metal-organic papers

[4-(Dimethylamino)pyridine-κN]bis(pentane-2,4-dionato-$\kappa^2 O,O'$)copper(II)

Leonard F. Lindoy,[a] **John C. McMurtrie**[b] **and David Schilter**[a]*

[a]Centre for Heavy Metals Research, School of Chemistry, F11, The University of Sydney, New South Wales 2006, Australia, and [b]School of Physical and Chemical Sciences, Queensland University of Technology, Queensland 4001, Australia

Correspondence e-mail:
d.schilter@chem.usyd.edu.au

Key indicators

Single-crystal X-ray study
$T = 150$ K
Mean σ(C–C) = 0.002 Å
R factor = 0.026
wR factor = 0.064
Data-to-parameter ratio = 18.5

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

The title complex, [Cu(C$_5$H$_7$O$_2$)$_2$(C$_7$H$_{10}$N$_2$)], is disposed about a twofold axis and forms a discrete molecule with the metal adopting a distorted trigonal–bipyramidal geometry within an NO$_4$ donor set.

Comment

Recent attention has been paid to the rational design and synthesis of metallo-supramolecular architectures (Lindoy & Atkinson, 2000). In particular, several architectures, including new rectangles, 'zig-zag' chain and chiral lattices, have been prepared in our laboratory (Clegg *et al.*, 2004, 2005, 2006). The title complex, (I), was considered a model system for the multinuclear systems referred to above and was obtained by the addition of an equimolar amount of 4-(dimethylamino)pyridine (dmap) to bis(pentane-2,4-dionato)copper(II) in dichloromethane solution. A colour change from blue to deep-green was observed and slow evaporation of this solution afforded green crystals suitable for X-ray analysis.

(I)
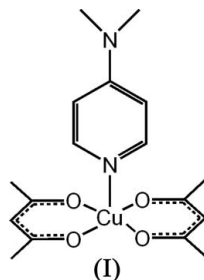
As expected, the structure, Fig. 1, confirms that complexation of dmap to bis(pentane-2,4-dionato)copper(II) has occurred, with the resultant five-coordinate copper(II) centre existing in a distorted trigonal–bipyramidal coordination environment; the complex has twofold symmetry. In this description, atoms N1, O1 and O1^i are positioned at the vertices of the trigonal plane, and atoms O2 and O2^i are at the axial positions (see Table 1 for symmetry code). The six-membered chelate rings are approximately planar and are twisted with respect to each other to form a twofold propeller with a dihedral angle (between the planes defined by the chelate rings) of close to 65°.

In a similar experiment to that described above, the use of two (rather than one) equivalents of dmap failed to induce six-coordination, giving (I) in quantitative yield. This result is in keeping with the addition of a single, strongly basic dmap ligand donating sufficient electron density to the metal centre to render the resulting five-coordinate copper(II) centre

effectively charge neutral, hence inhibiting further adduct formation.

Experimental

A stirred solution of bis(2,4-pentanedionato)copper(II) (0.200 g, 0.76 mmol) and 4-(dimethylamino)pyridine (0.093 g, 0.76 mmol) in dichloromethane solution (25 ml) was brought to reflux, during which time the reaction mixture became green. Subsequent cooling and slow evaporation of the reaction mixture afforded (I) (0.290 g, 99%) as green crystals that were employed for the X-ray crystallographic study. Analysis found: C 53.30, H 6.18, N 7.43%; calculated for $C_{17}H_{24}CuN_2O_4$: C 53.18, H 6.30, N 7.30%.

