

Table 3. Possible hydrogen bonds ( $\text{\AA},^\circ$ )

$X\cdots H\cdots Y$	$H\cdots Y$	$X\cdots Y$	$X\cdots H\cdots Y$
$\text{N}(1)\cdots\text{H}(1)\cdots\text{Cl}(2)^{\text{viii,ix}}$	2.63 (1)	3.576 (13)	158 (6)
$\text{N}(1)\cdots\text{H}(11)\cdots\text{Cl}(1)^{\text{v,vi}}$	2.35 (2)	3.298 (13)	161 (6)
$\text{N}(2)\cdots\text{H}(2)\cdots\text{Cl}(4)^{\text{v,vi}}$	2.35 (2)	3.288 (13)	154 (6)
$\text{N}(3)\cdots\text{H}(2)\cdots\text{Cl}(5)^{\text{v}}$	2.52 (2)	3.502 (10)	168 (9)

Symmetry code: (i)  $x, y, z$ ; (vi)  $-x, y, z$ ; (vii)  $x, y, \frac{1}{2}-z$ ; (viii)  $x-\frac{1}{2}, y-\frac{1}{2}, z$ ; (ix)  $x-\frac{1}{2}, y-\frac{1}{2}, z-\frac{1}{2}$ .

nature. The shortest  $\text{C}\cdots\text{Cl}$  distances are about 3.7 (1)  $\text{\AA}$ . Connection to the organic layer occurs via the hydrogen-bond system formed by the terminal  $\text{Cl}(4)$  and  $\text{Cl}(5)$  atoms and the ammonium and methyl groups. The distance 3.288 (13)  $\text{\AA}$  for the  $\text{N}(2)\cdots\text{H}(2)\cdots\text{Cl}(4)$  contact appears to be the shortest of this type in the structure. The third ammonium group  $[\text{N}(3)\text{H}_2]$  exhibits positional disorder relative to the mirror plane  $m$ . The  $\text{N}(3)$  atom was thus refined in two statistically equivalent positions, both with an occupancy factor of 0.5. The two statistically occupied positions correspond to two equivalent potential-energy minima in the room temperature

phase. Transition to the low temperature phase may cause a freezing of the  $[\text{N}(3)\text{H}_2]$  group in one preferred orientation.

Further studies on the dynamics of this cation group will give information on the character and phase-transition mechanism in  $[(\text{CH}_3)_2\text{NH}_2]_5\text{Cd}_3\text{Cl}_{11}$  crystals.

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## Structure of a Copper(II) Complex of the Deprotonated Anion of 3,10-Dimethyl-4,9-diaza-3,9-dodecadiene-2,11-dione Dioxime

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**Abstract.** Bis[ $\mu$ -3,10-dimethyl-4,9-diaza-3,9-dodecadiene-2,11-dione dioximato(1-)- $\mu$ -O, $N,N',N'',N'''$ ]-dicopper(II) diperchlorate  $[\text{Cu}(\text{C}_{12}\text{H}_{21}\text{N}_4\text{O}_2)]_2^{2+}\cdot 2\text{ClO}_4^-$ ,  $M_r = 832.6$ , monoclinic,  $P2_1/n$ ,  $a = 6.484$  (2),  $b = 21.711$  (4),  $c = 12.397$  (3)  $\text{\AA}$ ,  $\beta = 96.59$  (2)°,  $V = 1733.5$  (6)  $\text{\AA}^3$ ,  $Z = 2$ ,  $\lambda(\text{Mo } K\alpha) = 0.71073$   $\text{\AA}$ ,  $\mu = 14.51$   $\text{cm}^{-1}$ ,  $D_x = 1.595$   $\text{g cm}^{-3}$ ,  $T = 297$  K,  $R = 0.0448$ ,  $wR = 0.0452$  for 1897 independent reflections [ $I > 3\sigma(I)$ ]. The crystal contains a binuclear complex with two oxime groups as bridging ligands. The copper coordination is a buckled square pyramid. The four donor N atoms of the diazadioxime form a very slightly distorted plane and an oxime O atom of the other diazadioxime occupies the axial position. An oxime proton is lost from the ligand in forming the complex and the remaining oxime proton forms a hydrogen bond between the two oxime O atoms of the same molecule.

