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Preparation, Crystal and Molecular Structure of Aquadichlorocaffeinecopper(II)

G. BANDOLI,[a,c] M. CINGI BIAGINI,[b] D. A. CLEMENTE,[a,c] and G. RIZZARDI[c]

[a] *Laboratorio di Chimica e Tecnologia dei Radioelementi del CNR, Corso Stati Uniti Padova,* [b] *Istituto di Chimica Generale, Università di Messina e di Parma,* [c] *Istituto di Chimica Generale, Università di Padova, Italy*

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Preparation, crystal and molecular structure of aquadichlorocaffeinecopper(II), determined by three-dimensional X-ray data, are reported. The darkish green crystals are orthorhombic, space group $P2_12_12_1$ *with cell dimensions:* a = *16.370(9),* b = *13.432(7),* c = *5.814(6)* Å *and* Z = *4. The structure was solved by the heavy-atom method from 1221 reflections collected by counter, and refined by least-squares method to* R = *0.028. The geometry around copper is tetragonal pyramidal distorted towards trigonal bipyramidal, the* C_{2v} *symmetry being maintained. The caffeine imidazole nitrogen atom (Cu–N 1.98* Å*), oxygen atom from water (Cu–O 1.96* Å*) and* trans *chlorine atoms (Cu–Cl(1) 2.32, Cu–Cl(2) 2.25* Å*) lie at the corners of an approximate square as closest ligands to the copper. Through a screw-axis parallel to* c*, Cl(1) atom is placed at the apex of the pyramidal configuration (Cu–Cl(1)' 2.79* Å*); since only one chlorine atom forms a bridge between successive symmetry related copper atoms a polynuclear chain with alternating short and long Cu–Cl distances is formed. The single chain is further strengthened by Cl– – –HOH hydrogen bonds; moreover, symmetry-related chains are held together by O – – –HOH hydrogen bonds.*

Introduction

The co-ordination of divalent metal ions to substituted purines have become a very active area of research in the last decade or so [1]. In this contribution we present a portion of our work in this field [2, 3] related to the synthesis and the crystal structure of a caffeine-copper chloride complex. Our primary interest was the binding site or sites of the base to the metal and this work was also expected to provide information on the structural changes induced in the ligand molecule by the metal.

Experimental

Preparation of Aquadichlorocaffeinecopper(II)

An aqueous acidic solution of copper(II) chloride was added to an aqueous solution of the caffeine ligand (8:1 mol ratio). The mixture was then stirred for several hours during which time darkish green crystals precipitated. This crystalline product was collected and washed with ether. *Anal.* Calcd for $[CuCl_2(C_8H_{10}N_4O_2)H_2O]$: C, 27.72; H, 3.49; N, 16.16. Found: C, 27.70; H, 3.55; N, 16.10. The crystals are stable to air and to X-rays.

Crystal Data

$C_8H_{12}Cl_2CuN_4O_3$, M = 346.7. Orthorhombic, a = 16.370(9), b = 13.432(7), c = 5.814(6) Å, U = 1278.4 Å^3, D_m = 1.79 (by flotation in tetrabromoethane and chloroform), Z = 4, D_c = 1.80 g cm^{-3}, $F(000)$ = 700. Mo-K$_\alpha$ radiation, λ = 0.7107 Å; μ(Mo-K$_\alpha$) = 21.9 cm^{-1}. Preliminary Weissenberg and precession photographs showed systematic absences *h00*, $h = 2n + 1$; *0k0*, $k = 2n + 1$; and *00l*, $l = 2n + 1$, consistent with space group $P2_12_12_1$ (D_2^4, No. 19).

Data Collection and Reduction

The single crystal used for the collection of intensity data was *ca.* 0.17 × 0.15 × 0.54 mm^3 size, and was mounted with c roughly parallel to the Φ-axis of a Siemens on-line four circle diffractometer. The cell parameters and their standard deviations were calculated by least-squares refinement of the setting angles of 15 high-angle reflections (Cu-K$_\alpha$ radiation, λ = 1.54178 Å, take-off angle of 4.5° and a Na(Tl)I scintillation counter). The intensities of 1221 independent reflections (to ϑ 25°) were measured by use of Mo-K$_\alpha$ radiation (λ = 0.7107 Å) and the ϑ–2ϑ scan technique with a 'five-value' measuring procedure. Of these 48 were judged to be 'unobserved', having a net count $< 3\sigma$, and omitted in the subsequent refinement procedure. The 4,4,1 reflection was measured as a reference every 20 reflections, and its net count did not vary noticeably during data collection (*ca.* 4 days). The data were scaled by use of the reference reflection and Lorentz and polarization corrections were applied.

