metal-organic compounds

Tetrakis(μ-benzoato-$\kappa^2 O$:O)bis-{[4-(dimethylamino)pyridine-κN^1]-copper(II)}

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The title compound, $[Cu_2(C_7H_5O_2)_4(C_7H_{10}N_2)_2]$, is a crystallographically centrosymmetric binuclear complex, with Cu atoms [Cu$\cdots$Cu = 2.6982 (4) Å] bridged by four benzoate ligands. Each of the Cu atoms in this bunuclear copper(II) acetate hydrate analogue is present in an approximately square-pyramidal environment, with four O atoms in a plane and the pyridine N atom at the apical site. Selected geometric parameters are compared with values for related tetrabenzoate complexes of copper(II).

Comment

The N-heteroaromatic ligand 4-(dimethylamino)pyridine (DMAP) finds use as a homogeneous catalyst in cellulose acylation in the synthesis of biodegradable plastics (Satgé et al., 2004). DMAP is also known to form transition metal complexes which exhibit luminescence properties (Araki et al., 2005). Our interest in copper(II) carboxylates with DMAP evolves from their catalytic activity. Moreover, carboxylic acid complexes of copper(II) have properties of special interest in the fields of biology and magnetism (Cotton et al., 1999). In particular, the dimeric copper(II) carboxylates $[Cu_2(R\text{-}COO)_4L_2]$ are found to be antiferromagnetic and their magneto-structural correlation has been studied extensively (Kawata et al., 1992).

The title compound, $[Cu_2(\mu\text{-}C_6H_5CO_2)_4(DMAP)_2]$, (I), was previously synthesized by reacting metallic copper with dibenzoyl peroxide and DMAP (Zhang et al., 2003). The molecular structure of (I) as determined by us is analogous to that of copper(II) acetate hydrate and very similar to the structure reported by Zhang et al. (2003). It has a paddle-wheel type dimeric structure (Fig. 1) with an inversion centre located between the Cu ions. Each Cu atom is five-coordinate: the four equatorial O atoms belong to four bridging carboxyl groups and the N atom at the apical position is the pyridine N atom of the DMAP ligand. The Cu—O bond lengths are ca 1.97 Å, but the Cu1—N1 distance is longer [2.141 (1) Å]. The

Cu$\cdots$Cu distance of 2.6982 (4) Å in (I) is shorter than the corresponding distance of 2.711 (1) Å in $[Cu_2(C_6H_5COO)_4$-$(2,6\text{-diaminopyridine})_2]\cdot2CH_3CN$ (Lah et al., 2001) and 2.723 (1) Å in $[Cu_2(C_6H_5COO)_4(2\text{-amino-6-methylpyridine})_2]$

(I)
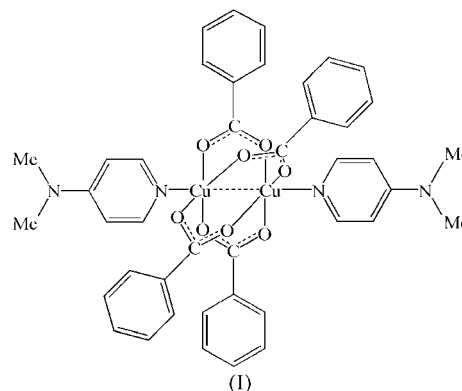
(Kozlevčar et al., 2004), but longer than those in $[Cu_2$-$(C_6H_5COO)_4(caffeine)]_2$ [2.647 (1) Å; Kawata et al., 1992], $[Cu_2(C_6H_5COO)_4(4\text{-ethylpyridine})_2]$ [2.6714 (6) Å; Das et al., 2007], $[Cu_2(C_6H_5COO)_4(N,N\text{-diethylnicotinamide})_2]$ [2.613 (1) Å; Hökelek et al., 1995], $[Cu_2(C_6H_5COO)_4(pyri\text{-}dine)_2]$ [2.681 (1) Å; Speier & Fulop, 1989] and $[Cu_2$-$(C_6H_5OO)_4(urea)_2]$ [2.633 (2) Å; Leban et al., 1997]. However, it is only marginally longer than the distance found previously for compound (I) [2.6976 (9) Å; Zhang et al., 2003].

