

## Structure of an Asymmetric Bridged Binuclear Copper(II) Complex

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(Received 7 December 1984; accepted 25 February 1985)

**Abstract.**  $\mu$ -{2,6-Bis[3-(dimethylamino)propylimino-methyl]-4-methylphenolato-*N,N',N'',N'''*, $\mu$ -O}- $\mu$ -hydroxo-diperchloratodicopper(II) monohydrate,  $C_{19}H_{32}Cl_2Cu_2N_4O_{10}\cdot H_2O$ .  $M_r = 692.5$ , monoclinic,  $C2/c$ ,  $a = 29.924$  (2),  $b = 12.289$  (1),  $c = 15.168$  (1),  $\beta = 91.84$  (1)°,  $V = 5575.3$  Å<sup>3</sup>,  $Z = 8$ ,  $D_m = 1.64$  (1),  $D_x = 1.650$  g cm<sup>-3</sup>, Mo  $K\alpha$ ,  $\lambda = 0.71069$  Å,  $\mu = 16.98$  cm<sup>-1</sup>,  $F(000) = 2848$ ,  $T = 296$  K, final  $R = 0.038$ , 3239 unique reflections. The asymmetric unit consists of the macrocyclic binuclear cation, two perchlorate ions and one water molecule. The two Cu atoms are asymmetrically bridged by a hydroxyl [Cu—O, 1.915 (3), 1.898 (3) Å] and a phenolate oxygen [Cu—O, 2.001 (2), 1.980 (2) Å]. The copper coordination polyhedra are distorted tetragonal pyramids with a roughly square-planar  $N_2O_2$  basal plane and two additional weakly bound ligands forming the apex, Cu(1)—O(water) = 2.346 (4) Å and Cu(2)—O (perchlorate) = 2.544 (3) Å.

**Introduction.** The crystal structure of the title compound has been determined as part of an investigation on asymmetric bridged dimeric copper(II) complexes modelling the active site in the dioxygen-carrying protein haemocyanin (Lorösch, Paulus & Haase, 1985). Asymmetric copper dimers are used to correlate structural and magnetic properties in order to understand the unusual magnetic behaviour of haemocyanin.

The multidentate ligand 2,6-bis{3-(dimethylamino)-propyliminomethyl}-4-methylphenol is able to form interesting binuclear copper(II) complexes in which the exogenous bridge can be exchanged selectively. The azido-bridged species has already been investigated (Lorösch *et al.*, 1985). The magnetic behaviour of the title compound, related to its structural features, will be discussed elsewhere (Lorösch, Quotschalla & Haase, 1985).

**Experimental.** Reaction of 2-hydroxy-5-methylisophthalaldehyde (Ullmann & Brittner, 1909) with 3-dimethylamino-1-propylamine (molar ratio 1:2) in methanolic solution gave the macrocyclic Schiff-base ligand *L*. Addition of copper perchlorate and dilution with water results in the crude product. Upon twofold recrystallization blue parallelepipeds were obtained;  $D_m$

by flotation in  $CHCl_3/CHBr_3$ ; crystal size  $0.3 \times 0.5 \times 0.6$  mm; cell constants and e.s.d.'s at 296 K from least-squares refinement of the  $2\theta$  values of 64 reflections. Data collected on a Stoe-Siemens four-circle diffractometer. 4043 intensities measured,  $2\theta_{max} = 45^\circ$ ,  $-32 \leq h \leq 32$ ,  $-13 \leq k \leq 13$ ,  $0 \leq l \leq 16$ ; 3 standard reflections, intensity variations < 4%; 3628 unique reflections,  $R_{int} = 0.020$ ; 389 unobserved with  $F_o < 3\sigma(F_o)$ ; numerical absorption correction, min. and max. transmission factors 0.3845 and 0.6279. Structure solved by direct methods with *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). C-bound H atoms placed in calculated positions (C—H = 1.08 Å), O-bound H atoms from difference Fourier map,  $U_H$  fixed at  $1.1 U_{eq}$  of carrying atom; non-hydrogen atoms refined by least squares with anisotropic thermal parameters, refinement based on  $F$ ;  $w = 1/\sigma^2(F_o)$ ; final difference Fourier map with peaks within  $\pm 0.51 e \text{ \AA}^{-3}$ . Final refinement, 367 variables, gave  $R = 0.038$ ,  $wR = 0.039$ ; max.  $\Delta/\sigma$  1.4, for C(11) methyl rotation, max.  $\Delta/\sigma$  for non-rotation parameter 0.2. Final positional and thermal parameters are given in Table 1.\* Calculations were performed on the Data General Eclipse S140 computer using a program package developed in the application laboratory of Stoe & Cie (Darmstadt) and on the IBM 3081 computer of the Technische Hochschule Darmstadt. Atomic scattering factors taken from *International Tables for X-ray Crystallography* (1974).

