

Discussion. Tous les atomes, y compris les atomes d'hydrogène ont pu être localisés. Dans le Tableau 1 sont indiqués les coordonnées atomiques et les facteurs thermiques équivalents (ou isotopes pour les atomes d'hydrogène). Le composé $[\text{Ni}_2\text{Cl}_4(\text{H}_2\text{O})_6] \cdot \text{C}_4\text{H}_{12}\text{N}_2^+ \cdot 2\text{Cl}^-$ est formé de chlorure de nickel hydraté $\text{Ni}_2\text{Cl}_4(\text{H}_2\text{O})_6$, de cations pipérazine $\text{C}_4\text{H}_{12}\text{N}_2^+$ (dont les distances sont résumées dans le Tableau 2) et de chlorures isolés $\text{Cl}(3)^-$, provenant du dichlorure de pipérazine. La cohésion de la structure est assurée d'une part par les liaisons ioniques entre les cycles de pipérazine et $\text{Cl}(3)^-$, d'autre part par les liaisons hydrogène allant des molécules d'eau et de la pipérazine aux différents atomes de chlore: le Tableau 2 donne les caractéristiques de ces liaisons hydrogène.

Comme dans $\text{C}_4\text{H}_{12}\text{N}_2^+ \cdot \text{Cu}_2\text{Cl}_6^{2-}$ (Daoud *et al.*, 1986) la molécule de pipérazine, qui est centrosymétrique, adopte la forme chaise (Fig. 1). Les distances C–N sont légèrement plus courtes dans le complexe de nickel, alors que les distances C–C sont identiques. La coordination du nickel est un octaèdre déformé (Fig. 1), constitué de trois atomes de chlore [trois distances longues de 2,393 à 2,417 (1) Å] et de trois molécules d'eau [trois distances courtes Ni–O de 2,025 à 2,099 (1) Å]. Deux octaèdres mettent en commun une arête Cl(1)–Cl(1) pour donner le dimère $[\text{Ni}_2\text{Cl}_4(\text{H}_2\text{O})_6]$. Ceci conduit à une courte distance Ni–Ni de 3,480 (1) Å dans le dimère comparable à la distance Cu–Cu de 3,423 (1) Å dans $\text{C}_4\text{H}_{12}\text{N}_2^+ \cdot \text{Cu}_2\text{Cl}_6^{2-}$. Par contre la plus courte distance Ni–Ni entre deux dimères est beaucoup plus grande [5,692 (1) Å] que la distance Cu–Cu correspondante [3,446 (1) Å]: il n'y aura probablement pas d'ordre magnétique entre les nickel analogue à celui observé dans le composé de cuivre (Daoud *et al.*, 1986), même à très basse température. Les atomes de chlore Cl(1) et Cl(2) ne sont accepteurs respectivement que de une et

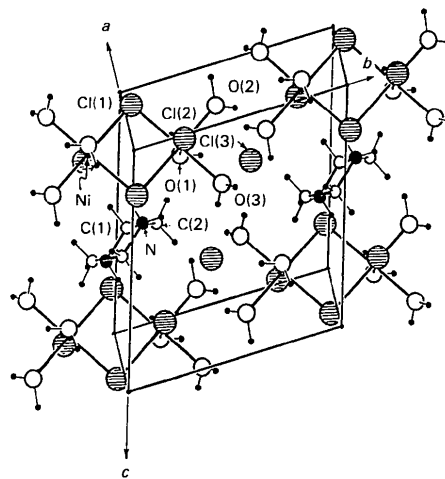


Fig. 1. Projection de la structure de $[\text{Ni}_2\text{Cl}_4(\text{H}_2\text{O})_6] \cdot \text{C}_4\text{H}_{12}\text{N}_2^+ \cdot 2\text{Cl}^-$ obtenue avec le programme ORTEPII (Johnson, 1976).

trois liaisons hydrogène, alors que le chlore isolé Cl(3) est accepteur de cinq liaisons fortes (Tableau 2). Cet atome joue un rôle important dans la cohésion de la structure: il est lié à quatre dimères différents et à une molécule de pipérazine.

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Structure of Bis(ethylenediamine)copper(II) Dichlorocuprate(I)

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Abstract. $[\text{Cu}(\text{C}_2\text{H}_8\text{N}_2)_2][\text{CuCl}_2]_2$, $M_r = 452.65$, monoclinic, $P2_1/c$, $a = 7.995$ (2), $b = 14.147$ (2), $c = 6.2331$ (6) Å, $\beta = 108.82$ (1)°, $V = 667.3$ (5) Å³, $Z = 2$, $D_m = 2.2$ (1), $D_x = 2.253$ Mg m⁻³, $\lambda(\text{Mo K}\alpha) = 0.71073$ Å, $\mu = 5.54$ mm⁻¹, $F(000) = 446$, $T = 295$ K, $R = 0.064$ for 1337 unique observed reflections.