**Introduction.** Copper(II)-diazadioxime complexes present considerable interest in bio-inorganic chemistry (Gagné, 1976; Gagné, Allison, Gall & Koval, 1977; Gagné, Allison & Ingle, 1979). They may serve as model compounds of copper enzymes with 'type 2' copper sites (Giordano & Bereman, 1974; Morpurgo, Giovagnoli & Rotilio, 1973; Richardson, Thomas, Rubin & Richardson, 1975). However, very little attention has been devoted to the crystal structures of this type of complex. The crystal structure of the copper(II) complex with the deprotonated anion of 3,9-dimethyl-4,8-diaza-3,8-undecadiene-2,10-dione dioxime has been reported by Bertrand, Smith & VanDerveer (1977). We report here the crystal structure of the copper(II) complex with the deprotonated anion of 3,10-dimethyl-4,9-diaza-3,9-dodecadiene-2,11-dione dioxime ( $\text{H}_{-1}\text{L}$  in formulae).

**Experimental.** Preparation of 3,10-dimethyl-4,9-diaza-3,9-dodecadiene-2,11-dione dioxime: 2,3-

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Table 1. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ )

$U_{eq}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}$
Cu	-75 (1)	4672 (1)	1463 (1)	33 (1)
Cl	7831 (3)	1676 (1)	9480 (1)	62 (1)
N(1)	1624 (6)	5309 (2)	880 (3)	33 (1)
N(2)	-217 (6)	5314 (2)	2583 (3)	36 (1)
N(3)	-1484 (7)	3963 (2)	2065 (3)	37 (2)
N(4)	1415 (7)	3976 (2)	846 (3)	37 (2)
O(1)	2964 (7)	4029 (2)	195 (4)	48 (2)
O(2)	2534 (5)	5221 (2)	-22 (3)	37 (1)
O(3)	6294 (14)	2025 (4)	9865 (6)	186 (5)
O(4)	9276 (10)	1539 (3)	10335 (5)	139 (3)
O(5)	7063 (13)	1134 (3)	9042 (5)	152 (4)
O(6)	8619 (10)	2032 (3)	8685 (5)	109 (3)
C(1)	1792 (8)	5825 (2)	1399 (4)	36 (2)
C(2)	727 (8)	5814 (3)	2398 (4)	40 (2)
C(3)	-1145 (10)	5190 (3)	3597 (4)	53 (2)
C(4)	-3468 (10)	5121 (3)	3411 (5)	59 (3)
C(5)	-4298 (9)	4645 (3)	2567 (5)	49 (2)
C(6)	-3332 (9)	4014 (3)	2674 (5)	50 (2)
C(7)	-733 (9)	3438 (2)	1869 (4)	39 (2)
C(8)	1029 (8)	3439 (2)	1181 (4)	38 (2)
C(9)	2990 (10)	6363 (3)	1064 (5)	55 (2)
C(10)	906 (12)	6366 (3)	3110 (6)	77 (3)
C(11)	-1491 (11)	2838 (3)	2249 (5)	62 (3)
C(12)	2123 (11)	2878 (3)	887 (6)	64 (3)

Butanedione monoxime (115.4 mmol) was dissolved in benzene (200 ml) in the presence of *p*-toluenesulfonic acid (0.1 g), and the solution was refluxed in an apparatus fitted with a Dean and Stark trap and under a nitrogen atmosphere. 1,4-Butanediamine (49 mmol) in benzene (100 ml) was added dropwise and the solution was refluxed for a further 11 h, then allowed to cool to room temperature. The solvent was removed under reduced pressure. The precipitate was washed with cold acetonitrile and recrystallized from methanol yielding a colorless product.

Preparation of  $\text{Cu}(\text{H}_{-1}\text{L})(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ : A hot methanol solution of  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (10 mmol in 30 ml) was added to a hot methanol solution of the ligand (20 mmol in 20 ml). As the deep black solution cooled, a black product precipitated. It was collected by filtration, washed with diethyl ether and dried in air.

A single crystal having the dimensions  $0.1 \times 0.2 \times 0.3$  mm was selected for indexing and intensity data collection on a MicroVAX II computer-controlled Nicolet *R3m/V* diffractometer, equipped with a graphite monochromator. The orientation and unit-cell parameters were determined by a least-squares fit of 17 peak maxima with  $12 < 2\theta < 27^\circ$ . The space group,  $P2_1/n$ , was unambiguously determined from the systematic absences:  $0k0$ ,  $k = 2n + 1$ ;  $h0l$ ,  $h + l = 2n + 1$ .  $\theta/2\theta$  scan data were collected at room temperature (297 K) for two octants of sphere ( $0 \leq h \leq 7$ ,  $-25 \leq k \leq 0$ ,  $-14 \leq l \leq 14$ ) out to the  $2\theta$  limit of  $50^\circ$  [ $(\sin\theta)/\lambda = 0.595 \text{ \AA}^{-1}$ ]. Scan width of  $1.0^\circ$  plus  $K\alpha$  separation and scan speed of  $2.93\text{--}14.65^\circ \text{ min}^{-1}$ .