Solution and Refinement of the Structure

The structure was solved by the standard heavy-atom method and refined by block-diagonal least-squares initially and by full-matrix least-squares

TABLE I. Positional and Thermal Parameters. Positional parameters of nonhydrogen atoms have been multiplied by 10^4. Positional parameters of hydrogen atoms have been multiplied by 10^3. Anisotropic thermal parameters have been multiplied by 10^4. Anisotropic temperature factor is of the form $\exp[-2\pi^2(h^2a^{*2}U_{11} + \cdots + 2hka^*b^*U_{12} + \cdots)]$. Standard deviations in parentheses refer to the last significant digits.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu	1962(0)	1156(0)	467(1)	300(3)	276(3)	341(3)	−26(3)	−44(3)	71(3)
Cl(1)	3056(1)	420(1)	2347(2)	309(6)	396(7)	272(6)	19(6)	−19(7)	55(6)
Cl(2)	886(1)	1839(1)	−1346(3)	414(7)	434(8)	731(12)	−16(7)	−199(8)	250(9)
O(10)	1235(2)	441(5)	2587(9)	290(22)	951(39)	431(26)	6(25)	−37(24)	303(29)
N(1)	3865(2)	4653(3)	1549(8)	352(23)	274(23)	384(24)	−22(20)	−47(22)	−28(23)
C(1)	4338(4)	5498(5)	2487(15)	595(43)	396(39)	550(39)	−140(34)	−154(40)	23(42)
C(2)	3186(3)	4350(4)	2815(8)	407(31)	298(26)	245(26)	104(24)	−46(25)	3(24)
O(2)	2970(2)	4802(2)	4536(6)	575(22)	480(20)	421(20)	−8(21)	58(25)	−165(22)
N(3)	2778(2)	3497(3)	2083(7)	290(20)	301(22)	304(24)	5(16)	77(19)	−12(21)
C(3)	2008(4)	3229(4)	3224(11)	420(30)	447(32)	518(38)	−56(34)	205(35)	−56(33)
C(4)	3048(3)	3019(3)	162(8)	278(21)	238(22)	293(26)	50(23)	2(26)	−12(22)
C(5)	3693(3)	3358(3)	−1115(8)	240(22)	273(25)	332(31)	46(22)	30(23)	17(25)
C(6)	4116(3)	4263(3)	−558(10)	210(22)	312(26)	422(29)	36(21)	−2(28)	134(30)
O(6)	4635(2)	4679(3)	−1736(7)	349(19)	430(22)	568(26)	−70(18)	65(19)	130(23)
N(7)	3800(2)	2681(3)	−2855(7)	373(23)	357(24)	276(25)	65(21)	90(22)	2(23)
C(7)	4470(4)	2643(5)	−4567(12)	517(33)	578(44)	431(41)	87(33)	266(36)	33(40)
C(8)	3234(3)	1984(4)	−2605(10)	441(31)	295(28)	368(31)	7(24)	54(28)	57(29)
N(9)	2741(2)	2150(3)	−749(7)	358(21)	269(20)	302(24)	−15(17)	47(21)	−6(23)

	x	y	z	B		x	y	z	B
H(11)	486(4)	534(6)	206(14)	5.0	H(71)	496(4)	261(6)	−352(14)	5.0
H(12)	440(4)	538(5)	401(14)	5.0	H(72)	453(5)	310(6)	−519(16)	5.0
H(13)	410(5)	591(6)	228(16)	5.0	H(73)	432(4)	202(5)	−581(13)	5.0
H(31)	210(5)	258(5)	375(13)	5.0	H(8)	311(4)	139(5)	−378(11)	5.0
H(32)	202(4)	362(5)	460(12)	5.0	H(101)	133(5)	31(7)	359(14)	5.0
H(33)	150(5)	346(5)	240(13)	5.0	H(102)	96(5)	63(7)	263(17)	5.0

procedure in the later stages. The copper and two chlorine positions were evident from a three-dimensional unsharpened Patterson map. These positions were refined (to a reliability index R of 0.29) and the next Fourier synthesis revealed all nonhydrogen atoms. Refinement proceeded normally using the block-diagonal least-squares approximation and converged initially at an R of 0.082 (to each reflection unit weight was assigned), varying the positional and individual isotropic temperature factors reduced R to 0.054. At this stage, the anomalous dispersion components for Cu and Cl were entered and a difference map showed ten peaks of 0.5–0.7 eÅ^{-3}, suggesting positions for the hydrogens of the caffeine ligand. Two further cycles of refinement were performed in which the positional parameters of all atoms, the anisotropic temperature factors of the nonhydrogen atoms were varied, with fixed isotropic temperature factors of H (B = 5.0 Å^2). Two peaks in the subsequent difference map, although not higher than the background by more than 0.15 eÅ^{-3}, were taken as the positions of the hydrogens of the water molecule and were entered in the last refinement cycle. The final R and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ were 0.028 and 0.026, respectively (observed data and $w = 1$). At this stage the model was checked to see if the correct enantiomer had been selected. Since only a single form (*hkl*) of the data had been collected, a least-squares calculation was run in which the Miller indices *hkl* were replaced by *hkl* for all reflections. This brought to R and R_w values of 0.038 and 0.040, respectively; this increase in R_w convinced us that the first model was correct.

