C(22)	0.6351 (4)	0.0894 (6)	0.3219 (3)	5.7 (1)
C(23)	0.5600 (3)	0.1759 (7)	0.3064 (3)	6.8 (1)
C(24)	0.5311 (3)	0.2412 (7)	0.2393 (3)	6.4 (1)
C(25)	0.5802 (3)	0.2192 (5)	0.1884 (3)	4.7 (1)
C(31)	0.8226 (2)	0.3056 (4)	0.1050 (2)	2.92 (8)
C(32)	0.8771 (3)	0.4225 (5)	0.0966 (3)	4.3 (1)
C(33)	0.9567 (3)	0.4468 (5)	0.1489 (3)	4.8 (1)
C(34)	0.9841 (3)	0.3563 (5)	0.2084 (3)	4.3 (1)
C(35)	0.9299 (3)	0.2415 (5)	0.2127 (2)	3.52 (9)
C(41)	0.8245 (3)	0.3892 (5)	0.4128 (2)	3.56 (9)
C(42)	0.8948 (3)	0.2836 (5)	0.4022 (3)	4.9 (1)
C(43)	0.7365 (3)	0.6111 (5)	0.3813 (2)	3.70 (9)
C(44)	0.6479 (3)	0.5461 (6)	0.3858 (3)	4.8 (1)
C(45)	0.7563 (3)	0.4456 (5)	0.2819 (2)	3.62 (9)
C(46)	0.7211 (4)	0.5511 (6)	0.2206 (2)	5.1 (1)
C(47)	0.8844 (3)	0.5924 (5)	0.3519 (2)	4.1 (1)
C(48)	0.9413 (3)	0.6495 (6)	0.4232 (3)	5.7 (1)

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

Co—S(1)	2.566 (1)	N(4)—C(47)	1.514 (5)
Co—S(2)	2.552 (1)	C(11)—C(12)	1.394 (6)
Co—S(3)	2.585 (1)	C(12)—C(13)	1.366 (7)
Co—N(1)	2.096 (3)	C(13)—C(14)	1.371 (7)
Co—N(2)	2.135 (3)	C(14)—C(15)	1.377 (7)
Co—N(3)	2.094 (3)	C(21)—C(22)	1.401 (6)
S(1)—C(11)	1.730 (4)	C(22)—C(23)	1.367 (9)
S(2)—C(21)	1.713 (5)	C(23)—C(24)	1.368 (8)
S(3)—C(31)	1.727 (4)	C(24)—C(25)	1.372 (7)
N(1)—C(11)	1.354 (5)	C(31)—C(32)	1.401 (6)
N(1)—C(15)	1.342 (5)	C(32)—C(33)	1.370 (7)
N(2)—C(21)	1.369 (6)	C(33)—C(34)	1.378 (7)
N(2)—C(25)	1.345 (6)	C(34)—C(35)	1.367 (6)
N(3)—C(31)	1.354 (5)	C(41)—C(42)	1.503 (6)
N(3)—C(35)	1.345 (5)	C(43)—C(44)	1.501 (7)
N(4)—C(41)	1.515 (5)	C(45)—C(46)	1.506 (7)
N(4)—C(43)	1.514 (5)	C(47)—C(48)	1.495 (7)
N(4)—C(45)	1.520 (6)		
S(1)—Co—S(2)	97.82 (4)	C(41)—N(4)—C(47)	111.4 (3)
S(1)—Co—S(3)	106.32 (4)	C(43)—N(4)—C(45)	110.9 (3)
S(1)—Co—N(1)	66.54 (9)	C(43)—N(4)—C(47)	108.5 (3)
S(1)—Co—N(2)	153.1 (2)	C(45)—N(4)—C(47)	108.9 (4)
S(1)—Co—N(3)	98.98 (9)	S(1)—C(11)—N(1)	113.5 (3)
S(2)—Co—S(3)	152.75 (5)	S(1)—C(11)—C(12)	126.4 (3)
S(2)—Co—N(1)	100.9 (1)	N(1)—C(11)—C(12)	120.0 (4)
S(2)—Co—N(2)	66.4 (2)	C(11)—C(12)—C(13)	119.6 (4)
S(2)—Co—N(3)	98.0 (1)	C(12)—C(13)—C(14)	120.1 (4)
S(3)—Co—N(1)	100.2 (1)	C(13)—C(14)—C(15)	118.5 (4)
S(3)—Co—N(2)	95.1 (2)	N(1)—C(15)—C(14)	122.1 (4)
S(3)—Co—N(3)	66.2 (1)	S(2)—C(21)—N(2)	113.8 (4)
N(1)—Co—N(2)	94.2 (1)	S(2)—C(21)—C(22)	127.3 (4)
N(1)—Co—N(3)	157.5 (1)	N(2)—C(21)—C(22)	119.0 (5)
N(2)—Co—N(3)	104.5 (1)	C(21)—C(22)—C(23)	119.7 (5)
Co—S(1)—C(11)	76.7 (1)	C(22)—C(23)—C(24)	120.9 (6)
Co—S(2)—C(21)	78.0 (2)	C(23)—C(24)—C(25)	118.1 (6)
Co—S(3)—C(31)	76.3 (1)	N(2)—C(25)—C(24)	122.4 (5)
Co—N(1)—C(11)	103.2 (2)	S(3)—C(31)—N(3)	113.8 (3)
Co—N(1)—C(15)	137.2 (3)	S(3)—C(31)—C(32)	126.5 (4)
C(11)—N(1)—C(15)	119.6 (4)	N(3)—C(31)—C(32)	119.8 (4)
Co—N(2)—C(21)	101.8 (3)	C(31)—C(32)—C(33)	119.3 (4)
Co—N(2)—C(25)	138.3 (3)	C(32)—C(33)—C(34)	120.7 (4)
C(21)—N(2)—C(25)	119.9 (4)	C(33)—C(34)—C(35)	117.7 (4)
Co—N(3)—C(31)	103.6 (3)	N(3)—C(35)—C(34)	123.1 (4)
Co—N(3)—C(35)	136.9 (3)	N(4)—C(41)—C(42)	116.4 (4)
C(31)—N(3)—C(35)	119.5 (4)	N(4)—C(43)—C(44)	115.0 (4)
C(41)—N(4)—C(43)	108.2 (4)	N(4)—C(45)—C(46)	116.2 (4)
C(41)—N(4)—C(45)	108.9 (13)	N(4)—C(47)—C(48)	115.5 (4)

