3)	−0.0083 (3)	0.3834 (2)	0.0452 (14)
O3	0.3994 (3)	−0.1021 (3)	0.4896 (2)	0.0525 (12)
O4	0.4324 (3)	0.0657 (3)	0.2880 (2)	0.0443 (11)
O5	0.5464 (2)	−0.0468 (2)	0.4521 (2)	0.0366 (9)
O6	0.3482 (3)	0.1550 (3)	0.3786 (2)	0.0533 (12)
O7	0.4524 (3)	−0.0514 (3)	0.2482 (3)	0.076 (2)
O8	1/2	0	0.3580 (2)	0.0337 (12)
C1	0.5289 (5)	0.1969 (4)	0.3705 (5)	0.071 (3)
C2	0.3035 (7)	−0.0213 (8)	0.3754 (9)	0.125 (5)
C3	0.3757 (6)	−0.1389 (5)	0.5310 (4)	0.080 (3)
C4	0.4133 (4)	0.1000 (4)	0.2438 (3)	0.051 (2)
C5	0.5709 (4)	−0.0681 (4)	0.5012 (3)	0.048 (2)
C6	0.3021 (7)	0.2005 (6)	0.3829 (7)	0.113 (5)
C7	0.4009 (6)	−0.0645 (5)	0.2172 (5)	0.078 (4)
C8	0.4937 (6)	0.2435 (5)	0.3902 (6)	0.105 (5)
C9	0.5963 (5)	0.2076 (6)	0.3881 (6)	0.089 (4)
C10	0.2801 (9)	−0.0795 (8)	0.3861 (10)	0.198 (10)
C11	0.2621 (7)	0.0168 (8)	0.3621 (8)	0.178 (8)
C12	0.3914 (6)	−0.1095 (6)	0.5804 (4)	0.082 (3)
C13	0.3056 (7)	−0.1499 (7)	0.5220 (6)	0.124 (6)
C14	0.3422 (4)	0.1041 (5)	0.2416 (4)	0.070 (3)
C15	0.4415 (5)	0.1649 (5)	0.2469 (6)	0.091 (4)
C16	0.5575 (5)	−0.1390 (5)	0.5085 (5)	0.086 (4)
C17	0.6400 (5)	−0.0570 (4)	0.5061 (4)	0.064 (3)
C18	0.3094 (5)	0.2535 (4)	0.3478 (6)	0.080 (3)
C19	0.2736 (6)	0.2075 (6)	0.4288 (7)	0.110 (5)
C20	0.4205 (9)	−0.0693 (10)	0.1618 (6)	0.133 (7)
C21	0.3770 (8)	−0.1304 (8)	0.2302 (9)	0.172 (10)

† Site occupancy = 0.90. ‡ Site occupancy = 0.10.

Table 2. *Selected geometric parameters (Å, °)*

Tb1—O6	2.061 (4)	Tb2—O8	2.520 (4)
Tb1—O4	2.226 (5)	Ti1—O7	1.783 (6)
Tb1—O1	2.281 (6)	Ti1—O8	1.865 (6)
Tb1—O2	2.322 (6)	Ti1—O4	2.021 (5)
Tb1—O5^{i}	2.391 (4)	O1—C1	1.423 (10)
Tb1—O8	2.6181 (9)	O2—C2	1.347 (15)
Tb2—O3	2.066 (5)	O3—C3	1.420 (10)
Tb2—O2	2.247 (6)	O4—C4	1.414 (9)
Tb2—O1^{i}	2.270 (6)	O5—C5	1.442 (8)
Tb2—O5^{i}	2.380 (5)	O6—C6	1.393 (9)
Tb2—O5	2.387 (5)	O7—C7	1.391 (12)
C3—O3—Tb2	172.4 (7)	C7—O7—Ti1	152.6 (7)
C6—O6—Tb1	178.7 (10)		

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

The absolute structure for the compound was chosen according to the Flack (1983) parameter. Site-occupation factors for the Tb and Er atoms were fixed at 0.9 and 0.1, respectively. All H atoms were placed in calculated positions with a common fixed displacement parameter of 0.08 Å^2. Methyl groups were constrained as rigid tetrahedra (C—H 0.98 Å) with H atoms freely rotating around the C—C bonds and riding on the C atoms. Tertiary H atoms were riding on tied C atoms (C—H 1.00 Å).

