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2,2′-Iminodipyridinium Tetrachlorocuprate(II)

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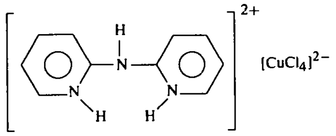
Abstract

The title structure, $(C_{10}H_{11}N_3)[CuCl_4]$, consists of isolated diprotonated 2,2′-iminodipyridinium cations and $CuCl_4^{2-}$ anions. The anions assume a flattened tetrahedral geometry, with *trans* Cl—Cu—Cl bond angles of 137.3 (1) and 139.2 (1)°. The Cu—Cl bond distances average 2.249 Å. The non-planar cations assume an *S-trans* configuration with one ring twisted 16.3 (6)° out of the central C—N—C plane and the other ring twisted 32.0 (7)° in the opposite sense. The cation configuration represents a balance of intramolecular repulsions and external hydrogen-bonding interactions, with N(1) and N(3) hydrogen bonding to Cl(3) [3.080 (5) Å] and Cl(2) [3.167 (5) Å], respectively, on one anion, while N(9) is involved in a weaker hydrogen bond to Cl(1) [3.486 (3) Å] of a second anion.

Comment

The title compound, (I), was prepared as part of our study of the structural characteristics of organoammonium salts of Cu^{II} halides.



(I)

An illustration of the asymmetric unit is shown in Fig. 1. Each pyridinium ring is nearly planar (maximum deviation 0.017 Å), but is twisted 45.7° with respect to the other. This twist is caused by repulsion of the H atoms on C(7) and N(9). The *S-trans* conformation minimizes internal electrostatic repulsions and provides maximum hydrogen-bonding capability. This twist comes at the expense of hyperconjugation of the amine C—N bonds. The hydrogen-bonding scheme (Fig. 2) indicates relative inefficiency as shown by the non-linearity of the N—H···Cl interaction.

The structural chemistry of more than 60 salts containing $CuCl_4^{2-}$ anions has been summarized recently (Halvorson, Patterson & Willett, 1990). The degree of flattening was shown to be roughly related to the strength of the *A*—H···Cl hydrogen bonding. The distortion in the present compound is in the middle of the observed range, consistent with the presence of a limited number of hydrogen-bonding interactions.

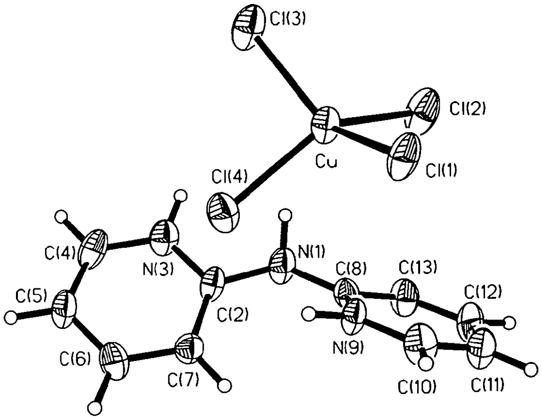


Fig. 1. Displacement ellipsoid plot illustrating the asymmetric unit of the title structure. Ellipsoids are plotted at the 50% probability level.

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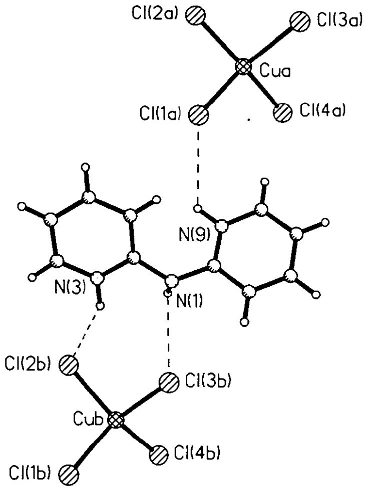

Fig. 2. Illustration of the hydrogen-bonding scheme.

Experimental

The compound was prepared by the reaction of a 1:1 mixture of 2,2′-iminodipyridine and $CuCl_2.2H_2O$ in a dilute hydrochloric acid solution. Crystals were grown over a period of several months by a temperature-gradient technique, using CH_3CN as a solvent.

