metal-organic compounds

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Tetra- μ -acetato- $\kappa^2 O:O'$ -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 $[Cu_2(Me-CO_2)_4(phpy)_2]$ (phpy is 4-phenylpyridine), consists of centrosymmetric dimers in which the Cu^{II} atoms display a squarepyramidal CuO₄N 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).



The crystal structure of (I) comprises dinuclear $[Cu_2(O_2C-Me)_4(phpy)_2]$ 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 [Cu₂(O₂CMe)₄(3-pyridylcarbinol)₂]·-CH₂Cl₂ (Melnik *et al.*, 1985), [Cu₂(O₂CMe)₄{ μ_3 -1,3,5-tris-(4-pyridyl)-2,4,6-triazine}₂]·MeOH (Batten *et al.*, 2000), [Cu₂-(O₂CMe)₄(*p*-pyridylnitronyl nitroxide)₂] (Dasna *et al.*, 2000), and [Cu₂(O₂CMe)₄(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 elliposids 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].

 $R_{\rm int} = 0.034$

 $h = 0 \rightarrow 27$

 $k = 0 \rightarrow 27$

 $l = -1 \rightarrow 18$

2 standard reflections

every 150 reflections

intensity decay: none

 $\theta_{\rm max} = 28^{\circ}$

It should be noted that, to the best of our knowledge, few compounds formulated as $[Cu_2(carboxylate)_4L_2]$ crystallize in high-symmetry space groups. The Cambridge Structural Database (CSD, Version 5.22 of October 2001; Allen & Kennard, 1993) was searched for all $[Cu_2(MeCO_2)_4L_2]$ compounds and only two, viz. (NMe₄)[Cu₂(MeCO₂)₄(SCN)₂] (Goodgame et al., 1969) and $[Cu_2(MeCO_2)_4(1,3,5-triphenyl-$ 2S-benzylisobiuret- O_{2}] (Singh *et al.*, 1984), were found to be tetragonal.

The discrete dimers in (I) are extended into a threedimensional 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 $J = -322 \text{ cm}^{-1}$ 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 $[Cu_2(O_2CMe)_4L_2]$ 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).

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To a solution of Cu(MeCO₂)₂ (0.5 mmol) in 1:1 (ν/ν) 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).

rystal aata	
$Cu_2(C_2H_3O_2)_4(C_{11}H_9N)_2]$	Mo $K\alpha$ radiation
$M_r = 673.64$	Cell parameters from 25
Fetragonal, I4 ₁ /a	reflections
a = 20.598 (4) Å	$\theta = 7 - 15^{\circ}$
$x = 14.070 (8) \text{\AA}$	$\mu = 1.48 \text{ mm}^{-1}$
$V = 5970 (4) \text{ Å}^3$	T = 293 (2) K
Z = 8	Block, green
$D_x = 1.499 \text{ Mg m}^{-3}$	$0.42 \times 0.36 \times 0.30 \text{ mm}$

Data collection

Siemens R3m four-circle
diffractometer
ω scans
Absorption correction: empirical
via ψ scan (North et al., 1968)
$T_{\min} = 0.543, \ T_{\max} = 0.642$
4097 measured reflections
3598 independent reflections
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	$(\Delta/\sigma)_{\rm max} < 0.001$
3598 reflections	$\Delta \rho_{\rm max} = 0.37 \ {\rm e} \ {\rm \AA}^{-3}$
192 parameters	$\Delta \rho_{\rm min} = -0.35 \text{ e } \text{\AA}^{-3}$
H-atom parameters constrained	

Table 1

Selected geometric parameters (Å, °).

Cu1-O1	1.975 (3)	Cu1-O2 ⁱ	1.987 (3)
Cu1-O4 ⁱ	1.979 (3)	Cu1-N1	2.150 (3)
Cu1-O3	1.984 (3)		
O1-Cu1-O4 ⁱ	88.94 (15)	O3-Cu1-O2 ⁱ	88.76 (15)
O1-Cu1-O3	89.63 (15)	O1-Cu1-N1	98.49 (12)
O4 ⁱ -Cu1-O3	167.80 (12)	O4 ⁱ -Cu1-N1	95.51 (12)
O1-Cu1-O2i	167.79 (12)	O3-Cu1-N1	96.69 (12)
$O4^i$ -Cu1-O2 ⁱ	90.08 (15)	O2 ⁱ -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: 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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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1496). Services for accessing these data are described at the back of the journal.

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