Nicotinium tetrachlorocuprate(II)

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The structure of the title compound, $(C_{10}H_{16}N_2)[CuCl_4]$, comprises two crystallographically non-equivalent tetrahedral $[CuCl_4]^{2-}$ anions, each of which is linked to two doubly protonated nicotinium cations *via* hydrogen bonds. There are two different types of hydrogen-bonding interactions present, namely (i) the protonated pyridinium groups exclusively form bifurcated hydrogen bonds to two *cis*-Cl atoms of both $[CuCl_4]^{2-}$ units and (ii) the protonated pyrrolidinium groups exclusively form a two-center hydrogen bond with a chloride of both $[CuCl_4]^{2-}$ units.

Comment

Considerable interest has been shown in recent years in tetrahalocuprate complexes containing various organic counter-cations (Desjardins *et al.*, 1983; Halvorson *et al.*, 1990; McDonald *et al.*, 1988; Straatman *et al.*, 1984). It is known that their hydrogen-bonding interactions (Glenn *et al.*, 1995; Marzotto *et al.*, 2001) and π-interactions between the aromatic rings of the organic cations (Luque *et al.*, 2002; Sertucha *et al.*, 1998) stabilize their crystal structures. These types of interactions control molecular recognition and self-assembly processes, and exercise important effects on solid-state structure and the properties of many compounds relevant to biological and material sciences (Desiraju & Steiner, 1999; Robinson *et al.*, 2000). In this work, we report the preparation and crystal structure of the title compound, (I). The doubly protonated nicotinium cation, $[C_{10}H_{16}N_2H_2]^{2+}$, contains two sites capable of forming hydrogen-bonding interactions with Cl atoms of the $[CuCl_4]^{2-}$ anion and the pyridine ring is capable of establishing a π-interaction in the crystalline state.

(I)
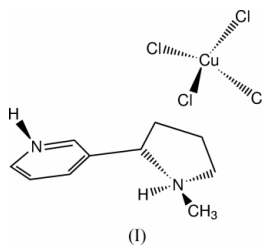
The asymmetric unit of the crystal structure (Fig. 1) of (I) comprises two nicotinium cations and two discrete $[CuCl_4]^{2-}$ anions held together by N—H···Cl hydrogen bonds. The $[CuCl_4]^{2-}$ anions are crystallographically non-equivalent and are approximately D_{2d}, somewhat flattened from tetrahedral as a result of hydrogen-bonding interactions with nicotinium cations. The two nicotinium cations are protonated at the atoms N1 and N9, and N13 and N21. The protonated pyridinium N atoms exclusively form a rare three-center hydrogen bond (bifurcated hydrogen bond) with two *cis*–Cl atoms of

both $[CuCl_4]^{2-}$ units. On the other hand, each of the protonated pyrrolidinium N atoms exclusively forms a common two-center hydrogen bond with a Cl atom of a $[CuCl_4]^{2-}$ unit. As a result, three Cl atoms of each $[CuCl_4]^{2-}$ anion participate in the hydrogen bonding with nicotinium cations. The hydrogen-bonding interactions are shown in Fig. 2.

The Cu1 and Cu2 centers are each coordinated by four Cl atoms, at average distances of 2.2465 (18) and 2.2390 (19) Å, respectively. These values are close to those observed in similar complexes (Halvorson *et al.*, 1990). The mean N···Cl distance of about 3.24 Å for the three-center hydrogen bond in both of the Cu1 and Cu2 sites is appreciably shorter than the mean distance of 3.40 Å suggested by previous results (Glenn *et al.*, 1995) for this type of hydrogen bond. There are no important bonding interactions among the tetrachlorocuprate anionic units, with the nearest non-bonded Cu···Cl distance in the unit cell being 5.577 (2) Å and the nearest Cu···Cu distance being 7.691 (1) Å. The nearest Cl···Cl contact distance of 4.375 (3) Å is considerably longer than the sum of their van der Waals radii. The aromatic pyridine rings of the cations are nearly perfectly planar, but the pyridine rings stacked in the parallel fashion are well separated from each other by the cell-unit distance, making a π-interaction between them impossible.

