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Crystal and Molecular Structure of Creatininium Tetrachlorocuprate(II)

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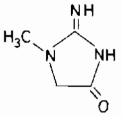
Preparation, crystal and molecular structure of creatininium tetrachlorocuprate(II) is described. The structure was solved by X-ray diffraction studies and was refined by least-squares methods to R = 0.041 for 1344 reflections. The compound is monoclinic, space group $P2_1/c$. The unit cell parameters are a = 8.080(3), b = 7.831(2), c = 13.922(3) Å, β = 113.77(2)°, V = 806.2 Å^3, d_c = 1.786, d_m = 1.77(1) g cm^{-3}, Z = 2. The $[CuCl_4]^{2-}$ ion is centrosymmetric and the copper atom is surrounded by four Cl atoms (Cu–Cl1 2.233(1), Cu–Cl2 2.268(1)) in a square planar arrangement. The creatininium cation is almost planar and each cation is linked to $[CuCl_4]^{2-}$ units through hydrogen bonding involving the amino and imino nitrogen atoms.

Introduction

2-Imino-1-methyl-4-imidazolidinone, commonly known as cretinine, is of considerable biological



interest as it plays an important role in the metabolism of proteins. It has more than one coordinating site to form metal complexes. Further, the exocyclic imino group is fairly basic and can get protonated resulting in the formation of a bulky creatininium cation. In continuation of our studies on the preparation and characterization of metal complexes with biologically important substances [1, 2], we report in this communication the preparation and crystal and molecular structure of creatininium tetrachlorocuprate(II).

Experimental

An alcoholic solution of copper(II) chloride is added to an aqueous solution of creatinine containing a few drops of 2n HCl in 1:2 molar ratio. The resulting solution is stirred for some time and kept aside for crystallization. The crystalline product formed after a few hours is filtered, washed with acetone and ether. *Anal.* Found: C 22.38, H 3.14, N 19.49, Cu 14.73. Calcd. for $C_8H_{16}N_6O_2Cl_4Cu$: C 22.15, H 3.73, N 19.38, Cu 14.65%.

The cell dimensions obtained by preliminary Weissenberg and precession photographs were refined by least-squares from diffractometer coordinates of 15 high-order reflections. The crystal is monoclinic, the cell dimensions being *a* = 8.080(3), *b* = 7.831(2), *c* = 13.922(3) Å, β = 113.77(2)°, V = 806.2 Å^3. The measured and calculated densities are 1.77(1) and 1.786 g cm^{-3} respectively for two molecules per unit cell. The systematic absences noticed from the photographs, 0k0, k = 2n + 1 and h0l, l = 2n + 1 suggested the space group $P2_1/c(C^5_{2h}$, No. 14).

The X-ray intensity data for a crystal of approximate dimensions 0.12 × 0.10 × 0.15 mm^3 were collected at 22 °C on a Syntex $P2_1$ four-circle diffractometer using MoKα radiation and a graphite monochromator. ($K\alpha_1$ = 0.70926 Å, $K\alpha_2$ = 0.71354 Å, ω–2θ scan, scintillation counter, take-off angle 6°). The sampling interval in 2θ for each reflection was from 1.0° below the calculated $MoK\alpha_1$ maximum to 1.0° above the calculated $MoK\alpha_2$ maximum. The scan rate, depending on the intensity of the reflection, changed from 2° per min to 15° per min (in 2θ). The background measurements with the total time for background counts equal to the scan time were made both at the start and end of each scan with the counter stationary. A standard reflection was measured for every 50 reflections. A complete set of 1766 reflections was measured up to $(\sin\theta)/\lambda$ = 0.64 Å^{-1}, out of which 1344 reflections were accepted as statistically above the background on the basis that $I \geqslant 1.96\ \sigma(I)$. The data reduction was done applying Lorentz and polarization corrections and a Wilson plot. The absorption coefficient is 17.4 cm^{-1} and hence no correction was applied.

The structure was solved by direct methods using the MULTAN programme system [3]. The correct solution was readily apparent from the combined figure of merit. Cu and Cl atoms were easily located

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TABLE I. Coordinates of the Atoms in the Unit Cell of Creatininium Tetrachlorocuprate(II).

	x	y	z
Cu	0.00000	0.00000	0.00000
Cl1	−0.03976(12)	−0.28206(12)	0.00127(10)
Cl2	0.29873(12)	−0.03428(12)	0.10148(9)
O	0.2092(4)	−0.3821(3)	0.3220(3)
N1	0.6315(5)	0.0456(4)	0.3960(3)
N2	0.3191(4)	0.0499(4)	0.3455(3)
N3	0.4520(4)	−0.1991(4)	0.3709(3)
C1	0.4745(5)	−0.0275(4)	0.3711(3)
C2	0.2879(6)	0.2316(5)	0.3263(5)
C3	0.1721(5)	−0.0738(5)	0.3165(4)
C4	0.2705(5)	−0.2409(5)	0.3348(3)
H1	0.733(5)	−0.027(5)	0.417(3)
H2	0.639(5)	0.143(5)	0.398(3)
H3	0.534(5)	−0.270(5)	0.385(3)
H4	0.105(5)	−0.066(5)	0.360(3)
H5	0.075(5)	−0.053(5)	0.229(3)
H6	0.194(5)	0.266(5)	0.339(3)
H7	0.211(5)	0.242(5)	0.254(3)
H8	0.391(5)	0.294(5)	0.366(3)