Data collection: *DIF*4 (Stoe & Cie, 1990). Cell refinement: *DIF*4. Data reduction: *X-RED* (Stoe & Cie, 1996). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AB1489). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). C**54**, 31–33

Bis(4-methoxybenzaldehyde thiosemicarbazonato-*S*,N^4)copper(II)

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Abstract

The Schiff base ligand in the title complex, $[Cu(C_9H_{10}N_3OS)_2]$, lost a proton from its tautomeric thiol form and coordinated to Cu^{II} *via* the mercapto S and β-N atoms. The geometry around Cu^{II} is square planar with two equivalent Cu—N and Cu—S bonds. The two phenyl rings and the coordination moieties are in one plane forming an extensive electronic delocalization system.

Comment

Transition metal organometallic and coordination complexes have emerged as potential building blocks for non-linear optical (NLO) materials due to the various

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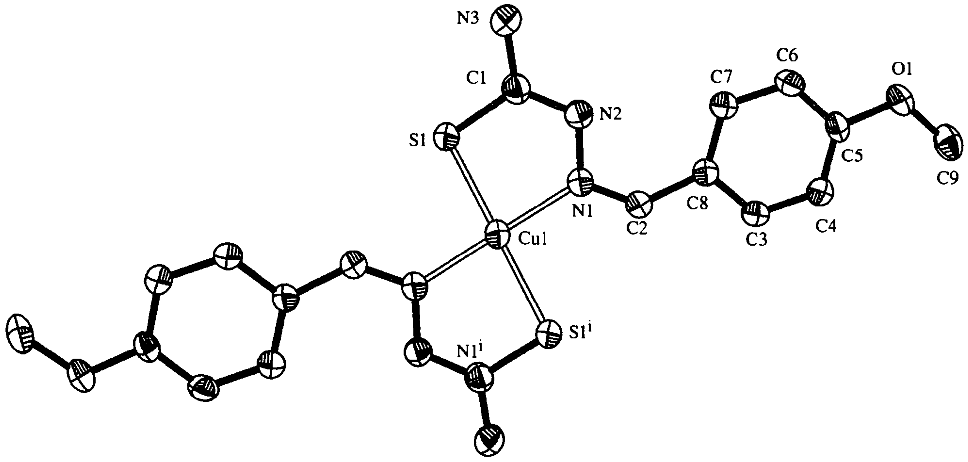
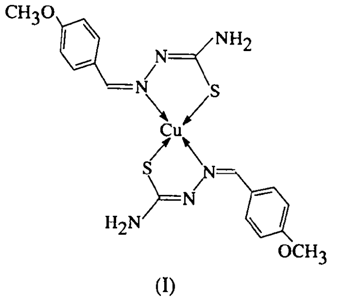


Fig. 1. View of the title compound. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry code: (i) $-x$, $-y$, $-z$.]

excited states present in these systems, as well as the ability to manipulate metal–organic ligand interactions (Long, 1995; Bella *et al.*, 1994). In comparison with organic molecules, metal complexes offer a wider variety of structures, with comparable or, in some cases, higher environmental stability and a much greater diversity of tunable electronic properties as a result of the coordinated metal center (Nalwa, 1991; Laidlaw *et al.*, 1994). Thiosemicarbazones are known to coordinate readily with transition metals to give stable complexes, forming a long π-conjugated system by deprotonation on complex formation (Podhye & Kauffman, 1985; Tian *et al.*, 1996). Therefore, it is expected that the metal dithiocarbazato may exhibit large second-order molecular hyperpolarizability. As part of our studies on the synthesis and non-linear optical properties of thio-Schiff base metal complexes, we report here the title structure, (I), the copper(II) complex with thiosemicarbazone derived from 4-methoxylbenzaldehyde.



(I)

The coordination geometry of copper(II) is square planar with two equivalent Cu—N and Cu—S bonds. The Schiff base loses a proton from its tautomeric thiol form and acts as a singly charged bidentate ligand coordinating to copper(II) *via* the mercapto S and β-N atoms. The copper(II) does not occupy the coordination chelate plane defined by S1, N1, N2 and C1 (mean deviation from the best plane is 0.062 Å); the distance of copper(II) to the plane is 0.16 Å. All bond distances in the side chain are intermediate between a formal single bond and a double bond, indicating the high electron delocalization in the π system of the whole molecule.

There is a short contact (Fig. 2) between Cu1 and N3 [Cu1···N3*A*($-x$, $1-y$, $-z$) 3.438 Å]. The intermolecular contact between N3 and O1*B*($-1-x$, $1-y$, $-z$) [3.163 (4) Å], indicates a soft intermolecular hydrogen bond [N3—H3···O1*B* 145.1 (3)°]. The second H atom on N3 seems to have no clear hydrogen-bond acceptor.

