chelate around one of the amino hydrogens (Table 3). Therefore a significant difference (~10°) between the angles C(15)—C(26)—C(25) [125·5 (4)°] and C(13)—C(36)—N(31) [115·9 (4)°] is also observed.

Two other kinds of hydrogen bonds (Table 3) exist in the cell packing, firstly between the bromide ion and the amino nitrogen N(16), and secondly between the bromide ion and the oxygen of a water molecule. These different hydrogen bridges may be classified as intra- and intermolecular, respectively.

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Structure of a Copper(II) Complex of the Deprotonated Anion of 3,3,6,6,9,9-Hexamethyl-4,8-diazaundecane-2,10-dione Dioxime

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Abstract. Aqua(3,3,6,6,9,9-hexamethyl-4,8-diazaundecane-2,10-dione dioximato)copper(II) perchlorate, $[Cu(C_{15}H_{31}N_4O_2)(H_2O)](ClO_4)$, $M_r = 480{\cdot}44$, monoclinic, $P2_1/c$, $a = 7{\cdot}918$ (1), $b = 20{\cdot}265$ (2), $c = 13{\cdot}707$ (4) Å, $\beta = 104{\cdot}34$ (2)°, $U = 2130{\cdot}7$ (2) Å^3, $Z = 4$, $D_x = 1{\cdot}498$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 1{\cdot}19$ mm^{-1}, $F(000) = 1011{\cdot}79$, room temperature, final $R = 0{\cdot}035$, $wR = 0{\cdot}030$ for 2924 observed reflections. The coordination about Cu^{II} is distorted square pyramidal with the deprotonated diazadioxime equatorial and the O atom of the aqua group axial. The Cu atom is significantly (0·202 Å) out of the plane of the four nitrogens and towards the O atom of the aqua group. This O atom forms hydrogen bonds with the neighbouring oxime and perchlorate O atoms. The C-methyl groups in this complex impose significant constraint resulting in an increase of the N(amine)—M—N(amine) angle, decrease of the N(amine)—M—N(oxime) angles and elongation of the O···O distance. The important bond distances are Cu—O = 2·321 (3), average Cu—N(oxime) = 1·953 (3), average Cu—N(amine) = 1·993 (3) and O···O = 2·509 (5) Å for the intramolecular hydrogen bond.

Introduction. The deprotonated diazadioxime metal complexes allow a comprehensive structural study of the variation in intramolecular hydrogen bonding with O···O distance for short hydrogen bonds (Gavel & Schlemper, 1979). Previously, structural studies have indicated that the O···O distance varies as a function of: (1) the size of the metal ion, (2) the constraint imposed by the methylene carbons bridging the amine N atoms, and (3) changing from an sp^3 amine nitrogen to an sp^2 imine nitrogen (Liss & Schlemper, 1975; Pal, Murmann, Schlemper, Fair & Hussain, 1986). The present study was undertaken to examine the steric effect of the copper(II) complex of deprotonated diazadioxime.

Experimental. The ligand, 3,3,6,6,9,9-hexamethyl-4,8-diazaundecane-2,10-dione dioxime (6,6-Me_2-PnAO), was prepared as described by Murmann (1957, 1958) and Vassian & Murmann (1967). Prepa-

0108-2701/90/122360-04$03.00

Table 1. *Atomic positional parameters and equivalent isotropic thermal parameters* (Å^2) *with e.s.d.'s in parentheses*

$$B_{iso} = \tfrac{8}{3}\pi^2(\mathbf{u}_{11} + \mathbf{u}_{22} + \mathbf{u}_{33}).$$

