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### Di- $\mu$ -chloro-bis[chloro(6,7,8,9,10,11,18,19-octahydro-5H,17H-dibenzof[*o*][1,5,9,13]-dioxadiazacyclohexadecane)copper(II)]<sup>†</sup>

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#### Abstract

The title complex, [CuCl<sub>2</sub>(C<sub>20</sub>H<sub>26</sub>N<sub>2</sub>O<sub>2</sub>)]<sub>2</sub>, has a centrosymmetrical dimeric structure linked by a pair of chloride bridges. Each Cu atom has the five-coordinated geometry of a distorted square pyramid. The axial sites are occupied by the bridging chlorides which are bound asymmetrically to Cu at distances of 2.8288 (14) and 2.2963 (12) Å. The Cu...Cu distance of 3.4294 (13) Å is too long to suggest a Cu—Cu bond in the dimeric unit.

<sup>†</sup> Alternative name: di- $\mu$ -chloro-bis{chloro[2,6-dioxo-14,18-diazatricyclo[18.4.0.0<sup>7,12</sup>]]tetracos-1(20),7(12),8,10,21,23-hexaene-*N,N'*-copper(II)}.

#### Comment

In recent years, various macrocyclic ligands have been the subject of an intense research effort because of their high selectivity towards metal ions. From the investigation of the interaction of N<sub>2</sub>O<sub>2</sub>-donor macrocycles with Cu<sup>II</sup> and high-spin Ni<sup>II</sup>, Andereg, Ekstrom, Lindoy & Smith (1980) reported that one of the major parameters affecting the metal-ion specificity for Ni<sup>II</sup> is the hole size in the macrocyclic ligand. It has been confirmed by X-ray studies of Ni<sup>II</sup> analogues (Adam *et al.*, 1979) that the nickel ion sits in the hole of the macrocycle and a clear correlation between macrocyclic hole size and thermodynamic stability has been observed. In contrast, such a correlation was not observed for Cu<sup>II</sup> complexes (Adam *et al.*, 1980). In an effort to elucidate the difference in behaviour for Cu<sup>II</sup> complexes, we have determined the structure of title complex, (I).

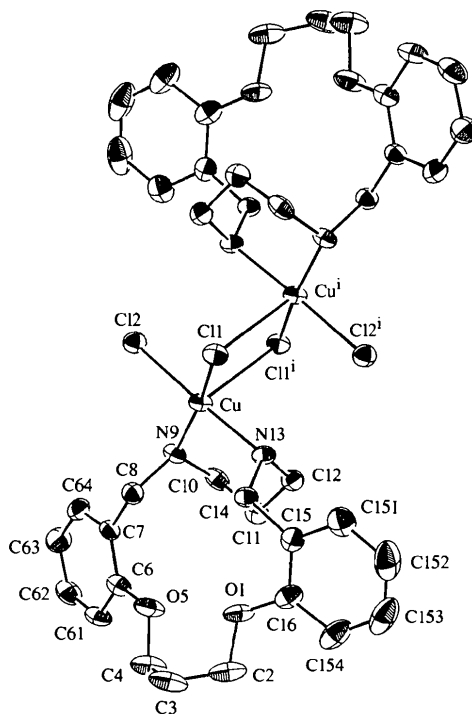
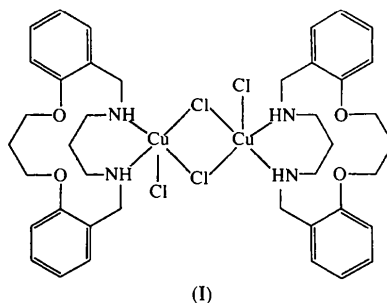


Fig. 1. Displacement ellipsoid plot (50% probability level) for the title complex with the atom-numbering scheme. H atoms have been omitted for clarity.

Each Cu atom has the five-coordinated geometry of a distorted square pyramid. The Cu atom is bound to two secondary amine N atoms in *cis* positions, to a terminal Cl2 and a bridging Cl1 atom in the basal plane of a square-planar geometry. The Cu—N distances are 2.025 (4) and 2.044 (4) Å, and the Cu—Cl distances in the basal plane are 2.2963 (12) and 2.2949 (14) Å. The axial site is occupied by the other bridging chloride [Cl1<sup>i</sup>; symmetry code: (i)  $-x, 1-y, -z$ ] which is at a much greater distance [2.8288 (14) Å] than Cl1 [2.2963 (12) Å] in the basal plane. The Cu···Cu<sup>i</sup> separation of 3.4294 (13) Å is similar to those of related dimeric Cu<sup>II</sup> complexes which have no Cu—Cu bond (Bailey, Fenton, Williams & Winter, 1989).

## Experimental

The title complex was prepared by adding a solution of the ligand in methanol dropwise to a hot methanolic solution of copper(II) chloride. The resulting precipitate was recrystallized from acetonitrile by slow evaporation of the solvent at room temperature.

