

(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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(measuring about 0.38 × 0.36 × 0.48 mm) was mounted nearly parallel to the *b* axis, and all subsequent measurements were carried out with a Picker FACS-I automated diffractometer. The crystal gave systematic absences (*Ok*l, *k* odd; *h*0l, *l* odd; *hk*0, *h* odd) characteristic of space group *Pbca*. Cell constants were determined by a least-squares refinement of 12 reflections (60 < |2θ| < 76°) measured with Cu *K*α radiation [$\lambda(\text{Cu } K\alpha_1) = 1.54050$, $\lambda(\text{Cu } K\alpha_2) = 1.54433$ Å]. The density was estimated from neutral buoyancy in a CCl₄/CH₃I mixture.

Intensities were measured with Zr-filtered Mo radiation (40 kV, 18 mA, take-off angle = 4°). Data were collected using the coupled θ ; 2 θ technique from 2 to 50°, with a scan rate of 1° min⁻¹ and range of 1.6(1 + 0.3 tan θ)°, and with 10 s background measurements at both extremities of the scan. A total of 1768 reflections were measured of which 1307 reflections having $|F_o| > 3\sigma(F_o)$ were used in the structure solution and refinement; $\sigma^2(F_o) = 1/w = (F_o/2I_n)^2 [I_s + (t_s/t_b)^2 I_b + (0.03I_n)^2]$, where *I*, *t*, *s*, *n* and *b* refer to intensity (counts), time (s), scan, net and background respectively. Three standard reflections measured after 50 data reflections showed an average intensity decrease of less than 1%. Intensities, which were corrected for absorption as a function of ϕ [linear $\mu = 0.751$ mm⁻¹; maximum/minimum transmission (calc.) = 1.07, (obs.) = 1.04] and Lorentz-polarization effects in the usual manner, were converted to structure amplitudes.

The structure was solved through the use of Fourier synthesis methods, and was refined by a full-matrix least-squares program which minimized the function $\sum w(|F_o| - |F_c|)^2$, utilized anisotropic temperature factors and included a correction for secondary extinction. Atomic scattering factors for nonhydrogen atoms were taken from the tabulations of Cromer & Waber (1965) and for H atoms the values of Stewart, Davidson & Simpson (1965) were used: corrections for real and imaginary anomalous-dispersion effects were applied to the scattering factors of the Cu and Cl atoms (Cromer & Liberman, 1970).

A difference Fourier electron density map contained peaks near all 10 expected H-atom positions. H atoms with $B = 4.0$ Å² and at idealized positions were introduced into the model structure and held fixed. Refinement converged to $R = [\sum w(|F_o| - |F_c|)^2 / \sum w(F_o)^2]^{1/2} = 0.051$ and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w(F_o)^2]^{1/2} = 0.048$; there were no significant shifts in the final cycle of refinement. Major peaks in the final difference Fourier electron density map have a maximum peak height of 0.5 e Å⁻³, and are located nearest O atoms in the perchlorate group. Atomic coordinates are listed in Table 1, Fig. 1 shows the atom numbering scheme and bonding distances and angles, and Fig. 2 is a perspective view of the complex. E.s.d.'s (from the least-squares matrix) are less than 0.007 Å and 0.6°

Table 1. Final positional parameters and equivalent isotropic thermal parameters

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} (Å ²) [†]
Cu	0.0	0.0	0.0	2.94 (6)
Cl	-0.09861 (10)	0.18632 (8)	-0.22770 (11)	3.42 (10)
O(1)	-0.1139 (2)	0.0390 (2)	0.1082 (3)	3.6 (3)
O(2)	-0.0931 (4)	0.0928 (3)	-0.1975 (4)	7.1 (5)
O(3)	-0.1983 (4)	0.2173 (4)	-0.2305 (5)	9.3 (6)
O(4)	-0.0484 (4)	0.2348 (3)	-0.1280 (4)	7.9 (5)
O(5)	-0.0535 (4)	0.2048 (3)	-0.3487 (4)	6.8 (4)
N(1)	-0.2053 (3)	0.0346 (3)	0.0493 (4)	3.0 (3)
N(2)	-0.0749 (3)	-0.1114 (2)	-0.0553 (4)	3.3 (3)
C(1)	-0.2389 (4)	-0.0446 (3)	0.0021 (4)	3.1 (4)
C(2)	-0.3318 (4)	-0.0461 (4)	-0.0605 (5)	3.8 (4)
C(3)	-0.3879 (4)	0.0316 (4)	-0.0739 (5)	4.0 (5)
C(4)	-0.3527 (4)	0.1102 (4)	-0.0205 (5)	4.1 (5)
C(5)	-0.2600 (4)	0.1114 (4)	0.0400 (5)	3.6 (4)
C(6)	-0.1701 (4)	-0.1247 (3)	0.0199 (5)	3.8 (4)
C(7)	-0.0918 (4)	-0.1179 (3)	-0.1947 (5)	4.1 (5)

$$^{\dagger} B_{eq} = \frac{1}{3} \sum_i \sum_j B_{ij} a_i^* a_j^* a_i \cdot a_j$$

