

Structure of *trans*-Dichlorobis(7-chloro-1,3-dihydro-1-methyl-5-phenyl-2*H*-1,4-benzodiazepin-2-one)copper(II), the Copper(II) Complex of Diazepam

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Abstract. $[\text{Cu}(\text{C}_{16}\text{H}_{13}\text{ClN}_2\text{O})_2\text{Cl}_2]$, $M_r = 703.9$, triclinic, $P\bar{1}$, $a = 12.584(2)$, $b = 17.108(2)$, $c = 7.383(1)$ Å, $\alpha = 96.57(1)$, $\beta = 99.15(2)$, $\gamma = 97.09(2)^\circ$, $U = 1542.6$ Å³ at 295 K, $D_x = 1.516$, D_m (flotation, trichloroethylene/carbon tetrachloride) = 1.534 Mg m⁻³, $Z = 2$, $\mu(\text{Mo } K\alpha) = 1.12$ mm⁻¹. The structure was determined from intensities of 5121 independent reflections and refined by block-diagonal least squares to an $R = 0.031$. The complexes are centrosymmetric, the Cu atoms being on the inversion centers. The coordination geometry around the Cu atom is square planar with two N atoms of the diazepam molecules and the two Cl atoms in *trans* position.

Introduction. It is well documented that copper exists in the human brain to assist its development, maintenance, and function. Therefore a study of interactions between copper and psychotherapeutic drugs may offer a clue in the elucidation of intricate phenomena in psychosis. In this report, we have carried out X-ray diffraction analysis of the Cu^{II} complex of diazepam (diazepam = 7-chloro-1,3-dihydro-1-methyl-5-phenyl-2*H*-1,4-benzodiazepin-2-one), $[\text{CuCl}_2(\text{diazepam})_2]$, which was obtained from an ethanol solution of diazepam and anhydrous CuCl₂. In the course of our study, an X-ray analysis on the complex $[\text{CuCl}_2(\text{diazepam})_2(\text{H}_2\text{O})_2 \cdot 0.33\text{CHCl}_3]$ has been reported (Mosset, Tuchagues, Bonnet, Haran & Sharrock, 1980). Structural differences between both complexes will be discussed.

A crystal of dimensions $0.51 \times 0.26 \times 0.26$ mm was mounted with **a** aligned on the φ axis of the Rigaku AFC-5 automatic four-circle diffractometer at the Institute for Molecular Science. Intensities of 7408 reflections with $2 < 2\theta < 55^\circ$ were measured using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å), of which 5121 independent reflections $[|F| > 3\sigma(|F|)]$ were used for the structure determination. The reflections were corrected for Lp but no correction was made for absorption.

