Redetermination of the crystal structure of bis(*N*-methyl-*N*-phenyl-dithiocarbamato-$\kappa^2 S,S'$)copper(II), $C_{16}H_{16}CuN_2S_4$

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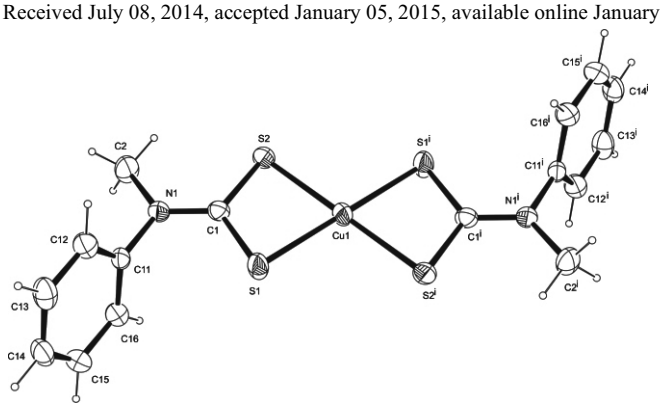

Abstract

$C_{16}H_{16}CuN_2S_4$, monoclinic, $P2_1/n$ (no. 14), a = 7.6067(2) Å, b = 6.5835(2) Å, c = 18.5042(5) Å, β = 97.2900(10)°, V = 919.2 Å^3, Z = 2, $R_{gt}(F)$ = 0.0243, $wR_{ref}(F^2)$ = 0.0626, T = 200 K.

Table 1. Data collection and handling.

Crystal:	green platelets, size 0.044×0.244×0.380 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	16.41 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II CCD, φ and ω
$2\theta_{max}$:	56.62°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	12501, 2287
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2012
$N(param)_{refined}$:	107
Programs:	SHELX, SAINT, SADABS, SHELXle, ORTEP-3, PLATON, MERCURY [8–13]

Source of material

An aqueous solution of copper(II)chloride dihydrate (0.21 g, 1.25 mmol) and ammonium *N*-methyl-*N*-phenyl dithiocarbamate (0.50 g, 2.5 mmol) were reacted together. Brown precipitates were obtained, which were filtered, and washed thoroughly with water and ethanol. The crude product was re-crystallized from a mixture of acetone and ethanol, and light brown crystals suitable for X-ray diffraction were obtained by slow evaporation of acetone and *n*-hexane solution at room temperature.

Experimental details

Carbon-bound H atoms were placed in calculated positions and were included in the refinement in the riding model approximation, with U_{iso}(H) set to 1.2U_{eq}(C). The H atoms of the methyl group was allowed to rotate with a fixed angle around the C–C bond to best fit the experimental electron density (HFIX 137 in the SHELX program suite [8]), with U_{iso}(H) set to 1.5 U_{eq}(C).

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Discussion

Dithiocarbamates are valuable compounds due to their interesting chemistry, and wide ranges of applications [1]. The anionic ligands [$^-S_2CNR_1R_2$] are versatile, and have been widely studied due to their ability to form complexes with most of the transition elements. The interesting redox chemistry of dithiocarbamate-containing transition metal complexes has significant biological implications, and among the transition metal ions. Copper dithiocarbamate is one of the preferred candidates for the development of anticancer agents [2]. It has also been employed as synthetic precursors for the deposition of CuS nanoparticles [3, 4]. Copper (II)bis(dithiocarbamate) complexes can assume either a monomeric or dimeric structure. While the monomeric structures adopt the square planar arrangement, the dimeric complexes have five-coordinate geometry at the copper ion [5]. The crystal structure of the title compound has been reported once before [6], where the data was obtained at room temperature and the structure reported in a non-standard space group, with the 3D coordinates of the methyl hydrogens not given. The title compound is a square planar complex of Cu(II) with two molecules of *N*-methyl-*N*-phenyl-dithiocarbamate. The complex is centrosymmetric with half the complex in the asymmetric unit. The phenyl rings are turned out the [CuS_4] plane with its least square plane making a 77.02(7)° dihedral angle. The Cu1 to S1 and S2 bond lengths determined here are 2.2803(5) and 2.3252(4) Å respectively while the bond lengths determined previously [6] are slightly shorter at 2.255(2) and 2.319(2) Å. The S–Cu–S bond angle of 77.63(2)° is slightly smaller than the previous reported [6] angle of 77.87°. The median metrical parameters for other Cu dithiocarbamate complexes whose structural data have been deposited with the Cambridge Structural Database [7] are 2.312 Å and 76.923° for the bond length and angle respectively. The only notable hydrogen bond is the intramolecular C2–H2A···S2 interaction with a distance of 2.57 Å. There are weak intermolecular C16–H16···π interactions with the Cu1, S1, S2, C1 ring linking complexes in an infinite chain along the *a* axis. The H16 to centroid distance is 2.76 Å. The dithiocarbamate phenyl rings are also linked with C14–H14···π interactions with a H14 to centroid distance of 2.86 Å.

