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Bis(1-methylguanidinium) tetrachloro-cuprate(II) and 4-(2-pyrimidin-1-io)-piperazinium tetrachlorocuprate(II)[1]

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The crystal structures of the title compounds, $(C_2N_3H_8)_2$-$[CuCl_4]$, (I), and $(C_8H_{14}N_4)[CuCl_4]$, (II), have been studied by X-ray diffraction. The structures consist of discrete $[CuCl_4]^{2-}$ anions with two monoprotonated $(C_2N_3H_8)^+$ cations for (I) and a diprotonated $(C_8N_4H_{14})^{2+}$ cation for (II). The $[CuCl_4]^{2-}$ anions of both compounds have flattened tetrahedral geometries. There are several N—H⋯Cl weak bonds that join the $[CuCl_4]^{2-}$ anions and the organic cations helping retain the pseudo-tetrahedral geometries of the anions.

Comment

The synthesis and characterization of copper halides in which organic ligands link metal centres have received considerable attention. One of the reasons for that is the fact that the copper environment of these compounds can adopt different geometries: tetrahedral, pseudo-tetrahedral or square-planar (Corzo-Suárez *et al.*, 1997). This coordination variety allows the study of the relationship between the different geometries and the structural and magnetic properties of these compounds. The $[CuCl_4]^{2-}$ anions of both compounds have a flattened tetrahedral geometry, which is the most common geometry reported for this anion in compounds of this kind (Díaz *et al.*, 1998).

In this communication, we report the X-ray analyses of two new compounds within this series. The structures show monoprotonated $(C_2N_3H_8)^+$ cations for (I) and diprotonated $(C_8N_4H_{14})^{2+}$ cations for (II). The results of the ESI mass spectrometric analyses (Colton & Traeger, 1992) corroborated the presence of the suggested cations. The general method of synthesis described below (see *Experimental*) for compounds within this series usually leads to $L_2[CuX_4]$ structures, in which L is a monoprotonated organic cation (Fernández, Doadrio *et al.*, 1996). However, we obtained diprotonated cations for (II). One of the reasons for that is the fact that this organic ligand is larger than the ligands used in other cases with a common method of synthesis. The distance between the two protonated N atoms (N1⋯N4) is 4.688 (5) Å.

(I)   (II)
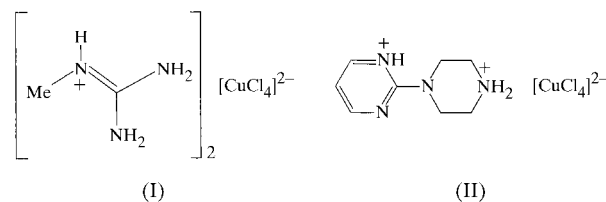
In compound (I), the geometry of the $[CuCl_4]^{2-}$ anion can be described as a flattened tetrahedron assuming the lowest energy structure for this kind of compound (Marcotrigiano *et al.*, 1979). The Cu—Cl bond distances (over 2.25 Å) are similar to those of other tetrachlorocuprates(II) (Fernández, Hartung *et al.*, 1996), but its symmetry in this case has a small deviation from D_{2d} (*trans* angle Cl—Cu—Cl = 130°) with *trans*-Cl—Cu—Cl = 145.15° (Melnik *et al.*, 1997). The N atoms help to keep the distorted geometry of the anion through several weak N—H⋯Cl bonds.

For compound (II), the geometry of the $[CuCl_4]^{2-}$ anion can be described as a distorted and flattened tetrahedron in which the distance Cu—Cl4 [2.238 (2) Å] is shorter than the other Cu—Cl distances, which are longer than 2.28 Å. One reason for that behaviour may be the absence of hydrogen bonds between the Cl4 and N atoms, while the other Cl atoms of the anion are linked with N1 and N4 *via* weak N—H⋯Cl bonds. Moreover, the distance Cu⋯Cl4($-x$, $-y$, $-z$) of 3.061 (4) Å is quite short. On the other hand, in compound (II), the pseudo-tetrahedral anion is more flattened than that described for compound (I), as we can see from the Cl—Cu—Cl angles. The widest Cl—Cu—Cl angle is 145.93 (4)° for compound (I) and 160.95 (5)° for compound (II).

Experimental

The title compounds were synthesized by the reaction of a solution of the ligand salt in a mixture of H_2O–EtOH (3:1) with a solution of $CuCl_2\cdot2H_2O$ in a 2:1 molar ratio of ligand–$CuCl_2\cdot2H_2O$. The ligand salts used in the synthesis were 1-methylguanidine hydrochloride for (I) and N-(2-pyrimidinyl)piperazine dihydrochloride for (II). To the resulting mixture, 12 M HCl was added and after 1 h stirring, the final solution was filtered off and allowed to crystallize at room temperature. After three months, many crystals appeared and were recrystallized from a 1:1 H_2O–EtOH mixture. The ESI mass spectrometry analyses were carried out by injecting solutions of the samples in acetonitrile–water (1:1) at a rate of 0.05 ml min^{-1} into a LC MS PLATFORMII spectometer.