from the E-map. The other non-hydrogen atoms were found from the next difference Fourier map after the isotropic refinement. All the H atoms were located from the subsequent difference Fourier map after the anisotropic refinement of the non-hydrogen atoms. The atomic scattering factors for Cu, Cl, O, N, C and H were taken from the International Tables [4]. Full-matrix least-squares refinement with anisotropic temperature factors for all non-hydrogen atoms and fixed isotropic temperature factors of 5.0 for all hydrogen atoms converged to residuals of R = 0.041 (including unobserved data, 0.062), $R_2 = 0.031$ where $R_1 = \Sigma \| F_o| - |F_c\| / \Sigma |F_o|$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w F_o^2]^{1/2}$.

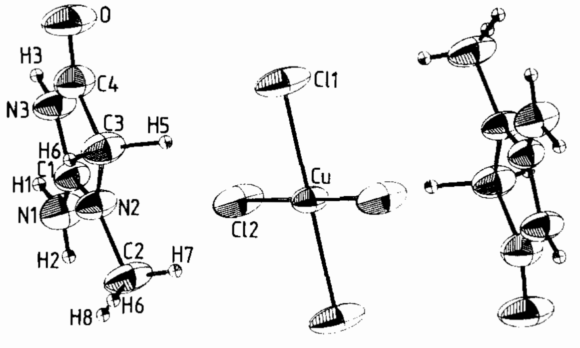

Figure 1. $CuCl_4^{2-}$ ion with neighboring creatininium cations, including atom designations.

The quantity minimized was $\Sigma w(|F_o| - |F_c|)^2$. The weighting scheme was based on counting statistics of the intensities. The shifts in the final cycle were below 0.02σ. The final difference Fourier map had no significant features. The final atomic coordinates and thermal parameters are given in Tables I and II. A Table of calculated and observed structure factors is available from the Editor.

Results and Discussion

The crystal structure consists of centrosymmetric $CuCl_4^{2-}$ ions and cationic creatininium units, both being linked through N–H...Cl hydrogen bonding involving imino and amino nitrogen atoms. An ORTEP plot of a $CuCl_4^{2-}$ ion with two neighboring cations, including the atom designations, is reproduced in Fig. 1. Fig. 2 gives a projection of the unit cell, showing the H bond system. The interatomic bond distances and bond angles are given in Table III.

TABLE II. Coefficients of the Anisotropic Temperature Factors.[a]

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	2.12(3)	1.81(2)	4.02(3)	−0.23(2)	0.79(2)	−0.06(3)
Cl1	2.62(4)	1.97(4)	9.33(8)	−0.30(3)	1.02(5)	0.38(5)
Cl2	2.50(4)	2.60(4)	7.48(7)	−0.09(3)	−0.27(4)	0.25(4)
O	5.06(16)	2.48(13)	8.98(22)	−1.05(12)	0.91(15)	−0.39(13)
N1	2.12(14)	3.09(15)	6.33(20)	0.25(12)	0.70(14)	0.22(15)
N2	1.95(13)	2.10(12)	5.28(18)	0.18(9)	0.61(12)	0.09(12)
N3	2.80(14)	2.25(13)	5.68(20)	0.59(11)	0.68(14)	−0.07(13)
C1	2.63(16)	2.35(15)	3.84(18)	0.12(13)	0.82(14)	−0.09(14)
C2	2.86(18)	2.46(18)	7.61(33)	0.58(15)	0.76(20)	0.27(20)
C3	2.63(18)	2.74(16)	5.99(27)	−0.32(14)	1.10(17)	0.05(17)
C4	3.54(18)	2.98(18)	4.98(24)	−0.19(15)	0.94(17)	−0.27(17)

[a] The isotropic temperature factors for the hydrogen atoms are fixed at 5.0. The anisotropic temperature factors are expressed in the form $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*]$.

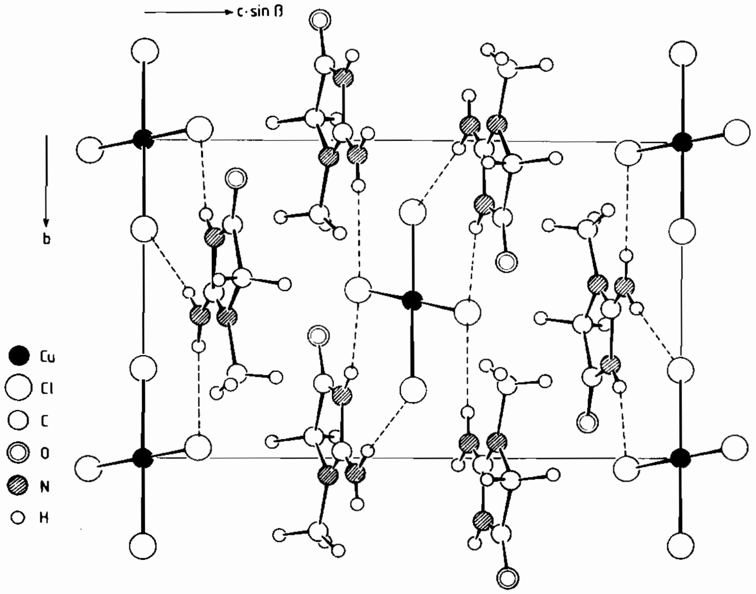

Figure 2. Projection of the unit cell, showing the intermolecular hydrogen bond system.

