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Key indicators

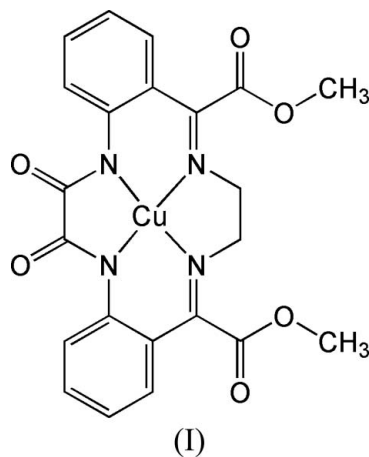
Single-crystal X-ray study
 $T = 293$ K
Mean $\sigma(\text{C}-\text{C}) = 0.005$ Å
Disorder in main residue
 R factor = 0.037
 wR factor = 0.105
Data-to-parameter ratio = 11.2For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.**[Dimethyl 5,6,7,8,15,16-hexahydro-6,7-dioxo-5,8,14,17-tetraazadibenzo[*a,g*]cyclotetradeca-3,9,13,17-tetraene-13,18-dicarboxylato- κ^4 N,N',N''',N'''']copper(II)**

In the title complex, $[\text{Cu}(\text{C}_{22}\text{H}_{18}\text{N}_4\text{O}_6)]$, the Cu^{II} atom is coordinated by four N atoms from a macrocyclic ligand with a square-planar geometry. Weak $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonding occurs between neighbouring Cu^{II} complexes in the crystal structure.

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Comment

Macrocyclic complexes have received considerable attention because of their applications in biology, medicine and chemical techniques (Costamanga *et al.*, 2000; McAuley *et al.*, 2000; Hubin, 2003; Liang & Sadler, 2004; Li *et al.*, 2005). Five $\text{Cu}L'$ complexes incorporating a macrocyclic oxamide Schiff base (L' is dialkyl 5,6,7,8,15,16-hexahydro-6,7-dioxo-5,8,14,17-tetraazadibenzo[*a,g*]cyclotetradecene-13,18-dicarboxylate) have been synthesized to date (Black & Moss, 1987; Gao *et al.*, 2000, 2001), of which three complexes have been characterized crystallographically (Gao *et al.*, 2000, 2001). Here, we report the crystal structure of the title complex, $\text{Cu}L$, (I) (L is dimethyl 5,6,7,8,15,16-hexahydro-6,7-dioxo-5,8,14,17-tetraazadibenzo[*a,g*]cyclotetradecene-13,18-dicarboxylate).



The molecular structure of (I) is illustrated in Fig. 1. The macrocyclic ligand L coordinates to the Cu^{II} atom through the imine N atoms and the deprotonated oxamide N atoms, with a square-planar geometry [maximum deviation 0.059 (3) Å for atom Cu1]. The plane of the oxamide group is tilted relative to the coordination plane with a dihedral angle of 11.2 (8)°. The benzene rings of L are nearly coplanar with the coordination plane, the dihedral angles between the coordination plane and the phenyl rings being 5.2 (8) and 2.9 (8)°.

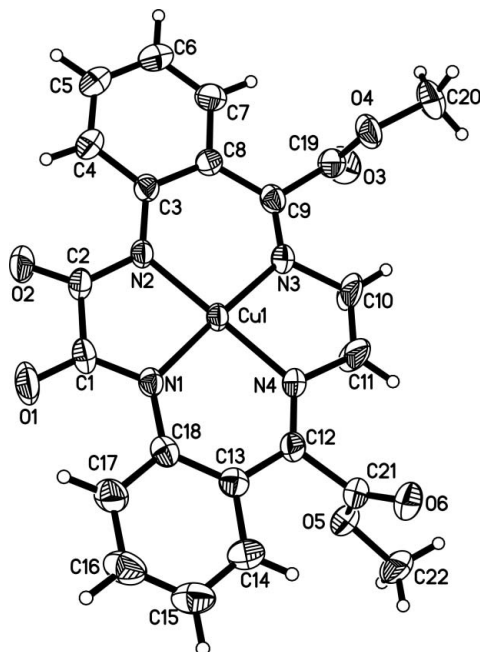


Figure 1
The molecular structure of (I), with 30% probability displacement ellipsoids. The minor disordered component has been omitted for clarity.

