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[3,6,9,12,23-Pentaazatetracyclo[22.4.0.0^{2,6}.0^{14,19}]-octacosa-1(28),12,14,16,18,24,26-heptaene-21,22-dione(2−)-$\kappa^5N^6,N^9,N^{12},N^{20},N^{23}$]copper(II)

Ya-Qiu Sun, Wen Dong, Guang-Ming Yang* and Dai-Zheng Liao*

Department of Chemistry, Nankai University, Tianjin 300071, People's Republic of China

Correspondence e-mail: coord@nankai.edu.cn

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Key indicators

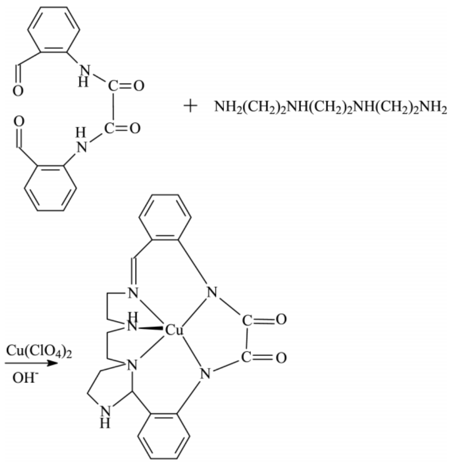
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.007 Å
R factor = 0.052
wR factor = 0.138
Data-to-parameter ratio = 14.9

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

In the title compound, [Cu($C_{22}H_{24}N_6O_2$)], the copper(II) ion is coordinated by five N atoms from the chelating macrocyclic ligand, forming a distorted square-pyramidal geometry. The complexes associate as dimers, disposed about a centre of symmetry, linked through weak intermolecular Cu···O coordination and N—H···O hydrogen bonding.

Comment

The coordination properties of *N*,*N*′-bisoxamides have been investigated thoroughly both in aqueous solution and in the solid state (Ruiz *et al.*, 1999). However, the insolubility of oxamide in common solvents and the hydrolytic reactions it undergoes under deprotonation to yield oxalate preclude an exhaustive exploration of its coordination chemistry (Armendarez & Nakamoto, 1966). These difficulties can be overcome, in the presence of metals ions and when the oxamide has another coordinating group at a position that can form five- or six-membered chelate rings as a consequence of deprotonation of the amide at high pH and subsequent coordination (Ojima & Nakamoto, 1980). Consequently, we designed and synthesized the macrocyclic oxamide complex, (I).



(I)

The crystal structure of the title complex is composed of monomeric copper(II) complexes (Fig. 1). The 2,3-dioxo-5,6,16,17-dibenzo-14,15-imidazolidinepentaazacycloheptadeca-7-ene ligand coordinates to the Cu ion in a chelating mode, leading to a significant distortion from square pyramidal, with Cu—N bonds lengths ranging from 1.950 (3) to 2.318 (4) Å. The N1—C1 bond length is 1.349 (5) Å, indicating this bond to be a partial double bond. Fig. 2 shows how the

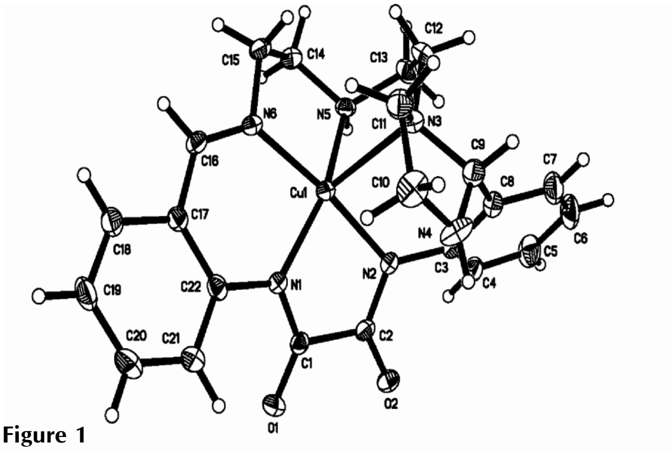


Figure 1
An *ORTEP* view of the title compound, showing displacement ellipsoids at the 50% probability level.

