Liu, M. C., Lin, T. S., Penketh, P. & Sartorelli, A. C. (1995). *J. Med. Chem.* **38**, 4234–4241.
Podhye, S. & Kauffman, G. B. (1985). *Coord. Chem. Res.* **63**, 127–164.
Siemens (1995). *SHELXTL Reference Manual*. Version 5.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Tanner, J. & Krause, K. (1994). *Rigaku J.* **11**, 4–7.
West, D. X., Liberta, A. E., Rajendran, K. G. & Hall, I. H. (1993). *Anticancer Drugs*, **4**, 241–246.

Acta Cryst. (1998). C**54**, 1397-1399

Bis[μ-(di-2-pyridyl ketone thiosemicarbazonato-N^1,N'',S:N')]bis[(acetato-O)-copper(II)] Dimethanol Solvate

Chun-Ying Duan,[a] Xiao-Zeng You[a] and T. C. W. Mak[b]

[a]*Coordination Chemistry Institute & State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, People's Republic of China, and* [b]*Department of Chemistry, The Chinese University of Hong Kong, Shatin, Hong Kong. E-mail: ccinu@netra.nju.edu.cn*

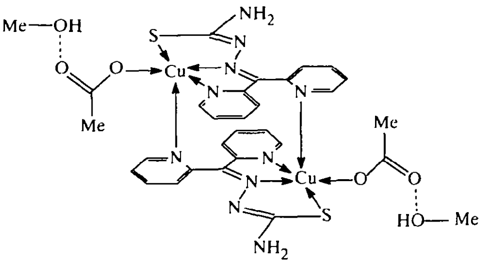
(Received 18 April 1997; accepted 30 March 1998)

Abstract

In the title compound, $[Cu_2(C_2H_3O_2)_2(C_{12}H_{10}N_5S)_2]$.$2CH_4O$, the coordination geometry about each Cu^{II} atom is distorted square pyramidal, with one pyridine N atom, the S atom and the imino N atom from the thiosemicarbazone ligand, together with one O atom from acetate, in the basal plane; a pyridyl N atom of an adjacent moiety occupies the apical position, serving as a bridge to form a centrosymmetric dimeric structure.

Comment

Thiosemicarbazones belong to a large group of thiourea derivatives, the biological activities of which are a function of the parent aldehyde or ketone (Podhye & Kauffman, 1985; Liberta & West, 1992). It has been postulated that many N-heterocyclic carbaldehyde thiosemicarbazones act as tridentate N_2S ligands which bond to iron or copper in the synthesis of precursors of DNA (West *et al.*, 1993; Liu *et al.*, 1995). The solution chemistry and crystal structure of pyridine-2-carbaldehyde thiosemicarbazone (*HL'*) (Biyuskin *et al.*, 1987), the active precursor complex [Cu*L'*(OAc)] (Bell & Theocharis, 1987), as well as many other N-heterocyclic carbaldehyde thiosemicarbazones (Brown & Agrawal, 1977, 1978*a*,*b*) and their metal complexes, have been studied (Farrarri *et al.*, 1989; Garcia-Tojal *et al.*, 1994). We report here the crystal structure of a new acetate-coordinated copper(II) thiosemicarbazone complex, (I), derived from di-2-pyridyl ketone.



(I)

The title complex (Fig. 1) has a dimeric structure. The coordination geometry about each copper(II) ion is square pyramidal. The pyridine N4 atom, the imino N3 atom and the thiosemicarbazone S1 atom, together with the acetate O1 atom, comprise the basal plane, while the apical position is occupied by the pyridine N5($\frac{1}{2}-x$, $\frac{3}{2}-y$, $-z$) atom of the symmetry-related half of the dimer. The basal plane shows appreciable tetrahedral distortion (mean deviation from the plane 0.16 Å), which deforms the square-pyramidal coordi-

