metal-organic compounds

Tetra-μ-acetato-κ²O:O′-bis[(4-phenyl-pyridine-κN)copper(II)]

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The title compound, $[Cu_2(C_2H_3O_2)_4(C_{11}H_9N)_2]$ or $[Cu_2(MeCO_2)_4(phpy)_2]$ (phpy is 4-phenylpyridine), consists of centrosymmetric dimers in which the Cu^{II} atoms display a square-pyramidal CuO_4N coordination, with four acetate O atoms in the basal plane [Cu—O 1.975 (3)–1.987 (3) Å] and the phpy N atom in the apical position [Cu—N 2.150 (3) Å]. The Cu atoms are 2.654 (1) Å apart and are bridged by four acetate groups. The discrete dimers are extended into a three-dimensional supramolecular array through intermolecular π–π-stacking interactions.

Comment

Studies of dicopper carboxylates exhibiting the lantern structure (Rusjan *et al.*, 2000) have been associated with a variety of interests (Mehrotra & Bohra, 1983; Kato & Muto, 1988). The structural and magnetic properties of this type of compound are important in the understanding of, for example, magnetic exchange in dinuclear compounds, and in the development of appropriate models to describe magnetic coupling between metal centres (Bleaney & Bowers, 1952; Kahn, 1993). We report here the synthesis, structure and magnetic properties of the title complex, (I).

(I)
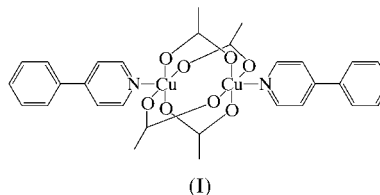
The crystal structure of (I) comprises dinuclear $[Cu_2(O_2CMe)_4(phpy)_2]$ species. As shown in Fig. 1, the dimer is located on a crystallographic inversion centre. The two Cu^{II} ions, 2.654 (1) Å apart, are bridged by the carboxylate groups of four acetate ligands. Each Cu atom is in a square-pyramidal environment, coordinated equatorially to four acetate O atoms [Cu—O 1.975 (3)–1.987 (3) Å] and apically to the phpy N atom [Cu—N 2.150 (3) Å].

The Cu···Cu separation and Cu—N(pyridyl) distances observed in (I) are very similar to the corresponding values reported previously, in the ranges 2.628–2.736 and 2.145–2.246 Å, respectively, in $[Cu_2(O_2CMe)_4(3\text{-pyridylcarbinol})_2]$·$CH_2Cl_2$ (Melnik *et al.*, 1985), $[Cu_2(O_2CMe)_4\{\mu_3\text{-}1,3,5\text{-tris-}(4\text{-pyridyl})\text{-}2,4,6\text{-triazine}\}_2]$·MeOH (Batten *et al.*, 2000), $[Cu_2(O_2CMe)_4(p\text{-pyridylnitronyl nitroxide})_2]$ (Dasna *et al.*, 2000), and $[Cu_2(O_2CMe)_4(\text{pyridine-}N)_2]$ (Uekusa *et al.*, 1989).
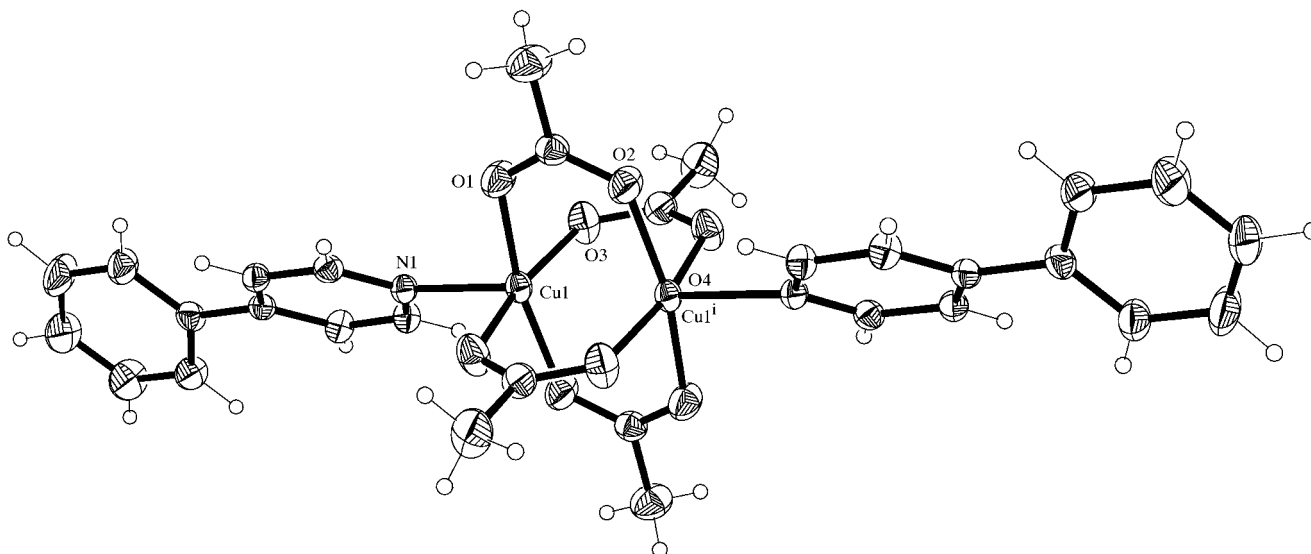