A listing of observed and calculated structure factors is given in a Table available from the Editor.

The final parameters with esd's after the last cycle of full-matrix least-squares refinement are listed in Table I. Average and maximum shifts in the final least-squares refinement were 0.1σ and 0.3σ, respectively. The weighting scheme was $w = \{1 + (|F_o| - b/a)^2\}^{-1}$, where a and b were derived from a quadratic curve of best fit for $|F_o| - |F_c|$ as a function of $|F_o|$; the final a value was 20 and b 60. Atomic scattering factors were taken from ref. 4 and the real and imaginary parts of the anomalous dispersion correction for copper and chlorine were taken from ref. 5.

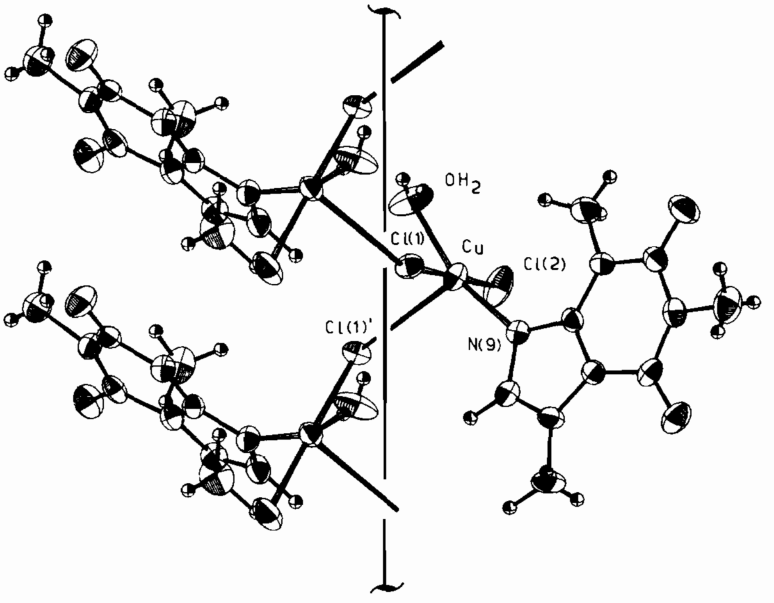

Figure 1. View of one polymeric singly bridged chain in $[CuCl_2(caffeine)H_2O]$. Atom Cl(1)' is related to Cl(1) by the screw-axis (↼) parallel to *c*. Cl–Cu–Cl bridges are shown; for clarity the hydrogen bonds running along the chain are omitted and hydrogen atoms are given artificially small. The drawings were performed using the program ORTEP (Johnson, 1970) and the thermal vibration ellipsoids are scaled to enclose 50% probability.

The crystal structure calculation system '*X*-ray 70' [6] was used for the solution and refinement of the structure. Calculations were carried out on the Consorzio Interuniversitario Italia Nord-Orientale – Casalecchio (Bologna)-CDC 6600 computer.

Description of the Structure and Discussion

Nature of the Aggregation

The crystal structure consists of polymeric chains $[CuCl_2(caffeine)H_2O]$ units linked by single Cu–Cl–Cu bridges and by Cl– – –HOH hydrogen bonds; moreover, O– – –HOH hydrogen bonds connect distinct chains (see further). A view of one segment of the polymer is given in Figure 1. The polymeric chains are singly bridged being constituted of pentacoordinated copper atoms linked by single Cu–Cl–Cu bridges, in fact, through a screw-axis parallel to *c*, Cl(1) atom is placed at the apex of a pyramidal configuration (Cl(1)'), the chains running along the crystallographic *c* axis. The interactions between $[CuCl_2(caffeine)H_2O]$ moieties are weak, being the bridge formed by one normal (2.32 Å) and one long (2.79 Å) Cu–Cl bond (Table II). This apical Cu–Cl(1)' bond indicates weak axial co-ordination, although extremely weak Cu–Cl separations as far as 3.50 Å are known [7] in systems like $CuLX_2$ (L = bidentate ligand and X = halogen) and CuA_2X_2 (A = monodentate ligand). The Cu–Cl(1)–Cu' angle at the bridge is 128.1° and the Cu– – –Cu' separation is 4.60 Å.