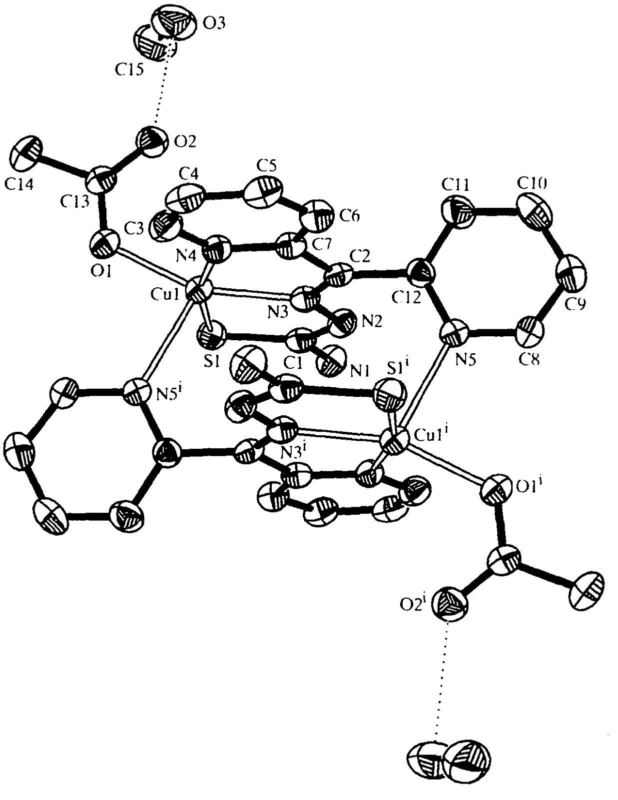


Fig. 1. View of the title compound. Displacement ellipsoids are shown at the 30% probability level. [Symmetry code: (i) $\frac{1}{2}-x$, $\frac{3}{2}-y$, $-z$.]

Acta Crystallographica Section C
ISSN 0108-2701 ©1998

nation polyhedron towards trigonal-bipyramidal geometry. The bond lengths in the basal plane agree well with those generally found in copper(II) complexes containing thiosemicarbazone derivatives acting as mononegative tridentate ligands (Farrarri *et al.*, 1989; Garcia-Tojal *et al.*, 1994).

While the thiosemicarbazone moiety in the 'free' ligand has an *E* configuration about both C2—N3 and C1—N2 (Duan *et al.*, 1996), the copper(II) complex has the *E* configuration about C2—N3, but a *Z* configuration about C1—N2, with the donors placed on the same side. The data in Table 1 show that all the bond distances in the side chain are intermediate between formal single and double bonds, pointing to extensive electron delocalization over the entire moiety.

The conformation of the title complex is stabilized by favourable π–π interactions between the planar chelate rings of symmetry-related ligands in the dimeric molecule. The overlap occurs between the chelate ring defined by atoms Cu1, N3, C2, C7 and N4 (mean and maximum deviations from best plane are 0.014 and 0.018 Å, respectively), and its counterpart ring, and between the basal pyridine ring defined by atoms N4, C3, C4, C5, C6 and C7 (mean and maximum deviations from the best plane are 0.0097 and 0.012 Å, respectively), and the *N*,*S*-chelate ring defined by atoms Cu1, S1, C1, N2 and N3 (mean and maximum deviations from the best plane are 0.0084 and 0.012 Å, respectively). The centre-to-centre distance is 3.48 (1) Å for the first pair of rings and 3.64 (1) Å for the second.

Hydrogen-bonding interaction occurs between the uncoordinated O atom of each acetate and the O atom of a methanol solvent molecule [O2···O3 2.862 (7) Å and O3—H3*B*···O2 178.7 (3)°].

Experimental

The title compound was synthesized by refluxing a methanol solution of di-2-pyridyl ketone thiosemicarbazone (0.51 g, 2 mmol) and copper acetate tetrahydrate (0.50 g, 2 mmol) for 4 h. The dark-green crystalline solid which formed was isolated and dried under vacuum. Good quality crystals were obtained by evaporating a methanol solution in air.

Crystal data

$[Cu_2(C_2H_3O_2)_2$-
$(C_{12}H_{10}N_5S)_2].2CH_4O$
$M_r = 821.89$
Monoclinic
$C2/c$
$a = 22.457\ (2)$ Å
$b = 13.346\ (1)$ Å
$c = 12.896\ (1)$ Å
$\beta = 113.66\ (1)°$
$V = 3540.2\ (5)$ Å^3
$Z = 4$
$D_x = 1.542$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 156 reflections
$\theta = 1.75$–$27.50°$
$\mu = 1.376$ mm^{-1}
$T = 293\ (2)$ K
Prism
0.36 × 0.28 × 0.25 mm
Dark blue

Data collection

Rigaku RAXIS IIC image-plate (IP) diffractometer
Oscillation IP scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.552$, $T_{max} = 0.709$
3719 measured reflections