TABLE III. Interatomic Distances and Bond Angles in the Crystal Structure of Creatininium Tetrachlorocuprate(II).

Distances (Å)		*Angles* (°)	
Cu Coordination			
Cu–Cl1 (Cl1')^a	2.233(1)	Cl1–Cu–Cl2	89.91(4)
Cu–Cl2 (Cl2')	2.268(1)	Cl1–Cu–Cl2'	90.09(4)
Creatininium Ion			
C1–N1	1.305(6)	N1–C1–N2	126.4(4)
C1–N2	1.308(5)	N1–C1–N3	123.4(4)
C1–N3	1.356(4)	N2–C1–N3	110.2(3)
C2–N2	1.451(5)	C1–N2–C2	125.5(3)
C3–C4	1.499(6)	C1–N2–C3	110.7(3)
C3–N2	1.458(5)	C2–N2–C3	122.6(3)
C4–N3	1.384(6)	N2–C3–C4	102.5(3)
C4–O	1.195(5)	C3–C4–N3	105.5(4)
		C3–C4–O	128.5(4)
		N3–C4–O	126.0(4)
		C4–N3–C1	110.9(3)

[a] The primed atoms are related to the unprimed ones by a centre of inversion at the Cu site.

The copper atom is strongly bonded to chlorine atoms in a square planar arrangement. Tetrahalogenocuprate(II) complexes generally assume distorted tetrahedral geometry, the square planar coordination being less common [5]. Even the known square planar tetrachlorocuprates may also be regarded as tetragonally distorted octahedral as the neighbouring chlorine atoms approach the copper atom in the axial positions at an average distance of 2.88 Å [6–8]. In the present complex the closest neighbours in axial positions are carbonyl oxygen atoms at distances of 3.637(3) Å which cannot be regarded as weak interactions.

In chlorocuprates with known structures Cu–Cl bond distances fall in the range 2.18 to 2.30 Å [9–17]. The average value of 2.251 Å observed in the present complex is very close to the sum of the covalent radii (2.27) [18]. A remarkable feature of the structure is the large apparent thermal vibration (expressed roughly by the B_{33} values, see Table II) perpendicular to the planes of the anions and cations. This effect (which was shown to be not a systematic

TABLE IV. N–H...Cl Hydrogen Bonding in the Structure of Creatininium Tetrachlorocuprate(II).

	Distances (Å)			*Angles* (°)
	N–H	H...Cl	N...Cl	N–H...Cl
N1–H1...Cl1	0.94(4)	2.29(4)	3.212(4)	166(3)
N1–H2...Cl2	0.76(4)	2.58(4)	3.337(4)	172(4)
N3–H3...Cl2	0.83(4)	2.44(4)	3.239(3)	163(4)

error of the data) indicates large librational motions of both units. For CuCl$_4^{2-}$ it can possibly be interpreted as a static or dynamical disorder of non-planar (*e.g.* distorted tetrahedral) ions, resulting in a planar centrosymmetric electron density picture.

Bond distances and bond angles within the creatininium cation are not much different from those observed in the unprotonated creatinine molecule (C1–N1 1.30, C1–N2 1.34, C1–N3 1.40, C2–N2 1.46, C3–64 1.47, C3–N2 1.40, C4–N3 1.37, C4–O 1.22 Å, with e.s.d's of 0.03 Å) [19]. A detailed comparison is not possible because of the limited accuracy of these early data.

The bond distances and angles in the creatininium cation indicate extensive electron delocalization in the "aromatic" part of the molecule, including N2, C1, N1, N3, C4, O, H1, H2, H3. This part is not quite planar. The maximum deviations from the best plane through this part are 0.058 Å for N3 and –0.040 Å for N1. The least squares equation for the plane containing all ring atoms and N1 is $0.3017x + 0.0049y - 0.9534z + 3.9837 = 0$, where x, y, z are related to the monoclinic axes of the crystal, the maximum deviations being again for N3 (0.054 Å) and N1 (–0.045 Å).

The atom C2 lies 0.18 Å above this plane. As in the unprotonated molecule [19] this means that the strongly non-planar N1 atom is asymmetric; the crystal contains *d* and *l* forms joined by the centre of inversion. In Table IV the hydrogen bond distances and angles are listed. In Fig. 2 they are indicated by dashed lines. Since Cl2 is linked to two different nitrogens, the Cl2–N bond distances are slightly longer than the Cl1–N ones.

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