

The ligand in the form N(1)–C(2)–C(3)–N(4) has the *gauche* conformation (–synclinal) usual for  $[\text{Cu}(\text{en})_2]^{2+}$ , with C(2) 0.44 (2) Å below and C(3) 0.13 (2) Å above the Cu(2), N(1), N(4) plane. The N(1)–C(2)–C(3)–N(4) torsion angle is 47 (2)° which is a normal value compared to other similar compounds. The torsion angle N(1)–C(2)–C(33)–N(44) is very small [3 (3)°] so it is doubtful whether the position N(1)–C(2)–C(33)–N(44) represents a 'true' conformation.

Disorder in an ethylenediamine ligand bound to Cu is also observed for the compound dichloro(ethylenediamine)copper(II) (Harvey & Lock, 1986).

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## Dichloro(mepirizole)copper(II)

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**Abstract.** Dichloro[4-methoxy-2-(5-methoxy-3-methylpyrazol-1-yl)-6-methylpyrimidine]copper(II),  $[\text{CuCl}_2 \cdot (\text{C}_{11}\text{H}_{14}\text{N}_4\text{O}_2)]$ ,  $M_r = 368.7$ , monoclinic,  $C2/c$ ,  $a = 14.177$  (5),  $b = 17.821$  (4),  $c = 12.119$  (2) Å,  $\beta = 106.13$  (2)°,  $V = 2942$  (3) Å<sup>3</sup>,  $Z = 8$ ,  $D_m = 1.66$  (2),  $D_x = 1.665$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo K}\alpha) = 0.71069$  Å,  $\mu = 1.86$  mm<sup>-1</sup>,  $F(000) = 1496$ ,  $T = 293$  K,  $R = 0.032$  for 1544 unique observed reflections and 181 variable parameters. The Cu<sup>2+</sup> ions are four-coordinated by two mepirizole N atoms and two Cl atoms; the N–Cu–N bite-angle value, 80.75 (9)°, is imposed by the planar

geometry of the ligand; the geometry of the CuN<sub>2</sub>Cl<sub>2</sub> chromophore is characterized by a substantial distortion from either square-planar or tetrahedral coordination: the Cl–Cu–Cl angle is 100.39 (4)° and the dihedral angle between the N–Cu–N and Cl–Cu–Cl planes is 56.8 (3)°.

**Introduction.** Mepirizole, 4-methoxy-2-(5-methoxy-3-methylpyrazol-1-yl)-6-methylpyrimidine (*L*), is a biologically active pyrimidyl-pyrazole derivative used as an anti-inflammatory agent (Takabatake, Kodama, Tanaka, Dohmori, Tachizawa & Naito, 1970). The crystal-structure determination of the title compound was undertaken as part of a continuing research project involving the synthesis, structure and properties of

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mepirizole metal complexes (Garcia, Molla & Borrás, 1985; Molla, Garcia, Borrás, Foces, Cano & Martínez, 1986). It was also of particular interest to confirm the molecular structure of this complex, previously established by spectroscopic techniques (Molla, Garcia & Borrás, 1985).