Crystal data

$(C_{10}H_{11}N_3)[CuCl_4]$
$M_r = 378.6$
Triclinic
$P\bar{1}$
$a = 7.786(2)$ Å
$b = 8.984(3)$ Å
$c = 11.696(4)$ Å
$\alpha = 108.21(2)°$
$\beta = 95.13(2)°$
$\gamma = 109.79(2)°$
$V = 713.6(4)$ Å^3
$Z = 2$
$D_x = 1.762$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 25 reflections
$\theta = 30–45°$
$\mu = 8.93$ mm^{-1}
$T = 295$ K
Needle
$0.38 \times 0.12 \times 0.04$ mm
Brownish green

Data collection

Nicolet *P*3 diffractometer
ω scans
Absorption correction:
ψ scan (*SHELXTL-Plus*; Sheldrick, 1990)
$T_{min} = 0.71$, $T_{max} = 0.86$
1958 measured reflections
1797 independent reflections
1716 observed reflections
$[|F| > 3\sigma(F)]$

$R_{int} = 0.064$
$\theta_{max} = 52.5°$
$h = 0 \rightarrow 8$
$k = -9 \rightarrow 8$
$l = -12 \rightarrow 12$
2 standard reflections monitored every 96 reflections
intensity decay: none

Refinement

Refinement on *F*
$R = 0.064$
$wR = 0.109$
$S = 1.74$
1716 reflections
166 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F) + 0.0035F^2]$
$(\Delta/\sigma)_{max} = 0.01$

$\Delta\rho_{max} = 1.49$ e Å^{-3}
$\Delta\rho_{min} = -0.75$ e Å^{-3}
Extinction correction: $F^* = F[1 + (0.002\chi \times F^2/\sin 2\theta)]^{1/4}$
Extinction coefficient: $\chi = 0.024$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Cu	0.6967 (1)	0.0093 (1)	0.2674 (1)	0.034 (1)
Cl(1)	0.8347 (2)	0.1048 (1)	0.1307 (1)	0.045 (1)
Cl(2)	0.7682 (2)	0.2620 (2)	0.4201 (1)	0.055 (1)
Cl(3)	0.7269 (2)	−0.1412 (2)	0.3844 (1)	0.048 (1)
Cl(4)	0.4382 (2)	−0.2005 (1)	0.1330 (1)	0.042 (1)
N(1)	0.1980 (7)	0.0173 (5)	0.3320 (4)	0.043 (2)
C(2)	0.0942 (7)	−0.1498 (6)	0.2620 (4)	0.033 (2)
N(3)	0.0850 (6)	−0.2578 (5)	0.3200 (4)	0.039 (2)
C(4)	−0.0220 (8)	−0.4260 (6)	0.2676 (5)	0.045 (3)
C(5)	−0.1173 (8)	−0.4913 (6)	0.1483 (5)	0.044 (2)
C(6)	−0.1070 (8)	−0.3809 (6)	0.0855 (5)	0.043 (2)
C(7)	−0.0045 (7)	−0.2115 (6)	0.1415 (5)	0.035 (2)
C(8)	0.2674 (7)	0.1516 (6)	0.2929 (4)	0.035 (2)
N(9)	0.3204 (6)	0.1265 (5)	0.1855 (3)	0.035 (2)
C(10)	0.3938 (8)	0.2520 (6)	0.1430 (5)	0.044 (2)
C(11)	0.4194 (8)	0.4155 (7)	0.2131 (5)	0.048 (3)
C(12)	0.3673 (8)	0.4455 (6)	0.3262 (6)	0.045 (2)
C(13)	0.2903 (8)	0.3150 (6)	0.3646 (5)	0.043 (2)

Table 2. *Selected geometric parameters* (Å, °)

Cu—Cl(1)	2.233 (2)	Cu—Cl(2)	2.256 (1)
Cu—Cl(3)	2.252 (2)	Cu—Cl(4)	2.256 (1)
N(1)—C(2)	1.367 (5)	N(1)—C(8)	1.381 (7)
C(2)—N(3)	1.334 (8)	C(4)—C(5)	1.359 (8)
N(3)—C(4)	1.353 (6)	C(6)—C(7)	1.358 (6)
C(5)—C(6)	1.394 (9)	C(8)—C(13)	1.384 (7)
C(8)—N(9)	1.333 (7)	C(10)—C(11)	1.375 (8)
N(9)—C(10)	1.345 (8)	C(12)—C(13)	1.356 (9)
C(11)—C(12)	1.391 (9)		
Cl(1)—Cu—Cl(2)	98.4 (1)	Cl(1)—Cu—Cl(3)	139.3 (1)
Cl(2)—Cu—Cl(3)	98.4 (1)	Cl(1)—Cu—Cl(4)	97.5 (1)
Cl(2)—Cu—Cl(4)	137.3 (1)	Cl(3)—Cu—Cl(4)	94.8 (1)
C(2)—N(1)—C(8)	128.2 (4)	N(1)—C(2)—N(3)	115.0 (4)
N(1)—C(2)—C(7)	125.7 (5)	N(3)—C(2)—C(7)	119.2 (4)
C(2)—N(3)—C(4)	122.9 (4)	N(3)—C(4)—C(5)	119.3 (6)
C(4)—C(5)—C(6)	118.6 (4)	C(5)—C(6)—C(7)	121.1 (5)
C(2)—C(7)—C(6)	118.8 (6)	N(1)—C(8)—N(9)	119.9 (5)
N(1)—C(8)—C(13)	121.6 (5)	N(9)—C(8)—C(13)	118.4 (5)
C(8)—N(9)—C(10)	123.2 (4)	N(9)—C(10)—C(11)	119.4 (5)
C(10)—C(11)—C(12)	118.6 (6)	C(11)—C(12)—C(13)	120.2 (5)
C(8)—C(13)—C(12)	120.2 (5)		

The bridging NH group was assumed to have trigonal planar geometry.

