metal-organic papers

# [29H,31H-Tetrabenzo[b,g,l,q]porphinato(2–)-κ⁴N²¹,N²²,N²³,N²⁴]copper(II)

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Key indicators

Single-crystal X-ray study
T = 93 K
Mean σ(C–C) = 0.008 Å
R factor = 0.099
wR factor = 0.266
Data-to-parameter ratio = 11.5

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

The molecule of the title comound, [Cu(C₃₆H₂₀N₄)], is not entirely planar in the crystal structure (i.e. not D_{4h}), but is slightly deformed, with only C_i symmetry. The molecules are stacked along the b axis in a herring-bone fashion.

Comment

We have recently reported that 29H,31H-tetrabenzo-[b,g,l,q]porphin (abbreviated to H₂P) exhibits an excellent field-effect transistor (FET) characteristic (Aramaki et al., 2004) and that the structure of H₂P is similar to that of metal-free β-phthalocyanine (i.e. the phthalocyanine analogue of H₂P) (Aramaki & Mizuguchi, 2003). An appealing feature of our FET system is the use of a soluble precursor of H₂P and its thermal transformation into H₂P directly on the substrate at about 473 K. The title compound (CuP), (I), is found to show an even better FET performance, as characterized by a high mobility of about 1.3 cm²/Vs (Aramaki et al., 2006), compared with about 0.017 cm²/Vs in H₂P (Aramaki et al., 2004). In this connection, the present structure analysis has been carried out in order to study the correlation between the crystal structure and the FET characteristics.

(I)
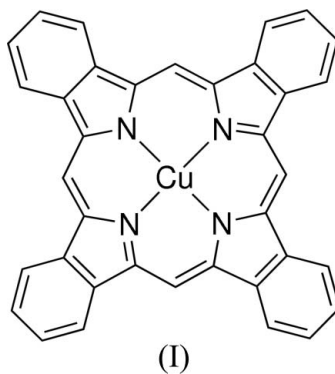
The molecular structure of (I) is shown in Fig. 1. The molecular symmetry is not D_{4h} but C_i, because the molecule, located on an inversion centre, is not entirely flat. The angles between the plane of the four N atoms [N1/N1ⁱ/N2/N2ⁱ; symmetry code: (i) $1 - x, 1 - y, 1 - z$] and the planes of the benzene rings C2–C7 and C11–C16 are 6.1 (2) and 5.4 (2)°, respectively; the angle between the benzene rings is 0.9 (2)°. The present situation is quite similar to that of H₂P, where the corresponding dihedral angles are 6.42 (1)–6.96 (1)° and 0.5 (1)°, respectively (Aramaki & Mizuguchi, 2003).

Fig. 2 shows the molecular arrangement of (I). The molecules are arranged in a herring-bone fashion along the b axis, which is typical of porphin (Aramaki & Mizuguchi, 2003) and
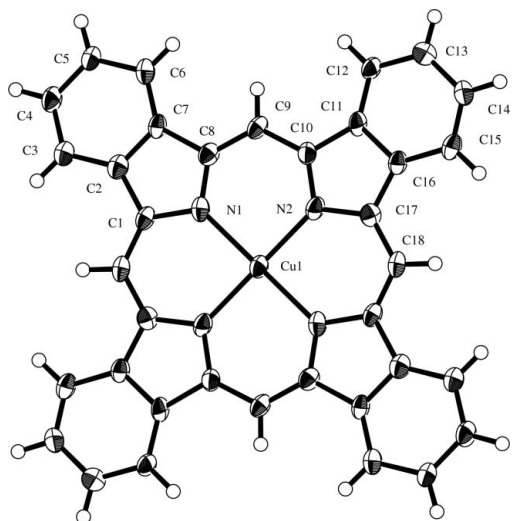
Figure 1
A view of the molecular structure of (I), showing 50% probability displacement ellipsoids. Unlabelled atoms are related to labelled atoms by the symmetry operation $(1 - x, 1 - y, 1 - z)$.

phthalocyanine compounds (Matsumoto *et al.*, 1999). As judged from the space group, lattice parameters and molecular arrangement, CuP is found to be isomorphous with H_2P (isomorphous replacement of 2H by Cu).

