

Fig. 1. A perspective view of the  $\text{CoBr}(\text{H}_2\text{O})[\text{H}(\text{g})]_2$  complex molecule. Thermal ellipsoids are drawn at the 50% probability level.

equatorial Co—N distances are virtually identical while the Co—Br separation is considerably larger, of course.

The complexes are linked by intermolecular H bridges *via* the  $\text{H}_2\text{O}$  ligands. This is indicated by a short O(3)—O''(1) distance of 2.60 (2) Å, where O''(1) is related to the O(1) position of Table 1 by the symmetry operation  $-x, 1-y, 1-z$ .

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## Structure of Di- $\mu$ -chloro-bis[chloro(1,2-cyclohexanedione dioxime- $N,N'$ )copper(II)], [ $\text{Cu}_2(\text{C}_6\text{H}_{10}\text{N}_2\text{O}_2)_2\text{Cl}_4$ ]

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**Abstract.**  $M_r = 553.22$ , monoclinic,  $P2_1/n$ ,  $a = 6.957(2)$ ,  $b = 19.161(4)$ ,  $c = 7.660(2)$  Å,  $\beta = 93.34(2)^\circ$ ,  $V = 1019.4$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.80$  g cm<sup>-3</sup>, Mo  $K\alpha$  radiation,  $F(000) = 556$ ,  $\mu = 26.5$  cm<sup>-1</sup>,  $R(R_w) = 0.028(0.032)$  for 1786 observed independent reflections measured at  $295 \pm 2$  K. Monomers are linked into discrete, centrosymmetric dimers by two Cl

\* Correspondence about preparation and properties should be addressed to M. Mégnamisi-Bélobmé, about the structure to H. Endres.

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bridges. The coordination around Cu is a distorted square pyramid. The cyclohexane rings adopt a twisted conformation.

**Introduction.** The title compound was prepared in the course of research which aims to provide more examples of magnetic coordination compounds suitable for investigation of superexchange (Andoseh, Douglas, Egharevba & Mégnamisi-Bélobmé, 1982). So far, our interest has focused on the synthesis, structural and

magnetic study of dimers consisting of adducts of Cu<sup>II</sup> halides, CuX<sub>2</sub> (X = Cl<sup>-</sup>, Br<sup>-</sup>), with various  $\alpha,\beta$ -dione dioximes ( $\alpha,\beta$ -Hdodo) as chelating ligands. An accurate knowledge of the structure of these materials is an indispensable prerequisite for reliable interpretations of magnetic data. Recently we reported the structures of two such di- $\mu$ -halo-bis[halo( $\alpha,\beta$ -Hdodo)copper(II)] dimers (Endres, 1978; Endres, Andoseh & Mégnamisi-Bélombé, 1981), whereas the structure of the CuCl<sub>2</sub> adduct with 2,3-butanedione dioxime had been reported earlier (Svedung, 1969). In the following we describe the synthesis and crystal structure of the analogous adduct of CuCl<sub>2</sub> with 1,2-cyclohexanedione dioxime (nioxime) which is to our knowledge only the fourth structurally characterized example of this type of Cu<sup>II</sup> dimer.

**Experimental.** 340 mg (2.5 mmol) of finely powdered anhydrous CuCl<sub>2</sub> were suspended at room temperature in 30 ml acetone. To the well-stirred suspension, a fine powder of 350 mg (~2.5 mmol) nioxime (97%, as purchased from EGA Chemicals) was added in small portions. The mixture turned deep green and a dark green crystalline body precipitated. Stirring was continued for 30 min, and 50 ml of dry diethyl ether (Et<sub>2</sub>O) were added. After stirring for a further 20 min, the solid was separated by filtration, washed with dry Et<sub>2</sub>O, and air dried at ambient temperature. Yield: 580 mg (84%) of green microcrystals which were recrystallized from a 1:1 acetone/Et<sub>2</sub>O mixture. M.p. 447–448 K (vigorous decomposition). To grow crystals for the X-ray investigation, a saturated solution in a 1:1 acetone/Et<sub>2</sub>O mixture was allowed to evaporate in a refrigerator over a period of six days. The compound is fairly soluble in acetone (green), very soluble in H<sub>2</sub>O (red-brown), but virtually insoluble in Et<sub>2</sub>O. Lattice parameters from an orientation matrix calculated from the setting angles of 25 reflections centered on a diffractometer (Syntex R3, monochromatic Mo K $\alpha$  radiation). Data collection ( $\theta$ -2 $\theta$  scans background-peak-background, 2 $\theta$   $\leq$  60°) yielded 1786 observed independent reflections with  $I > 2.5\sigma(I)$ ; 1092 reflections classified as unobserved; empirical absorption correction ( $\psi$  scans) applied (minimum transmission factor 0.76, taking maximum transmission as unity). The Cu position from a Patterson map, all the other non-H atoms from a Fourier synthesis; refinement [anisotropic temperature factors,  $\sum w(\Delta F)$  minimized] resulted in  $R = 0.041$ ; all H positions, from a difference Fourier map, included in the refinement ('cascade matrix' least squares) with individual isotropic temperature factors;  $w = 1/\sigma^2(F)$ , final  $R(R_w) = 0.028$  (0.032); largest features in final difference Fourier map +0.30 and -0.32 e Å<sup>-3</sup>. Nova 3 computer, plots drawn on a Tektronix plotter; SHELXTL program system (Sheldrick, 1981), which uses scattering factors from *International Tables for X-ray Crystallography* (1974) and takes anomalous dispersion into account.