Environment of Copper

The molecular structure around the copper atom may be described as distorted tetragonal pyramid (Fig. 2) or as distorted trigonal bipyramid. In the first description the caffeine imidazole N(9) atom, O(10) atom from water and *trans* Cl(1) and Cl(2) atoms lie at the corners of an approximate square as closest ligands to the copper. Moreover, the puckering of the basal plane is large (Table III, plane (1)), the *trans* Cl(1) and Cl(2) lying 0.17–0.16 Å above the least-squares plane through the four ligating atoms, while O(10) and N(9) lie 0.17–0.16 Å below it. The copper atom is above this plane (0.15 Å) towards the apical chlorine (Table III), the fifth long bond (2.79 Å), Cu–Cl(1)', being approximately normal to this plane. As commonly observed in similar tetragonal pyramidal complexes [7–9], the metal atom is displaced towards the top of the pyramid in the range 0.13–0.33 Å. In the sixth co-ordination direction of an imagined octahedral configuration around the copper (*i.e.*: *trans* to Cl(1)'), the methyl group C(3) is found at a distance of 3.12 Å. As a result, one of the hydrogen atoms linked to this carbon (H(31)) is situated at 2.71 Å from the copper and approximately in the sixth octahedral position, H(31)–Cu–Cl(1)' angle being 174°. Similar copper contacts in the region of the sixth octahedron position have been reported for several copper(II) complexes [10]. The relative high displacements of the atoms N(9), O(10), Cl(1) and Cl(2) from the basal plane are imputable to a distortion of the tetragonal pyramid towards the trigonal bipyramid geometry.

TABLE II. Bond Lengths and Bond Angles. Standard deviations for the last significant figure are shown in parentheses.[a]

Bond Lengths (Å)

Cu–Cl(1)	2.319(2)	C(2)–O(2)	1.22(1)	C(6)–O(6)	1.23(1)	C(3)–H(32)	0.96(7)
Cu–Cl(2)	2.248(2)	C(2)–N(3)	1.39(1)	N(7)–C(7)	1.48(1)	C(3)–H(33)	1.01(8)
Cu–O(10)	1.96(1)	N(3)–C(3)	1.47(1)	N(7)–C(8)	1.33(1)	C(7)–H(71)	1.01(7)
Cu–N(9)	1.98(1)	N(3)–C(4)	1.36(1)	C(8)–N(9)	1.37(1)	C(7)–H(72)	0.72(8)
Cu–Cl(1)'[b]	2.788(2)	C(4)–C(5)	1.37(1)	C(1)–H(11)	0.92(7)	C(7)–H(73)	1.13(7)
N(1)–C(1)	1.48(1)	C(4)–N(9)	1.38(1)	C(1)–H(12)	0.91(8)	C(8)–H(8)	1.07(7)
N(1)–C(2)	1.39(1)	C(5)–N(7)	1.37(1)	C(1)–H(13)	0.69(8)	O(10)–H(101)	0.63(8)
N(1)–C(6)	1.39(1)	C(5)–C(6)	1.44(1)	C(3)–H(31)	0.94(7)	O(10)–H(102)	0.52(9)

Bond Angles (°)

Cl(1)–Cu–O(10)	87.9(3)	C(3)–N(3)–C(2)	118.4(8)	Cu–N(9)–C(4)	132.1(7)
O(10)–Cu–Cl(2)	91.1(3)	C(3)–N(3)–C(4)	122.2(8)	Cu–N(9)–C(8)	123.6(7)
Cl(2)–Cu–N(9)	93.6(2)	N(3)–C(4)–N(9)	126.6(8)	N(7)–C(8)–H(8)	126
N(9)–Cu–Cl(1)	87.6(2)	N(3)–C(4)–C(5)	122.6(8)	N(9)–C(8)–H(8)	121
Cl(1)–Cu–Cl(2)	178.8(1)	N(9)–C(4)–C(5)	110.8(8)	Cu–O(10)–H(101)	125
O(10)–Cu–N(9)	161.0(4)	C(4)–C(5)–C(6)	122.1(9)	Cu–O(10)–H(102)	109
Cl(1)'–Cu–Cl(1)	89.5(1)	C(5)–C(6)–N(1)	112.0(8)	H(101)–O(10)–H(102)	108
Cl(1)'–Cu–O(10)	91.8(4)	O(6)–C(6)–N(1)	121.6(8)	N(1)–C(1)–H(11)	102
Cl(1)'–Cu–Cl(2)	89.8(1)	O(6)–C(6)–C(5)	126.4(10)	N(1)–C(1)–H(12)	107
Cl(1)'–Cu–N(9)	106.7(2)	C(4)–C(5)–N(7)	106.1(8)	N(1)–C(1)–H(13)	105
C(2)–N(1)–C(6)	126.1(8)	C(6)–C(5)–N(7)	131.8(9)	N(3)–C(3)–H(31)	104
C(1)–N(1)–C(6)	117.3(9)	C(5)–N(7)–C(8)	107.4(8)	N(3)–C(3)–H(32)	103
C(1)–N(1)–C(2)	116.6(10)	C(7)–N(7)–C(5)	127.8(8)	N(3)–C(3)–H(33)	115
N(1)–C(2)–N(3)	117.5(8)	C(7)–N(7)–C(8)	124.5(9)	N(7)–C(7)–H(71)	101
O(2)–C(2)–N(1)	121.2(9)	N(7)–C(8)–N(9)	112.6(9)	N(7)–C(7)–H(72)	114
O(2)–C(2)–N(3)	121.3(9)	C(8)–N(9)–C(4)	103.1(8)	N(7)–C(7)–H(73)	107
C(2)–N(3)–C(4)	118.9(8)				