	x	y	z	B_{iso}
Cu	0·72664 (6)	0·46484 (2)	0·12128 (3)	2·12 (2)
Cl	1·1998 (1)	0·34646 (5)	0·43181 (7)	3·28 (5)
O(1)	0·7454 (3)	0·5354 (1)	−0·0605 (2)	3·0 (1)
O(2)	0·6579 (3)	0·4165 (1)	−0·0864 (2)	3·4 (1)
O(3)	1·1300 (4)	0·4063 (1)	0·3842 (2)	4·9 (2)
O(4)	1·2558 (5)	0·3067 (2)	0·3622 (3)	8·7 (2)
O(5)	1·3444 (4)	0·3608 (2)	0·5131 (2)	6·3 (2)
O(6)	1·0679 (5)	0·3126 (2)	0·4656 (3)	8·5 (2)
O(7)	1·0149 (3)	0·4302 (1)	0·1665 (2)	3·4 (1)
N(1)	0·7697 (3)	0·5399 (1)	0·0418 (2)	2·3 (1)
N(2)	0·7492 (3)	0·5349 (1)	0·2249 (2)	2·0 (1)
N(3)	0·6274 (4)	0·3936 (1)	0·1914 (2)	2·1 (1)
N(4)	0·6582 (4)	0·4010 (2)	0·0116 (2)	2·5 (1)
C(1)	0·8375 (5)	0·5914 (2)	0·0890 (3)	2·4 (2)
C(2)	0·9028 (8)	0·6487 (2)	0·0418 (3)	4·2 (2)
C(3)	0·8562 (5)	0·5917 (2)	0·2028 (2)	2·3 (2)
C(4)	0·7856 (6)	0·6555 (2)	0·2371 (3)	3·9 (2)
C(5)	1·0507 (5)	0·5841 (2)	0·2554 (3)	3·5 (2)
C(6)	0·7944 (4)	0·5117 (2)	0·3313 (2)	2·2 (2)
C(7)	0·6637 (4)	0·4608 (2)	0·3518 (2)	2·5 (2)
C(8)	0·7178 (5)	0·4485 (2)	0·4663 (2)	3·4 (2)
C(9)	0·4768 (5)	0·4881 (2)	0·3228 (3)	3·4 (2)
C(10)	0·6791 (5)	0·3933 (2)	0·3046 (2)	2·6 (2)
C(11)	0·6393 (5)	0·3270 (2)	0·1434 (3)	2·7 (2)
C(12)	0·8092 (6)	0·2915 (2)	0·1913 (3)	4·0 (2)
C(13)	0·4860 (6)	0·2835 (2)	0·1521 (3)	4·5 (2)
C(14)	0·6363 (5)	0·3411 (2)	0·0324 (3)	2·8 (2)
C(15)	0·6184 (7)	0·2854 (2)	−0·0413 (3)	4·5 (2)

ration of the title complex: A hot methanol solution of $Cu(ClO_4)_2.6H_2O$ (10 mmol in 30 ml) was added to a hot methanol solution of the ligand (20 mmol in 20 ml). Dark red crystals were obtained as the solution was cooled. The crystals were collected by filtration, washed with diethyl ether and dried in air.

Recrystallized from methanol solution. CAD-4 diffractometer, graphite monochromator, dark red crystal (0·30 × 0·5 × 0·5 mm) used for data collection, unit-cell parameters from 24 reflections with $15 < \theta < 30°$, data collected by ω–2θ scans with scan parameters $2(0{\cdot}8 + 0{\cdot}35\tan\theta)°$ and with scan speed 20/10 to 20/3° min^{-1}, three standard reflections ($\overline{41}3$, $2\overline{7}2$ and 272) checked every 2 h varied within $2\sigma(I)$. Max. $(\sin\theta/\lambda) = 0{\cdot}7035$ Å^{-1} ($-9 \leq h \leq 9$, $0 \leq k \leq 24$, $0 \leq l \leq 24$), 4324 reflections were collected, 2924 were significant with $I > 2{\cdot}5\sigma(I)$. Empirical absorption correction was based on azimuthal rotation from reflections 040, $\overline{1},\overline{13},\overline{1}$ and 1,21,0 (North, Phillips & Mathews, 1968). The minimum and maximum transmission factors were 0·97 and 0·99, respectively. The structure was solved by direct methods using *MULTAN*82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982). Full-matrix least-squares refinement was carried out on positional and anisotropic thermal parameters of non-H atoms over 2924 reflections. The function minimized was $\sum w(|F_o| - |F_c|)$, where $w = 1/\sigma^2(F)$ from counting statistics. Positions of the H atoms were all located from the difference Fourier map, and were not refined. The B values of the H atoms were initially assigned as 5·0 Å^2 and refined. In the last stage of least-squares calculation, the $R(F)$ factor reduced to 0·035, GOF = 2·90, $(\Delta\rho)_{max} = 0{\cdot}39$ e Å^{-3}, $(\Delta/\sigma)_{max} = 0{\cdot}01$. Atomic scattering factors were from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Table 2. *Bond lengths* (Å) *and bond angles* (°), *and hydrogen-bond lengths* (Å) *and angles* (°)