**Experimental.** Brown crystals from 1:1 mixture of  $\text{CuCl}_2$  and mepirizole in ethanol. Crystal used:  $0.2 \times 0.2 \times 0.3$  mm.  $D_m$  by flotation in a chloroform-1,1,2,2-tetrabromoethane mixture. Systematic absences from precession photographs:  $hkl$ ,  $h + k = 2n + 1$ ;  $h0l$ ,  $l = 2n + 1$ ; space group  $Cc$  or  $C2/c$ ; centrosymmetric space group assumed on the basis of convincing intensity statistics. Enraf-Nonius CAD-4 diffractometer. Unit cell: least squares on 25 reflections with  $7 < \theta < 17^\circ$ . Intensity measurements by  $\omega$ - $2\theta$  scans, variable speed, pre-scan speed  $10^\circ \text{ min}^{-1}$  in  $\omega$ ,  $\sigma_I/I$  for final scan 0.015, maximum time allowed for final scan 90 s, minimum scan speed  $1.25^\circ \text{ min}^{-1}$  in  $\omega$ , width  $1.1^\circ + 0.35^\circ \tan \theta$  in  $\omega$ , background  $\frac{1}{4}$  of scan width fore and aft, Mo  $K\alpha$  radiation (graphite monochromator); 2437 ( $+h$ ,  $+k$ ,  $\pm l$ ) reflections measured ( $1.5 < \theta < 24^\circ$ ;  $h_{\text{max}} = 16$ ,  $k_{\text{max}} = 20$ ,  $l_{\text{max}} = 13$ ). Three standards for orientation, every 200 reflections, three standards for count, every 7200 s: no appreciable trends;  $p = 0.04$  ('instability constant'), used in  $\sigma_I^2 = S + I^2B + p^2I^2$ ,  $I = S - tB$ . Calculations by *SDP* (Enraf-Nonius, 1979), illustrations by *ORTEP* (Johnson, 1976), VAX 11-730 DEC computer. Structure solution by Patterson method, full-matrix least-squares refinement based on  $F$  magnitudes, function minimized:  $\sum w(\Delta F)^2$ ;  $w = 1/\sigma_F^2$ ; 1544 unique observed reflections used ( $I > 2\sigma_I$ ). Atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974). Absorption corrections unnecessary because of shape of crystal and small  $\mu$ . H atoms from  $\Delta\rho$  maps, not refined, idealized positions ( $\text{C}-\text{H} = 0.98 \text{ \AA}$ ,  $\text{H}-\text{C}-\text{H} = 109.5^\circ$ ), arbitrary isotropic temperature factor  $B = 5 \text{ \AA}^2$ . Final  $R = 0.032$ ,  $wR = 0.042$ ,  $S = 1.67$ ,  $(\Delta/\sigma)_{\text{max}} < 0.03$ . Max. peak height in final  $\Delta\rho$  map  $= 0.5 \text{ e \AA}^{-3}$ ; most of the highest residual peaks situated in the middle of covalent bonds and ascribable to the asphericity effect.

**Discussion.** Final positional and equivalent isotropic thermal parameters for non-H atoms are listed in Table 1.\* Selected bond lengths and angles are given in Table 2. Atoms are labelled according to Fig. 1. The crystal structure is made of discrete molecules; the overall geometry of the molecule is planar with Cl atoms

\* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43545 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

protruding from both sides of this plane. A stereoview of the molecular packing is shown in Fig. 2.

No other crystal structures of metal complexes with the mepirizole ligand have been reported to date with the exception of that of bis(mepirizole)copper(II) perchlorate,  $[\text{CuL}_2](\text{ClO}_4)_2$  (Molla *et al.*, 1986). In both

Table 1. Atomic parameters and their e.s.d.'s

	x	y	z	$B_{\text{eq}}^*(\text{\AA}^2)$
Cu	0.34559 (4)	0.34491 (3)	0.24078 (4)	3.27 (1)
Cl(1)	0.41560 (8)	0.34762 (7)	0.10111 (8)	4.63 (3)
Cl(2)	0.21103 (9)	0.41289 (6)	0.1632 (1)	4.57 (3)
O(12)	0.3786 (2)	0.1388 (2)	0.5456 (2)	4.41 (7)
O(15)	0.3799 (2)	0.3521 (2)	0.7473 (2)	4.62 (7)
N(1)	0.3559 (2)	0.3598 (2)	0.4073 (3)	2.82 (7)
N(3)	0.3698 (2)	0.2902 (2)	0.5789 (3)	2.99 (7)
N(7)	0.3672 (2)	0.2311 (2)	0.4083 (2)	2.74 (7)
N(8)	0.3629 (2)	0.2376 (2)	0.2932 (2)	2.71 (7)
C(2)	0.3636 (3)	0.2972 (2)	0.4696 (3)	2.57 (8)
C(4)	0.3727 (3)	0.3540 (2)	0.6347 (3)	3.61 (9)
C(5)	0.3687 (3)	0.4232 (2)	0.5812 (4)	4.1 (1)
C(6)	0.3608 (3)	0.4251 (2)	0.4661 (3)	3.45 (9)
C(9)	0.3666 (3)	0.1686 (2)	0.2553 (3)	3.06 (8)
C(10)	0.3736 (3)	0.1163 (2)	0.3421 (3)	3.49 (9)
C(11)	0.3748 (3)	0.1567 (2)	0.4398 (3)	3.23 (8)
C(13)	0.4017 (4)	0.0611 (3)	0.5759 (4)	5.5 (1)
C(14)	0.3594 (3)	0.1541 (2)	0.1314 (4)	4.2 (1)
C(16)	0.3837 (3)	0.2798 (3)	0.8014 (4)	4.5 (1)
C(17)	0.3618 (4)	0.4967 (2)	0.4026 (4)	5.1 (1)

\* Anisotropically refined atoms are given in the form of the equivalent isotropic thermal parameter defined as:  $\frac{1}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$ .