The structure was solved by the direct-methods routine *SOLV* in the *SHELXTL* (Sheldrick, 1986) package. Refinement was straight forward. Final refinement was carried out with the *SHELXTL-Plus* program package (Sheldrick, 1990) on a MicroVAX 3100 Workstation.

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: CR1092). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Dichloro[(1*R*,2*R*)-*N*-(2-pyridylmethylene)-1,2-cyclohexanediamine]copper(II)

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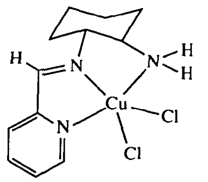
Abstract

The crystal structure of $[CuCl_2(C_{12}H_{17}N_3)]$, containing a five-coordinate Cu^{II} atom with distorted trigonal-bipyramidal coordination, is reported. The absolute configuration (1*R*,2*R*) has been verified.

Comment

We are interested in the synthesis and the structural chemistry of Cu complexes containing multidentate ligands (Wong, Gao & Wong, 1993). The tridentate ligand (1*R*,2*R*)-*N*-(2-pyridylmethylene)-1,2-cyclohexanediamine, containing three different types of N donor atoms, was prepared by condensation of an equimolar mixture of 2-pyridinecarboxaldehyde and (1*R*,2*R*)-1,2-diaminocyclohexane (L_1).



(I)

An *ORTEP*II plot (Johnson, 1976) of the molecule, (I), is shown in Fig. 1. The Cu atom has a distorted trigonal-bipyramidal environment, consisting of two Cl and three N atoms of the ligand L_1. An increase in the Cu—N distances from Cu—N(imine) 1.983 (4), through Cu—N(NH_2) 2.020 (4) to Cu—N(pyridine) 2.064 (4) Å, was observed. The Cu—Cl distances are significantly different [2.295 (1) and 2.396 (1) Å]. The cyclohexyl ring defined by C(1)–C(6) is in a chair conformation.

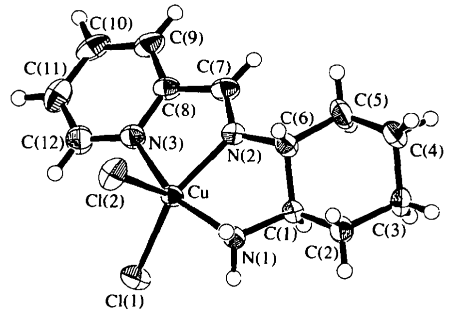


Fig. 1. An *ORTEP*II (Johnson, 1976) drawing of the molecule with 50% probability ellipsoids showing the numbering scheme. H atoms are shown as spheres of arbitrary radii.

Experimental

The title compound was prepared by treating $CuCl_2$ with an equivalent amount of L_1 in methanol. The reaction mixture was heated under reflux for 30 min. The solvent was removed under vacuum to give a blue residue which was redissolved in a minimum amount of water. Slow evaporation of the aqueous solution (2–3 d) at room temperature afforded blue crystals suitable for X-ray analysis.

Crystal data

$[CuCl_2(C_{12}H_{17}N_3)]$
$M_r = 337.83$
Orthorhombic
$P2_12_12_1$
$a = 8.235\ (2)$ Å
$b = 8.602\ (1)$ Å
$c = 19.604\ (1)$ Å
$V = 1388.7\ (3)$ Å^3
$Z = 4$
$D_x = 1.615$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10$–$14°$
$\mu = 1.95$ mm^{-1}
$T = 293$ K
Block
0.34 × 0.30 × 0.28 mm
Blue

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
$T_{min} = 0.845$, $T_{max} = 0.998$
2906 measured reflections
2459 independent reflections
2201 observed reflections $[F_o > 3\sigma(F_o)]$

$R_{int} = 0.016$
$\theta_{max} = 25°$
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 10$
$l = 0 \rightarrow 22$
3 standard reflections
frequency: 120 min
intensity decay: <2%

Refinement

Refinement on F
$R = 0.031$
$wR = 0.042$

$w = 4F_o^2/[\sigma^2(F_o^2) + 0.04(F_o^2)^2]$
$(\Delta/\sigma)_{max} = 0.02$