**Discussion.** The title compound crystallizes with the binuclear  $(LCu_2-OH)^{2+}$  cation, two perchlorate groups and one water molecule in the asymmetric unit. Selected interatomic distances and angles are given in Table 2.

The binuclear cation is represented in Fig. 1 including the numbering system used here. The macrocyclic Schiff base acts as a quinque-dentate ligand as is known from the literature (Okawa, Tokii, Nonaka,

\* Lists of structure factors, anisotropic thermal parameters, calculated hydrogen atom parameters, bond lengths and angles and least-squares planes and a figure showing a unit-cell projection have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42098 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Muto & Kida, 1973). The two Cu atoms are bridged by the hydroxyl group, O(1), and by the oxygen atom O(2) of the quinquedentate ligand. The two imino and the two amino N atoms of the ligand complete the roughly square-planar coordination of the two Cu atoms. Each

Table 1. Atomic positional parameters and equivalent isotropic temperature factors ( $\text{\AA}^2$ ) of the non-hydrogen atoms with e.s.d.'s in parentheses

$$B_{\text{eq}} = \frac{2}{3}\pi^2(U_{11} + U_{22} + U_{33}).$$

	x	y	z	$B_{\text{eq}}$
Cu(1)	0.39136 (2)	0.12252 (4)	0.16312 (3)	3.14
Cu(2)	0.35491 (1)	0.35158 (4)	0.16779 (3)	3.01
O(1)	0.3367 (1)	0.2038 (2)	0.1610 (2)	3.5
N(1)	0.3574 (1)	-0.0162 (3)	0.1221 (2)	3.9
C(1)	0.3170 (2)	-0.0350 (4)	0.1768 (4)	5.7
C(2)	0.3413 (2)	0.0075 (4)	0.0316 (3)	5.7
C(3)	0.3826 (2)	-0.1199 (3)	0.1245 (3)	4.9
C(4)	0.4295 (2)	-0.1114 (4)	0.0915 (4)	5.5
C(5)	0.4608 (2)	-0.0483 (4)	0.1530 (3)	5.1
N(2)	0.4524 (1)	0.0704 (3)	0.1497 (2)	3.6
C(6)	0.4858 (1)	0.1314 (3)	0.1364 (3)	3.8
O(2)	0.4132 (1)	0.2756 (2)	0.1777 (2)	3.0
C(7)	0.4519 (1)	0.3165 (3)	0.1541 (2)	2.9
C(8)	0.4880 (1)	0.2491 (3)	0.1332 (3)	3.2
C(9)	0.5284 (1)	0.2951 (4)	0.1088 (3)	3.7
C(10)	0.5353 (1)	0.4058 (4)	0.1025 (3)	3.9
C(11)	0.5784 (1)	0.4539 (4)	0.0738 (3)	5.0
C(12)	0.4998 (1)	0.4717 (4)	0.1263 (3)	3.8
C(13)	0.4589 (1)	0.4302 (3)	0.1514 (3)	3.1
C(14)	0.4251 (1)	0.5084 (3)	0.1763 (3)	3.5
N(3)	0.3833 (1)	0.4910 (3)	0.1865 (2)	3.3
C(15)	0.3557 (1)	0.5834 (3)	0.2131 (3)	4.1
C(16)	0.3189 (1)	0.6059 (3)	0.1431 (4)	5.0
C(17)	0.2835 (1)	0.5210 (3)	0.1371 (3)	4.5
N(4)	0.2981 (1)	0.4115 (3)	0.1063 (2)	3.6
C(18)	0.3095 (2)	0.4157 (4)	0.0119 (3)	5.2
C(19)	0.2593 (1)	0.3376 (4)	0.1148 (4)	5.1
Cl(1)	0.30492 (4)	0.28673 (9)	0.37310 (8)	4.47
O(3)	0.3193 (1)	0.3717 (3)	0.3169 (2)	5.8
O(4)	0.2857 (1)	0.2022 (3)	0.3202 (3)	8.4
O(5)	0.3421 (1)	0.2440 (4)	0.4199 (3)	8.8
O(6)	0.2737 (1)	0.3273 (4)	0.4323 (3)	9.0
Cl(2)	0.08596 (5)	0.29550 (11)	0.10215 (9)	5.86
O(7)	0.0965 (2)	0.2489 (4)	0.0223 (3)	10.4
O(8)	0.0671 (2)	0.3996 (4)	0.0869 (4)	11.6
O(9)	0.0597 (2)	0.2338 (4)	0.1563 (4)	12.3
O(10)	0.1276 (2)	0.3156 (6)	0.1475 (3)	13.9
O(11)	0.3940 (1)	0.0857 (4)	0.3150 (3)	5.7