Weak C—H···O hydrogen bonding (Table 2) stabilizes the crystal structure.

Experimental

Dimethyl 2,2'-(oxalyldiimino)bis(phenylglyoxylate) was prepared by the literature method of Black & Moss (1987). Dimethyl 2,2'-(oxalyldiimino)bis(phenylglyoxylate) (0.05 mmol), Cu(OAc)₂·H₂O (0.05 mmol) and ethylenediamine (0.05 mmol) were dissolved in a solution of triethylamine (0.3 ml) and methanol (12 ml). The mixture was refluxed for 20 h and then filtered. Crystals of (I) were obtained from the filtrate. Spectroscopic analysis: IR (KBr, ν , cm⁻¹): 1743, 1650, 1605, 1595, 1476, 1140. (IR spectra were recorded on a BIO-RAD FTS 3000 infrared spectrophotometer). The crystals remain solid up to 505 K, at which temperature they decompose. Analysis, calculated for CuC₂₂H₁₈N₄O₆: C 53.06, H 3.64, N 11.25%; found: C 53.19, H 3.72, N 11.36%.

Crystal data

[Cu(C₂₂H₁₈N₄O₆)]
 $M_r = 497.94$
 Monoclinic, $P2_1/c$
 $a = 9.6256$ (15) Å
 $b = 15.676$ (3) Å
 $c = 13.502$ (2) Å
 $\beta = 97.223$ (2)°
 $V = 2021.1$ (5) Å³
 $Z = 4$

$D_x = 1.636$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 2259 reflections
 $\theta = 2.5$ – 23.2°
 $\mu = 1.13$ mm⁻¹
 $T = 293$ (2) K
 Block, brown
 $0.24 \times 0.20 \times 0.14$ mm

Data collection

Bruker SMART APEX II CCD
 area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.694$, $T_{\max} = 0.854$
 10870 measured reflections

3567 independent reflections
 2529 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.036$
 $\theta_{\text{max}} = 25.0^\circ$
 $h = -10 \rightarrow 11$
 $k = -16 \rightarrow 18$
 $l = -16 \rightarrow 16$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.105$
 $S = 1.01$
 3567 reflections
 319 parameters
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0592P)^2 + 0.1852P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.29$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.20$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Cu1—N1	1.919 (2)	N1—C18	1.395 (4)
Cu1—N2	1.918 (2)	N2—C3	1.403 (4)
Cu1—N3	1.940 (3)	N3—C9	1.280 (4)
Cu1—N4	1.940 (3)	N4—C12	1.276 (4)
N2—Cu1—N1	88.06 (11)	N2—Cu1—N3	93.84 (11)
N2—Cu1—N4	174.45 (12)	N1—Cu1—N3	175.81 (10)
N1—Cu1—N4	93.78 (11)	N4—Cu1—N3	83.99 (11)

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$C10'-H10D\cdots O6^i$	0.97	2.39	3.155 (12)	136
$C20-H20B\cdots O2^{ii}$	0.96	2.40	3.319 (5)	159

Symmetry codes: (i) $-x, -y, -z + 1$; (ii) $x - 1, -y + \frac{1}{2}, z - \frac{1}{2}$.

Atoms C10 and C11 are disordered over two sites with the same occupancy of 0.5. Methyl H atoms were placed in calculated positions with C—H = 0.96 Å and torsion angles refined to fit the electron density, with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$. Other H atoms were placed in calculated positions with C—H = 0.93 (aromatic) or 0.97 Å (methylene), and refined in riding mode, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: SMART (Bruker, 1997); cell refinement: SAINT (Bruker, 1997); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 1997); software used to prepare material for publication: SHELXTL.

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