Cu—O(7)	2·321 (3)	N(3)—C(11)	1·515 (4)
Cu—N(1)	1·950 (3)	N(4)—C(14)	1·269 (5)
Cu—N(2)	1·985 (3)	C(1)—C(2)	1·483 (5)
Cu—N(3)	2·000 (3)	C(1)—C(3)	1·530 (5)
Cu—N(4)	1·955 (3)	C(3)—C(4)	1·529 (5)
Cl—O(3)	1·423 (3)	C(3)—C(5)	1·538 (5)
Cl—O(4)	1·401 (3)	C(6)—C(7)	1·536 (5)
Cl—O(5)	1·416 (3)	C(7)—C(8)	1·543 (4)
Cl—O(6)	1·420 (3)	C(7)—C(9)	1·537 (5)
O(1)—N(1)	1·370 (3)	C(7)—C(10)	1·531 (5)
O(2)—N(4)	1·379 (3)	C(11)—C(12)	1·523 (6)
N(1)—C(1)	1·274 (5)	C(11)—C(13)	1·528 (5)
N(2)—C(3)	1·504 (4)	C(11)—C(14)	1·542 (5)
N(2)—C(6)	1·488 (4)	C(14)—C(15)	1·498 (5)
N(3)—C(10)	1·502 (4)		

O(7)—Cu—N(1)	95·1 (1)	O(2)—N(4)—C(14)	117·9 (3)
O(7)—Cu—N(2)	96·7 (1)	N(1)—C(1)—C(2)	124·6 (3)
O(7)—Cu—N(3)	97·5 (1)	N(1)—C(1)—C(3)	116·3 (3)
O(7)—Cu—N(4)	94·1 (1)	C(2)—C(1)—C(3)	119·1 (3)
N(1)—Cu—N(2)	81·0 (1)	N(2)—C(3)—C(1)	106·6 (3)
N(1)—Cu—N(3)	167·3 (1)	N(2)—C(3)—C(4)	108·5 (3)
N(1)—Cu—N(4)	98·1 (1)	N(2)—C(3)—C(5)	112·2 (3)
N(2)—Cu—N(3)	98·6 (1)	C(1)—C(3)—C(4)	111·5 (3)
N(2)—Cu—N(4)	169·1 (1)	C(1)—C(3)—C(5)	108·1 (3)
N(3)—Cu—N(4)	79·9 (1)	C(4)—C(3)—C(5)	109·9 (3)
O(3)—Cl—O(4)	109·3 (2)	N(2)—C(6)—C(7)	112·4 (3)
O(3)—Cl—O(5)	109·4 (2)	C(6)—C(7)—C(8)	105·4 (3)
O(3)—Cl—O(6)	109·1 (2)	C(6)—C(7)—C(9)	111·1 (3)
O(4)—Cl—O(5)	108·9 (2)	C(6)—C(7)—C(10)	113·3 (3)
O(4)—Cl—O(6)	109·1 (2)	C(8)—C(7)—C(9)	109·1 (3)
O(5)—Cl—O(6)	111·0 (2)	C(8)—C(7)—C(10)	104·7 (3)
Cu—N(1)—O(1)	121·3 (2)	C(9)—C(7)—C(10)	112·7 (3)
Cu—N(1)—C(1)	117·8 (2)	N(3)—C(10)—C(7)	113·7 (3)
O(1)—N(1)—C(1)	120·6 (3)	N(3)—C(11)—C(12)	112·1 (3)
Cu—N(2)—C(3)	111·0 (2)	N(3)—C(11)—C(13)	110·1 (3)
Cu—N(2)—C(6)	115·6 (2)	N(3)—C(11)—C(14)	106·0 (3)
C(3)—N(2)—C(6)	115·4 (2)	C(12)—C(11)—C(13)	109·1 (3)
Cu—N(3)—C(10)	117·4 (2)	C(12)—C(11)—C(14)	108·0 (3)
Cu—N(3)—C(11)	111·1 (2)	C(13)—C(11)—C(14)	111·4 (3)
C(10)—N(3)—C(11)	114·5 (3)	N(4)—C(14)—C(11)	115·4 (3)
Cu—N(4)—O(2)	122·2 (2)	N(4)—C(14)—C(15)	124·4 (3)
Cu—N(4)—C(14)	119·2 (2)	C(11)—C(14)—C(15)	120·1 (3)