The Cu^{II} ions are placed on centres of symmetry and coordinated to four N atoms and two Cl^- ions arranged in a distorted octahedral configuration with the N atoms in a plane. Some of the atoms in the ethylenediamine ligand have disordered positions. The Cu^{I} ions are tetrahedrally coordinated to four Cl^- ions. The Cu^{I}

ions and the Cl⁻ ions constitute infinite chains of distorted tetrahedra extended along the *c* axis. The tetrahedra are joined on edges.

Introduction. Mixed-valence transition-metal complexes have been studied intensively during the last decades. Dark-brown-coloured oligomeric chlorocuprates have been characterized crystallographically in a few cases (Mori, 1960). Over a century ago Ritthausen (1853) prepared a blue Cu^I, Cu^{II} ammine chloride which Harris (1948) showed to have the composition [Cu^{II}·(NH₃)₄][CuCl₂]₂·H₂O. The crystal structures of this compound and its Br⁻ and I⁻ analogues have been reported (Baglio, Weakliem, Demelio & Vaughan, 1970; Baglio & Vaughan, 1970). This class of compounds consists of discrete tetraamminecopper(II) cations and extended-chain dichlorocuprate(I) anions.

The corresponding bis(ethylenediamine)copper(II) complex could not be prepared by Harris (1948), but instead he isolated a compound with the composition [Cu(en)₂][Cu₃Cl₅] and prepared the dark-coloured [Cu(en)₂][CuI₂]₂, the crystal structure of which has been reported (Freckmann & Tebbe, 1980). From a reaction mixture containing reducing mercapto-benzaldehyde we have isolated the title compound as a byproduct (Toftlund, Becher, Olesen & Pedersen, 1985).

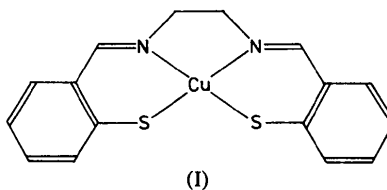
Experimental. Small red-violet prisms of bis(ethylenediamine)copper(II) dichlorocuprate(I) were obtained in low yield along with blue-green crystals of (I) by reflux of a mixture of 1,2-bis[*N*-(2-*tert*-butylthiophenyl)-iminomethyl]ethane and copper(II) chloride in 2-methoxyethanol for 18 h. *D_m* by flotation in a mixture of CHBr₃ and CHCl₃. Crystal: 0.23 × 0.20 × 0.07 mm, Enraf-Nonius CAD-4F diffractometer, graphite-monochromatized Mo *K*α radiation, lattice parameters from setting angles for 25 reflections with 8.45 < θ < 11.62°. 1938 unique reflections (*h*-11→10, *k*0→19, *l*0→8) with 2.0 < θ < 30.0°, 1337 with *I* > 2.5σ(*I*) used in refinement process together with 'less-than' reflections [*I* < 2.5σ(*I*)] with calculated values greater than the observed (1742 contributing reflections). Mixed ω/2θ-scan technique, scan angle = 1.20° + 0.35° tan θ. Standard reflections $\bar{2}60$, $\bar{2}\bar{4}\bar{2}$, and 25 $\bar{2}$ used for orientation control every 100 reflections, $\bar{2}\bar{4}\bar{2}$ used for intensity check every 10 800 s of exposure time, standard intensity variations < 2.2% of mean value. Lp correction, absorption ignored; Patterson, Fourier and direct methods, full-matrix least-squares refinement of anisotropic non-H atoms. Abnormal parameters connected with the C atoms led to the conclusion that some disorder must exist in the ethylenediamine ligand. After some trials C(3) and N(4) were split into disordered positions. These were treated isotropically and given fixed population parameters during the last cycles of least-squares refinement.