Table 2. Selected bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) with e.s.d.'s in parentheses

Cu(1)—Cu(2)	3.021 (1)		
Cu(1)—O(1)	1.915 (3)	Cu(2)—O(1)	1.898 (3)
Cu(1)—O(2)	2.001 (2)	Cu(2)—O(2)	1.980 (2)
Cu(1)—N(1)	2.071 (3)	Cu(2)—N(4)	2.050 (3)
Cu(1)—N(2)	1.951 (3)	Cu(2)—N(3)	1.929 (3)
Cu(1)—O(11)	2.346 (4)	Cu(2)—O(3)	2.544 (3)
Cu(1)—O(1)—Cu(2)	104.7 (1)		
Cu(1)—O(2)—Cu(2)	98.7 (1)		
O(1)—Cu(1)—O(2)	77.7 (1)	O(1)—Cu(2)—O(2)	78.7 (1)
O(1)—Cu(1)—O(11)	96.8 (1)	O(1)—Cu(2)—O(3)	90.8 (1)
O(1)—Cu(1)—N(1)	90.8 (1)	O(1)—Cu(2)—N(4)	95.0 (1)
O(1)—Cu(1)—N(2)	166.0 (1)	O(1)—Cu(2)—N(3)	169.1 (1)
O(2)—Cu(1)—O(11)	94.1 (1)	O(2)—Cu(2)—O(3)	111.8 (1)
O(2)—Cu(1)—N(1)	164.3 (1)	O(2)—Cu(2)—N(4)	156.9 (1)
O(2)—Cu(1)—N(2)	91.0 (1)	O(2)—Cu(2)—N(3)	91.4 (1)
O(11)—Cu(1)—N(1)	97.9 (1)	O(3)—Cu(2)—N(4)	90.2 (1)
O(11)—Cu(1)—N(2)	92.1 (1)	O(3)—Cu(2)—N(3)	88.8 (1)
N(1)—Cu(1)—N(2)	98.7 (1)	N(3)—Cu(2)—N(4)	95.9 (1)

Cu atom has an additional weakly bound axial ligand: a perchlorate oxygen, O(3), in the case of Cu(2) and a water molecule, O(11), in the case of Cu(1). The resulting coordination of Cu is therefore tetragonal pyramidal (see Fig. 2). The basal plane of the Cu(1) coordination polyhedron is essentially planar [maximum deviation 0.027 (5)  $\text{\AA}$ ] whereas the four equatorial atoms about Cu(2) show considerable distortions from planarity [maximum deviation 0.235 (5)  $\text{\AA}$ ]. Both Cu atoms deviate from their basal planes [mean value 0.17 (1)  $\text{\AA}$ ], shifted towards the apex.

Fig. 2 illustrates the interaction between the cation, the two perchlorate ions and the water molecule. The short contacts [O(1)...O(4) 2.897 (5)  $\text{\AA}$ ; O(11)...O(5) 2.982 (6)  $\text{\AA}$ ; O(11)...O(8) ( $\frac{1}{2}-x$ ,  $y-\frac{1}{2}$ ,  $\frac{1}{2}-z$ ) 2.947 (6)  $\text{\AA}$ ] are consistent with hydrogen bonds of type O—H...O. A projection of the unit cell is displayed in Fig. 3.\* The essentially two-dimensional cations are oriented nearly perpendicular to the *c* axis with a small deviation of the aromatic ring system from this orientation. This part of the cation shows overlapping with neighbouring cations. No intermolecular interaction between asymmetric units occurs.

This work has been supported by the Deutsche Forschungsgemeinschaft. JL thanks the Fonds der Chemischen Industrie, Frankfurt, for a scholarship.

\* Fig. 3 has been deposited. See deposition footnote.

