Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

(Acetato-κ*O*)(2-acetylpyridine 4-methylthiosemicarbazonato-κ^3N,N',S)copper(II) monohydrate

Emmanuel Ngwang Nfor,[a]* Xiao-Zeng You,[a] Liu Wei[a] and Grace Iniama[b]

[a]State Key Laboratory of Coordination Chemistry, Coordination Chemistry Institute, Nanjing University, Nanjing 210093, People's Republic of China, and [b]Department of Chemistry, University of Calabar, PMB 1115 Calabar, Cross River State, Nigeria

Correspondence e-mail: nforemma@yahoo.com

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.005 Å
R factor = 0.040
wR factor = 0.102
Data-to-parameter ratio = 15.1

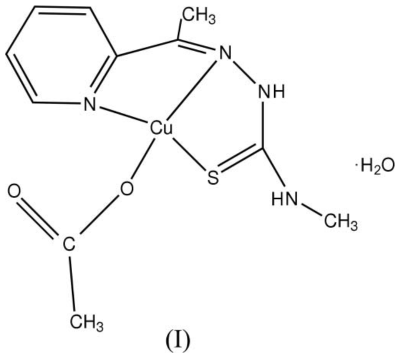
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 5 January 2006
Accepted 19 January 2006
Online 27 January 2006

In the title compound, $[Cu(C_9H_{10}N_4S)(C_2H_3O_2)]\cdot H_2O$, the Cu atom adopts a slightly distorted square-planar coordination geometry. The 2-acetylpyridine thiosemicarbazone group is very close to planar. The computed bond valencies for the Cu centre are ν(Cu—N) = 0.349 and 0.404 valence units (v.u.), ν(Cu—S) = 0.627 v.u., and ν(Cu—O) = 0.483 v.u. There is an out of plane Cu—O(acetate) bond [2.639 (13) Å], which makes a contribution of 0.08 v.u. The computed valency of the Cu atom is thus 1.94 v.u. Hydrogen bonds between pairs of molecules create dimers.

Comment

Heterocyclic thiosemicarbazones are important because of their potentially beneficial biological activity (Scovill *et al.*, 1982). These activities are due to their ability to chelate trace metals. It has been reported that copper ions enhance the antitubercular activity of thiosemicarbazone, leading to an increased interest in the chemistry of transition metal chelates of thiosemicarbazone and its derivatives. (Campbell, 1975; Kovala-Demertzi *et al.*, 1997; Siripaisampipat*et al.*, 2003). In the title compound, (I) (Fig. 1), the coordination of the Cu atom has a distorted square-planar geometry. The 2-acetylpyridine thiosemicarbazone group is very close to planar; the maximum deviation from the mass-weighted least-squares plane calculated for all 2-acetylpyridine thiosemicarbazone atoms is 0.050 (7) Å for C7. Atom Cu1 is 0.043 (4) Å from this plane, in the same direction as atoms N1 and S1. Thus, atom Cu1 lies in this plane, within experimental error. This ligand plane makes an angle of 4.52 (13)° with the Cu coordination plane.



(I)

It has been stated that the correlation between bond length and bond valence represents a measure of bond strength independent of atomic sizes (Brown, 1994). The applicaion of this correlation allows us to compare the relative importance of Cu—N, Cu—S and Cu—O bonds in (I), and to check the valence sum rule for coordinated atoms (Brown, 2002). The valence sum rule states that the sum of the valencies of the bond formed by an atom is equal to the valency (formal oxidation state) of the atom (Brown, 2002). The bond valencies in (I) were computed as $\nu = \exp[(R_{ij} - d_{ij})/0.37]$ (Brown, 1992, 1997; O'Keeffe & Brese, 1991), where R_{ij} is the bond valence parameter. The values of the $R_{\rm Cu-N}$, $R_{\rm Cu-S}$ and $R_{\rm Cu-O}$ bonds were taken as 1.61, 1.86 and 2.05, respectively (Brese & O'Keeffe, 1991). The computed bond valencies of Cu are Cu1—N1 = 0.349 valence units (v.u.), Cu1—N2 = 0.404 v.u., Cu1—S1 = 0.627 v.u. and Cu1—O1 = 0.483 v.u. and for the out-of-plane bond Cu1—O2 = 0.08 v.u. Thus, the computed valency of the atom Cu1 is 1.94 v.u. Although this computed bond valency is less than the formal oxidation state of +2, this is much less than the error of 0.25–0.30 (Palenik, 2003), which is quite a reasonable value. According to the bond-valence calculation, it can be stated that the bond strength of Cu1—N1 < Cu—N2 < Cu1—O1 < Cu1—S1. The Cu1—N1 and Cu1—N2 bonds have comparable strength and they are distinctly weaker than the Cu1—O1 and Cu1—S1 bonds, which are of comparable strength.