### Crystal data

[Cu<sub>2</sub>Cl<sub>4</sub>(C<sub>20</sub>H<sub>26</sub>N<sub>2</sub>O<sub>2</sub>)<sub>2</sub>]  
*M<sub>r</sub>* = 921.78  
 Monoclinic  
*P*2<sub>1</sub>/*c*  
*a* = 7.529 (2) Å  
*b* = 13.278 (2) Å  
*c* = 20.457 (3) Å  
 $\beta$  = 92.14 (2)°  
*V* = 2043.7 (7) Å<sup>3</sup>  
*Z* = 2  
*D<sub>x</sub>* = 1.498 Mg m<sup>-3</sup>  
*D<sub>m</sub>* not measured

Mo *K*α radiation  
 $\lambda$  = 0.71069 Å  
 Cell parameters from 25 reflections  
 $\theta$  = 11.34–12.67°  
 $\mu$  = 1.348 mm<sup>-1</sup>  
*T* = 293 (2) K  
 Block  
 0.25 × 0.20 × 0.20 mm  
 Light green

### Data collection

Enraf–Nonius CAD-4 diffractometer  
 $\omega/2\theta$  scans  
 Absorption correction: none  
 3152 measured reflections  
 3152 independent reflections  
 2414 reflections with  $I > 2\sigma(I)$

$\theta_{\max}$  = 24.98°  
 $h = -8 \rightarrow 8$   
 $k = 0 \rightarrow 15$   
 $l = 0 \rightarrow 24$   
 3 standard reflections  
 frequency: 180 min  
 intensity decay: <2.3%

### Refinement

Refinement on *F*<sup>2</sup>  
 $R[F^2 > 2\sigma(F^2)] = 0.050$   
 $wR(F^2) = 0.100$   
*S* = 1.062  
 3152 reflections  
 276 parameters  
 All H atoms refined  
 $w = 1/[\sigma^2(F_o^2) + (0.0392P)^2 + 1.0274P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.416 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.247 \text{ e } \text{Å}^{-3}$   
 Extinction correction: none  
 Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Cu—N9	2.025 (4)	C64—C7	1.371 (6)
Cu—N13	2.044 (4)	C7—C8	1.516 (6)
Cu—Cl2	2.2949 (14)	C8—N9	1.492 (6)
Cu—Cl1	2.2963 (12)	N9—C10	1.475 (6)
Cu—Cl1 <sup>i</sup>	2.8288 (14)	C10—C11	1.500 (6)
O1—C16	1.355 (6)	C11—C12	1.499 (6)
O1—C2	1.417 (6)	C12—N13	1.482 (5)
C2—C3	1.483 (8)	N13—C14	1.493 (5)
C3—C4	1.488 (8)	C14—C15	1.498 (6)
C4—O5	1.429 (6)	C15—C151	1.369 (7)
O5—C6	1.367 (6)	C15—C16	1.400 (7)
C6—C7	1.381 (6)	C151—C152	1.382 (9)
C6—C61	1.391 (6)	C152—C153	1.371 (10)
C61—C62	1.369 (7)	C153—C154	1.360 (10)
C62—C63	1.347 (8)	C154—C16	1.393 (7)
C63—C64	1.380 (7)		
N9—Cu—N13	91.2 (2)	C64—C7—C8	121.1 (4)
N9—Cu—Cl2	87.5 (1)	C6—C7—C8	121.7 (5)
N13—Cu—Cl2	176.7 (1)	N9—C8—C7	114.4 (4)
N9—Cu—Cl1	164.4 (1)	C10—N9—C8	115.2 (4)
N13—Cu—Cl1	87.6 (1)	C10—N9—Cu	117.1 (3)
Cl2—Cu—Cl1	94.48 (4)	C8—N9—Cu	111.2 (3)
N9—Cu—Cl1 <sup>i</sup>	98.8 (1)	N9—C10—C11	112.8 (4)
N13—Cu—Cl1 <sup>i</sup>	88.0 (1)	C12—C11—C10	113.8 (4)
Cl2—Cu—Cl1 <sup>i</sup>	89.20 (5)	N13—C12—C11	113.6 (4)
Cl1—Cu—Cl1 <sup>i</sup>	96.69 (4)	C12—N13—C14	114.6 (4)
Cu—Cl1—Cu <sup>i</sup>	83.31 (4)	C12—N13—Cu	115.5 (3)
C16—O1—C2	118.5 (4)	C14—N13—Cu	112.7 (3)
O1—C2—C3	111.0 (5)	N13—C14—C15	113.6 (4)
C2—C3—C4	118.0 (6)	C151—C15—C16	118.0 (5)
O5—C4—C3	109.6 (5)	C151—C15—C14	120.8 (5)
C6—O5—C4	118.1 (4)	C16—C15—C14	121.1 (5)
O5—C6—C7	116.3 (4)	C15—C151—C152	121.5 (7)
O5—C6—C61	122.6 (5)	C153—C152—C151	119.1 (7)
C7—C6—C61	121.1 (5)	C154—C153—C152	121.5 (7)
C62—C61—C6	119.1 (5)	C153—C154—C16	118.9 (7)
C63—C62—C61	121.1 (5)	O1—C16—C154	123.1 (6)
C62—C63—C64	119.1 (6)	O1—C16—C15	116.2 (4)
C7—C64—C63	122.4 (5)	C154—C16—C15	120.7 (6)
C64—C7—C6	117.2 (4)		

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

The title structure was solved by direct methods and refined by full-matrix least squares with anisotropic displacement factors for the non-H atoms. The C-bonded H-atom positions were calculated geometrically (aliphatic: 0.97; phenyl: 0.93 Å) and constrained to ride on the relevant C atoms. The positions of the N-bonded H atoms were found from a difference Fourier synthesis. All H atoms were refined isotropically.