3553 independent reflections
2519 reflections with $I > 2\sigma(I)$
$R_{int} = 0.013$
$\theta_{max} = 26.73°$
$h = -28 \rightarrow 26$
$k = 0 \rightarrow 16$
$l = 0 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.064$
$wR(F^2) = 0.255$
$S = 1.024$
3537 reflections
226 parameters
H atoms riding (fixed U_{iso})
$w = 1/[\sigma^2(F_o^2) + (0.080P)^2 + 0.015P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.544$ e Å^{-3}
$\Delta\rho_{min} = -0.429$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Cu1—O1	1.981 (3)	N2—C1	1.328 (6)
Cu1—N3	1.999 (4)	N2—N3	1.350 (5)
Cu1—N4	2.018 (4)	N3—C2	1.310 (5)
Cu1—S1	2.2747 (13)	N4—C3	1.340 (6)
Cu1—N5^{i}	2.406 (3)	N5—Cu1^{i}	2.406 (3)
S1—C1	1.752 (5)	C2—C7	1.462 (6)
N1—C1	1.340 (6)	C2—C12	1.503 (6)
O1—Cu1—N3	158.82 (13)	N4—Cu1—S1	164.47 (11)
O1—Cu1—N4	96.00 (14)	O1—Cu1—N5^{i}	87.55 (12)
N3—Cu1—N4	80.79 (15)	N3—Cu1—N5^{i}	113.12 (12)
O1—Cu1—S1	98.61 (10)	N4—Cu1—N5^{i}	88.16 (12)
N3—Cu1—S1	83.69 (11)	S1—Cu1—N5^{i}	97.67 (9)

Symmetry code: (i) $\frac{1}{2} - x, \frac{3}{2} - y, -z$.

Data were collected on a Rigaku RAXIS IIC image-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* program based on Fourier-coefficient fitting to the intensities of symmetry-equivalent reflections (Tanner & Krause, 1994; Krause & Phillips, 1992; Higashi, 1995). All non-H atoms were refined anisotropically. All H atoms were placed in calculated positions (C—H 0.96 Å), assigned fixed isotropic displacement parameters [$1.2U_{eq}$(parent atom)] and allowed to ride.

Data collection: *BIOTEX* (Krause & Phillips, 1992). Cell refinement: *BIOTEX*. Data reduction: *BIOTEX*. Program(s) used to solve structure: *SHELXTL* (Siemens, 1995). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

This research was supported by the State Science and Technology Commission, National Nature Science Foundation of China, through a Key Research Project grant.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1118). Services for accessing these data are described at the back of the journal.

References

Bell, C. F. & Theocharis, C. R. (1987). *Acta Cryst.* C**43**, 26–27.

Biyuskin, V. N., Samus, Y. M., Samus, N. M. & Bake, I. O. (1987). *J. Struct. Chem. (Engl. Transl.)*, **28**, 119–121.

Brown, J. N. & Agrawal, K. C. (1977). *Acta Cryst.* B**33**, 980–981.

Brown, J. N. & Agrawal, K. C. (1978*a*). *Acta Cryst.* B**34**, 1002–1011.

Brown, J. N. & Agrawal, K. C. (1978*b*). *Acta Cryst.* B**34**, 2078–2081.

Duan, C.-Y., Wu, B.-M. & Mak, T. C. W. (1996). *J. Chem. Soc. Dalton Trans.* pp. 3485–3490.

Farrarri, M. B., Fava, G. G., Tarasconi, P. & Pelizzi, C. (1989). *J. Chem. Soc. Dalton Trans.* pp. 361–365.

Garcia-Tojal, J., Urtiaga, M. K., Cortes, R., Lezama, L., Arriortua, M. I. & Rojo, T. J. (1994). *J. Chem. Soc. Dalton Trans*, pp. 2233–2238.

Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.

Krause, K. L. & Phillips, G. N. (1992). *J. Appl. Cryst.* **25**, 146–164.

Liberta, A. E. & West, D. X. (1992). *Biometal*, **5**, 121–126.

Liu, M. C., Lin, T. S., Penketh, P. & Sartorelli, A. C. (1995). *J. Med. Chem.* **38**, 4234–4241.

Podhye, S. & Kauffman, G. B. (1985). *Coord. Chem. Res.* **63**, 127–164.

Siemens (1995). *SHELXTL Reference Manual.* Version 5.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Tanner, J. & Krause, K. (1994). *Rigaku J.* **11**, 4–7.

West, D. X., Liberta, A. E., Rajendran, K. G. & Hall, I. H. (1993). *Anticancer Drugs*, **4**, 241–246.