In the crystal structure of (I) the molecules are linked by intermolecular O—H···O hydrogen bonds (Table 2) creating a dimer between pairs of molecules. The stacking of the molecules along the *a* axis is accounted for by *π*–*π* bonding (Hunters & Sanders, 1990) (Fig. 2).

Experimental

The title compound was prepared according to the method of Kovala-Demertzi *et al.* (1997). The crystal used for data collection was grown from a dimethylformamide–water (3:1 *v*/*v*) solution by slow evaporation at room temperature.

Crystal data

$[\mathrm{Cu(C_9H_{10}N_4S)(C_2H_3O_2)}]\cdot\mathrm{H_2O}$
$M_r = 347.88$
Monoclinic, $P2_1/c$
$a = 7.0091$ (18) Å
$b = 11.116$ (3) Å
$c = 19.336$ (5) Å
$\beta = 99.442$ (4)°
$V = 1486.1$ (7) Å^3
$Z = 4$
$D_x = 1.555$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 2923 reflections
$\theta = 0$–26°
$\mu = 1.62$ mm^{-1}
$T = 293$ (2) K
Rectangular block, brown
0.30 × 0.12 × 0.07 mm

Data collection

Bruker APEX area-detector diffractometer
φ and *ω* scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
$T_{\min} = 0.792$, $T_{\max} = 0.893$
7772 measured reflections
2906 independent reflections
2299 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.057$
$\theta_{\max} = 26.0°$
$h = -8 \rightarrow 8$
$k = -13 \rightarrow 10$
$l = -23 \rightarrow 23$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.102$
$S = 1.00$
2906 reflections
192 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0519P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.44$ e Å^{-3}
$\Delta\rho_{\min} = -0.46$ e Å^{-3}

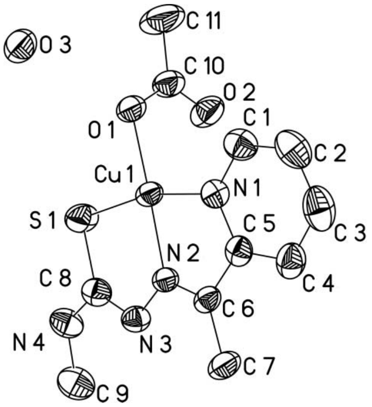


Figure 1
The molecular structure of (I), with the atom numbering, showing displacement ellipsoids at the 30% probability level. H atoms have been omitted for clarity.

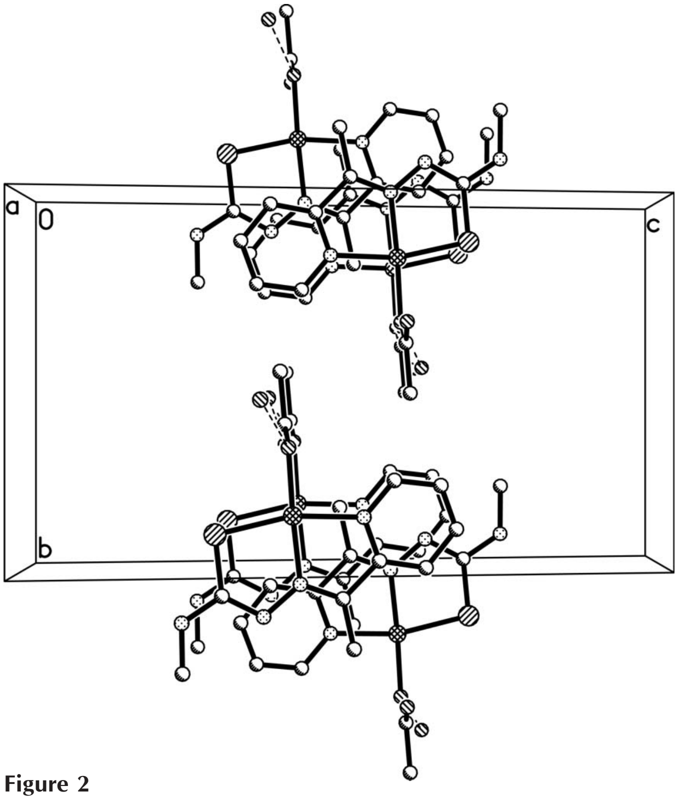


Figure 2
Part of the crystal packing of (I), viewed along the *b* axis. Hydrogen bonds are shown as dashed lines. H atoms have been omitted for clarity.

