

sites. Another mixed-valence salt studied is the (hydrazinium)₂Cu₃Cl₆ salt, which has both bonded Cu^I—Cl—Cu^{II} bridges and bonded/semicoordinate Cu^I—Cl...Cu^{II} bridges (Scott & Willett, 1990). All of these compounds display the class II behavior of Robin & Day (1967) with broad intervalence absorption bands in the visible region of the spectrum (Scott, 1990). This transition probably arises *via* the strong Cu^I—Cl—Cu^{II} bridges present in these salts.

The Cu^I...Cl—Cu^{II} interactions in the title compound involve the two long Cu^I...Cl contacts of 2.895 and 3.224 Å, shown as dashed lines in Fig. 1(a). The presence of such weak linkages makes the crystallographic assignment of the salt as a class I or class II mixed-valence system ambiguous. Clearly, the non-linearity of the CuCl₂⁻ anion shows that some small perturbation is induced at the Cu^I site. Nevertheless, the interaction must be much less than that in (Et₄N)Cu₂Cl₄ (Willett, 1987) and related systems (Scott, 1990). Spectroscopic investigation will not be much assistance, since the visible region of the spectrum is dominated by the broad tail of a BV electronic transition.

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Structure of Dichlorobis(2-chloroimidazole)copper(II)

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Abstract. [CuCl₂(C₃H₃ClN₂)₂], *M*_r = 339.5, monoclinic, *C*2/*c*, *a* = 7.988 (1), *b* = 12.276 (2), *c* = 11.633 (2) Å, β = 90.4 (2)°, *V* = 1140.7 (3) Å³, *Z* = 4, *D*_x = 1.98 g cm⁻³, λ(Mo *K*α) = 0.7107 Å, μ = 27.01 cm⁻¹, *F*(000) = 668, room temperature, *R* = 0.030 for 1257 reflections with *F* > 7σ(*F*). The structure consists of discrete four-coordinate molecular units. The 2-chloroimidazole ligands are bonded through the N(3) atoms. The coordination about the Cu atom is intermediate between tetrahedral and square planar.

Introduction. Coordination about the Cu atom in complexes of the type CuL₂X₂, containing pyridines and azoles, is found to depend also upon effects of non-bonding groups on the ligands. For example, in complexes with *X* = Cl, the metal is five-coordinate for *L* = 2-methylpyridine (Marsh, Hatfield & Hodgson, 1982) and six-coordinate for *L* = pyridine (Morosin, 1975), four-coordinate for *L* = *N*-methylimidazole (van Ooijen, Reedijk & Spek, 1979) and five-coordinate for *L* = imidazole (Lundberg, 1972). This paper reports the structure of the 2-

chloroimidazole complex $[\text{CuCl}_2(\text{C}_3\text{H}_3\text{ClN}_2)_2]$. Metal complexes of 2-chloroimidazole have not been described previously.

Experimental. The ligand was prepared according to the literature (Takeuchi, Kirk & Cohen, 1979). Crystals of the complex were obtained by slow evaporation of an aqueous solution of CuCl_2 and the ligand in the molar ratio 1:2 containing hydrochloric acid.

Crystal dimensions approximately $0.2 \times 0.2 \times 0.4$ mm. Cell dimensions and intensity data were measured on a Philips PW1100 diffractometer; θ - 2θ scan; lattice parameters from 25 reflections with $7 < \theta < 13^\circ$. 1388 unique reflections ($R_{\text{int}} = 0.04$) were collected in the range $6 < 2\theta < 56^\circ$ ($h: -9 \rightarrow 8$; $k: -15 \rightarrow 15$; $l: 0 \rightarrow 9$); of these 1257 with $F > 7\sigma(F)$ were classified as observed; three standard reflections monitored every 180 reflections, 10% variation; Lorentz and polarization corrections applied; no absorption corrections applied. The Cu atom was first located from a Patterson map through *SHELXS86*

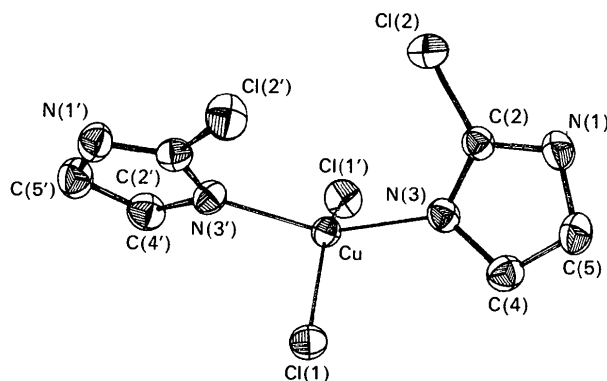


Fig. 1. Molecular scheme with atomic numbering.