Table 1. Atomic positional parameters ($\times 10^5$ for Cu and Cl, $\times 10^4$ for C, N and O, $\times 10^3$ for H) and equivalent isotropic thermal parameters with *e.s.d.*'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq} (Å ²)
Cu(A)	0	0	0	2.44 (1)
Cu(B)	50000	50000	50000	2.44 (1)
Cl(1)A	-1790 (7)	9994 (4)	22018 (12)	4.31 (3)
Cl(1)B	59305 (7)	46095 (7)	75394 (12)	5.27 (5)
Cl(2)A	-62351 (6)	-11957 (5)	4975 (15)	5.12 (2)
Cl(2)B	7612 (8)	57258 (7)	118643 (13)	5.96 (5)
N(1)A	-1927 (2)	-2322 (1)	1049 (3)	2.93 (7)
C(1')A	-1885 (3)	-3177 (2)	591 (4)	3.78 (9)
C(2)A	-974 (2)	-1854 (2)	1898 (4)	2.89 (7)
O(2')A	-118 (2)	-2113 (1)	2221 (3)	3.99 (6)
C(3)A	-1060 (2)	-978 (2)	2370 (4)	2.73 (7)
N(4)A	-1227 (2)	-639 (1)	628 (3)	2.48 (5)
C(5)A	-2237 (2)	-799 (1)	-363 (3)	2.39 (7)
C(6)A	-4153 (2)	-1089 (1)	38 (4)	2.61 (7)
C(7)A	-4988 (2)	-1546 (2)	567 (4)	2.99 (7)
C(8)A	-4846 (2)	-2259 (2)	1225 (4)	3.25 (7)
C(9)A	-3842 (2)	-2502 (2)	1346 (4)	3.21 (7)
C(10)A	-2950 (2)	-2044 (1)	877 (3)	3.58 (7)
C(11)A	-3118 (2)	-1326 (1)	198 (3)	2.34 (7)
C(12)A	-2490 (2)	-449 (1)	-2098 (4)	2.58 (7)
C(13)A	-1952 (2)	286 (2)	-2323 (4)	3.10 (7)
C(14)A	-2155 (3)	588 (2)	-3971 (5)	4.04 (8)
C(15)A	-2932 (3)	181 (2)	-5397 (4)	4.83 (11)
C(16)A	-3500 (3)	-534 (2)	-5175 (4)	4.73 (9)
C(17)A	-3275 (3)	-857 (3)	-3549 (3)	3.46 (7)
N(1)B	3172 (2)	6995 (1)	6329 (3)	3.47 (7)
C(1')B	2740 (3)	7574 (2)	5198 (6)	5.82 (12)
C(2)B	4256 (2)	6930 (2)	6443 (4)	3.76 (8)
O(2')B	4859 (2)	7337 (1)	5684 (4)	5.98 (8)
C(3)B	4632 (2)	6290 (2)	7540 (4)	3.38 (8)
N(4)B	4075 (2)	5515 (1)	6562 (3)	2.46 (5)
C(5)B	3083 (2)	5312 (1)	6731 (3)	2.20 (6)
C(6)B	1938 (2)	5568 (2)	9129 (4)	2.71 (7)
C(7)B	1402 (2)	6069 (2)	10136 (4)	3.34 (7)
C(8)B	1363 (2)	6844 (2)	9801 (4)	3.64 (8)
C(9)B	1923 (2)	7133 (2)	8504 (4)	3.38 (8)
C(10)B	2539 (2)	6660 (1)	7541 (4)	2.65 (7)
C(11)B	2511 (2)	5857 (1)	7814 (3)	2.29 (6)
C(12)B	2478 (2)	4530 (1)	5815 (3)	2.30 (7)
C(13)B	3014 (2)	3878 (1)	5459 (4)	2.93 (7)
C(14)B	2431 (3)	3158 (2)	4575 (4)	4.00 (9)
C(15)B	1313 (2)	3078 (2)	4063 (4)	4.59 (9)

Table 1 (cont.)

