Tetrakis(μ_2-4-tolylthioacetato-$\kappa^2 O$:O')bis-[(pyridine-κN)copper(II)]

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Key indicators

Single-crystal X-ray study
T = 275 K
Mean σ(C–C) = 0.005 Å
R factor = 0.037
wR factor = 0.120
Data-to-parameter ratio = 18.2

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

The two symmetry-independent molecules of the title dinuclear complex, [Cu$_2$(C$_9$H$_9$O$_2$S)$_4$(C$_5$H$_5$N)$_2$], lie on centers of inversion located midway between the Cu atoms. Four carboxylate anions function as bridges to the two Cu atoms and each Cu atom is coordinated by a pyridine molecule.

Comment

There is an enormous number of copper(II) carboxylates whose two carboxylate units function in the μ_2-bridging mode to link two Cu atoms across a center of symmetry, as noted from a cursory inspection of the Cambridge Structural Database (Version 5.25; Allen, 2002). The sixth coordination site of the metal atom is typically completed by an oxygen- or a nitrogen-donor ligand. Among these dinuclear copper tetra-carboxylate adducts are several having a mercapto entity in the acetate residue such as, for example, the adducts iso-propylthioacetate quinoline (Ouchi *et al.*, 1983), 2,4-dichloro-5-methylphenylthioacetate acetone (Kennard *et al.*, 1985), 2-(2-chlorophenylthio)-2-methylpropionate water (Chan, Mak, Yip, Smith *et al.*, 1987), 2-methyl-2-(phenylthio)propionate ethanol (Chan, Mak, Yip, Kennard *et al.*, 1987) and 2,4-di-chloro-5-methylphenylthioacetate acetone (Smith *et al.*, 1985).

(I)
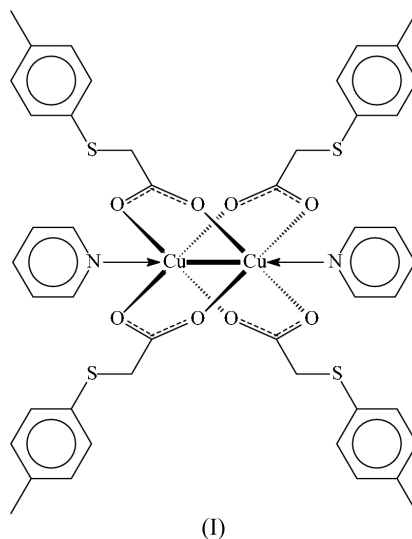
The 4-tolylthiolyl substituent attached to the acetate ligand in the present pyridine adduct, (I), does not significantly alter the bond dimensions around the Cu atoms. The compound crystallizes as two independent molecules, each of which lies on a center of inversion (Fig. 1). Bond dimensions involving the metal atom are similar to reported values. The Cu—Cu distance compares well with that found in tetraacetatodi-pyridinedicopper, whose structure has been determined
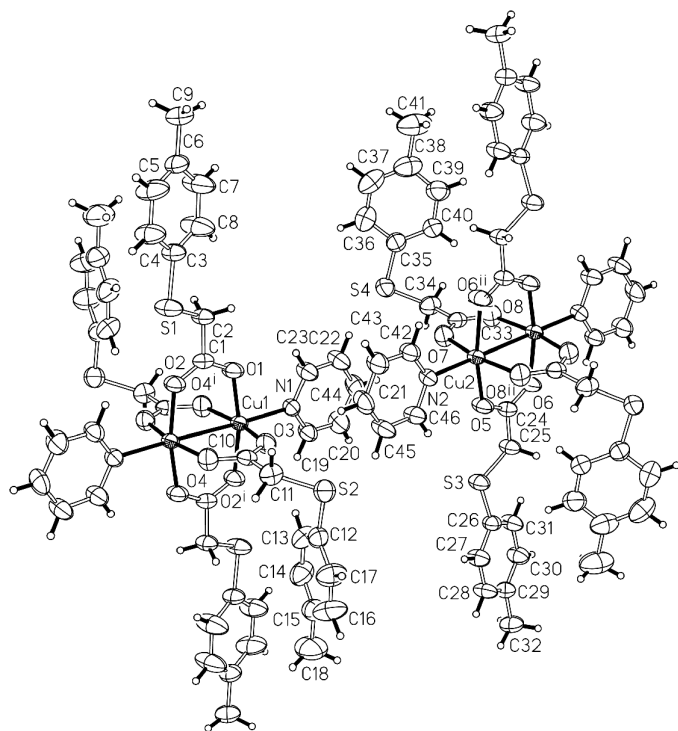
Figure 1
ORTEPII plot (Johnson, 1976) of the two symmetry-independent molecules of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are drawn as spheres of arbitrary radii. [Symmetry codes: (i) $1 - x$, $1 - y$, $1 - z$; (ii) $2 - x$, $1 - y$, $2 - z$.]
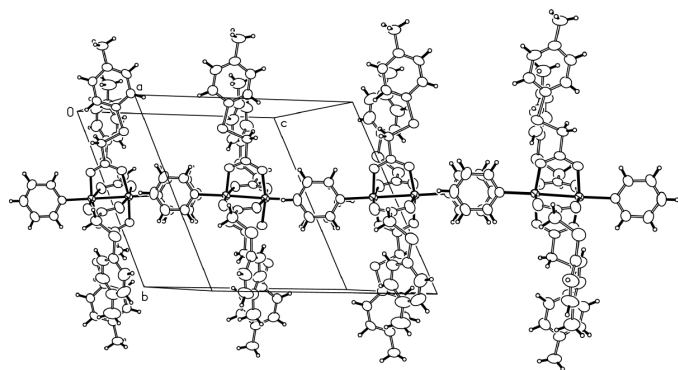