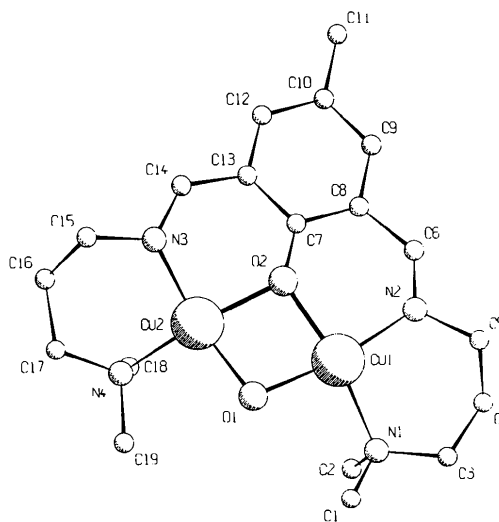


Fig. 1. Perspective view of the binuclear cation, with the labelling scheme used. H atoms have been omitted.

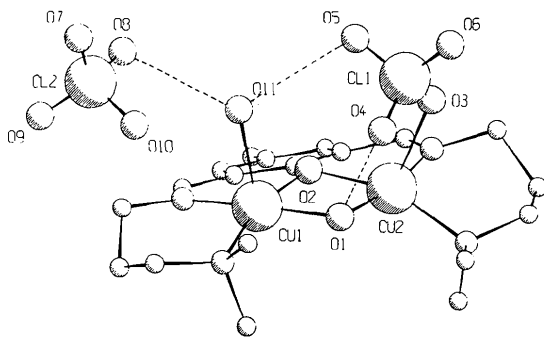


Fig. 2. The Cu-coordination polyhedra. Broken lines show the hydrogen-bond network.

*Acta Cryst.* (1985), **C41**, 899–902

## Structure of *trans*-Amminebis(ethylenediamine)fluorochromium(III) Perchlorate, [CrF(NH<sub>3</sub>)(C<sub>2</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>

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(Received 17 August 1984; accepted 28 February 1985)

**Abstract.**  $M_r = 407.1$ , monoclinic,  $P2_1/c$ ,  $a = 14.815$  (4),  $b = 9.526$  (3),  $c = 11.585$  (3) Å,  $\beta = 110.95$  (2)°,  $V = 1526.8$  (7) Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 1.776$  (10),  $D_x = 1.771$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 11.72$  cm<sup>-1</sup>,  $F(000) = 836$ ,  $T = 297$  K,  $R = 0.058$  for 1423 reflections (all included). Constraints were used to deal with one disordered ethylenediamine group. The bond lengths found were Cr–F, 1.862 (3); Cr–NH<sub>3</sub>, 2.093 (6) Å. The bond angles N–Cr–N are 81.9° (av.) within, and 98.1° (av.) between, the chelate rings. The other angles at Cr are less than 3° from orthogonality. The shortest of the interionic hydrogen bonds [N...F = 2.768 (9) Å] is from NH<sub>3</sub> to F, between *c*-glide-plane-related cations.

**Introduction.** Pseudo-octahedral complexes of the type *trans*- and *cis*-[MX(NH<sub>3</sub>)(en)<sub>2</sub>]<sup>2+</sup>, where *X* is an acido ligand, are useful analogues of acidopentammines and have been utilized in studies of the stereochemistry of thermal (House, 1977) and, more recently, photochemical kinetics (Kirk, 1981). For the cobalt complexes in particular, a large number of compounds have been synthesized and studied kinetically. In contrast, only recently have a few of the analogous chromium compounds been prepared and characterized (Kirk & Kelly, 1974; Wong & Kirk, 1975) but these have proved important photochemically. The literature

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assignment of stereochemistry for these was based on solubilities, chromatographic properties, UV and IR spectroscopy (Wong & Kirk, 1975), and in one instance (Kirk & Kelly, 1974), comparison to the Co<sup>III</sup> analogue by X-ray powder photography. In light of the importance of this type of compound in the studies that are currently being used to test and illuminate the nature of ligand labilization in photochemistry and theory of the photostereochemistry of *d*<sup>3</sup> systems (Vanquickenborne & Ceulemans, 1983), we thought it desirable to undertake a single-crystal-structure determination on at least one of the compounds to confirm that its stereochemistry had been correctly assigned in the previous work. That isomer of [CrF(NH<sub>3</sub>)(en)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> that was previously assigned as *trans* was chosen for study for several reasons. Firstly, it in particular gave well formed crystals showing good extinction. Several of the other compounds, notably the *cis* compounds, did not crystallize well. The choice of the fluoro compound also presented the opportunity to investigate the nature of the Cr<sup>III</sup>–F bond, an entity little studied in complexes to date. A recent study (Clamp, Connelly, Taylor & Louttit, 1980) of [CrF(NO)(dppe)<sub>2</sub>], where dppe = 1,2-bis(diphenylphosphino)ethane, yielded a Cr–F bond length of 1.880 Å, deemed by the authors to involve Cr<sup>III</sup>. There may be some suspicion, however, as to whether this