	x	y	z	B _{eq} (Å ²)
C(16)B	773 (2)	3717 (2)	4414 (4)	4.06 (8)
C(17)B	1351 (2)	4443 (2)	5283 (4)	3.11 (7)
H(1)A	-164 (2)	-89 (2)	307 (4)	3.0 (0.6)
H(2)A	-35 (2)	-68 (2)	314 (4)	3.3 (0.6)
H(3)A	-428 (2)	-60 (1)	-43 (3)	2.5 (0.5)
H(4)A	-545 (2)	-256 (2)	162 (4)	4.4 (0.7)
H(5)A	-372 (2)	-295 (2)	174 (4)	3.2 (0.6)
H(6)A	-156 (2)	56 (2)	-137 (4)	3.4 (0.6)
H(7)A	-175 (2)	106 (2)	-408 (4)	4.5 (0.7)
H(8)A	-312 (3)	35 (2)	-658 (5)	6.2 (0.9)
H(9)A	-404 (3)	-80 (2)	-610 (5)	6.1 (0.9)
H(10)A	-367 (2)	-134 (2)	-343 (4)	3.6 (0.6)
H(11)A	-245 (3)	-340 (2)	-24 (5)	6.0 (0.9)
H(12)A	-182 (3)	-343 (2)	167 (4)	5.2 (0.8)
H(13)A	-123 (3)	-322 (2)	9 (5)	6.3 (0.9)
H(1)B	446 (2)	634 (2)	881 (4)	3.2 (0.6)
H(2)B	546 (2)	633 (2)	755 (4)	3.4 (0.6)
H(3)B	196 (2)	503 (2)	934 (4)	3.6 (0.6)
H(4)B	96 (2)	717 (2)	1044 (4)	3.7 (0.7)
H(5)B	190 (2)	768 (2)	821 (4)	4.3 (0.7)
H(6)B	375 (2)	389 (2)	586 (4)	3.0 (0.6)
H(7)B	283 (2)	273 (2)	439 (4)	4.1 (0.7)
H(8)B	91 (3)	257 (2)	350 (4)	5.2 (0.8)
H(9)B	-2 (3)	368 (2)	405 (4)	5.1 (0.8)
H(10)B	98 (2)	490 (2)	550 (4)	3.8 (0.7)
H(11)B	196 (3)	745 (2)	493 (5)	6.0 (0.9)
H(12)B	297 (4)	754 (3)	392 (7)	10.9 (1.4)
H(13)B	299 (4)	805 (3)	565 (7)	11.8 (1.6)

The structure determination and refinements were performed using the *Universal Crystallographic Computation Program System UNICS III* (Sakurai & Kobayashi, 1978). Coordinates of the Cu atom were obtained from a Patterson map and subsequent Fourier syntheses gave the positions of all the remaining non-H atoms. They were refined with individual

anisotropic thermal parameters. The positions of all the H atoms were determined from difference Fourier maps. When the shifts of all parameters were less than 0.1 of the e.s.d. except for that of the H atoms, the refinement was terminated with an $R = 0.031$. Atomic scattering factors including anomalous scattering were taken from *International Tables for X-ray Crystallography* (1974). Final atomic coordinates are listed in Table 1.*

Discussion. The packing diagram is shown in Fig. 1. Two independent complex molecules are in the unit cell. They lie at the origin (complex *A*) or at point $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36287 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

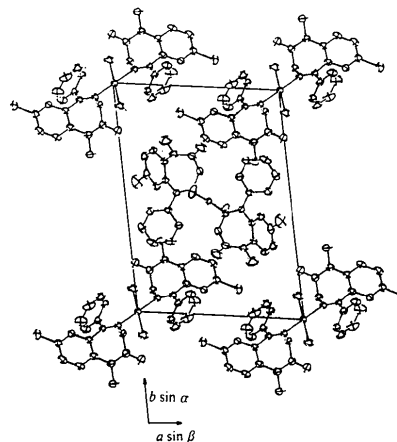


Fig. 1. Molecular packing viewed along *c*: 50% probability ellipsoids (*ORTEP*, Johnson, 1965).