Figure 2
ORTEPII plot (Johnson, 1976), illustrating the π–π stacking interactions that lead to the formation of a chain.

several times [Cu—Cu = 2.641 (1) Å; Uekusa *et al.*, 1989]. In the title compound, (I), the pyridine donor of one molecule is stacked over that of an adjacent molecule at a distance of about 3.7 Å; the weak π—π interaction gives rise to a chain structure (Fig. 2).

Experimental

Copper nitrate hexahydrate (1.48 g, 5 mmol) and an excess of pyridine (1 ml) were added to a hot aqueous solution of 4-tolylthio acetic acid (0.91 g, 5 mmol). The blue solution was set aside for several days to allow the growth of crystals. Elemental analysis calculated for $C_{23}H_{23}CuNO_4S_2$: C 54.69, H 4.59, N 2.77%; found: C 54.74, H 4.52, N 2.74%.

Crystal data

[Cu2(C9H9O2S)4(C5H5N)2]	$Z = 2$
$M_r = 1010.17$	$D_x = 1.479$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 13.341$ (3) Å	Cell parameters from 19327
$b = 13.981$ (3) Å	reflections
$c = 14.185$ (3) Å	$\theta = 3.0$–$27.5°$
$\alpha = 70.33$ (1)°	$\mu = 1.18$ mm^{-1}
$\beta = 75.80$ (1)°	$T = 275$ (2) K
$\gamma = 66.64$ (1)°	Block, blue
$V = 2268.0$ (8) Å^3	$0.38 \times 0.26 \times 0.17$ mm

Data collection

Rigaku R-AXIS RAPID diffractometer	10252 independent reflections
	7833 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.020$
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)	$\theta_{max} = 27.5°$
	$h = -16 \rightarrow 17$
$T_{min} = 0.704$, $T_{max} = 0.825$	$k = -18 \rightarrow 18$
22338 measured reflections	$l = -18 \rightarrow 18$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.037$	$w = 1/[\sigma^2(F_o^2) + (0.0764P)^2]$
$wR(F^2) = 0.120$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{max} = 0.001$
10252 reflections	$\Delta\rho_{max} = 0.48$ e Å^{-3}
563 parameters	$\Delta\rho_{min} = -0.31$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—Cu1^i	2.6797 (7)	Cu2—O5	1.968 (2)
Cu1—O1	1.968 (2)	Cu2—Cu2^{ii}	2.6729 (7)
Cu1—O2^i	1.979 (2)	Cu2—O6^{ii}	1.975 (2)
Cu1—O3	1.980 (2)	Cu2—O7	1.977 (2)
Cu1—O4^i	1.978 (2)	Cu2—O8^{ii}	1.979 (2)
Cu1—N1	2.161 (2)	Cu2—N2	2.143 (2)
O1—Cu1—O2^i	167.11 (7)	O5—Cu2—O6^{ii}	166.97 (7)
O1—Cu1—O3	88.88 (8)	O5—Cu2—O7	89.78 (9)
O1—Cu1—O4^i	89.34 (8)	O5—Cu2—O8^{ii}	88.63 (8)
O1—Cu1—N1	95.73 (7)	O5—Cu2—N2	96.52 (7)
O2^i—Cu1—O3	89.85 (8)	O6^{ii}—Cu2—O7	89.29 (9)
O2^i—Cu1—O4^i	89.00 (8)	O6^{ii}—Cu2—O8^{ii}	89.33 (9)
O2^i—Cu1—N1	97.15 (7)	O6^{ii}—Cu2—N2	96.49 (7)
O3—Cu1—O4^i	166.93 (7)	O7—Cu2—O8^{ii}	166.89 (8)
O3—Cu1—N1	98.41 (8)	O7—Cu2—N2	96.76 (8)
O4^i—Cu1—N1	94.65 (8)	O8^{ii}—Cu2—N2	96.35 (8)

Symmetry codes: (i) $1 - x$, $1 - y$, $1 - z$; (ii) $2 - x$, $1 - y$, $2 - z$.

The methyl groups were allowed to rotate to fit the electron density [C—H = 0.96 Å and $U_{iso}(H) = 1.5U_{eq}(C)$]; the other H atoms were positioned geometrically [aromatic C—H$_{aromatic}$ 0.93 Å and aliphatic C—H = 0.97 Å, $U_{iso}(H) = 1.2U_{eq}(C)$]. All H atoms were included in the refinement in the riding-model approximation.

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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