Experimental

[1,4,8,11,15,18,22,25-Octahydro-1,4:8,11:15,18:22,25-tetraethano-29H,31H-tetrabenzo[b,g,l,q]porphinato(2−)-$\kappa N^{29},\kappa N^{30},\kappa N^{31},\kappa N^{32}$]-copper(II) is a precursor that gives the title compound (CuP), (I), by thermal decomposition. The precursor was prepared according to the method of Ito *et al.* (2000). Single crystals of (I) were grown directly by thermal decomposition of the precursor at about 610 K in a closed system under high vacuum. A number of tiny needle crystals were obtained over a period of 72 h.

Crystal data

$[Cu(C_{36}H_{20}N_4)]$	$Z = 2$
$M_r = 572.11$	$D_x = 1.599$ Mg m^{-3}
Monoclinic, $P2_1/n$	Cu $K\alpha$ radiation
$a = 12.339$ (2) Å	$\mu = 1.58$ mm^{-1}
$b = 6.5940$ (12) Å	$T = 93$ K
$c = 14.908$ (3) Å	Needle, black
$\beta = 101.537$ (12)°	$0.10 \times 0.02 \times 0.02$ mm
$V = 1188.5$ (4) Å^3	

Data collection

Rigaku R-AXIS RAPID-F imaging-plate diffractometer	11140 measured reflections
	2161 independent reflections
ω scans	1347 reflections with $F^2 > 2\sigma(F^2)$
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)	$R_{int} = 0.206$
$T_{min} = 0.860, T_{max} = 0.969$	$\theta_{max} = 68.3°$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.099$	$w = 1/[\sigma^2(F_o^2) + (0.1369P)^2]$
$wR(F^2) = 0.266$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{max} < 0.001$
2161 reflections	$\Delta\rho_{max} = 1.43$ e Å^{-3}
188 parameters	$\Delta\rho_{min} = -0.55$ e Å^{-3}
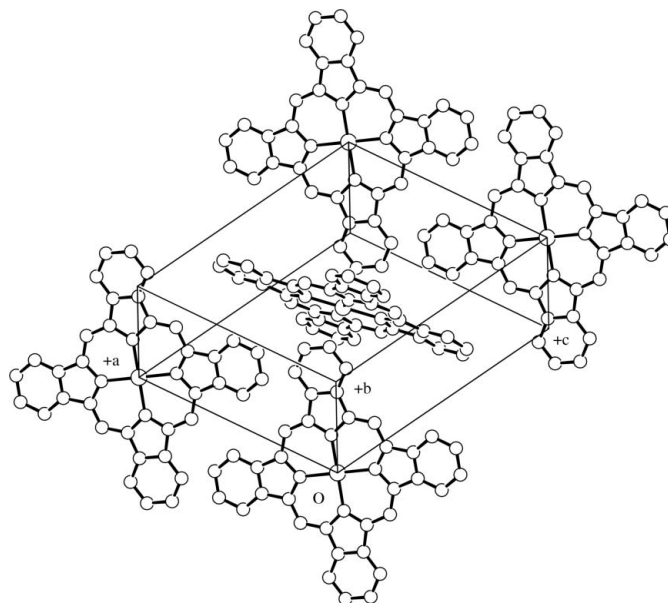
Figure 2
The packing arrangement in (I). H atoms have been omitted

Table 1
Selected geometric parameters (Å, °).

Cu1—N1	2.027 (5)	N1—C8	1.373 (8)
Cu1—N2	2.001 (4)	N2—C10	1.374 (8)
N1—C1	1.395 (8)	N2—C17	1.391 (8)
N1—Cu1—N2	90.0 (2)		

All H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H = 0.95 Å and with $U_{iso}(H) = 1.2U_{eq}(C)$. The highest residual density peak of 1.43 e Å^{-3} is located 1.2 Å from atoms N1 and Cu1.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2005); program(s) used to solve structure: *SIR2002* (Burla *et al.*, 2003); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *CrystalStructure*.

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