**Discussion.** Atomic coordinates are listed in Table 1,\* bond distances and angles in Table 2. A view of the centrosymmetric chloro-bridged dimer is shown in Fig. 1. This geometry corresponds to that found in previous di- $\mu$ -halo-bis[halo( $\alpha,\beta$ -Hdodo)copper(II)] complexes quoted above. In all these the crystal structure contains discrete dimers, and the coordination around Cu is a

\* Lists of structure factors, anisotropic thermal parameters, and bond lengths and angles involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38397 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates ( $\times 10^4$ ) and isotropic temperature factors ( $\times 10^3$ ) equivalent to the refined anisotropic values (except for H, where refined isotropic values are listed)

For non-H atoms,  $U = \frac{1}{3} \text{trace } \bar{U}$ ,  $\bar{U}$  signifying the diagonalized  $U_{ij}$  matrix.

	x	y	z	U(Å <sup>2</sup> )
Cu	2078 (1)	181 (1)	11357 (1)	35 (1)
Cl(1)	1354 (1)	605 (1)	8655 (1)	41 (1)
Cl(2)	1219 (1)	1094 (1)	12949 (1)	51 (1)
O(1)	2547 (4)	-149 (1)	15192 (3)	46 (1)
O(2)	3721 (4)	-812 (2)	8687 (3)	56 (1)
N(1)	2907 (4)	-351 (1)	13515 (3)	33 (1)
N(2)	3353 (4)	-673 (1)	10412 (3)	37 (1)
C(1)	3578 (4)	-967 (2)	13343 (4)	32 (1)
C(2)	3946 (4)	-1146 (2)	11505 (4)	33 (1)
C(3)	4873 (5)	-1824 (2)	11072 (5)	45 (1)
C(4)	5824 (5)	-2172 (2)	12692 (5)	52 (1)
C(5)	4430 (7)	-2205 (2)	14144 (6)	59 (2)
C(6)	3966 (6)	-1475 (2)	14800 (5)	47 (1)
H(1)	1925 (70)	245 (24)	14985 (64)	146 (21)
H(2)	3207 (41)	-560 (15)	8278 (38)	47 (9)
H(3)	3809 (47)	-2120 (16)	10503 (42)	48 (10)
H(4)	5732 (43)	-1736 (15)	10267 (40)	37 (9)
H(5)	6984 (43)	-1942 (15)	13043 (39)	53 (10)
H(6)	6209 (45)	-2627 (16)	12373 (42)	53 (10)
H(7)	3254 (51)	-2431 (18)	13663 (45)	61 (12)
H(8)	4860 (45)	-2475 (17)	15094 (43)	60 (10)
H(9)	2886 (43)	-1485 (16)	15570 (41)	55 (10)
H(10)	5128 (46)	-1312 (17)	15506 (42)	63 (11)

Table 2. Bond distances (Å) and angles (°)