[a] Taking into account the accuracy of cell parameters. [b] ½ – x, y, – ½ + z

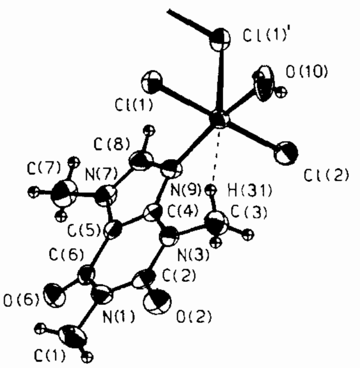

Figure 2. Co-ordination geometry around one copper atom in [$CuCl_2$(caffeine)H_2O]. The atom numbering system is shown. Cu–H(31) interaction is indicated by a dashed line.

The trigonal plane is constituted, in this description, of N(9), O(10) and Cl(1)' atoms, while Cl(1) and Cl(2) are in the axial direction. Indeed, Cu, Cl(1)', N(9), O(10) atoms are coplanar and the 'chlorines line' is normal to the basal plane (89.9°) (Table III). The angles of the trigonal plane are noticeably different from 120°; this is duc, without doubt, to the H(31)–Cu distance that is contained in this plane (the deviation of H(31) from this plane is 0.18 Å only) and lies between the N(9) and O(10) atoms forcing the N(9)–Cu–O(10) angle to 161°.

Muetterties and Guggenberger [11] have shown that distortions of C_{4v} geometry in ML_5 complexes are towards the D_{3h} geometry following, in any case, the C_{2v} Berry pathway. Here too the C_{2v} symmetry is nearly maintained, if we see N(9) and O(10) as atoms of the same nature. Distances and angles in the 'inner core' of the complex are comparable with those found in other similar complexes in equivalent co-ordination situations [1, 7]. In particular, the distances Cu–Cl(1) and Cu–Cl(2) (2.32 and 2.25 Å, respectively) are close to the sum of the covalent radii (2.27 Å) given by Pauling [12]. The significant lengthening of the first distance can be ascribed to the bridging and hydrogen bonding involving Cl(1) atom. The Cu–Cl bond length to the fifth co-ordination site (2.79 Å) is in the range reported for a variety of dimeric and polymeric copper(II) complexes [7, 13, 14] and longer than the sum of the ionic radii (2.62 Å) [12]. It is noteworthy that in the structure of catena-μ-imidazolato-chlorido-diimidazolo-copper (II) [15], where the chlorine atom lies at the apex of a tetragonal pyramidal configuration just as in this structure but without bridging two copper atoms, the

TABLE III. Least-squares Planes with the Deviations (Å) of Relevant Atoms in Square Brackets. The equation of a plane is given by $Px + Qy + Rz = S$, where x, y and z are in fractional unit-cell co-ordinates.

	P	Q	R	S
Plane (1):				
Basal Plane	1.165	−9.216	−4.209	−1.186
[Cl(1) 0.17, O(10) −0.17, Cl(2) 0.16, N(9) −0.16, Cu 0.15, Cl(1)′ 2.92, C(3) −2.91]				
Plane (2):				
Imidazole Ring	10.241	−7.072	3.347	1.037
[C(4), C(5), N(7), C(8), N(9) 0.00, Cu 0.31, C(7) 0.14, N(3) 0.03, C(6) −0.02]				
Plane (3):				
Pyrimidine Ring	10.258	−7.554	3.136	0.881
[N(1) 0.05, C(2) −0.02, N(3) −0.02, C(4) 0.02, C(5) 0.02, C(6) −0.05, Cu 0.40, C(1) 0.19, O(2) −0.04, C(3) −0.25, O(6) −0.20]				
Plane (4):				
Xanthine Ring	10.273	−7.299	3.241	1.002
[N(1) 0.07, C(2) 0.01, N(3) −0.03, C(4) −0.02, C(5) −0.02, C(6) −0.07, N(7) 0.02, C(8) 0.03, N(9) 0.00, Cu 0.32, C(1) 0.25, C(7) 0.18, C(3) −0.25, O(6) −0.22, O(2) 0.01]				
Plane (5):				
Cu, N(9), O(10), Cl(1)′	12.624	−5.846	2.701	1.978
[Cu −0.05, N(9) 0.02, O(10) 0.02, Cl(1)′ 0.01, Cl(1) 2.27, Cl(2) −2.30, H(31) 0.18]				

The equation of least-squares line (L) defined by Cl(1), Cu, Cl(2) in parametric form is: $X = 0.1968 + 0.0475T$; $Y = 0.1138 - 0.0311T$; $Z = 0.0489 + 0.0808T$
[Cl(1) 0.01, Cl(2) 0.01, Cu 0.02]

Angles (°) between the mean planes and between planes (1) and (5) and the line L (for a plane and a line, the angle is to the normal of the plane)