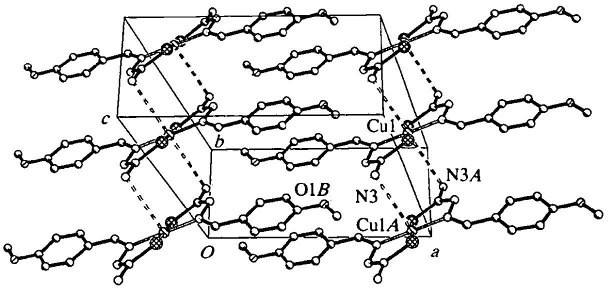


Fig. 2. Packing diagram viewed down the c axis. See text for symmetry codes.

Experimental

The title compound was synthesized by refluxing the methanol solution of thiosemicarbazone (0.42 g, 2 mmol) and copper acetate tetrahydrate (0.50 g, 2 mmol) for 4 h. The dark green crystalline solid formed was isolated and dried under vacuum. Good quality crystals were obtained by evaporating a methanol solution in air.

Crystal data

$[Cu(C_9H_{10}N_3OS)_2]$
$M_r = 480.06$
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å

Monoclinic
$P2_1/c$
$a = 12.504\,(3)$ Å
$b = 5.5750\,(10)$ Å
$c = 14.450\,(2)$ Å
$\beta = 102.300\,(10)°$
$V = 984.2\,(3)$ Å^3
$Z = 2$
$D_x = 1.620$ Mg m^{-3}
D_m not measured

Cell parameters from 136 reflections
$\theta = 1.75–27.50°$
$\mu = 1.351$ mm^{-1}
$T = 293\,(2)$ K
Prism
0.32 × 0.22 × 0.16 mm
Dark blue

Data collection

Rigaku RAXIS IIC imaging-plate diffractometer
Oscillation IP photos
Absorption correction: *ABSCOR* (Higashi, 1995)
$T_{\min} = 0.65$, $T_{\max} = 0.88$
2362 measured reflections
2260 independent reflections

1777 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.018$
$\theta_{\max} = 27.50°$
$h = 0 \rightarrow 16$
$k = 0 \rightarrow 7$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.132$
$S = 1.068$
2260 reflections
133 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.08P)^2 + 0.13P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.390$ e Å^{-3}
$\Delta\rho_{\min} = -0.446$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Cu1—N1$^{\rm i}$	1.922 (2)	N1—C2	1.290 (4)
Cu1—N1	1.922 (2)	N1—N2	1.400 (3)
Cu1—S1	2.1842 (7)	N2—C1	1.307 (3)
Cu1—S1$^{\rm i}$	2.1842 (7)	N3—C1	1.340 (4)
S1—C1	1.740 (3)		
N1$^{\rm i}$—Cu1—N1	180.0	N1$^{\rm i}$—Cu1—S1$^{\rm i}$	84.86 (7)
N1$^{\rm i}$—Cu1—S1	95.14 (7)	S1—Cu1—S1$^{\rm i}$	180.0

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

Data were collected on a Rigaku RAXIS IIC imaging-plate diffractometer using Mo $K\alpha$ radiation from a rotating-anode generator operating at 50 KV and 90 mA ($2\theta_{\max} = 55.2°$, 60 oscillation frames in the range of 0–180°), exposure 8 min per frame. Absorption corrections were made using the *ABSCOR* (Higashi, 1995) program based on Fourier-coefficient fitting to the intensities of symmetry-equivalent reflections (Tanner & Krause, 1990*a*,*b*; Kraus & Phillips, 1992; Higashi, 1995). All the non-H atoms were refined anisotropically. All H atoms were placed in calculated positions (C—H 0.96 Å), assigned fixed isotropic displacement parameters 1.2 times the equivalent isotropic *U* value of the attached atom and allowed to ride on their respective parent atoms.

Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1994). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1119). Services for accessing these data are described at the back of the journal.

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Aqua(dicyanonitrosomethanido-*O*)bis(1,10-phenanthroline-*N*,*N'*)copper(II) Dicyanonitrosomethanide

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Abstract

The crystal structure of the title complex, $[\mathrm{Cu\{ONC(CN)_2\}(C_{12}H_8N_2)_2(H_2O)}][\mathrm{ONC(CN)_2}]$, is composed of discrete $[\mathrm{Cu(dcnm)(H_2O)(phen)_2}]^+$ cations and dcnm anions [phen is 1,10-phenanthroline and dcnm is dicyanonitrosomethanide, $\mathrm{ONC(CN)_2^-}$]. The coordination polyhedron of the Cu$^{\rm II}$ atom is a distorted elongated tetragonal bipyramid with a $\mathrm{CuN_4O_2}$ chromophore. The water molecule occupies an axial position, while the dcnm anion occupies an equatorial position.

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