Cu-Cl(1)	2.252 (1)	N(2)-C(2)	1.285 (4)
Cl(2)	2.233 (1)	Cu-N(2)-O(2)	127.4 (2)
N(1)	1.998 (2)	C(2)	118.0 (2)
N(2)	2.016 (3)	O(2)-N(2)-C(2)	114.6 (3)
Cl'(1)	2.822 (1)	C(1)-C(2)	1.486 (4)
Cl(1)-Cu-Cl(2)	99.6 (1)	C(6)	1.494 (5)
N(1)	169.2 (1)	N(1)-C(1)-C(2)	113.2 (3)
N(2)	92.4 (1)	C(6)	125.2 (3)
Cl'(1)	92.6 (1)	C(2)-C(1)-C(6)	121.6 (3)
Cl(2)-Cu-N(1)	91.2 (1)	C(2)-C(3)	1.496 (5)
N(2)	165.7 (1)	N(2)-C(2)-C(1)	112.8 (3)
Cl'(1)	99.6 (1)	C(3)	126.4 (3)
N(1)-Cu-N(2)	76.8 (1)	C(1)-C(2)-C(3)	120.7 (3)
Cl'(1)	86.2 (1)	C(3)-C(4)	1.526 (5)
N(2)-Cu-Cl'(1)	87.5 (1)	C(2)-C(3)-C(4)	111.8 (3)
Cu-Cl(1)-Cu'	87.4 (1)	C(4)-C(5)	1.519 (6)
O(1)-N(1)	1.379 (3)	C(3)-C(4)-C(5)	110.4 (3)
O(2)-N(2)	1.386 (4)	C(5)-C(6)	1.526 (6)
N(1)-C(1)	1.279 (4)	C(4)-C(5)-C(6)	111.1 (3)
Cu-N(1)-O(1)	124.6 (2)	C(1)-C(6)-C(5)	112.5 (3)
C(1)	118.4 (2)		
O(1)-N(1)-C(1)	116.3 (2)		

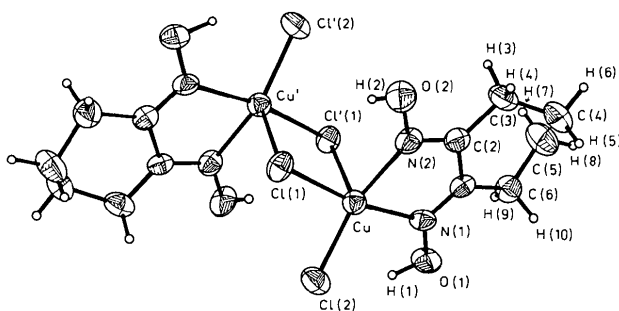


Fig. 1. A perspective view of the centrosymmetric di- $\mu$ -chloro-bis[chloro(1,2-cyclohexanedione dioxime)copper(II)] complex with the numbering scheme. Thermal ellipsoids are drawn at the 50% probability level, H atoms as small spheres with a radius of 0.1 Å.

distorted square pyramid. The two halide ions and the two oxime N atoms form the base, whilst a halide ion of the adjacent monomer occupies the apical position. In the title compound the cyclohexane ring of the dioxime ligand adopts a twisted conformation.

Interdimer H bonding occurs with distances  $H(2)-O''(1) = 2.51(3)$ ,  $O(2)-O''(1) = 3.032(4)$  Å, where  $O''(1)$  is generated from the  $O(1)$  position of Table 1 by the symmetry operation  $x, y, z - 1$ .

Possible magnetic interactions are primarily determined by the geometry of the structural core  $Cu_2X_2$  in which the angle  $Cu-X-Cu$  is of crucial importance. For the four  $[CuX_2(\alpha, \beta\text{-Hodo})]_2$  structures determined so far, data characteristic of this core are compared in Table 3. The connection between magnetic properties and this structural feature has recently been discussed by Marsh, Hatfield & Hodgson (1982).

The  $CuBr_2$  adduct of nioxime, however, has a different structure where dimerization occurs *via* bridging O atoms (Mégnamisi-Bélobmé & Endres, 1983).

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## 10-Chlorophenothiantimonin, $C_{12}H_8ClSSb$

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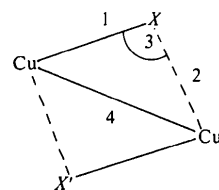
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**Abstract.**  $M_r = 341.5$ , orthorhombic,  $Pnma$ ,  $a = 1204.03(3)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.88$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 26.6$  cm<sup>-1</sup>,  $F(000) = 656$ ,  $T = 294$  K. Final  $R = 0.025$  for 969 observed reflections. This is the first structure report of a heterocyclic molecule

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Table 3. Comparison of geometries of the  $Cu_2X_2$  cores in di- $\mu$ -halo-bis[halo( $\alpha, \beta$ -dione dioxime)copper(II)] dimers (lengths in Å, angles in deg)



Ligand	X	(1)	(2)	(3)	(4)	X-X'
a	Cl	2.24	2.70	88	3.445	3.57
a	Br	2.387	2.883	85.59	3.599	3.881
b	Br	2.358	3.427	78.1	3.737	4.544
c	Cl	2.252	2.822	87.4	3.530	3.690

Ligands and references: (a) 2,3-Butanedione dioxime.  $X = \text{Cl}$ : Svedung (1969).  $X = \text{Br}$ : Endres (1978). (b) Diphenylethanedione dioxime: Endres, Andoseh & Mégnamisi-Bélobmé (1981). (c) 1,2-Cyclohexanedione dioxime: this work.

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