Table 2. Interatomic distances ( $\text{\AA}$ ), bond angles ( $^\circ$ ) and relevant torsion angles ( $^\circ$ )

Cu-Cl(1)	2.188 (1)	N(3)-C(4)	1.318 (4)
Cu-Cl(2)	2.235 (1)	N(7)-N(8)	1.385 (3)
Cu-N(1)	2.001 (2)	N(7)-C(2)	1.402 (4)
Cu-N(8)	2.008 (2)	N(7)-C(11)	1.377 (4)
O(12)-C(11)	1.309 (4)	N(8)-C(9)	1.320 (4)
O(12)-C(13)	1.445 (4)	C(4)-C(5)	1.387 (5)
O(15)-C(4)	1.341 (4)	C(5)-C(6)	1.370 (5)
O(15)-C(16)	1.438 (4)	C(6)-C(17)	1.490 (5)
N(1)-C(2)	1.334 (4)	C(9)-C(10)	1.392 (4)
N(1)-C(6)	1.355 (4)	C(9)-C(14)	1.495 (4)
N(3)-C(2)	1.307 (4)	C(10)-C(11)	1.380 (4)
Cl(1)-Cu-Cl(2)	100.39 (4)	N(1)-C(2)-N(3)	128.7 (3)
Cl(1)-Cu-N(1)	148.88 (8)	N(1)-C(2)-N(7)	114.2 (3)
Cl(1)-Cu-N(8)	102.90 (7)	N(3)-C(2)-N(7)	117.0 (3)
Cl(2)-Cu-N(1)	99.62 (8)	O(15)-C(4)-N(3)	118.9 (3)
Cl(2)-Cu-N(8)	131.65 (7)	O(15)-C(4)-C(5)	118.7 (3)
N(1)-Cu-N(8)	80.75 (9)	N(3)-C(4)-C(5)	122.4 (3)
C(11)-O(12)-C(13)	115.2 (3)	C(4)-C(5)-C(6)	118.7 (3)
C(4)-O(15)-C(16)	118.0 (3)	N(1)-C(6)-C(5)	119.4 (3)
Cu-N(1)-C(2)	115.6 (2)	N(1)-C(6)-C(17)	118.0 (3)
Cu-N(1)-C(6)	128.5 (2)	C(5)-C(6)-C(17)	122.5 (3)
C(2)-N(1)-C(6)	115.8 (3)	N(8)-C(9)-C(10)	111.2 (3)
C(2)-N(3)-C(4)	114.9 (3)	N(8)-C(9)-C(14)	120.8 (3)
N(8)-N(7)-C(2)	117.9 (2)	C(10)-C(9)-C(14)	128.0 (3)
N(8)-N(7)-C(11)	109.7 (2)	C(9)-C(10)-C(11)	106.3 (3)
C(2)-N(7)-C(11)	132.4 (3)	O(12)-C(11)-N(7)	119.0 (3)
Cu-N(8)-N(7)	111.4 (2)	O(12)-C(11)-C(10)	134.4 (3)
Cu-N(8)-C(9)	142.2 (2)	N(7)-C(11)-C(10)	106.6 (3)
N(7)-N(8)-C(9)	106.2 (2)		
C(5)-C(4)-O(15)-C(16)	-179.9 (2)	C(2)-N(1)-C(6)-C(17)	174.5 (4)
C(10)-C(11)-O(12)-C(13)	-11.5 (3)	N(7)-N(8)-C(9)-C(14)	177.6 (3)
N(3)-C(2)-N(7)-C(11)	-1.2 (3)		

complexes, the pyrazole and pyrimidine rings are planar: deviations (Å) of atoms from their least-squares plane for  $[\text{CuLCl}_2]$  are N(7): 0.005 (3), N(8): -0.004 (3), C(9): 0.001 (4), C(10): 0.002 (4), C(11): -0.005 (4) and N(1): 0.017 (3), C(2): -0.017 (4), N(3): 0.005 (3), C(4): 0.006 (4), C(5): -0.005 (5), C(6): -0.006 (4); the dihedral angle between the two planes is  $3.5^\circ$ , indicating a large degree of overall electronic delocalization. The Cu atom is situated in the plane of the pyrimidine ring [deviation 0.000 (1) Å] but deviates by 0.094 (1) Å from the plane of the pyrazole ring.