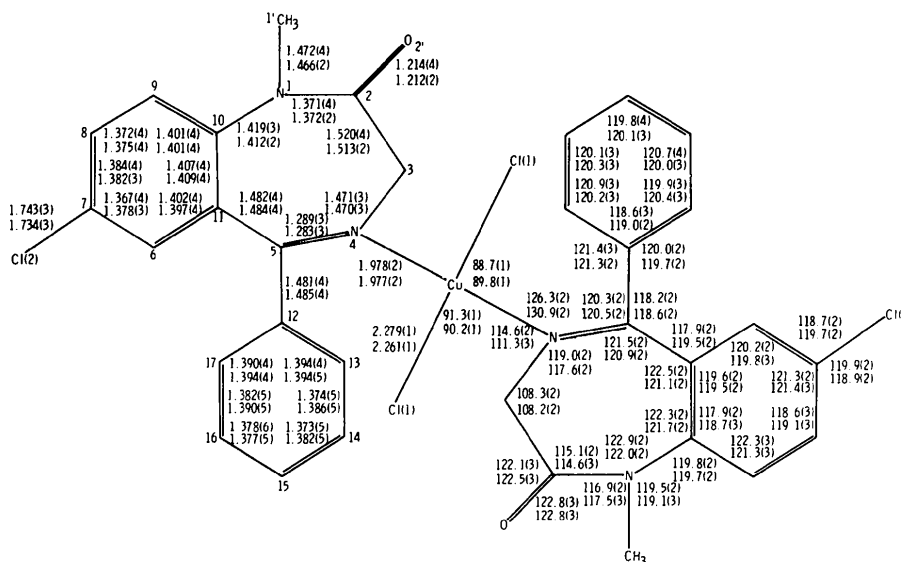


Fig. 2. Bond distances (Å) and angles (°) for complex *A* (upper values) and complex *B*.

(complex *B*). Their stacking cohesions are van der Waals interactions.

Bond lengths and angles within the molecules are given in Fig. 2 with the atom numbering. The complexation of the diazepam molecule to the Cu atom does not affect markedly its geometry as in the case of Mosset *et al.* (1980).

The phenyl ring bonded to C(5) (see Fig. 2) is in close proximity to the central Cu atom in complex *A*. The Cu—C(13) distance of 2.892 (3) Å [Cu—H(6) distance of 2.41 Å] is much shorter than that in complex *B* [3.046 (3) Å] and that in the study of Mosset *et al.* (1980) [3.01 (1) Å]. The Cu—Cl bonds in complexes *A* and *B* are slightly different in length. This could be due to the close contact between the Cu atom and the phenyl ring bonded to C(5) in complex *A*. On the other hand, the Cu—N bond distances for complexes *A* and *B* are not influenced by this short contact. However, they are slightly shorter than those in the study of Mosset *et al.* (1980) [1.990 (8) Å].

The dihedral angle between the CuCl₂N₂ plane and the phenyl ring bonded to C(5) for complex *A* [65.1 (4)°] is smaller than that for complex *B* [71.1 (4)°], while the dihedral angle between the

CuCl₂N₂ plane and the Cl-substituted phenyl ring for complex *A* [60.7 (4)°] is larger than that for complex *B* [52.0 (4)°]. The difference could be attributed to the short contact mentioned above. The phenyl rings in the diazepam molecules are at dihedral angles of 116.7 (4) and 113.7 (4)° for complexes *A* and *B* respectively.

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Bis[2-(methylaminomethyl)pyridine 1-oxide]copper(II) Diperchlorate

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Abstract. [Cu(C₇H₁₀N₂O)₂](ClO₄)₂, *M_r* = 538.8, orthorhombic, *Pbca*, *a* = 13.0888 (5), *b* = 14.7638 (6), *c* = 10.3534 (4) Å at 298.7 (5) K, *V* = 2000.70 (13) Å³, *Z* = 4, *D_m* = 1.79 (2), *D_c* = 1.788 Mg m⁻³. The structure was solved by the Fourier synthesis method and refined to a conventional *R* of 0.051 for the 143 parameters varied and 1307 reflections used in the refinement. In this centrosymmetric complex there are four bonds from Cu to *trans* N and O donor atoms with an average bond distance of 1.976 (5) Å, and two longer bonds to ClO₄⁻ O atoms of 2.747 (4) Å. Other O atoms in the anion are involved in intra- and intermolecular hydrogen bonding.

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Introduction. The title compound is one in a series of complexes containing ring-substituted pyridine 1-oxide ligands, and for which a correlative study between EPR spectral results and bonding parameters (as determined by X-ray techniques) is being made (West & Kohrman, 1979; West & Hartley, 1980). The ligand in this example is capable of forming a six-membered chelate ring. For comparative purposes a structure is known for another series complex containing a five-membered chelate ring (West, Pavkovic & Brown, 1980).

Crystals of the purple compound (provided by Professor D. X. West) were obtained upon slow evaporation from a nitromethane solution. A fragment

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