Data collection: *SDP* (Frenz, 1985). Cell refinement: *SDP*. Data reduction: *SDP*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1126). Services for accessing these data are described at the back of the journal.

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### Bis[(anhydro-*meso*-rhodochlorinato-XV methyl ester)zinc(II)]

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#### Abstract

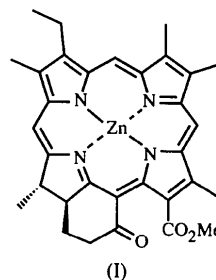
The title compound, bis[(methyl 8,13-diethyl-2,2<sup>1</sup>,2<sup>2</sup>,2<sup>3</sup>-tetrahydro-3,7,12,17-tetramethyl-2<sup>3</sup>-oxo-3*H*-benzo[*at*]-porphyrin-18-carboxylato- $\kappa^4N$ )zinc(II)], [Zn(C<sub>33</sub>H<sub>34</sub>N<sub>4</sub>O<sub>3</sub>)<sub>2</sub>], has similar structural characteristics to the naturally occurring factor F430 and forms dimers that are held together by axial interactions between the zinc(II) center and the cyclohexanone carbonyl O atom of a neighboring macrocycle [Zn—O 2.204 (3) Å]. These dimers form infinite stacks in the crystal stabilized by  $\pi$ – $\pi$  interactions between the aromatic ring systems.

#### Comment

The structure of the cofactor F430 of methyl coenzyme M reductase involved in methanogenesis has been determined unambiguously as a nickel hydrocorphin (Färber *et al.*, 1991). The structure is characterized by a high degree of saturation of the basic porphyrin system and the presence of a fused cyclohexanone ring. The latter structural feature is also found in derivatives of the anhydro-*meso*-porphyrin-XV series, which can be chemically synthesized from chlorophyll derivatives (Smith & Simpson, 1987).

The zinc(II) complex of anhydro-*meso*-rhodochlorin methyl ester, (I), shows the same *trans* arrangement of the H atoms at C17 and C18 as found in cofactor F430, with a C17—C18 single bond of 1.451 (7) Å.

The structural characteristics of the macrocycle system are typical for chlorins (Scheidt & Lee, 1987). The ring system shows a moderate degree of ruffling, *i.e.* a non-planar macrocycle distortion with tilting of the pyrrole rings against the mean plane (Scheidt & Lee, 1987). The average deviation of the 24 atoms comprising the tetrapyrrole system from their least-squares plane is 0.132 Å. The largest deviations from planarity are observed for some C<sub>b</sub> positions and the *meso*-C atoms, the latter being displaced alternately above and below the mean plane by 0.2–0.3 Å. The structure of the corresponding nickel(II) isobacteriochlorin [(anhydro-*meso*-rhodoisobacteriochlorinato)nickel(II)] shows a significantly higher degree of S<sub>4</sub> ruffling (Renner *et al.*, 1991).



Interestingly, the presence of the fused cyclohexanone ring leads to the formation of a bischlorin structure, consisting of two macrocycles, related to each other by an inversion center and held together using the carbonyl O atom of the cyclohexanone ring of one macrocycle as an axial ligand to the zinc center of another (Fig. 1). Thus, the core geometry is similar to that of pentacoordinate zinc(II) porphyrins, with the zinc center located 0.22 Å above the mean plane of the molecule and a Zn—O bond length of 2.204 (3) Å.

This bond length is comparable to that found in monomeric pentacoordinate zinc(II) porphyrins with water or alcohols as axial ligands (Scheidt & Lee, 1987), but is shorter than those found in the polymeric (2,3,7,8,12,13,17,18-octaethyl-5,10,15,20-tetranitroporphyrinato)zinc(II), where a nitro O atom serves as an axial ligand [Zn—O 2.485 (5) Å; Senge & Smith, 1994], and in a cyclophane-type zinc(II) porphyrin benzoquinone, which has a quinone O atom as an axial ligand [Zn—O 2.532 (3) Å; Staab, Krieger, Anders & Rückemann, 1994]. Axial coordination of carbonyl O atoms to metal centers of neighboring macrocycles is often found in chlorophyll aggregates (Abraham & Rowan, 1991) and in the solid-state structures of covalently linked zinc(II) porphyrin quinones (Staab, Krieger, Anders & Rückemann, 1994; Senge & Kurreck, 1997).

The bischlorin is further characterized by weak  $\pi$ – $\pi$  interactions. The interplanar separation (*i.e.* the distance between the centers of the planes defined by the four N atoms) of the ring systems in a given dimer is 3.95 (1) Å.