	O···O	O—H···O
O(2)—H(O21)···O(1)	2·509 (5)	176·7 (1)
O(7)—H(O72)···O(1)^{i}	2·751 (5)	176·1 (1)
O(7)—H(O71)···O(3)	2·935 (5)	150·0 (1)

Symmetry code: (i) $2 - x, 1 - y, -z$.

Discussion. Table 1 lists atomic coordinates and Table 2 bond lengths and angles.* A perspective view

* 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 53216 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Selected bond lengths* (Å) *and bond angles* (°) *for* Cu^{II}*–diaminedioxime complexes*

	(I)	(II)	(III)	(IV)	(V)
Cu—N(amine)	1·979	1·99 (1)	1·985 (3)	2·036 (4)	2·038 (4)
	2·012	1·99 (1)	2·000 (3)	2·047 (3)	2·029 (4)
Cu—N(oxime)	1·938	1·96 (1)	1·950 (3)	1·958 (4)	1·950 (4)
	1·944	1·96 (1)	1·955 (3)	1·986 (4)	1·967 (4)
Cu—O(apical)	2·185 (4)	2·40 (1)	2·321 (3)	2·287 (4)	2·300 (4)
O···O	2·698 (6)	2·46 (2)	2·509 (5)	2·421 (5)	2·531 (5)
O···H	1·95	1·23 (2)	1·451 (3)	1·437 (3)	1·695
O—H	0·75	1·23 (2)	1·058 (2)	0·991	0·840
N(amine)—Cu—N(amine)	87·8 (2)	96·3 (6)	98·6 (1)	104·6 (2)	106·7 (2)
N(amine)—Cu—N(oxime)	83·1 (2)	81·4 (5)	79·9 (1)	79·6 (2)	79·9 (2)
	82·0 (2)	81·4 (5)	81·0 (1)	80·3 (2)	78·6 (2)

Notes: (I) [Cu(EnAO-H)$_2$](ClO_4)$_2$ (Gavel & Schlemper, 1979); (II) [Cu(PnAO-H)](ReO_4) (Liss & Schlemper, 1975); (III) [Cu(6,6-Me$_2$-PnAO-H)(H_2O)](ClO_4) (this work); (IV) [Cu(BnAO-H)(H_2O)](ClO_4) (Pal *et al.*, 1986); (V) [Cu(BnAO-H)$_2$](ClO_4)$_2$ (Pal *et al.*, 1986).