Experimental

(S)-(−)-Nicotine (0.24 g, 1.5 mmol), dissolved in an ethanol-triethylorthoformate mixture (15.0 ml; 5:1 v/v), was added to an excess of concentrated HCl. To this solution, 1.0 mmol of anhydrous $CuCl_2$, dissolved in an ethanol–triethylorthoformate mixture (5.0 ml; 5:1 v/v), was added. The resulting solution was stirred vigorously for 2 h at room temperature and was then refrigerated overnight. The bright yellow precipitate which appeared was collected by filtration and washed with cold absolute ethanol and dried under vacuum. The yield of the product was 0.28 g (76.03% based on $CuCl_2$) based on $CuCl_2$. The orange crystals used for analysis were obtained by recrystallization from absolute ethanol. Analysis calculated for $C_{10}H_{16}Cl_4CuN_2$: C 32.50, H 4.36, N 7.58%; found: C 32.70, H 4.39, N 7.63%.

Crystal data

$(C_{10}H_{16}N_2)[CuCl_4]$	$Z = 2$
$M_r = 369.59$	$D_x = 1.602$ Mg m^{-3}
Triclinic, $P1$	Mo $K\alpha$ radiation
$a = 7.6919 (8)$ Å	Cell parameters from 50
$b = 8.1526 (9)$ Å	reflections
$c = 12.2337 (15)$ Å	$\theta = 5.0–15.3°$
$\alpha = 87.249 (9)°$	$\mu = 2.10$ mm^{-1}
$\beta = 88.694 (8)°$	$T = 293 (2)$ K
$\gamma = 89.414 (7)°$	Block, orange
$V = 766.05 (15)$ Å^3	$0.50 \times 0.45 \times 0.26$ mm

Data collection

Bruker $P4$ diffractometer	$\theta_{max} = 27.5°$
$2\theta/\omega$ scans	$h = -1 \rightarrow 9$
Absorption correction: ψ scan	$k = -10 \rightarrow 10$
(North *et al.*, 1968)	$l = -15 \rightarrow 15$
$T_{min} = 0.663$, $T_{max} = 0.988$	3 standard reflections
4302 measured reflections	every 97 reflections
4302 independent reflections	intensity decay: none
3327 reflections with $I > 2\sigma(I)$	

Figure 1
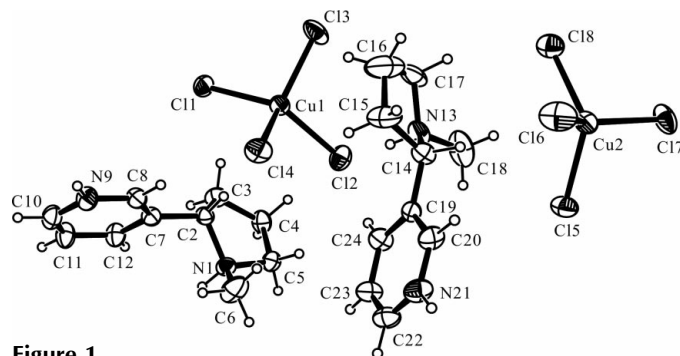*ORTEP*-3 (Farrugia, 1997) diagram of (I), showing the atom-numbering scheme and 30% probability ellipsoids.
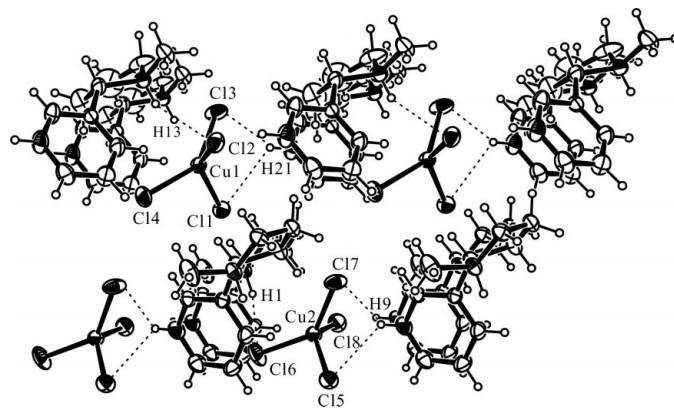