The sample for analysis was mounted on a glass fibre in a random orientation. The structure was solved by direct methods. A total of four atoms were located from an *E* map, the remaining atoms being located in the succeeding difference Fourier syntheses. H atoms were located and added to the structure-factor calculations, but their positions were not refined. Calculations were performed on a Compaq computer using the *MolEN* package (Fair, 1990).

The financial support of NNSFC and CPNKPFR is gratefully acknowledged.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AS1185). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C**52**, 632–634

A Bis(6-methyl-2-pyridylmethyl) Thioether (DMPT) Copper(II) Complex, $[Cu(OSO_2CF_3)_2(C_{14}H_{16}N_2S)].CH_2Cl_2$

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(*Received 10 July 1995; accepted 11 September 1995*)

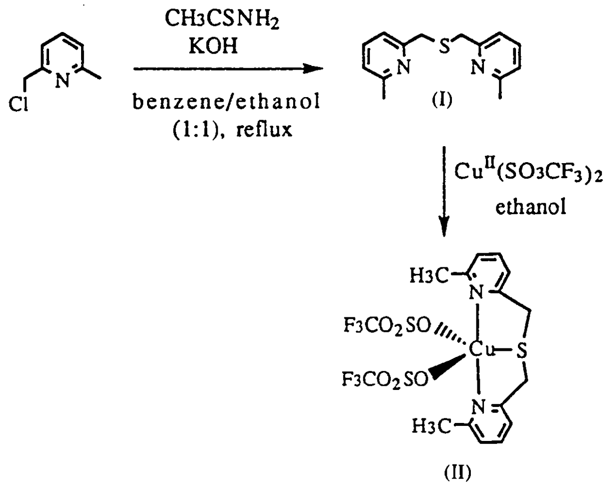
Abstract

The X-ray crystal structure determination of the title copper derivative, [bis(6-methyl-2-pyridylmethyl) sulfide-*N*,*N*′,*S*]bis(trifluoromethylsulfonato-*O*)copper(II) dichloromethane solvate, shows that this compound contains monomeric $[Cu(DMPT)(OSO_2CF_3)_2]$ molecules in which the Cu^{II} ion is surrounded by a tridentate DMPT

ligand [Cu—N1 2.001 (4), Cu—N2 1.977 (4) and Cu—S3 2.319 (1) Å] and by a pair of trifluoromethylsulfonato ligands [Cu—O1 2.205 (4) and Cu—O4 2.043 (3) Å] in a distorted tetragonal-pyramidal environment.