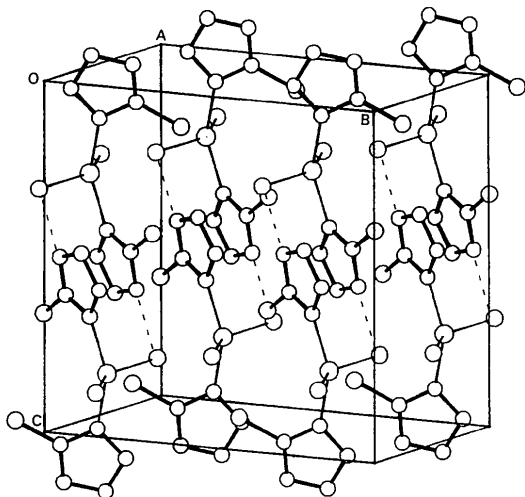


Fig. 2. Crystal packing of the title compound; *b* horizontal, *c* vertical.

Table 1. Fractional coordinates of non-H atoms with equivalent isotropic thermal parameters (\AA^2)

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	1.000000	0.13679 (3)	0.250000	0.0254 (1)
Cl(1)	0.73523 (6)	0.07668 (4)	0.27217 (4)	0.0338 (1)
Cl(2)	0.87747 (9)	0.36926 (5)	0.38913 (6)	0.0470 (2)
N(1)	1.0138 (3)	0.2712 (2)	0.5718 (2)	0.0385 (5)
N(3)	1.0313 (2)	0.1769 (1)	0.4126 (1)	0.0284 (4)
C(2)	0.9760 (2)	0.2674 (2)	0.4606 (2)	0.0306 (5)
C(4)	1.1108 (3)	0.1203 (2)	0.5008 (2)	0.0345 (6)
C(5)	1.0991 (3)	0.1771 (2)	0.5989 (2)	0.0402 (7)

Table 2. Bond lengths (\AA) and angles ($^\circ$)

Cu—Cl(1)	2.257 (1)	Cu—N(3)	1.968 (2)
Cl(2)—C(2)	1.693 (2)	N(1)—C(2)	1.328 (3)
N(1)—C(5)	1.377 (3)	N(3)—C(2)	1.321 (3)
N(3)—C(4)	1.389 (3)	C(4)—C(5)	1.341 (3)
N(3)—Cu—N(3')	151.1 (1)	Cl(1)—Cu—Cl(1')	141.8 (1)
Cl(1)—Cu—N(3)	94.9 (1)	Cl(1)—Cu—N(3')	94.5 (1)
Cu—N(3)—C(4)	129.7 (1)	Cu—N(3)—C(2)	125.2 (1)
C(2)—N(1)—C(5)	107.6 (2)	C(2)—N(3)—C(4)	105.1 (2)
N(1)—C(2)—N(3)	111.6 (2)	N(3)—C(4)—C(5)	109.6 (2)
N(1)—C(5)—C(4)	106.2 (2)	Cl(2)—C(2)—N(3)	124.7 (2)
Cl(2)—C(2)—N(1)	123.7 (2)		

$$\text{N(1)} \cdots \text{Cl(1)} (1\frac{1}{2} - x, \frac{1}{2} - y, 1 - z) \quad 3.284 (4)$$

(Sheldrick, 1986); then, a difference Fourier map revealed the other atoms (*SHELX76*; Sheldrick, 1976); anisotropic refinement of all non-H atoms and isotropic refinement of H atoms; the refinement converged to final $R = 0.030$, $wR = 0.035$, 83 parameters, $w = 1/[\sigma^2(F) + 0.002021F^2]$, $S = 0.975$, $(\Delta/\sigma)_{\text{max}} = 1.056$, $\Delta\rho_{\text{max}} = 0.889 \text{ e \AA}^{-3}$; atomic scattering factors for C, H, N, Cl from *SHELX76* and for Cu from *International Tables for X-ray Crystallography* (1974, Vol. IV).*