Figure 2
A view of hydrogen-bonding mode in the (010) plane of the unit cell, showing selected atom labels and 30% probability ellipsoids (Farrugia, 1997).

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.038$	$\Delta\rho_{max} = 0.70$ e Å^{-3}
$wR(F^2) = 0.099$	$\Delta\rho_{min} = -0.71$ e Å^{-3}
$S = 1.05$	Extinction correction: *SHELXL*97
4302 reflections	Extinction coefficient: 0.0251 (16)
290 parameters	Absolute structure: Flack (1983),
H-atom parameters constrained	781 Friedel pairs
$w = 1/[\sigma^2(F_o^2) + (0.0406P)^2$	Flack parameter = −0.037 (17)
$+ 0.6259P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1
Selected geometric parameters (Å, °).

Cu1—Cl1	2.2264 (17)	N1—C5	1.489 (10)
Cu1—Cl2	2.2774 (19)	N1—C6	1.502 (11)
Cu1—Cl3	2.2605 (18)	C8—N9	1.329 (10)
Cu1—Cl4	2.2216 (19)	N9—C10	1.336 (10)
Cu2—Cl5	2.2349 (18)	N13—C14	1.485 (9)
Cu2—Cl6	2.236 (2)	N13—C17	1.495 (9)
Cu2—Cl7	2.2412 (18)	N13—C18	1.464 (11)
Cu2—Cl8	2.244 (2)	C20—N21	1.346 (9)
N1—C2	1.511 (7)	N21—C22	1.338 (10)
Cl1—Cu1—Cl2	135.32 (8)	Cl5—Cu2—Cl7	98.73 (8)
Cl1—Cu1—Cl3	96.68 (7)	Cl5—Cu2—Cl8	131.17 (9)
Cl1—Cu1—Cl4	98.89 (7)	Cl6—Cu2—Cl7	135.29 (11)
Cl2—Cu1—Cl3	99.20 (9)	Cl6—Cu2—Cl8	96.80 (9)
Cl2—Cu1—Cl4	95.22 (8)	Cl7—Cu2—Cl8	100.20 (9)
Cl3—Cu1—Cl4	139.84 (9)	C8—N9—C10	122.7 (6)
Cl5—Cu2—Cl6	100.44 (9)	C20—N21—C22	123.2 (7)

Table 2
Hydrogen-bonding geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
N1—H1$\cdots$Cl6$^{\text{i}}$	0.91	2.45	3.282 (6)	152
N9—H9$\cdots$Cl7$^{\text{ii}}$	0.86	2.40	3.145 (7)	145
N9—H9$\cdots$Cl5$^{\text{ii}}$	0.86	2.70	3.336 (6)	132
N13—H13$\cdots$Cl2	0.91	2.35	3.156 (6)	148
N21—H21$\cdots$Cl3$^{\text{iii}}$	0.86	2.35	3.141 (7)	153
N21—H21$\cdots$Cl1$^{\text{iii}}$	0.86	2.78	3.357 (7)	125

Symmetry codes: (i) $1 + x, y, z - 1$; (ii) $x, 1 + y, z - 1$; (iii) $x - 1, y - 1, z$.

The positional parameters of the H atoms were calculated geometrically (C—H = 0.96–0.98 Å and N—H = 0.86–0.91 Å) and constrained to ride on their parent atoms, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{CH}, \text{CH}_2,$ and NH) or $1.5U_{\text{eq}}(\text{CH}_3)$.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Bruker, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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