Compound (I)

Crystal data

$(C_2N_3H_8)_2[CuCl_4]$	$D_x = 1.700$ Mg m^{-3}
$M_r = 353.57$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 25
$a = 11.372$ (3) Å	reflections
$b = 8.042$ (2) Å	$\theta = 15–20°$
$c = 15.621$ (9) Å	$\mu = 2.335$ mm^{-1}
$\beta = 104.71$ (2)°	$T = 293$ (2) K
$V = 1381.8$ (9) Å^3	Prismatic, green
$Z = 4$	$0.46 \times 0.26 \times 0.17$ mm

Data collection

Nonius CAD-4 diffractometer	$\theta_{max} = 34.97°$
$\omega–2\theta$ scans	$h = -18 \rightarrow 17$
Absorption correction: empirical	$k = 0 \rightarrow 12$
(*XABS*2; Parkin *et al.*, 1995)	$l = 0 \rightarrow 25$
$T_{min} = 0.335$, $T_{max} = 0.672$	3 standard reflections
3302 measured reflections	every 200 reflections
3039 independent reflections	frequency: 60 min
2078 reflections with $I > 2\sigma(I)$	intensity decay: 10.9%
$R_{int} = 0.034$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0651P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.040$	$+ 0.3729P]$
$wR(F^2) = 0.117$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.086$	$(\Delta/\sigma)_{max} < 0.001$
3039 reflections	$\Delta\rho_{max} = 0.50$ e Å^{-3}
69 parameters	$\Delta\rho_{min} = -1.41$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °) for (I).

Cu1—Cl1	2.2471 (8)	Cu1—Cl2	2.2611 (12)
Cl1^i—Cu1—Cl1	144.36 (4)	Cl1—Cu1—Cl2	95.43 (3)
Cl1—Cu1—Cl2^i	94.86 (3)	Cl2^i—Cu1—Cl2	145.93 (4)

Symmetry codes: (i) $-x, y, \frac{1}{2} - z$.

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N2—H2$B\cdots$Cl2^i	0.85	2.52	3.270 (3)	123
N1—H1$A\cdots$Cl1^{ii}	0.86	2.52	3.325 (3)	155
N1—H1$B\cdots$Cl2^{iii}	0.86	2.63	3.356 (3)	144
N3—H3$\cdots$Cl2^i	0.85	2.69	3.470 (3)	152

Symmetry codes: (i) $1 - x, 1 - y, -z$; (ii) $1 - x, y, \frac{1}{2} - z$; (iii) $\frac{1}{2} - x, \frac{1}{2} - y, -z$.

Compound (2)

Crystal data

$(C_8N_4H_{14})[CuCl_4]$	$D_x = 1.793$ Mg m^{-3}
$M_r = 371.57$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 25
$a = 9.205$ (7) Å	reflections
$b = 16.13$ (3) Å	$\theta = 15–20°$
$c = 9.391$ (7) Å	$\mu = 2.346$ mm^{-1}
$\beta = 99.24$ (6)°	$T = 293$ (2) K
$V = 1376$ (3) Å^3	Prismatic, brown
$Z = 4$	$0.28 \times 0.23 \times 0.20$ mm

Data collection

Nonius CAD-4 diffractometer	$\theta_{max} = 29.97°$
$\omega–2\theta$ scans	$h = -12 \rightarrow 12$
Absorption correction: empirical	$k = 0 \rightarrow 22$
(*XABS*2; Parkin *et al.*, 1995)	$l = 0 \rightarrow 13$
$T_{min} = 0.532$, $T_{max} = 0.626$	3 standard reflections
4363 measured reflections	every 200 reflections
3994 independent reflections	frequency: 60 min
2756 reflections with $I > 2\sigma(I)$	intensity decay: 3.2%
$R_{int} = 0.079$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0669P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.051$	$+ 0.6687P]$
$wR(F^2) = 0.135$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.038$	$(\Delta/\sigma)_{max} < 0.001$
3994 reflections	$\Delta\rho_{max} = 0.53$ e Å^{-3}
154 parameters	$\Delta\rho_{min} = -0.99$ e Å^{-3}
H-atom parameters constrained	

Table 3
Selected geometric parameters (Å, °) for (2).

Cu1—Cl4	2.2386 (19)	Cu1—Cl1	2.2849 (19)
Cu1—Cl2	2.284 (2)	Cu1—Cl3	2.287 (2)
Cl4—Cu1—Cl2	93.23 (8)	Cl4—Cu1—Cl3	160.96 (5)
Cl4—Cu1—Cl1	93.24 (7)	Cl2—Cu1—Cl3	92.58 (9)
Cl2—Cu1—Cl1	141.49 (6)	Cl1—Cu1—Cl3	93.46 (6)

Table 4
Hydrogen-bonding geometry (Å, °) for (2).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$\cdots$Cl1^i	0.86	2.30	3.123 (7)	160
N4—H4$B\cdots$Cl2^{ii}	0.90	2.40	3.187 (4)	146
N4—H4$A\cdots$Cl3	0.90	2.43	3.280 (4)	158

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

For both compounds, H atoms were geometrically calculated using a riding model and fixed displacement parameters of U(H) = 1.2U of the attached atom. For compound (I), the final difference Fourier maps show some electron-density holes deeper than 1 e Å^{-3} close to the Cu atom.

For both compounds, data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CRYSDA* (Beurskens *et al.*, 1992); data reduction: *REFLEX* (García-Granda *et al.*, 2000); program(s) used to solve structure: *DIRDIF* (Beurskens *et al.*, 1992); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); software used to prepare material for publication: *PARST* (Nardelli, 1995) and *SHELXL*97.

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