Discussion. The structure of the title compound (I) consists of discrete four-coordinate $\text{CuCl}_2(\text{C}_3\text{H}_3\text{ClN}_2)_2$ units. The molecular unit is shown in Fig. 1 with the atom-numbering scheme, the crystal packing in Fig. 2. Positional parameters for non-H atoms are listed in Table 1, bond lengths and angles in Table 2. The $\text{C}_3\text{H}_3\text{ClN}_2$ ligand is planar, deviations from the least-squares plane being less than 0.03 \AA . Each molecule is linked with two neighbouring molecules through two pairs of $\text{N—H} \cdots \text{Cl}$ hydrogen bonds to form infinite chains along the $[001]$ direction. The intermolecular contacts $\text{Cl(1)} \cdots \text{Cl(2)} (1\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z)$ of $3.285 (2) \text{ \AA}$ are consistent with

* Lists of structure factors, anisotropic thermal parameters, least-squares planes, possible hydrogen-bond geometries and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53859 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

non-bonded atomic radii for chlorine between 1.58 and 1.78 Å (Nyburg & Faerman, 1985).

The coordination about the Cu atom is intermediate between tetrahedral and square planar. The dihedral angle between the planes (Cl, Cu, Cl') and (N, Cu, N') is 95.7 (1)°. The Cu—N bond lengths are consistent with those of other Cu²⁺ complexes with imidazoles. The Cu—Cl bond lengths are typical for bonds of Cu²⁺ with non-bridging chloride anions. There are no close halide approaches from adjacent molecules to the Cu atom, the intermolecular Cu...Cl distances being larger than 4.0 Å. The intramolecular Cu...Cl(2) distance is 3.427 (2) Å.

The structure of the complex is different from that of the analogous complex with imidazole (II). The coordination in [CuCl₂(C₃H₄N₂)₂] is a distorted square pyramid, with two N and two Cl atoms in an approximately square plane [Cu—N 1.973 (12) and 1.992 (12), Cu—Cl 2.321 (4) and 2.365 (4) Å, N—Cu—N 174.3 (10) and Cl—Cu—Cl 166.9 (3)°], and a Cl atom from an adjacent unit occupying the apical site [Cu—Cl 2.751 (6) Å; Lundberg, 1972].

The configuration of (I) is similar to that of the analogous complex with *N*-methylimidazole, CuCl₂(C₄H₆N₂)₂ (III): Cu—N 1.962 (4) and 1.975 (5), Cu—Cl 2.260 (3) and 2.256 (2) Å, N—Cu—N 149.7 (1) and Cl—Cu—Cl 143.6 (1)°

(van Ooijen, Reedijk & Spek, 1979). However, the conformations about the Cu—N bonds are different in the two complexes. In (III) the Cl atoms lie very close to the planes through the imidazole rings. In (I) the Cu—Cl vectors are tipped from the planes through the 2-chloroimidazole ligands at angles higher than 40°. The dihedral angle between these planes is 52.7 (2)°. The resulting Cl(2)...Cl(2') intramolecular contact is 3.795 (6) Å.

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Synthesis and Structure of Hexakis(thiourea)ruthenium(II) Trifluoromethanesulfonate

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Abstract. [Ru(CH₄N₂S)₆][CF₃SO₃]₂, *M_r* = 855.9, monoclinic, *P*2₁/*a*, *a* = 11.173 (1), *b* = 11.064 (1), *c* = 13.722 (1) Å, β = 113.96 (1)°, *V* = 1550.1 (3) Å³, *Z* = 2, *D_x* = 1.834 Mg m⁻³, λ(Mo *K*α) = 0.71069 Å, μ(Mo *K*α) = 1.10 mm⁻¹, *T* = 295 K, *F*(000) = 860, *R* = 0.026 for 3609 observed reflections. The synthesis, solution properties and structure of the title complex are described. The [Ru(tu)₆]²⁺ (tu =

thiourea) cations lie on crystallographic inversion centres and the [CF₃SO₃]⁻ anions in general positions. The tu ligands are S bonded [mean Ru—S 2.421 (3) Å] and the six S atoms define an elongated trigonal antiprism centred on the metal atom.

Introduction. The title complex was isolated during a study of the kinetics of the replacement of coordinated water in [Ru(H₂O)₆]²⁺ (Patel, 1988). In aqueous solution the [Ru(tu)₆]²⁺ ion can be oxidized to [Ru^{III}{SC(NH)NH₂}]₃ in which the deprotonated

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