The  $\text{Cu}^{2+}$  ions are four-coordinated by two mepirizole N atoms [N(1) and N(8)] and two Cl atoms forming a strongly distorted tetrahedral  $\text{CuN}_2\text{Cl}_2$  chromophore with Cu-N and Cu-Cl distances falling in the usual ranges (Hathaway, 1983; O'Brien, 1984). The Cu-N coordination distances compare well with the Cu-N distances [1.974 (8) Å] reported for the bis(mepirizole)copper(II) perchlorate complex. In the same way the N(1)-Cu-N(8) bite angles are very close { $80.75$  (9) and  $80.8$  (3) $^\circ$  for  $[\text{CuLCl}_2]$  and  $[\text{CuL}_2](\text{ClO}_4)_2$ , respectively} and strongly reduced from the regular tetrahedral angle of  $109.5^\circ$ ; clearly,

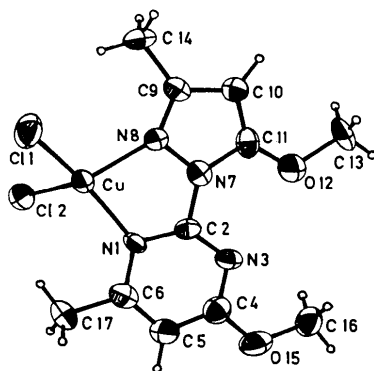


Fig. 1. Perspective view of the complex molecule showing atom labelling. H atoms are given an arbitrary isotropic temperature factor.

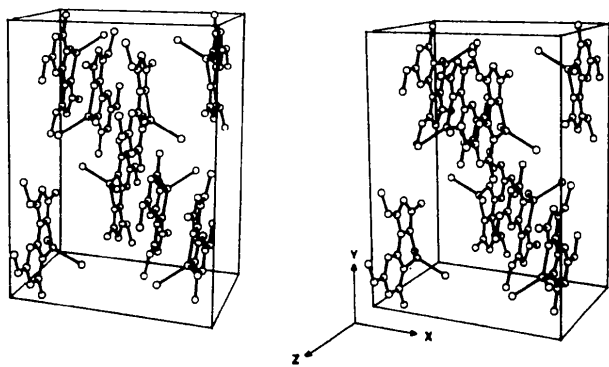


Fig. 2. Stereoview of the molecular packing.

the bite-angle value is imposed by the planar geometry of the ligand. The geometry of the  $\text{CuN}_2\text{Cl}_2$  chromophore is characterized by a substantial distortion from either square-planar or tetrahedral coordination: the Cl(1)-Cu-Cl(2) angle is  $100.39$  (4) $^\circ$  and there is a twist of the N(1)-Cu-N(8) plane with respect to the Cl(1)-Cu-Cl(2) plane to give a dihedral angle of  $56.8$  (3) $^\circ$ . Such geometry is also observed for the  $\text{CuN}_4$  chromophore in  $[\text{CuL}_2](\text{ClO}_4)_2$ .

This twisted tetrahedral structure has been observed previously in the  $\text{CuO}_2\text{Cl}_2$  (Mathew & Palenik, 1971) and  $\text{CuN}_2\text{Br}_2$  (Ray, Tyagi & Hathaway, 1982) chromophores and described as a compressed distorted tetrahedron. As there is no obvious intramolecular steric constraint to hinder the tetrahedral coordination, we rather like describing the distortion as resulting from a compromise between a tendency to adopt the square-planar coordination and steric interactions indicated by the non-bonded distances Cl(1)⋯Cl(2) = 3.397 (1), Cl(1)⋯C(14) = 3.582 (4) and Cl(2)⋯C(17) = 3.431 (4) Å. van der Waals radii for Cl and -CH<sub>3</sub> are 1.80 and 2.0 Å, respectively (Pauling, 1960).

The tetrahedral distortion of the  $\text{CuN}_2\text{Cl}_2$  chromophore is in full agreement with electronic spectra and magnetic measurements previously reported (Molla *et al.*, 1985).

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