Table 2. Bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ )

Cu—N(1)	1.957 (4)	Cu—N(2)	1.977 (4)
Cu—N(3)	1.978 (4)	Cu—N(4)	1.992 (5)
Cu—O(2a)	2.266 (3)	Cl—O(3)	1.380 (9)
Cl—O(4)	1.364 (6)	Cl—O(5)	1.366 (7)
Cl—O(6)	1.395 (6)	N(1)—O(2)	1.337 (5)
N(1)—C(1)	1.291 (7)	N(2)—C(2)	1.281 (7)
N(2)—C(3)	1.479 (7)	N(3)—C(6)	1.491 (8)
N(3)—C(7)	1.275 (7)	N(4)—O(1)	1.364 (7)
N(4)—C(8)	1.271 (7)	O(2)—Cu	2.266 (3)
C(1)—C(2)	1.486 (8)	C(1)—C(9)	1.488 (8)
C(2)—C(10)	1.485 (9)	C(3)—C(4)	1.505 (9)
C(4)—C(5)	1.524 (8)	C(5)—C(6)	1.506 (8)
C(7)—C(8)	1.502 (8)	C(7)—C(11)	1.487 (8)
C(8)—C(12)	1.478 (8)	O(1)—H(1a)	0.74 (6)
N(1)—Cu—N(2)	80.5 (2)	N(1)—Cu—N(3)	173.0 (2)
N(2)—Cu—N(3)	102.8 (2)	N(1)—Cu—N(4)	94.3 (2)
N(2)—Cu—N(4)	150.2 (2)	N(3)—Cu—N(4)	79.7 (2)
N(1)—Cu—O(2a)	90.7 (1)	N(2)—Cu—O(2a)	113.3 (1)
N(3)—Cu—O(2a)	93.6 (1)	N(4)—Cu—O(2a)	95.9 (1)
O(3)—Cl—O(4)	108.1 (4)	O(3)—Cl—O(5)	111.5 (5)
O(4)—Cl—O(5)	107.9 (4)	O(3)—Cl—O(6)	106.1 (4)
O(4)—Cl—O(6)	113.3 (4)	O(5)—Cl—O(6)	110.0 (4)
Cu—N(1)—O(2)	122.0 (3)	Cu—N(1)—C(1)	116.7 (4)
O(2)—N(1)—C(1)	121.3 (4)	Cu—N(2)—C(2)	114.2 (4)
Cu—N(2)—C(3)	121.7 (4)	C(2)—N(2)—C(3)	123.7 (5)
Cu—N(3)—C(6)	124.5 (3)	Cu—N(3)—C(7)	114.9 (4)
C(6)—N(3)—C(7)	120.6 (5)	Cu—N(4)—O(1)	125.8 (3)
Cu—N(4)—C(8)	116.6 (4)	O(1)—N(4)—C(8)	117.2 (5)
N(1)—O(2)—Cu	107.9 (3)	N(1)—C(1)—C(2)	112.4 (5)
N(1)—C(1)—C(9)	124.0 (5)	C(2)—C(1)—C(9)	123.6 (5)
N(2)—C(2)—C(1)	116.1 (5)	N(2)—C(2)—C(10)	125.8 (5)
C(1)—C(2)—C(10)	118.1 (5)	N(2)—C(3)—C(4)	112.7 (4)
C(3)—C(4)—C(5)	116.2 (5)	C(4)—C(5)—C(6)	116.5 (5)
N(3)—C(6)—C(5)	111.9 (5)	N(3)—C(7)—C(8)	116.0 (5)
N(3)—C(7)—C(11)	125.2 (5)	C(8)—C(7)—C(11)	118.8 (5)
N(4)—C(8)—C(7)	112.2 (5)	N(4)—C(8)—C(12)	123.9 (5)
C(7)—C(8)—C(12)	123.8 (5)		

Three standard reflections were monitored every 50 reflections and showed no sign of crystal deterioration. The data were corrected for absorption, Lorentz and polarization effects. Corrections for absorption effects were based on a  $\psi$  scan of a few suitable reflections with  $\chi$  values close to  $90^\circ$ . Estimated maximum and minimum transmission factors were 0.987 and 0.777. 3396 reflections were collected, 3011 unique, of which 1897 were observed reflections with  $I \geq 3.0\sigma(I)$ . The structure was solved by direct methods. The positions for all non-H atoms were deduced from an *E* map and were refined with anisotropic temperature factors. All H atoms except H(1a) included in the refinement were placed in their calculated positions and were refined with a fixed *U* value ( $0.08 \text{ \AA}^2$ ). H(1a) was deduced from a difference Fourier map and was refined with isotropic temperature factor. At convergence  $R = 4.48\%$ ,  $wR = 4.53\%$ ,  $w = [\sigma^2(F) + 0.0005F^2]^{-1}$ ,  $\sigma^2(F)$  from counting statistics,  $S = 1.49$ ,  $(\Delta/\sigma)_{\max} = 0.024$ ,  $(\Delta\rho)_{\max} = 0.52$ ,  $(\Delta\rho)_{\min} = -0.51 \text{ e \AA}^{-3}$  [scattering factors were taken from *International Tables for X-ray Crystallography* (1974)]. All calculations were performed on a MicroVAX II computer system using the *SHELXTL-Plus* program (Sheldrick, 1987). Atomic parameters are