Comment

Copper-coordination chemistry has become a diverse field of interest because of the frequent occurrence of such metal centres in biological systems (Beinert, 1991). Indeed, the study of heterobinuclear copper-containing complexes continues to be an area of intense activity. These studies are largely centred on magneto–structural correlations between the metal centres, catalysis and biomimicry. In our attempt to generate, by self-assembly, asymmetric binuclear iron–copper systems, which are of potential interest as structural and functional models for the cytochrome a_3 heme–copper moiety, known to be the active site for dioxygen binding and reduction in cytochrome *c* oxydases (Babcock & Wikström, 1992), we prepared the title monomeric Cu^{II} complex, (II), according to the following reaction scheme.



Complex (II) crystallizes in the triclinic system, space group $P\bar{1}$, with two molecules per unit cell. As illustrated in Fig. 1, the five-coordinate Cu^{II} ion is in a distorted tetragonal-pyramidal (TP) environment. This distorted TP stereochemistry is readily recognized by the values of the bond angles in the equatorial plane (which are all near 90°), the displacement of the Cu^{II} atom from this plane toward an axial ligand, and the elongation of the Cu–ligand bond distance along the pseudo-tetragonal axis. Indeed, the axial Cu–ligand distance is significantly longer than the equatorial distances because in such a geometry, the unpaired electron of the d^9 cupric ion lies in the $d_{x^2-y^2}$ orbital, which is directed toward the equatorial atoms. The equatorial portion is Cu—(N1,N2,S3,O4), with bond distances of 2.001 (4), 1.977 (4), 2.043 (3) and 2.319 (1) Å, respectively, and bond angles ranging from 85.0 (1) to 91.5 (2)°. The axial ligand atom is O1 bonded at a distance of 2.205 (4) Å from the metal (metric data are compiled in Table 2). The dichloromethane molecule does not make any close contacts with the complex molecule.

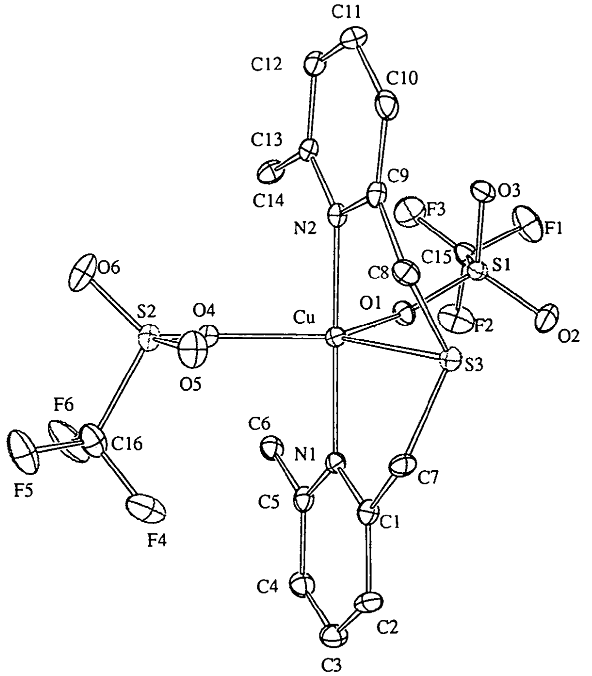


Fig. 1. Perspective *ORTEP* (Johnson, 1965) plot of complex (II) showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are omitted for clarity.