Crystal data

$[Cu(C_5H_7O_2)_2(C_7H_{10}N_2)]$	$Z = 8$
$M_r = 383.92$	$D_x = 1.458$ Mg m^{-3}
Orthorhombic, $Fdd2$	Mo $K\alpha$ radiation
$a = 11.3708\ (11)$ Å	$\mu = 1.27$ mm^{-1}
$b = 27.215\ (3)$ Å	$T = 150\ (2)$ K
$c = 11.3000\ (11)$ Å	Prism, green
$V = 3496.9\ (6)$ Å^3	$0.49 \times 0.32 \times 0.26$ mm

Data collection

Bruker SMART 1000 CCD diffractometer	8108 measured reflections
ω scans	2107 independent reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	2048 reflections with $I > 2\sigma(I)$
$T_{min} = 0.633$, $T_{max} = 0.718$	$R_{int} = 0.029$
	$\theta_{max} = 28.3°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0425P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.026$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.064$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.05$	$\Delta\rho_{max} = 0.91$ e Å^{-3}
2107 reflections	$\Delta\rho_{min} = -0.24$ e Å^{-3}
114 parameters	Absolute structure: Flack (1983), 968 Friedel pairs
H-atom parameters constrained	Flack parameter: 0.042 (11)

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	2.0156 (12)	Cu1—N1	2.119 (2)
Cu1—O2	1.9301 (10)		
O1—Cu1—O2	91.86 (5)	O2—Cu1—N1	90.60 (5)
O1—Cu1—N1	116.48 (4)	O2—Cu1—O2^i	178.79 (9)
O1^i—Cu1—O2	87.60 (5)		

Symmetry code: (i) $-x + \frac{3}{2}, -y + \frac{1}{2}, z$.

C-bound H atoms were included in idealized positions and refined using a riding-model approximation with aromatic and methyl C—H bond lengths fixed at 0.95 and 0.98 Å, respectively, and with $U_{iso}(H)$ values fixed at $1.2U_{eq}$(aromatic C) and $1.5U_{eq}$(methyl C).

Data collection: SMART (Siemens, 1995); cell refinement: SAINT (Siemens, 1995); data reduction: SAINT and XPREP (Siemens, 1995); program(s) used to solve structure: SIR97 (Altomare et al., 1999); program(s) used to refine structure: SHELXL97 (Sheldrick,
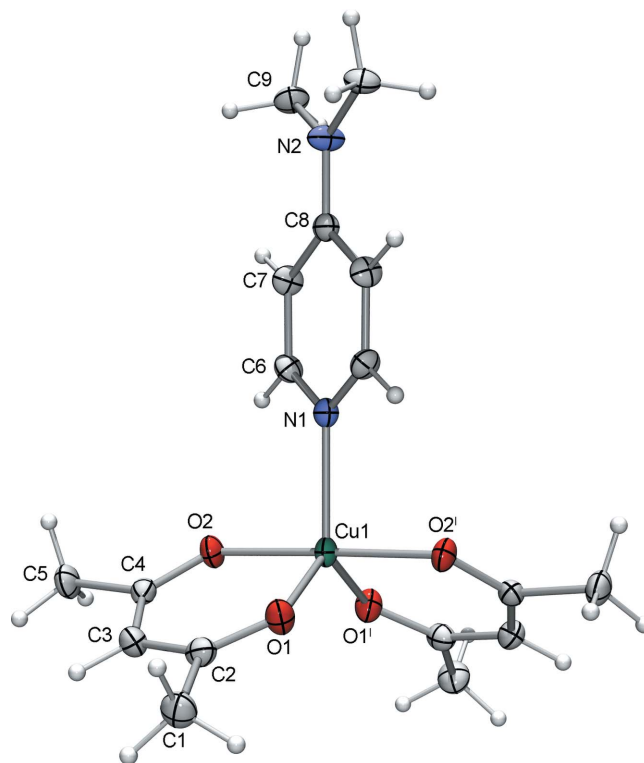

Figure 1
An ORTEP-3 (Farrugia, 1997) representation of (I), shown with 50% probability ellipsoids. [Symmetry operation (i): $\frac{3}{2} - x, \frac{1}{2} - y, z$.]

1997); molecular graphics: ORTEP-3 (Farrugia, 1997) and WinGX32 (Farrugia, 1999); software used to prepare material for publication: enCIFer (Allen et al., 2004).

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