given in Table 1, bond distances and angles are given in Table 2.\*

**Discussion.** The crystals contain a binuclear complex with two oxime groups as bridging ligands (Fig. 1). The copper(II) coordination is a buckled square pyramid. The four donor N atoms of diazadioxime form a very slightly distorted plane; an oxime O atom of another diazadioxime occupies the axial position. Maximum deviation of these four atoms from the least-squares plane is 0.209 Å. The Cu atom is displaced from the best plane of the four donor N atoms by 0.297 Å toward the apex of the pyramid. The equatorial Cu—N distances span a very narrow range, 1.957 (4)–1.993 (5) Å, which are significantly shorter than the Cu—N distances for copper(II)-tetraamine complexes (Lu, Liang, Wu & Chung, 1986).

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52855 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

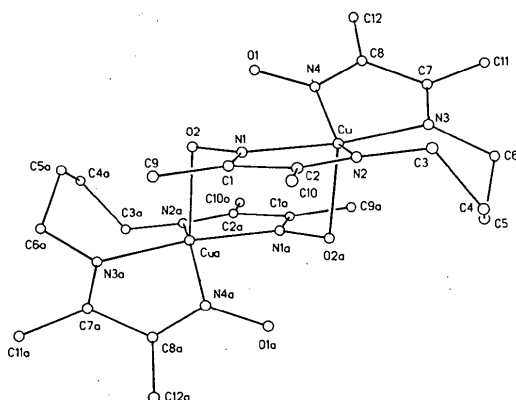


Fig. 1. Side view of the binuclear unit with numbering scheme.

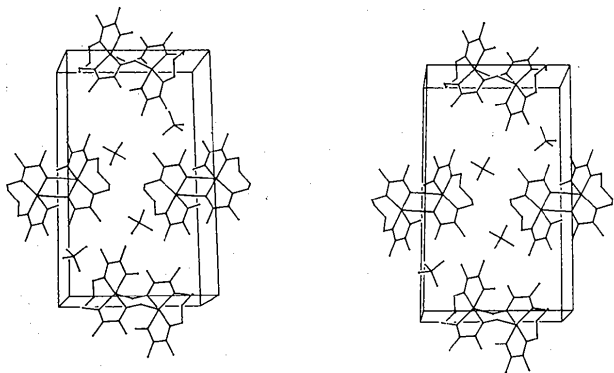


Fig. 2. Stereoscopic drawing of the molecules packing in a unit cell. **a** into the plane of the paper, **b** vertical, **c** horizontal.

An oxime proton is lost from the ligand in forming the complex and the remaining oxime proton forms a hydrogen bond between the two oxime O atoms of the same molecule. The O(1)—O(2) distance (2.608 Å) is similar to the hydrogen-bonded oxygen–oxygen distances observed in structures of other copper–oxime complexes (Bliss & Schlemper, 1975; Vaciego & Zamibonelli, 1970). A packing diagram is shown in Fig. 2.

The copper(II) complex of the deprotonated anion of 3,9-dimethyl-4,8-diaza-3,8-undecadiene-2,10-dione dioxime (compound *A*) has been reported by Bertrand, Smith & VanDerveer (1977). Comparing the results for *A* and the complex studied in this work (compound *B*), we found the following significant differences: (1) For *A*, the interaction of Cu<sup>II</sup> with the oxime O atom of the adjacent complex forms singly bridged polynuclear chains; for *B*, the interaction of Cu<sup>II</sup> with the oxime O atom forms a doubly bridged binuclear species. (2) For *A*, the Cu<sup>II</sup> coordination is a distorted octahedron; for *B*, it is a distorted square pyramid. (3) The N—Cu—N chelate angles for the two five-membered chelate rings of compound *A* [81.6 (2)–80.6 (2)°] are larger than those of *B* [79.7 (2)–80.5 (2)°]. (4) The Cu—N bond distances of compound *A* [1.937 (5)–1.961 (5) Å] are shorter than those of *B* [1.957 (4)–1.993 (5) Å].

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