Table 1. Fractional coordinates (×10⁴) and isotropic or equivalent isotropic thermal parameters of non-H atoms with e.s.d.'s in parentheses

PP, the population parameter, is quoted when it is different from unity. $B_{eq} = \frac{4}{3} \sum_i \sum_j \beta_{ij} (\mathbf{a}_i \cdot \mathbf{a}_j)$.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> / <i>B</i> _{eq} (Å ²)	PP
Cu(1)	3154 (2)	2458 (1)	6221 (2)	5.4 (1)	
Cu(2)	0	0	0	2.39 (9)	
Cl(1)	1239 (3)	1596 (2)	7884 (3)	3.2 (1)	
Cl(2)	4625 (3)	1588 (2)	4282 (3)	3.0 (1)	
N(1)	2558 (9)	5330 (5)	6414 (12)	3.1 (5)	
N(4)	123 (17)	6024 (9)	2741 (21)	2.9 (3)	0.65 (10)
N(44)	-65 (31)	5816 (17)	2471 (40)	3.0 (5)	0.35 (10)
C(2)	3170 (13)	5819 (10)	4759 (20)	5.5 (9)	
C(3)	1835 (19)	6466 (11)	3484 (26)	4.5 (3)	0.65 (10)
C(33)	1787 (36)	6069 (20)	2594 (48)	4.4 (5)	0.35 (10)

Positional H parameters calculated and not refined. $\sum w(\Delta|F|)^2$ minimized, final *R*=0.064, *wR*=0.077. Average $w(\Delta|F|)^2$ was almost independent of $|F_o|$ by using $w = 1/\{1 + [(F_o - 8.0)/46]^2\}$, *S* = 3.06, (Δ/σ)_{max} = 1.08. Minimum and maximum in final Δρ map: -1.6 and 1.6 e Å⁻³. Scattering factors from *International Tables for X-ray Crystallography* (1974). Computer programs from XRAY76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). The positional and isotropic thermal parameters are given in Table 1.*



Discussion. The Cu^I centres are tetrahedrally coordinated to four Cl⁻ ions. These tetrahedra are joined on edges and extend as infinite chains along the *c* axis (Fig. 1). The mean Cl—Cu(1) distance in the title compound (2.397 Å) compares well with the Cl—Cu^I distance in the related compound tetraamminecopper(II) dichlorocuprate(I) monohydrate [2.359 (6) Å] (Baglio & Vaughan, 1970). However, the chain polymeric anions in the two compounds differ with respect to bonding relationships to Cu^{II}. There is no bonding between the halide ions and Cu^{II} in tetraamminecopper(II) dichlorocuprate(I) monohydrate whereas a weak Cl—Cu(2) bonding probably occurs in bis(ethylenediamine)copper(II) dichlorocuprate(I) (Fig. 1). The bond distance Cu(1)—Cl(1) is significantly longer than Cu(1)—

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43550 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Cl(2). An explanation of this might be that Cl(1) coordinates to both Cu(1) and Cu(2) while Cl(2) only coordinates to Cu(1) (Fig. 2). The Cu(1)—Cu(1) distance is 3.119 (2) Å but 2.734 (4) Å in bis(ethylenediamine)copper(II) dichlorocuprate(I) monohydrate (Baglio & Vaughan, 1970). Table 2 compares bond lengths and angles in the title compound with those of related compounds.

Tetraamminecopper(II) complexes with strict planar coordination geometry are very rare. The ligand-field theory predicts that the energy for the $d-d$ transitions for such a planar $\text{Cu}^{\text{II}}\text{N}_4$ complex is blue-shifted compared to any system having a ligand interaction along the fourfold axis. Thus, certain anhydrous salts of $[\text{Cu}(\text{en})_2]^{2+}$ are pink (Procter, Hathaway & Nicholls, 1968). Very recently Lee, Lee, Juang & Chung (1985) reported the structure of the perchlorate of a red macrocyclic tetraamminecopper(II) complex with a long apical Cu—Cl distance of 2.716 (11) Å. A rather

long apical Cu(2)—Cl(1) coordination distance [2.943 (2) Å] is observed in the title compound. The Cu(2)—Cl(1) distance is significantly longer than the corresponding distance in aquachlorobis(ethylenediamine)copper(II) chloride [2.81 (1) Å] (Ball, Hall, Rickard & Waters, 1967). Thus, we assign the unexpected red colour of the title compound to the unusually weak interaction between the $[\text{Cu}(\text{en})_2]^{2+}$ complex and the chlorocuprate anion.

The bond distances and bond angles in the $[\text{Cu}(\text{en})_2]^{2+}$ complex are normal (within the standard deviations), but probably not so well defined due to the disordered positions C(3), C(33), N(4) and N(44). It is likely that C(2) is also disordered, but reliable 'split' positions for C(2) could not be found.