(1)–(2)	89.4	(1)–(5)	89.0	(2)–(5)	11.7	(4)–(5)	11.6
(1)–(3)	87.7	(2)–(3)	2.9	(3)–(4)	1.5	(1)–(L)	89.9
(1)–(4)	89.2	(2)–(4)	1.4	(3)–(5)	11.9	(5)–(L)	1.1

Cu–Cl distance is 2.56 Å. The distance Cu–N(9) (1.98 Å) is a normal bond length as can be seen in a paper by Ivarsson, Lundberg and Ingri [16] (where Cu–N(imidazole) distances which are within the range 1.95–2.01 Å are tabulated) and significantly shorter than in (dichloro)bis(9-methyl-6-oxopurine)(diaquo)copper(II) (2.055 Å) [17a] and (dichloro)tris(1,2-dimethylimidazole)copper(II) (2.144 Å) [17b]. Of interest is the orientation of the xanthine ring relative to the copper co-ordination polyhedron. For a d^9 system in C_{4v} geometry Rossi and Hoffmann [18] predict that a basal π donor should prefer a $ba_{\perp}$ instead of a $ba_{\parallel}$ interaction. In the $ba_{\perp}$ orientation the p_z orbital of $a^{\parallel}$ symmetry is perpendicular to the pseudo-C_{4v} axis with resulting considerable π interaction between the p_z orbital of N(9) and the d_{xy} orbital of Cu(II); consequently, the angle between the xanthine ring and the basal plane of C_{4v} symmetry is nearly 90° (here 89.2°). The $ba_{\perp}$ orientation is quite common in C_{4v} symmetry as found for example in $[Cu(NO_3)_2(caffeine)(H_2O)_3]$ [19], in the dimeric $[Cu_2(adenine)_4(H_2O)_2](ClO_4)_4 \cdot 2H_2O$ [9a] and in $[Cu(6\text{-hydroxypurine})_2Cl]Cl \cdot 3H_2O$ [9b]. The Cu–OH_2 separation (1.96 Å) is normal for a basal distance in C_{4v} symmetry, whereas the corresponding apical distance is longer (*ca.* 2.2 Å).

Geometry of Caffeine Ligand

The caffeine ligand is unidentate; the N(9) atom is 0.10 Å out of the Cu,C(4) and C(8) plane, indicating a slight deviation from sp^2 hybridization. The binding of copper to N(9) has no appreciable effect on the ligand geometry. A comparison between the dimensions in the 1:1 molecular complex formed by caffeine and 5-chlorosalicylic acid [20a], in the 1:2 molecular complex of caffeine and barbital [20b] or in caffeine hydrate [21] and the present compound reveals a very slight effect on the bonds adjacent to the co-ordination site N(9), the lengthening being only 0.03 Å in N(9)–C(8) and

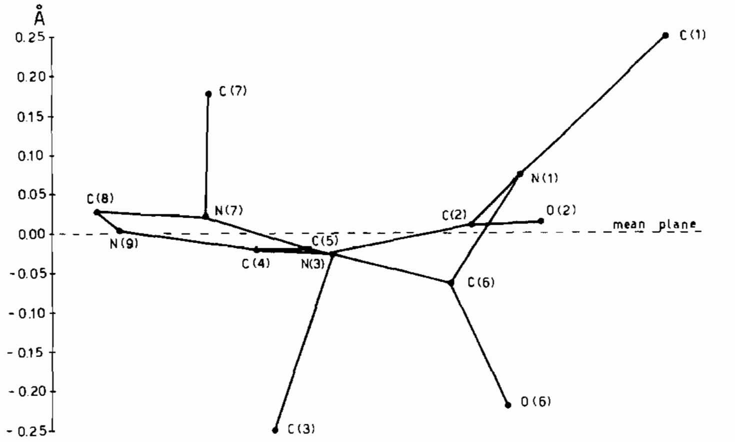

Fig. 3. The puckering of the caffeine ring. The scale of the ordinate is artificially expanded to magnify the feature.