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(2A)	4*e*	0.1270	0.5121	0.0795	0.059
H(2B)	4*e*	0.0509	0.4882	0.1558	0.059
H(2C)	4*e*	–0.0689	0.4259	0.0817	0.059
H(12)	4*e*	0.1813	0.1927	0.2561	0.036
H(13)	4*e*	0.0428	–0.0191	0.3336	0.043
H(14)	4*e*	–0.1787	–0.2433	0.2853	0.047

Table 2. continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(15)	4*e*	–0.2677	–0.2525	0.1602	0.048

Table 2. continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(16)	4*e*	–0.1287	–0.0434	0.0822	0.039

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu(1)	2*d*	½	0	0	0.0308(2)	0.0258(2)	0.0294(2)	–0.0004(1)	0.0143(1)	0.0022(1)
S(1)	4*e*	0.31794(7)	–0.09481(7)	0.08290(3)	0.0465(3)	0.0237(2)	0.0487(3)	0.0070(2)	0.0303(2)	0.0101(2)
S(2)	4*e*	0.35693(6)	0.30251(6)	0.02086(2)	0.0377(2)	0.0231(2)	0.0294(2)	–0.0037(2)	0.0146(2)	0.0029(2)
N(1)	4*e*	0.1228(2)	0.2220(2)	0.11429(7)	0.0278(7)	0.0200(6)	0.0294(7)	–0.0005(5)	0.0093(5)	0.0021(5)
C(1)	4*e*	0.2488(2)	0.1538(2)	0.07757(8)	0.0287(8)	0.0216(7)	0.0232(7)	–0.0040(6)	0.0060(6)	0.0007(6)
C(2)	4*e*	0.0521(3)	0.4292(3)	0.1073(1)	0.045(1)	0.0246(9)	0.052(1)	0.0098(8)	0.0211(9)	0.0081(8)
C(11)	4*e*	0.0400(2)	0.0895(2)	0.16256(9)	0.0241(7)	0.0202(7)	0.0295(8)	0.0023(6)	0.0114(6)	0.0006(6)
C(12)	4*e*	0.0911(2)	0.1008(3)	0.23673(9)	0.0286(8)	0.0316(9)	0.0315(8)	0.0005(7)	0.0059(7)	0.0014(7)
C(13)	4*e*	0.0085(3)	–0.0243(3)	0.2824(1)	0.039(1)	0.039(1)	0.0311(9)	0.0095(8)	0.0129(7)	0.0091(8)
C(14)	4*e*	–0.1236(3)	–0.1567(3)	0.2538(1)	0.043(1)	0.0290(9)	0.050(1)	0.0037(8)	0.0277(9)	0.0092(8)
C(15)	4*e*	–0.1755(3)	–0.1631(3)	0.1796(1)	0.038(1)	0.032(1)	0.053(1)	–0.0107(8)	0.0192(9)	–0.0053(8)
C(16)	4*e*	–0.0936(2)	–0.0395(3)	0.1333(1)	0.0332(9)	0.0327(9)	0.0335(9)	–0.0060(7)	0.0109(7)	–0.0048(7)

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