Based on structural data available in the Cambridge Structural Database (CSD; Allen, 2002), it has previously been observed (Sundberg et al., 1996) that for dimeric copper(II) acetate-type complexes there is a relationship between the Cu$\cdots$Cu separation and the distance by which the central Cu atom moves away from the least-squares plane of the four coordinated O atoms. On the basis of data available for 123 such complexes, we found that the longer the Cu$\cdots$Cu distance within the dimer, the greater the deviation of the Cu
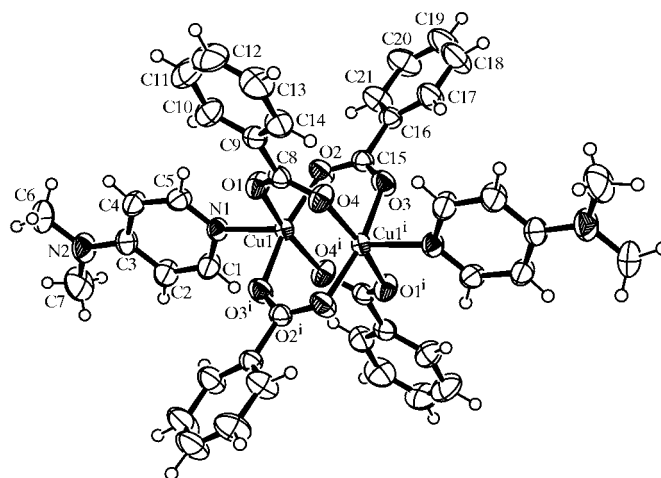

Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry code: (i) $-x$, $1 - y$, $-z$.]

atom from the mean O_4 plane. We have tabulated some available data for complexes of the type $[Cu_2(C_6H_5COO)_4L_2]$ (L = pyridine or substituted pyridine) in Table 2, with a view to seeing how well the earlier conclusions hold true for the tetrabenzoates of copper(II). As can be seen from the data, there are several compounds for which there is no correlation of the above nature. On the other hand, it is observed from the tabulated data that whenever there are substituents on the 2- and/or 6-position of the axial pyridine ligand, the Cu—N distance is relatively long. Again, with the exception of $[Cu_2(C_6H_5COO)_4(4,7\text{-dichloroquinoline})_2]$, the Cu···Cu distances are also long in complexes having ligands of this type. This suggests that steric factors due to the apical ligand may influence the Cu···Cu as well as the Cu—N distances.

The distorted nature of the CuO_4N square pyramid can be understood from the O—Cu—O and O—Cu—N angles. While the former are in the range 88.08 (6)–166.41 (5)°, the latter are in the range 89.88 (6)–103.85 (6)°. The deviations from linearity of the two O—Cu—O angles ($\simeq 166°$) for the two pairs of *trans* O atoms are particularly notable. However, the angles and bonds in the copper coordination environment in (I) are of comparable magnitude *vis á vis* the corresponding values found for several $[Cu_2(C_6H_5COO)_4L_2]$ compounds (Kawata *et al.*, 1992).

The Cu atom is 0.1878 (6) Å from the mean plane formed by the four equatorial O atoms. On the other hand, the coordinated N atom also lies in the same direction, at a distance of 2.312 (1) Å from the plane. The dihedral angle between the planes through Cu1/O2/C15/O3/Cu1^i/O2^i/C15^i/O3^i and Cu1/O1/C8/O4/Cu1^i/O1^i/C8^i/O4^i [symmetry code: (i) $-x, 1-y, -z$] is 88.74 (3)°, which is close to the ideal value of 90°, the observed difference being attributable to packing effects in a crystal of low symmetry. The corresponding value for the complex $[Cu_2(C_6H_5COO)_4(N,N\text{-diethylnicotin-amide})_2]$ (Hökelek *et al.*, 1995) is 88.9 (1)°.

Following the method given by Kawata *et al.* (1992), the rotation angles of the phenyl group relative to the carboxyl group in the bridging benzoate ions, φ_{rot}, and the bending angles of the COO group relative to the Cu—O···O—Cu plane, φ_{bend}, can be calculated. For an isolated binuclear complex, the φ_{rot} and φ_{bend} values are expected to be close to zero (with minimum strain energy). However, in the present structure, (I), the corresponding values are 3.85 (31) and 15.66 (21)°, and 3.71 (28) and 0.91 (25)°, respectively. The deviation of these values from zero is likely to be a consequence of the molecular packing in the crystal lattice. The deviations lead to an improvement in packing effeciency. In such cases, the increased intermolecular strain is compensated for by favourable intermolecular interactions.

The comparison of bond lengths and angles observed here for compound (I) and those reported previously by Zhang *et al.* (2003) shows that, while the crystallographic and geometric parameters are very similar, the s.u. values and the residuals observed in the present work are much improved. This improvement is an outcome of the use of a greater number of reflections in the present work. Moreover, the intensity data used earlier were not corrected for absorption effects.

Experimental

CuCl$_2$·2H$_2$O (0.34 g, 2 mmol) was dissolved in methanol (25 ml). To this solution, sodium benzoate (C_6H_5COONa; 0.576 g, 4 mmol) was added and the mixture was stirred for *ca* 10 min to obtain a green–blue solution. 4-(Dimethylamino)pyridine (0.488 g, 4 mmol) was added and the mixture was stirred for an additional 2 h. The resulting green product was filtered off, washed with small volumes of methanol and dried in a vacuum desiccator over fused CaCl$_2$ (yield 75%). Single crystals of (I) suitable for X-ray diffraction were obtained from a methanol solution of the title complex by slow evaporation.