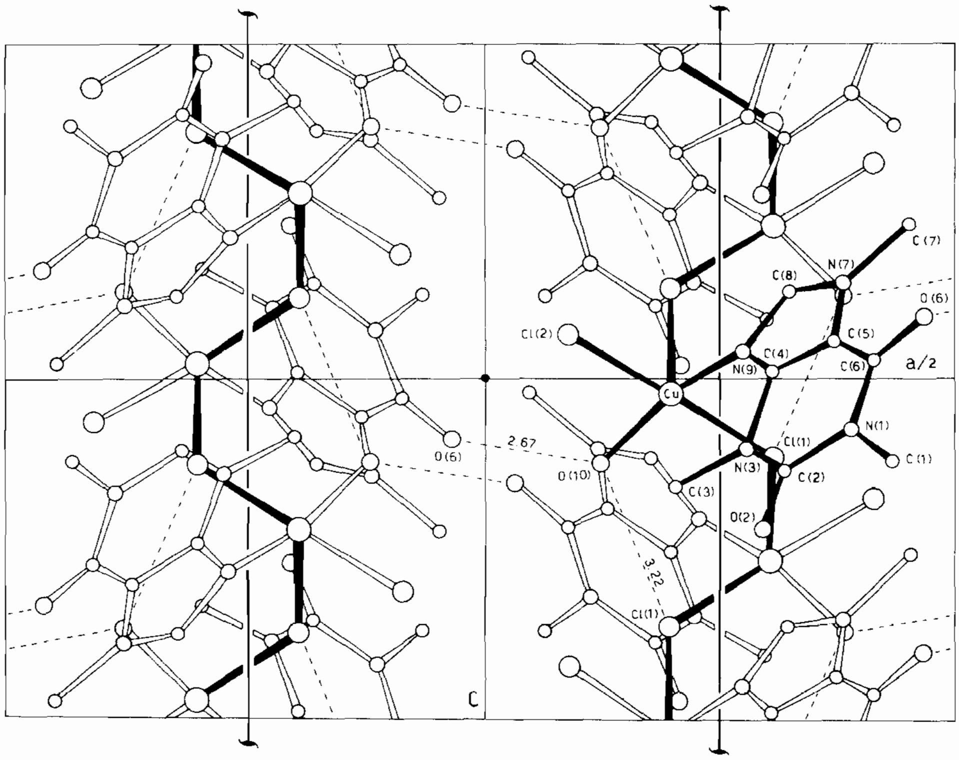

Fig. 4. A view down the *b* axis of the crystal packing. Hydrogen bonds are indicated by dashed lines.

0.02 Å in N(9)–C(4) bond without the expected opening of the C(4)–N(9)–C(8) angle. The caffeine ligand is significantly non planar, dihedral angle between pyrimidine and imidazole rings being 2.9° (Table III). This finding is not unusual as a variety of purine derivatives structures have been observed to be significantly non planar [22] ; there is a significant fold about the C(4)–C(5) bond (dihedral angle in the range 2–3°). The imidazole ring is, however, quite planar (maximum deviation 0.003 Å), while the pyrimidine ring retains a significant degree of non planarity (deviations within ±0.054 Å). This lack of planarity cannot be ascribed to a departure from trigonal geometry for the pyrimidine atoms (only N(3) is 0.06 Å out of the plane defined by its three nearest bonded atoms), but to the circumstance that some torsion angles are as large as 10.5°. Then an accurate description of the caffeine geometry in the present compound makes use of three planes (Figure 3): a) the imidazole ring + C(6) and N(3) atoms; b) N(1), C(1), C(6), C(2); c) N(1), C(2), O(2), N(3) with the dihedral angles between ab, ac and bc of 9.0, 3.4 and 6.5°, respectively.

TABLE IV. Hydrogen Bond Distances and Angles.

Bond D – H – – – A	Position of Acceptor Atom	Distances (Å)			Angle (°)
		D–H[a]	H– – –A	D– – –A	D–H– – –A
i) within the same chain					
O(10)–H(101)– – –Cl(1)	$1/2 - x, \bar{y}, 1/2 + z$	0.63	2.60	3.22	169
ii) between different chains					
O(10)–H(102)– – –O(6)	$-1/2 + x, 1/2 - y, \bar{z}$	0.52	2.27	2.67	137

[a] These distances are shorter than the true O–H separation but also shorter than the apparent X-ray O–H distance. This further shortening might be ascribed to the relatively high thermal motion of water oxygen.

TABLE V. Selected Distances.

(a) Selected Intramolecular Distances (Å)				(b) Selected Intermolecular Distances (Å) *	
Cu–C(8)	2.96	Cl(1)–H(101)	2.92	O(2)– – – – –C(2)^{I}	2.92
Cu–C(4)	3.07	Cl(2)–O(10)	3.01	H(32)– – – – –N(1)^{I}	2.96
Cu–C(3)	3.21	Cl(2)–N(9)	3.08	O(2)– – – – – –N(3)^{I}	2.98
Cu–H(102)	2.18	Cl(2)–H(102)	2.83	O(2)– – – – – –H(33)^{I}	3.00
Cu–H(101)	2.38	C(2)–H(32)	2.38	Cl(1)– – – – –H(8)^{II}	2.60
Cu–H(31)	2.71	C(2)–H(12)	2.52	H(12)– – – – –O(6)^{II}	2.67
Cu–H(8)	3.12	C(2)–H(13)	2.59	H(31)– – – – –C(8)^{II}	2.93
Cl(1)–O(10)	2.98	O(2)–H(32)	2.22	O(10)– – – – –H(8)^{III}	2.80
Cl(1)–N(9)	2.98	O(2)–H(12)	2.48	Cl(2)– – – – –H(72)^{IV}	3.00
		O(2)–H(13)	2.71		

*Roman numerals as superscripts refer to atoms in the equivalent positions, relative to the reference molecule at x, y, z:
I $1/2 - x, 1 - y, 1/2 + z$; II $x, y, 1 + z$; III $1/2 - x, y, 1/2 + z$; IV $-1/2 + x, 1/2 - y, -1 - z$.