Experimental

A mixture of 2-chloromethyl-6-methylpyridine (10.54 g, 74 mmol) (Baker, Buggle, McOmie & Watkins, 1958), thioacetamide (2.90 g, 39 mmol) and KOH (4.50 g, 80 mmol) in 140 ml of benzene/ethanol (1:1) was refluxed for 20 h. The solution was evaporated to dryness, diethyl ether added to the residue, the solution filtered from insoluble products and the filtrate concentrated again to yield the product (I) (8.9 g; 97% yield): m.p. 346.5–347.5 K; ^{1}H NMR (CDCl$_3$) δ 2.5 (*s*, 6H, CH$_3$), 3.8 (*s*, 4H, CH$_2$), 7.0 (*d*, 2H, ArH), 7.2 (*d*, 2H, ArH), 7.5 p.p.m. (*t*, 2H, ArH). In order to prepare the copper complex (II), a solution of (I) (0.5 g, 2.05 mmol) in 10 ml of absolute ethanol was added dropwise to a solution of Cu(SO$_3$CF$_3$)$_2$ (0.74 g, 2.05 mmol) in 20 ml of absolute ethanol. The resulting dark green solution was stirred at room temperature for 30 min, whereupon several volumes of diethyl ether were added to precipitate a green solid. After filtration, the solid was washed with diethyl ether and dried under vacuum, resulting in 1.02 g of green crystalline material (82%). Analysis found (calculated): C 31.3 (31.71), H 2.8 (2.66), N 4.0 (4.62), S 15.4% (15.87%). Single crystals of this complex suitable for X-ray analysis were obtained by slow diffusion of diethyl ether into a dichloromethane solution of (II) at 298 K.

Crystal data

$[Cu(CF_3O_3S)_2(C_{14}H_{16}N_2S)]$.-
CH_2Cl_2
$M_r = 691.0$
Triclinic
$P\bar{1}$
$a = 12.391\ (4)$ Å
$b = 13.403\ (4)$ Å
$c = 8.849\ (3)$ Å
$\alpha = 98.35\ (2)°$
$\beta = 89.96\ (2)°$
$\gamma = 62.55\ (2)°$
$V = 1286.5\ (8)$ Å^3
$Z = 2$
$D_x = 1.784$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.54184$ Å
Cell parameters from 25 reflections
$\theta = 20$–$22°$
$\mu = 6.16$ mm^{-1}
$T = 173$ K
Plate
0.30 × 0.14 × 0.04 mm
Blue

Data collection

Phillips PW1100/16 diffractometer
$\theta/2\theta$ scans
Absorption correction: refined from ΔF (*DIFABS*; Walker & Stuart, 1983)
$T_{min} = 0.73$, $T_{max} = 1.00$
2655 measured reflections
2655 independent reflections

2173 observed reflections $[I > 3\sigma(I)]$
$\theta_{max} = 51°$
$h = -11 \rightarrow 11$
$k = -12 \rightarrow 11$
$l = 0 \rightarrow 8$
3 standard reflections
frequency: 60 min
intensity decay: 1.1%

Refinement

Refinement on F
$R = 0.037$
$wR = 0.060$
$S = 1.364$
2173 reflections
334 parameters
H-atom parameters not refined
$w = 1/\sigma^2(F^2)$, where $\sigma^2(F^2) = \sigma_{cs}^2 + (0.08I)^2$