Figure 1
A view of the molecule of (I) illustrating the coordination environment of the Cu atom. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii [symmetry code: (i) $1 - x$, $1 - y$, $1 - z$].

It should be noted that, to the best of our knowledge, few compounds formulated as [Cu₂(carboxylate)₄L_2] crystallize in high-symmetry space groups. The Cambridge Structural Database (CSD, Version 5.22 of October 2001; Allen & Kennard, 1993) was searched for all [Cu₂(MeCO₂)₄L_2] compounds and only two, *viz.* (NMe₄)[Cu₂(MeCO₂)₄(SCN)₂] (Goodgame *et al.*, 1969) and [Cu₂(MeCO₂)₄(1,3,5-triphenyl-2*S*-benzylisobiuret-*O*)₂] (Singh *et al.*, 1984), were found to be tetragonal.

The discrete dimers in (I) are extended into a three-dimensional supramolecular array (Fig. 2) through intermolecular π–π-stacking interactions. Adjacent dimers stack into a one-dimensional supramolecular chain in an off-set fashion, whereby the separation of the phenyl rings of the phpy ligands is 3.6395 Å, suggesting significant π–π-stacking interactions. Neighbouring chains are arranged in a crosswise fashion, resulting in a three-dimensional supramolecular array with approximately square channels running along the *c* axis. The intermolecular Cu···Cu distances are one-half of the length of the *a* axis.

Variable-temperature magnetic susceptibility data were obtained from a Quantum Design SQUID magnetometer with a polycrystalline sample in a 5.0 kG field over the temperature range 4–298 K. Experimental magnetic susceptibility data were corrected for the diamagnetism of the constituent atoms (Kahn, 1993). Compound (I) shows a strong intramolecular antiferromagnetic interaction, which can be attributed to Cu···Cu superexchange through the carboxylate groups. The cryomagnetic data were fitted to the Bleaney–Bowers equation (Ginsberg, 1971). The best-fit parameters were found to be $J = -322$ cm⁻¹ and $g = 2.2$, with a reliability factor $R = 3.2 \times 10^{-6}$ [$R = \Sigma(\chi_{obs} - \chi_{calc})^2/\Sigma(\chi_{obs})^2$], by the non-linear least-squares fitting procedure. These values for the magnetic parameters agree with those already reported for [Cu₂(O₂CMe)₄L_2] compounds, where L coordinates *via* N atoms (308–353 cm⁻¹; Kato & Muto, 1988; Kawata *et al.*, 1992; Melnik *et al.*, 1985).