Crystal Packing

The packing is shown in a drawing viewed along *b* (Figure 4). Hydrogen bonds are reported in Table IV and are also shown as thin dotted lines in Fig. 4. The infinite chains, developing along the screw-axis and formed by the Cl(1)′ atoms bridging successive copper atoms, are strengthened by hydrogen bonds between water oxygen atom and Cl(1)′ (3.22 Å) and on the other hand symmetry-related chains are held together by hydrogen bonds between the water molecule and the carbonyl oxygen atom O(6) (O(10)– – –O(6) of 2.67 Å). As typical of purines [7, 22, 23], this carbonyl oxygen atom is linked *via* hydrogen bonds. This occurs also when O(6) atom might interact with the metal center; in the present complex, however, this possibility is rejected *a priori*, bearing the N(7) atom a methyl group. There are no other significant short intra- or intermolecular contacts in the structure (Table V).

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References

1 T. R. Harber and H. Freiser, *J. Am. Chem. Soc., 80,* 1132 (1958); G. E. Cheney, H. Freiser and Q. Fernando, *J. Am. Chem. Soc., 81,* 2611 (1959); J. A. Carrabine and M. Sundaralingam, *J. Am. Chem. Soc., 92,* 369 (1970) and refs. therein; E. Sletten and A. Apeland, *Acta Cryst., B31,* 2019 (1975) and refs. therein.

2 M. Biagini Cingi and L. Oleari, *Atti VIII Convegno Nazionale Chimica Inorganica, Jesolo, D7,* (1975).

3 M. Biagini Cingi, R. Borromei and L. Oleari, *Inorg. Chim. Acta, 11,* 167 (1974).

4 D. T. Cromer and J. T. Waber, *Acta Cryst., 18,* 104 (1965).

5 D. T. Cromer, *Acta Cryst., 18,* 17 (1965).

6 'X-ray' 70' *System of Programs, University of Maryland, Technical Report, TR 64 6.*

7 R. A. Bream, E. Dixon Estes and D. J. Hodgson, *Inorg. Chem., 14,* 1672 (1975) and refs. therein.

8 D. J. Hodgson and J. A. Ibers, *Inorg. Chem., 8,* 1282 (1969); D. S. Brown, F. W. B. Einstein and D. G. Tuck, *Inorg. Chem., 8,* 14 (1969).

9 (a) P. De Meester and A. C. Skapski, *J. Chem. Soc. A,* 2167 (1971); (b) E. Sletten, *Acta Cryst., B25,* 1480 (1969); (c) A. Terzis, A. L. Beauchamp and R. Rivest, *Inorg. Chem., 12,* 1166 (1973).

10 M. Bonamico, G. Dessy, A. Mugnoli, A. Vaciago and L. Zambonelli, *Acta Cryst., 19,* 886 (1965) and refs. therein.

11 E. L. Muetterties and L. J. Guggenberger, *J. Am. Chem. Soc., 96,* 1748 (1974).

12 L. Pauling, "The Nature of Chemical Bond", Cornell University Press, Ithaca, 1960.

13 B. K. S. Lundberg, *Acta Chem. Scand., 26,* 3977 (1972).

14 J. A. J. Jarvis, *Acta Cryst., 15,* 964 (1962).

15 B. K. S. Lundberg, *Acta Chem. Scand., 26,* 3902 (1972).

16 G. Ivarsson, B. K. S. Lundberg and N. Ingri, *Acta Chem. Scand., 26,* 3005 (1972).

17 (a) E. Sletten, *Chem. Comm.,* 558 (1971) and *Acta Cryst., B30,* 1961 (1974); (b) F. Huq and A. C. Skapski, *J. Chem. Soc. A,* 1927 (1971).

18 A. Rossi and R. Hoffmann, *Inorg. Chem., 14,* 365 (1975).

19 M. Biagini Cingi, A. Chiesi Villa, A. Gaetani Manfredotti and C. Guastini, *Cryst. Struct. Comm., 1,* 363 (1972).

20 (a) E. Shefter, *J. Pharm. Sci., 57,* 1163 (1968); (b) M. Craven and G. L. Gartland, *Acta Cryst., B30,* 1191 (1974).

21 D. J. Sutor, *Acta Cryst., 11,* 453 (1958).

22 J. Sletten and L. H. Jensen, *Acta Cryst., B25,* 1608 (1969); E. Sletten, J. Sletten and L. H. Jensen, *Acta Cryst., B25,* 1330 (1969); G. Nygjerd and E. Sletten, *Acta Chem. Scand., 27,* 2902 (1973); W. M. MacIntyre, *Biophys. J., 4,* 495 (1964).

23 T. J. Kistenmacher, D. J. Szalda and L. G. Marzilli, *Inorg. Chem., 14,* 1686 (1975) and refs. therein.