Crystal data

$[Cu_2(C_7H_5O_2)_4(C_7H_{10}N_2)_2]$	$V = 1981.71$ (10) Å^3
$M_r = 855.86$	$Z = 2$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 10.4339$ (3) Å	$\mu = 1.13$ mm^{-1}
$b = 11.1284$ (3) Å	$T = 293$ (2) K
$c = 17.1616$ (5) Å	$0.33 \times 0.30 \times 0.22$ mm
$\beta = 96.0140$ (1)°	

Data collection

Bruker SMART CCD area-detector diffractometer	19035 measured reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	4112 independent reflections
$T_{min} = 0.707$, $T_{max} = 0.789$	3511 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.019$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.026$	253 parameters
$wR(F^2) = 0.072$	H-atom parameters constrained
$S = 1.03$	$\Delta\rho_{max} = 0.28$ e Å^{-3}
4112 reflections	$\Delta\rho_{min} = -0.27$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—O4^i	1.9711 (12)	Cu1—Cu1^i	2.6982 (4)
Cu1—O2	1.9726 (13)	O1—C8	1.255 (2)
Cu1—O3^i	1.9791 (13)	O2—C15	1.255 (2)
Cu1—O1	1.9796 (12)	O3—C15	1.250 (2)
Cu1—N1	2.1410 (14)	O4—C8	1.258 (2)
O4^i—Cu1—O2	89.42 (6)	O4^i—Cu1—N1	97.89 (6)
O4^i—Cu1—O3^i	88.08 (6)	O2—Cu1—N1	103.85 (6)
O2—Cu1—O3^i	166.26 (6)	O3^i—Cu1—N1	89.88 (6)
O4^i—Cu1—O1	166.41 (5)	O1—Cu1—N1	95.62 (5)
O2—Cu1—O1	88.73 (6)	O1—C8—O4	125.49 (16)
O3^i—Cu1—O1	90.53 (6)	O3—C15—O2	125.66 (16)

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

Structure determination work was carried out using the *WinGX* platform (Farrugia, 1999). All H atoms belonging to the phenyl groups of the benzoate ligands and to the pyridine ring of the DMAP ligand were placed in calculated positions, with C—H = 0.93–0.96 Å and U_{iso}(H) = 1.2 or 1.5 times U_{eq}(C). No restraints were applied for any other parameters during structure refinement.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *publCIF* (Westrip, 2007).

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Table 2
Comparison of geometric parameters (Å) for some copper(II) benzoate dimers of general formula $[Cu_2(C_6H_5COO)_4L_2]$.

DENA is *N,N*-diethylnicotinamide, DAP is 2,6-diaminopyridine, β-pic is 3-methylpyridine, Dquin is 4,7-dichloroquinoline, 4-Mequin is 4-methylquinoline, 7-Mequin is 7-methylquinoline, Etpy is 4-ethylpyridine and AMP is 2-amino-6-methylpyridine. The fourth column lists the shift of the Cu atom from the mean O_4 plane.

Compound	Cu···Cu	Cu—N	Cu shift	Reference
$Cu_2OBz_4(DENA)_2$	2.613 (1)	2.162 (1)	0.190 (1)	*a*
$Cu_2OBz_4(MeCN)_2$	2.632 (5)	2.177 (1)	0.196 (7)	*b*
$Cu_2OBz_4(py)_2$	2.658 (1)	2.170 (3)	0.217 (1)	*c*
$Cu_2OBz_4(\beta$-pic$)_2$	2.664 (1)	2.151 (4)	0.217 (2)	*d*
$Cu_2OBz_4(Dquin)_2$	2.665 (1)	2.235 (2)	0.215 (1)	*d*
$Cu_2OBz_4(Etpy)_2$	2.671 (6)	2.173 (3)	0.175 (8)	*e*
$Cu_2OBz_4(4$-Mequin$)_2$	2.688 (1)	2.207 (2)	0.230 (1)	*d*
$Cu_2OBz_4(7$-Mequin$)_2$	2.688 (1)	2.226 (5)	0.189 (3)	*d*
$Cu_2OBz_4(DMAP)_2$	2.698 (4)	2.312 (1)	0.187 (7)	*f*
$Cu_2OBz_4(DAP)_2$	2.711 (1)	2.263 (4)	0.244 (2)	*b*
$Cu_2OBz_4(AMP)_2$	2.723 (1)	2.283 (7)		*g*

Notes: (*a*) Hökelek *et al.* (1995); (*b*) Lah *et al.* (2001); (*c*) Speier & Fulop (1989); (*d*) Kawata *et al.* (1992); (*e*) Das *et al.* (2007); (*f*) present work; (*g*) Kozlevčar *et al.* (2004).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3150). Services for accessing these data are described at the back of the journal.

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