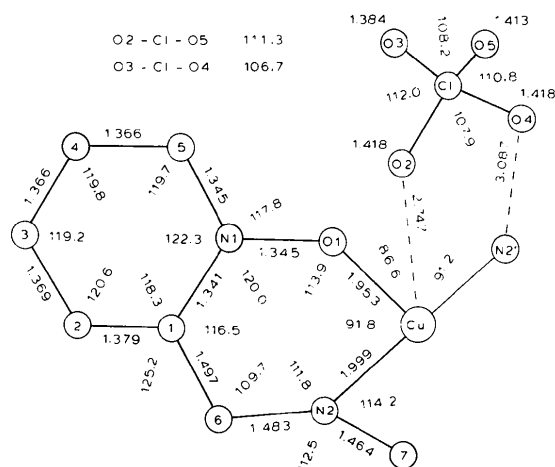


Fig. 1. A diagrammatic representation of a molecule of [Cu(C₇H₁₀N₂O)₂](ClO₄)₂ showing bond distances (Å) and angles (°). Bond distances and angles involving Cu have e.s.d.'s of 0.003–0.004 Å and 0.11–0.15°; other distances and angles have e.s.d.'s of 0.004–0.007 Å and 0.26–0.52°.

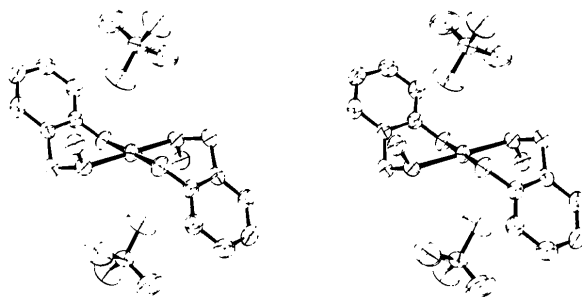


Fig. 2. A stereoview of a molecule of [Cu(C₇H₁₀N₂O)₂](ClO₄)₂ (Johnson, 1965).

for bond distances and angles. E.s.d.'s involving bonds to Cu are less than 0.004 Å and 0.2°.*

Discussion. The coordination geometry about Cu is of the 4 + 2 type. The major coordination plane is composed of *trans* chelated-ligand donor atoms, and the 'bite' distance across donor atoms is 2.838 (5) Å. The Cu—O(2) 'semi-coordinated' bond vector of 2.747 Å makes an angle of 86.4° to the major coordination plane. The next shortest contact between Cu and any ClO₄⁻ O atom is 3.77 Å.

Atoms in the pyridine ring have an average deviation from the best-fit plane through them of 0.009 (6) Å. The plane of the ring is inclined 53.4° to the major coordination plane. The Cu-coordinated O(1) atom is displaced by 0.04 Å from the best-fit ring plane, and the O(1)—N(1)—C(1)—C(6) torsion angle is 0.3 (6)°.

Two ClO₄⁻ O atoms are hydrogen-bonded to the amine H atom H(N2). An intramolecular hydrogen

* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36300 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

bond to O(4) is present with a N(2)—O(4) distance of 3.087 Å and N(2)—H(N2)—O(4) angle of 146.7°, and a weaker intermolecular hydrogen bond to O(5) is also present with a N(2)—O(5) distance of 3.343 Å and N(2)—H(N2)—O(5) angle of 138.4°. It is noteworthy that the remaining ClO₄⁻ O atom O(3), which has no contacts to H(N2) under 3.0 Å, has the shortest O—Cl bond distance and largest temperature factor of any atom in the anion.

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The Structure of μ -Aqua-bis(μ -trifluoroacetato-*O,O'*)-bis[(*N,N,N',N'*-tetramethylethylenediamine)(trifluoroacetato)nickel(II)]

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Abstract. [Ni₂(C₂F₃O₂)₄(C₆H₁₆N₂)₂H₂O]. C₂₀H₃₄F₁₂N₄Ni₂O₉, *M_r* = 819.9, monoclinic, *P*2₁/*n*, *a* = 17.183 (5), *b* = 13.879 (5), *c* = 15.509 (5) Å, β = 114.39 (2)°, *Z* = 4, *D_c* = 1.617 Mg m⁻³, μ (Mo *K* α) = 1.24 mm⁻¹. Final *R* = 0.071 for 2012 reflections. The molecule is binuclear, with a Ni—Ni distance of 3.676 (3) Å. The central Ni atoms are octahedrally coordinated and bridged by a H₂O molecule and two carboxylate groups in *syn-syn* configuration. The noncoordinated O atoms of the unidentate carboxylate groups form intramolecular hydrogen bonds with the bridging H₂O molecule.

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Introduction. The green crystals were obtained by slow evaporation of ethanol solution containing nickel(II) trifluoroacetate and *N,N,N',N'*-tetramethylethylenediamine. A single crystal of dimensions 0.25 × 0.30 × 0.35 mm was selected for the intensity measurements. Cell dimensions were determined by a least-squares treatment of 23 well-centered reflections on a Syntex *P*2₁ diffractometer. Intensities were collected (5 < 2 θ < 50°) by the ω -scan method with a variable scan rate from 2.55 to 29.3° min⁻¹ and graphite-monochromatized Mo *K* α radiation (λ = 0.71069 Å). Standards monitored about every 98 reflections showed

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