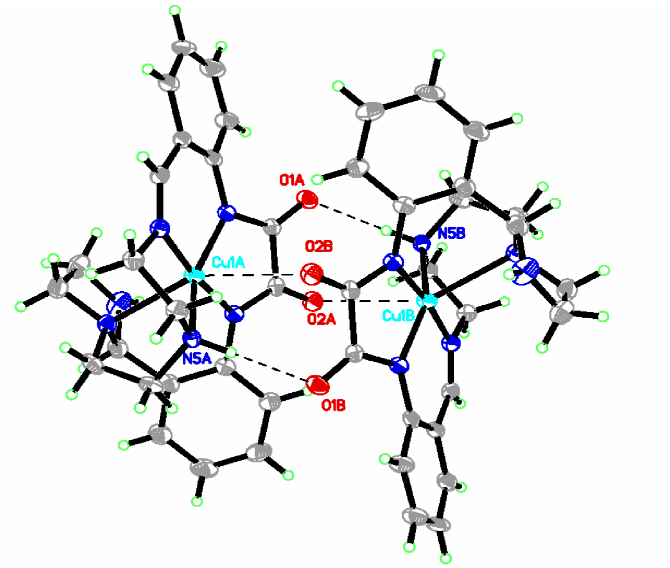


Figure 2
View of weak coordination interactions and hydrogen bonds in the dimer.

complexes associate as dimers disposed about a centre of symmetry, with an intermolecular Cu1$\cdots$O2^{i} distance of 3.129 (3) Å and a hydrogen-bonding contact distance, N5$\cdots$O1^{i}, of 2.974 (5) Å [symmetry code: (i) $1 - x, -y, 1 - z$].

Experimental

The title compound was prepared by refluxing and stirring diformyloxanilide (2.49 g, 0.01 mol), triethylenetetramine (2.96 g, 0.02mol) and copper(II) perchlorate (3.70 g, 0.01 mol) for 3.5 h in 50 ml of MeOH in the presence of four drops of 2 *M* NaOH. The mixture was cooled and filtered. The resulting deep-green filtrate, kept at room temperature for several days, gave rise to deep-green crystals suitable for X-ray analysis. Analysis calculated for $C_{22}H_{24}CuN_6O_2$: C 56.45, H 5.16, N 17.96%; found: C 56.43, H 5.21, N 17.87%.

Crystal data

$[Cu(C_{22}H_{24}N_6O_2)]$
$M_r = 468.01$
Monoclinic, $P2_1/n$
$a = 13.178$ (7) Å
$b = 11.587$ (6) Å
$c = 14.516$ (7) Å
$\beta = 112.949$ (8)°
$V = 2041.0$ (18) Å^3
$Z = 4$

$D_x = 1.523$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 755 reflections
$\theta = 2.5$–23.1°
$\mu = 1.10$ mm^{-1}
$T = 293$ (2) K
Block, green
0.26 × 0.24 × 0.20 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.650$, $T_{max} = 0.802$
11 388 measured reflections

4174 independent reflections
2632 reflections with $I > 2\sigma(I)$
$R_{int} = 0.060$
$\theta_{max} = 26.4°$
$h = -10 \rightarrow 16$
$k = -13 \rightarrow 14$
$l = -18 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.138$
$S = 1.06$
4174 reflections
281 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0669P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.60$ e Å^{-3}
$\Delta\rho_{min} = -0.57$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0131 (10)

H atoms were constrained as riding atoms, with C—H distances of 0.93, 0.97 and 0.98 Å, and N—H distances of 0.86 and 0.91 Å. U_{iso}(H) values were set at $1.1U_{eq}$ of the parent atom.

Data collection: *SMART-NT* (Bruker, 1998); cell refinement: *SMART-NT*; data reduction: *SAINT-NT* (Bruker, 1998); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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