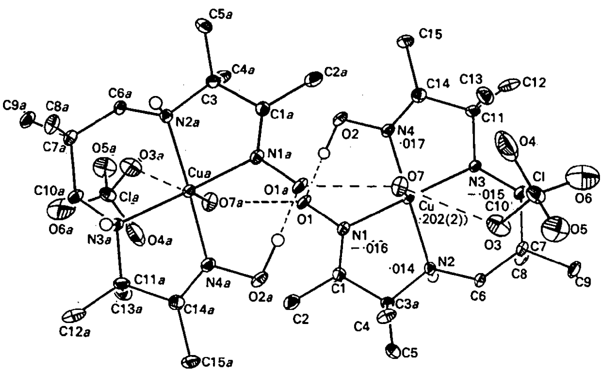

Fig. 1. Perspective view showing the atom-numbering scheme (Johnson, 1976); the hydrogens at the chiral centres are plotted as plain circles, the other atoms as shaded spheres. A neighbouring molecule with symmetry code $2-x, 1-y, -z$ is also plotted to indicate the intermolecular hydrogen bonding. Displacements of four donor N atoms and Cu^{II} from the best plane of the four N atoms are also indicated. The e.s.d.'s of the displacements for the N atoms are 0·004 Å. The oxime and amine hydrogens are plotted as plain circles.

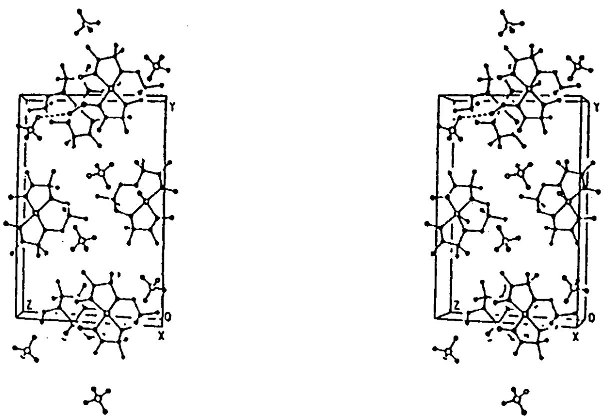

Fig. 2. A stereoscopic view, showing how the molecules are packed in a unit cell.

of two neighbouring molecules with deviation of Cu^{II} and donor atoms from the diaminedioxime plane is shown in Fig. 1. A stereoscopic view of molecules packed in a unit cell is plotted in Fig. 2.

The copper coordination is slightly distorted square pyramidal with the deprotonated diazadioxime equatorial and the O atom of the aqua group axial as shown in Fig.1. The four donor N atoms of the diazadioxime lie almost in a plane with maximum deviation of 0·017 Å; the Cu^{II} atom is significantly (0·202 Å) out of this plane towards the aqua group. The two H atoms of the amine groups are on the same side; however, the aqua group is on the other side of this plane. The configuration of the two chiral N centres is 4*RS* and 8*SR*. The central six-membered chelate ring is in a stable chair conformation, and both terminal five-membered rings are in a stable *gauche* conformation. The axial aqua O atom forms inter- and intramolecular hydrogen bonds with the oxime and perchlorate O atoms as shown in Fig. 1. The hydrogen-bond distances and angles are listed in Table 2.

In addition to this complex, the X-ray crystal structures of copper(II) complexes of a few deprotonated tetradentate diaminedioximes, [{Cu(EnAO-H)}$_2$](ClO_4)$_2$ (EnAO: 3,3,8,8-tetramethyl-4,7-diazadecane-2,9-dione dioxime) (Gavel & Schlemper, 1979), [Cu(PnAO-H)](ReO_4) (PnAO: 3,3,9,9-tetramethyl-4,8-diazaundecane-2,10-dione dioxime) (Liss & Schlemper, 1975), [Cu(BnAO-H)(H_2O)]ClO_4 and [{Cu(BnAO-H)}$_2$](ClO_4)$_2$ (BnAO: 3,3,10,10-tetramethyl-4,9-diazadodecane-2,11-dione dioxime) (Pal *et al.*, 1986), have previously been reported. Some selected structural data for these complexes are listed in Table 3. It is interesting to note that all of these complexes are five-coordinate distorted square-pyramidal copper(II) complexes with the deprotonated diaminedioxime equatorial. As listed in this table, the N—*M*—N angles in these complexes are distorted significantly from ideal square-planar values. The N(amine)—*M*—N(amine) angle increases in the order [{Cu(EnAO-H)}$_2$](ClO_4)$_2$ < [Cu(PnAO-H)](ReO_4) < [Cu(6,6-Me$_2$-PnAO-H)-(H_2O)](ClO_4) < [Cu(BnAO-H)(H_2O)](ClO_4) and [{Cu(BnAO-H)}$_2$](ClO_4)$_2$; the average N(amine)—