Table 1
Selected geometric parameters (Å, °).

Cu1—N2	1.945 (2)	Cu1—S1	2.2230 (11)
Cu1—O1	1.948 (2)	Cu1—O2	2.639 (13)
Cu1—N1	2.001 (2)		
N2—Cu1—O1	175.50 (9)	C1—N1—Cu1	128.0 (2)
N2—Cu1—N1	80.93 (9)	C5—N1—Cu1	112.61 (19)
O1—Cu1—N1	96.90 (10)	C6—N2—Cu1	117.3 (2)
N2—Cu1—S1	84.98 (7)	N3—N2—Cu1	123.79 (18)
O1—Cu1—S1	96.94 (7)	C10—O1—Cu1	107.8 (2)
N1—Cu1—S1	165.61 (7)	C8—S1—Cu1	95.09 (11)

m380 Nfor *et al.* • $[\mathrm{Cu(C_9H_{10}N_4S)(C_2H_3O_2)}]\cdot\mathrm{H_2O}$ *Acta Cryst.* (2006). E**62**, m379–m381

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3B···O2^{i}	0.63 (4)	2.19 (4)	2.786 (4)	160 (5)
O3—H3A···O1	0.88 (5)	1.99 (5)	2.860 (4)	171 (4)

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

H atoms attached to C atoms were placed at calculated positions (aromatic C—H = 0.93 Å and methyl C—H = 0.96 Å) and were allowed to ride on their parent atoms. Methyl groups were allowed to rotate around the C—C bond. The H atoms of the water molecule were located in difference Fourier syntheses and refined with the restrained O—H distance 0.85 (2) Å. All H atoms were assigned $U_{\rm iso}$(H) values of $XU_{\rm eq}$(host), with X = 1.2 for aromatic and water H atoms, and X = 1.5 for methyl H atoms.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Bruker, 2002); software used to prepare material for publication: *SHELXL97*.

ENN gratefully acknowledges the Third World Academy of Science (TWAS) for a postdoctoral fellowship.

References

Brese, N. E. & O'Keeffe, M. (1991). *Acta Cryst.* B**47**, 192–197.

Brown, I. D. (1992). *Acta Cryst.* B**48**, 553–572.

Brown, I. D. (1994). *Bond-length–Bond-Valence Relationship in Inorganic Solids. Structure correlation*, Part III, edited by H. B. Burgi & J. D. Duritz, pp. 405–429. Weinheim/New York. VCH Publishers.

Brown, I. D. (1997). *Acta Cryst.* B**53**, 381–393.

Brown, I. D. (2002). *The Chemical Bond in Inorganic Chemistry. The Bond Valence Model*, IUCr Monograph on Crystallography 12. Oxford University Press.

Bruker (2002). *SADABS* (Version 2.03), *SAINT* (Version 6.02), *SMART* (Version 5.62) and *SHELXTL* (Version 6.10). Bruker AXS Inc., Madison, Winsonsin, USA.

Campbell, M. J. M. (1975). *Coord. Chem. Rev.* **15**, 279–319.

Hunters, C. A. & Sanders, J. K. M. (1990). *J. Am. Chem. Soc.* **112**, 5525–5534.

Kovala-Demertzi, D., Domopoulou, A., Demertzi, M. A., Papageorgiou, A. & West, D. X. (1997). *Polyhedron*, **16**, 3625–3633.

O'Keeffe, M. & Brese, N. E. (1991). *J. Am. Chem. Soc.* **113**, 3226–3229.

Palenik, G. J. (2003). *Inorg. Chem.* **42**, 2725–2728.

Scovill, J. P., Klayman, D. L. & Franchino, C. F. (1982). *J. Med. Chem.* **25**, 1261–1264.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Siripaisampipat, S., Lhuachan, S. & Chaichit, N. (2003). *Eur. J. Inorg. Chem.* 263–267.

Acta Cryst. (2006). E**62**, m379–m381 Nfor *et al.* • $[Cu(C_9H_{10}N_4S)(C_2H_3O_2)]\cdot H_2O$ **m381**