Acta Cryst. (1998). C**54**, 1399–1401

1,4-Dimethylpyridinium (1,3-Dithiole-2-thione-4,5-dithiolato)(isothiocyanato)diphenylstannate(1−)

Abdullah Khan,[a] John N. Low,[b] James L. Wardell[a] and George Ferguson[c]

[a]*Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen, Aberdeen AB9 2UE, Scotland,* [b]*NCR Advanced Mechatronics Research Centre, Department of Applied Physics and Electronic & Mechanical Engineering, University of Dundee, Dundee DD1 4HN, Scotland, and* [c]*Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1. E-mail: j.n.low@dundee.ac.uk*

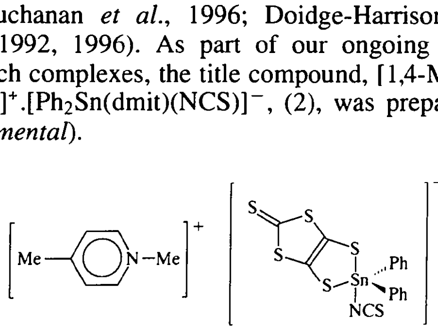
(*Received 23 March 1998; accepted 14 April 1998*)

Abstract

In the title compound, 1,4-dimethylpyridinium [4,5-dimercapto-1,3-dithiole-2-thionato(2−)-S^4,S^5](isothiocyanato)diphenylstannate(1−), ($C_7H_{10}N$)[Sn(NCS)(C_6H_5)$_2$(C_3S_5)], the anion has distorted trigonal-bipyramidal coordination at the Sn atom, with the thiocyanato N and a thiolato S atom axial [Sn—N 2.262 (3), Sn—S 2.5917 (10) Å and N—Sn—S 164.58 (8)°]. The remaining thiolato S and two phenyl C atoms complete the equatorial coordination at Sn [Sn—S 2.4399 (10), and Sn—C 2.137 (4) and 2.139 (4) Å].

Comment

The 1,3-dithiole-2-thione-4,5-dithiolate (dmit) ligand, (1), forms complexes with various metals, including tin (Buchanan *et al.*, 1996; Doidge-Harrison *et al.*, 1991, 1992, 1996). As part of our ongoing research into such complexes, the title compound, [1,4-Me_2-pyridinium]$^+$.[Ph_2Sn(dmit)(NCS)]$^-$, (2), was prepared (see *Experimental*).



(2)

Our analysis shows that the asymmetric unit of (2) contains two [1,4-Me_2-pyridinium]$^+$ cations, each of which lies about independent inversion centres (with consequent disorder of *para*-C and *para*-N atoms), and a [Ph_2Sn(dmit)(NCS)]$^-$ anion (Fig. 1) in a general position.

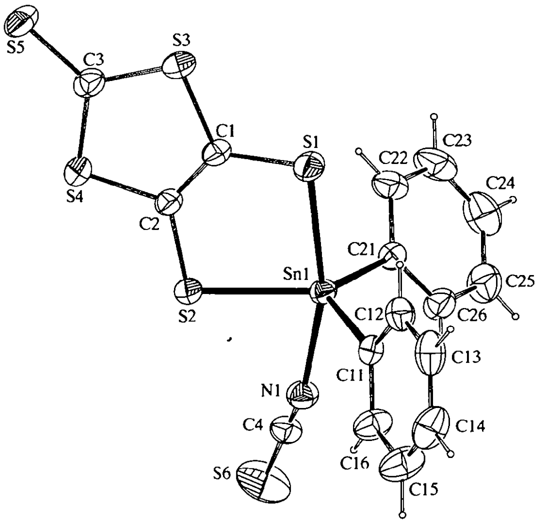


Fig. 1. A view of the anion in (2) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

The anion contains a pentacoordinate Sn atom, with a distorted trigonal-bipyramidal geometry. The chelating dmit ligand is bonded to Sn *via* the dithiolate S atoms in axial [Sn1—S1 2.5917 (10) Å] and equatorial [Sn1—S2 2.4399 (10) Å] sites, with a bite angle of 86.37 (3)°; the corresponding values in [NBu_4][Me_2Sn(dmit)Cl], (3), are 2.662 (3), 2.451 (3) Å and 84.5 (1)°, respectively (Doidge-Harrison *et al.*, 1991). The bite angles of the dmit ligand in (2) and (3) can be compared with those in other organotin–dmit complexes, *e.g.* 85.7 (2) and 85.8 (1)° in pentacoordinate [NBu_4][*R*Sn(dmit)$_2$] (*R* = Bu and Ph, respectively) (Doidge-Harrison *et al.*,