$(\Delta/\sigma)_{max} = 0.07$
$\Delta\rho_{max} = 0.61$ e Å^{-3}
$\Delta\rho_{min} = -0.38$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	B_{eq}
Cu	0.30022 (5)	0.27622 (5)	0.32952 (7)	2.15 (2)
N1	0.3433 (3)	0.3251 (3)	0.5352 (4)	2.18 (9)
N2	0.2895 (3)	0.2294 (3)	0.1100 (4)	2.27 (9)
C1	0.4594 (4)	0.3051 (4)	0.5457 (5)	2.5 (1)
C2	0.4981 (4)	0.3386 (4)	0.6808 (6)	3.4 (1)
C3	0.4157 (5)	0.3954 (4)	0.8039 (6)	3.7 (1)
C4	0.2977 (5)	0.4174 (4)	0.7940 (6)	3.2 (1)
C5	0.2613 (4)	0.3805 (4)	0.6578 (5)	2.7 (1)
C6	0.1331 (5)	0.4031 (4)	0.6451 (6)	3.0 (1)
C7	0.5441 (4)	0.2500 (4)	0.4027 (6)	2.8 (1)
C8	0.5056 (4)	0.1795 (4)	0.0935 (6)	2.9 (1)
C9	0.3970 (4)	0.1799 (4)	0.0196 (6)	2.5 (1)
C10	0.4027 (5)	0.1390 (4)	−0.1316 (6)	3.2 (1)
C11	0.2979 (5)	0.1479 (4)	−0.1994 (6)	3.4 (1)
C12	0.1914 (5)	0.1983 (4)	−0.1104 (6)	3.2 (1)
C13	0.1867 (4)	0.2372 (4)	0.0442 (5)	2.4 (1)
C14	0.0692 (4)	0.2910 (4)	0.1412 (6)	3.4 (1)
C15	0.1357 (5)	0.0356 (4)	0.4322 (7)	3.7 (1)
C16	0.1913 (5)	0.6258 (4)	0.4055 (7)	4.1 (1)
C17	0.1765 (6)	−0.1598 (6)	−0.0014 (8)	7.3 (2)
S1	0.2676 (1)	0.04589 (9)	0.3605 (1)	2.48 (3)
S2	0.2108 (1)	0.5146 (1)	0.2458 (1)	2.82 (3)
S3	0.5063 (1)	0.1483 (1)	0.2874 (1)	2.55 (3)
O1	0.2313 (3)	0.1659 (2)	0.4083 (4)	2.78 (8)
O2	0.3654 (3)	−0.0285 (3)	0.4384 (4)	4.1 (1)
O3	0.2753 (3)	0.0115 (3)	0.1986 (4)	3.40 (9)
O4	0.1766 (3)	0.4413 (2)	0.3205 (4)	2.43 (8)
O5	0.3379 (3)	0.4620 (3)	0.1976 (4)	4.0 (1)
O6	0.1263 (3)	0.5731 (3)	0.1420 (4)	4.7 (1)
F1	0.1574 (3)	−0.0718 (3)	0.4079 (5)	6.3 (1)
F2	0.1122 (3)	0.0729 (3)	0.5822 (4)	5.47 (9)
F3	0.0369 (3)	0.0965 (3)	0.3666 (4)	5.6 (1)
F4	0.2745 (4)	0.5843 (3)	0.5046 (5)	7.0 (1)
F5	0.1998 (3)	0.7095 (2)	0.3596 (5)	6.2 (1)
F6	0.0829 (3)	0.6661 (3)	0.4801 (5)	7.1 (1)
Cl1	0.1614 (2)	−0.0738 (2)	−0.1369 (2)	8.11 (7)
Cl2	0.2804 (2)	−0.3022 (2)	−0.0612 (3)	9.39 (7)

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

Cu—N1	2.001 (4)	Cu—N2	1.977 (4)
Cu—O1	2.205 (4)	Cu—O4	2.043 (3)
Cu—S3	2.319 (1)		
N1—Cu—S3	85.0 (1)	N1—Cu—N2	167.5 (2)
N1—Cu—O1	95.9 (2)	N1—Cu—O4	90.2 (2)
S3—Cu—N2	86.2 (1)	S3—Cu—O1	99.9 (1)
S3—Cu—O4	142.6 (1)	N2—Cu—O1	94.3 (2)
N2—Cu—O4	91.5 (2)	O1—Cu—O4	117.6 (1)

Cell reduction gave a monoclinic C-centred unit cell, but in this cell equivalent reflections were in very bad agreement $[R_{int}(I) = 0.65]$. Therefore, the real cell is triclinic, pseudo monoclinic. A total number of 2655 reflections were collected over the range $3 < \theta < 51°$. The resulting data set was analysed using the Enraf-Nonius *SDP*/VAX package (Frenz, 1978). The raw step-scan data were converted to intensities using the Lehmann–Larsen method (Lehmann & Larsen, 1974) and corrected for Lorentz and polarization factors. The structure was solved using the heavy-atom method. H atoms were introduced in the structure-factor calculations as fixed contributors [C—H = 0.95 Å, B(H) = 1.3 × B_{eq}(C) Å^2]. Refinement was by the full-matrix least-squares technique.

The authors express their thanks to the Centre National de la Recherche Scientifique for financial support, and to the Ministère de la Recherche et de la Technologie for a research grant to AD.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PA1205). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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