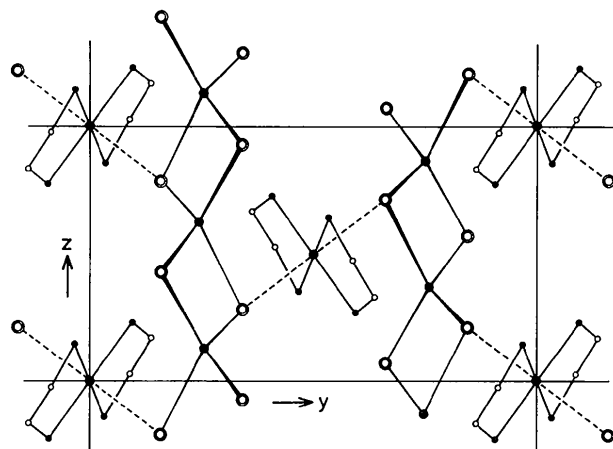


Fig. 1. Projection of the crystal structure down the x axis. Large filled circles: Cu atoms; large open circles: Cl atoms.

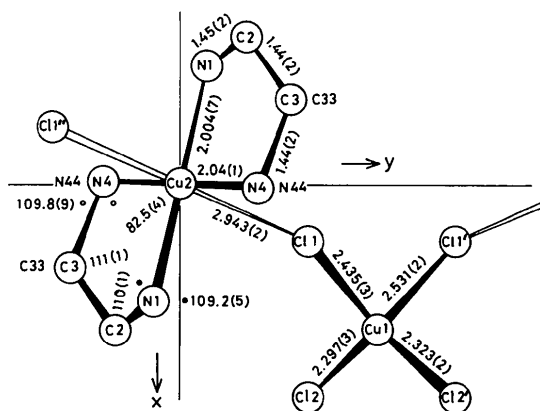


Fig. 2. Bond distances (Å), angles ($^{\circ}$), and the atom-numbering scheme for $[\text{Cu}(\text{en})_2][\text{CuCl}_2]_2$ shown on a z -axis projection. E.s.d.'s in parentheses. Cl(1)→Cl(1'): $(x, y, z) \rightarrow (x, \frac{1}{2}-y, z-\frac{1}{2})$. Cl(2)→Cl(2'): $(x, y, z) \rightarrow (x, \frac{1}{2}-y, \frac{1}{2}+z)$. The bond distances and bond angles associated with the conformation Cu(2), N(1), C(2), C(33), N(44) are: C(2)—C(33): 1.48 (3), C(33)—N(44): 1.50 (4), Cu(2)—N(44): 1.94 (3) Å; N(44)—Cu(2)—N(1): 88.5 (7), N(1)—C(2)—C(33): 116 (1), C(2)—C(33)—N(44): 115 (2), C(33)—N(44)—Cu(2): 109 (2) $^{\circ}$.

Table 2. Bond lengths (Å) and angles ($^{\circ}$) in $[\text{Cu}(\text{en})_2][\text{CuCl}_2]_2$ compared with corresponding bonds in related compounds

Compound	Reference	Cu—N	N—C	C—C	N—Cu—N	Cu—N—C	N—C—C
$[\text{Cu}(\text{en})_2][\text{CuCl}_2]_2$		2.006 (6)	1.45 (1)		84.3 (2)	109.0 (4)	115 (1)
		2.003 (5)	1.45 (1)	1.40 (1)		109.2 (6)	112.1 (8)
$[\text{Cu}(\text{en})_2](\text{NO}_3)_2$	(1)	2.04 (1)	1.48 (3)	1.55 (3)	86.2	108.5	109.6
		2.01 (1)	1.49 (3)			109.1	108.5
$[\text{CuCl}(\text{H}_2\text{O})(\text{en})_2]\text{Cl}$	(2)	1.98 (2)	1.46 (4)	1.49 (4)	85.1	107.3	102.9
		2.00 (2)	1.48 (4)	1.54 (4)	85.3	107.8	107.4
		2.00 (2)	1.49 (4)			107.9	108.5
		2.02 (2)	1.53 (4)			110.7	110.7
$[\text{Cu}(\text{en})_2](\text{BF}_4)_2$	(3)	2.02 (1)	1.48 (2)	1.56 (3)	86.4 (5)	107 (1)	107 (1)
		2.03 (1)	1.49 (2)			108 (1)	108 (1)
$[\text{Cu}(\text{en})_2][\text{CuI}_2]_2$	(4)	2.01	1.48	1.49	85	108	108

References: (1) Komiyama & Lingafelter (1964). (2) Ball, Hall, Rickard & Waters (1967). (3) Brown, Lee & Melsom (1968). (4) Freckmann & Tebbe (1980).

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) Å³, $Z = 8$, $D_m = 1.66$ (2), $D_x = 1.665$ Mg m⁻³, $\lambda(\text{Mo K}\alpha) = 0.71069$ Å, $\mu = 1.86$ mm⁻¹, $F(000) = 1496$, $T = 293$ K, $R = 0.032$ for 1544 unique observed reflections and 181 variable parameters. The Cu²⁺ 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 CuN₂Cl₂ 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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