M—N(oxime) angle decreases in the order [{Cu(EnAO-H)}$_2$](ClO$_4$)$_2$ > [Cu(PnAO-H)](ReO$_4$) > [Cu(6,6-Me$_2$-PnAO-H)(H$_2$O)](ClO$_4$) > [Cu(BnAOH)-(H$_2$O)](ClO$_4$) and [{Cu(BnAO-H)}$_2$](ClO$_4$)$_2$. This is related to two factors: (1) the size of the central chelate ring and (2) the number of the C-methyl groups of the central chelate ring. Generally, the N(amine)—M—N(amine) angle increases and the average N(amine)—M—N(oxime) angle decreases as the size of the central chelate ring increases and as the number of the C-methyl groups of the central ring increases. The average M—N(amine) bond distance is slightly longer than the average M—N(oxime) bond distance. It is significant to note that the M—N(amine) bond distances of these complexes are shorter than those of the analogous copper(II) complexes of tetraamines (Fawcett, Rudich, Toby, Lalancette, Potenza & Schuger, 1980). The O···O distance increases in the order: [Cu(BnAO-H)(H$_2$O)](ClO$_4$) < [Cu(PnAO-H)](ReO$_4$) < [Cu(6,6-Me$_2$-PnAO-H)(H$_2$O)](ClO$_4$) < [{Cu(BnA-OH)}$_2$](ClO$_4$)$_2$ < [{Cu(EnAO-H)}$_2$](ClO$_4$)$_2$. As pointed out by Pal *et al.* (1986) there are two factors which tend to elongate the O···O separation: (1) the constraint caused by the diaminedioxime ligand in the complex and (2) dimerization through a hydrogen-bonded oxime oxygen of copper(II). The constraint due to the C-methyl groups in [Cu(6,6-Me$_2$-PnAO-H)(H$_2$O)](ClO$_4$) contributes to the elongation of the O···O distance; therefore, the O···O distance in [Cu(6,6-Me$_2$-PnAO-H)(H$_2$O)](ClO$_4$) is larger than that in [Cu(PnAO-H)](ReO$_4$). Among these complexes the constraint imposed by the ethylene bridge in EnAO-H is the largest (Pal *et al.*, 1986); consequently, the O···O distance in [{Cu(EnAO-H)}$_2$](ClO$_4$)$_2$ is larger than that in any other complex.

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Structure of [P(CH$_3$)$_4$]$_2$CuBr$_4$ at 293 K

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Abstract. Tetramethylphosphonium tetrabromocuprate(II), [P(CH$_3$)$_4$]$_2$CuBr$_4$, M_r = 565·08, monoclinic, $P2_1/b11$, a = 9·493 (2), b = 31·673 (1), c = 13·046 (1) Å, α = 90·17 (2)°, V = 3922·5 Å^3, Z = 8, D_m = 1·909 (3), D_x = 1·911 Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, μ = 9·874 mm^{-1}, $F(000)$ = 2168, T = 293 K, R = 0·064 for 2368 unique observed reflections. Differential scanning calorimetry showed two phase transitions at 193 and 404 K, respectively. The space group, $Pmcn$, and the cell parameters of the high-temperature phase have also been determined by X-ray precession photographs. The monoclinic structure can be described as a commensurate distortion (with wave vector $\mathbf{q} = 1/2\,\mathbf{b}_0^*$) of the orthorhombic phase.

Introduction. Compounds belonging to the A_2BX_4 family have been exhaustively studied in the last few years. The main reason is the rich variety of commensurate and incommensurate (IC) phases pre-

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