Figure 2
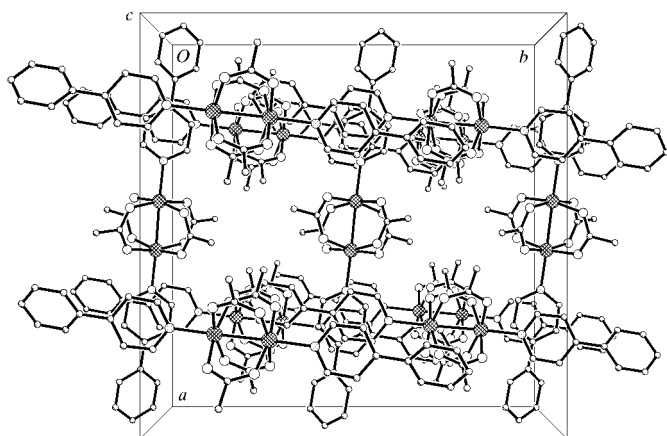A perspective view of the molecular packing of (I).

Experimental

To a solution of Cu(MeCO₂)₂ (0.5 mmol) in 1:1 (*v*/*v*) MeCN–H₂O (10 ml), a solution of phpy (0.5 mmol) in MeOH (5 ml) was added slowly with stirring over a period of 15 min at 333 K. Deep-green block-shaped crystals of (I) were deposited within 5 d (90% yield).

Crystal data

[Cu₂(C₂H₃O₂)₄(C₁₁H₉N)₂]	Mo *Kα* radiation
$M_r = 673.64$	Cell parameters from 25
Tetragonal, $I4_1/a$	reflections
$a = 20.598\,(4)$ Å	$\theta = 7\text{–}15°$
$c = 14.070\,(8)$ Å	$\mu = 1.48$ mm⁻¹
$V = 5970\,(4)$ Å³	$T = 293\,(2)$ K
$Z = 8$	Block, green
$D_x = 1.499$ Mg m⁻³	$0.42 \times 0.36 \times 0.30$ mm

Data collection

Siemens *R3m* four-circle	$R_{int} = 0.034$
diffractometer	$\theta_{max} = 28°$
ω scans	$h = 0 \rightarrow 27$
Absorption correction: empirical	$k = 0 \rightarrow 27$
via ψ scan (North *et al.*, 1968)	$l = -1 \rightarrow 18$
$T_{min} = 0.543$, $T_{max} = 0.642$	2 standard reflections
4097 measured reflections	every 150 reflections
3598 independent reflections	intensity decay: none
2304 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0698P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.053$	$+ 0.2836P]$
$wR(F^2) = 0.140$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.03$	$(\Delta/\sigma)_{max} < 0.001$
3598 reflections	$\Delta\rho_{max} = 0.37$ e Å⁻³
192 parameters	$\Delta\rho_{min} = -0.35$ e Å⁻³
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.975 (3)	Cu1—O2ⁱ	1.987 (3)
Cu1—O4ⁱ	1.979 (3)	Cu1—N1	2.150 (3)
Cu1—O3	1.984 (3)		
O1—Cu1—O4ⁱ	88.94 (15)	O3—Cu1—O2ⁱ	88.76 (15)
O1—Cu1—O3	89.63 (15)	O1—Cu1—N1	98.49 (12)
O4ⁱ—Cu1—O3	167.80 (12)	O4ⁱ—Cu1—N1	95.51 (12)
O1—Cu1—O2ⁱ	167.79 (12)	O3—Cu1—N1	96.69 (12)
O4ⁱ—Cu1—O2ⁱ	90.08 (15)	O2ⁱ—Cu1—N1	93.73 (12)

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

Methyl H atoms were located in difference syntheses and were refined using idealized rigid groups which were allowed to rotate but not tip. Other H atoms were positioned geometrically and refined using a riding model, with C—H distances in the range 0.93–0.96 Å. In both cases, $U_{iso}(H)$ values were set at $1.2U_{eq}(C)$.

Data collection: *R3m Software* (Siemens, 1990); cell refinement: *R3m Software*; data reduction: *R3m Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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