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Interaction of Metal Ions with 8-Azapurines. Synthesis and Structure of Tetrachlorobis-2-[(5-amino-4-carboxamidinium)[1,2,3]triazole]copper(II) Monohydrate

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Abstract: The reaction of copper(II) chloride with 8-azaadenine in 0.36 *M* hydrochloric acid solution brings about ring opening at C(2) of the azapurine to form tetrachlorobis-2-[(5-amino-4-carboxamidinium)[1,2,3]triazole]copper(II) monohydrate, $[CuCl_4(N_6C_3H_7)_2]\cdot H_2O$, hereinafter referred to as $[CuCl_4(HACT)_2]\cdot H_2O$. The composition and geometry of this complex have been verified by single-crystal X-ray crystallography using data collected by counter methods on an automatic diffractometer. The material crystallizes in the monoclinic space group $C2/c$ with four molecules in a cell of dimensions a = 15.153 (14) Å, b = 6.962 (4) Å, c = 18.274 (16) Å, and β = 121.47 (6)°. The observed and calculated densities are 1.90 (3) and 1.93 g cm^{-3}, respectively. Least-squares refinement of the structure has led to a final value of the conventional R factor (on F) of 0.042 using 1131 independent intensities. The complex consists of monomeric $CuCl_4$ $(HACT)_2$ units which are hydrogen bonded to the water molecules. The geometry at the copper(II) centers is tetragonally distorted octahedral, the base plane being formed by two trans chlorine atoms and two trans N(8) atoms of the $HACT^+$ ligands, while the axial ligands are the remaining chlorides; the copper atoms lie on a crystallographic inversion center. The in-plane Cu-N and Cu-Cl distances of 2.049 (3) and 2.258 (2) Å, respectively, are normal, as is the axial Cu-Cl separation of 2.967 (2) Å. The triazole portion of the ligand is planar, but the copper atom and the N and C atoms of the amidine moiety are out of this plane. The ligand bond lengths suggest four principal resonance contributors to the bonding in $HACT^+$. The hydrogen bonding in the crystals is complex, with all available donor and acceptor atoms apparently participating. Since neither adenine nor 8-azaguanine undergoes hydrolysis in weakly acidic solution, it appears probable that copper coordination at N(8) may assist ring opening at C(2) in 8-azapurines.

The interactions of metal ions with nucleic acid constituents have been the subjects of numerous recent chemical, spectroscopic, and crystallographic studies;[2-16] this demonstrated interest in this field is due primarily to the biological significance of metal-nucleic acid and peptide-metal-nucleic acid interactions in living systems.[15,17-19] Crystallographic studies have demonstrated that individual transition metal ions can bind in a variety of different ways to a given purine or pyrimidine base, which may in part explain the observation[19] that some metal ions (e.g., Cu^{2+}, Cd^{2+}, Hg^{2+}) lower the thermal denaturation temperature of DNA while others (e.g., Zn^{2+}, Mn^{2+}, Mg^{2+}) have the reverse effect. Thus, for example, Zn^{2+} binds to N(7) in adenine[10] while Cu^{2+} binds[5] to N(9); moreover, Zn^{2+} binds to N(9) in guanine.[11] Thus, these two metal ions would be expected to produce different effects on the hydrogen bonding scheme in a polynucleotide and, hence, a different degree of stabilization (or destabilization).

The syntheses and structures of aza analogs of the nucleic acid constituents have also been widely studied during the past 2 or 3 years,[20-31] mainly as a result of the demonstrated but varying potency of some of these species (notably 8-azaguanine) as antineoplastic agents.[32,33] On the basis of structural models, it has been suggested that the biological activity of the ortho aza nucleosides (i.e., 6-azapyrimidine or 8-azapurine nucleosides) may result from changes in their hydrogen bonding ability brought about by conformation changes.[34] This postulate has recently received partial confirmation from theoretical[35] and crystallographic studies, which have shown that the conformations of ortho aza nucleosides about the glycosyl bond are in a different angular range than are those of the naturally occurring nucleosides.[26,27,29,30]

Since azapurines and azapyrimidines, therefore, are in common use in medical therapy, it is apparent that the interactions of naturally occurring metal ions with these bases are also of great importance. To our knowledge, however, no such studies have been reported to date, although we have noted in the literature[31] that $HgCl_2$ interacts sufficiently with 6-azauracil to allow the dissolution of this insoluble base in aqueous medium. Similarly, Zn^{2+} and Cu^{2+} form complexes with 6-azauracil and 6-azathymine, respectively, in aqueous solution,[36] but in all of these cases it is the uncomplexed base which crystallizes from the solution.

In order to overcome this lack of information, we have initiated a program of synthetic and structural chemistry to investigate this significant area. We report here the results of our study of the interaction of Cu^{2+} with 8-azaadenine in weakly acidic aqueous medium.

Experimental Section

The complex was prepared by the addition of 25 ml of 4×10^{-2} *M* aqueous copper(II) chloride solution to a 25-ml solution of 4×10^{-2} *M* 8-azaadenine dissolved in 0.36 *M* hydrochloric acid. The resulting mixture was warmed (less than 50°) and allowed to stand at room temperature; after several days, olive green crystals precipitated from the solution. The initial preparation of the complex did not yield sufficient material for elemental analysis, but the density and cell constants were consistent with the formulation $Cu(HAA)_2Cl_4$, where HAA is the protonated 8-azaadenine cation; it was on this basis that the structural analysis was initiated. As the structure analysis proceeded it became apparent that this formulation was incorrect and that the six-membered ring of the purine was no longer intact (vide infra). A subsequent preparation yielded more material, and chemical analysis confirmed that the complex was tetrachlorobis-2-[(5-amino-4-carboxamidinium)[1,2,3]triazole]copper(II) monohydrate, $CuCl_4(HACT)_2 \cdot H_2O$. Anal. Calcd for $CuCl_4N_{12}C_6H_{16}O$: C, 15.09; N, 35.19; H, 3.38. Found:[37] C, 15.03; N, 35.26; H, 3.18.

On the basis of precession photographs, the crystals were assigned to the monoclinic system. The observed systematic absences of $(h + k)$ odd for hkl, l odd for the $h0l$ plane, and k odd for $0k0$ suggested that the space group was either $C2/c$ or Cc. Subsequent refinement of the structure revealed that the space group was $C2/c$. The lattice constants, obtained by the least-squares method of Busing and Levy,[38] are a = 15.153 (14) Å, b = 6.962 (4) Å, c = 18.274 (16) Å, and β = 121.47 (6)°. A density of 1.93 g cm^{-3} calculated for four formula units in the cell is in acceptable agreement with the value of 1.90 (3) g cm^{-3} obtained by flotation in diiodomethane–methylene chloride solution. Hence, the Cu atom is constrained to lie either on the inversion center or on the twofold axis.

A parallelepiped crystal in which the faces were $(11\bar{1})$, $(\bar{1}\bar{1}1)$, $(\bar{1}11)$, $(1\bar{1}\bar{1})$, (100), and $(\bar{1}00)$ was chosen for data collection. The distance between faces $(11\bar{1})$ and $(\bar{1}\bar{1}1)$ was 0.173 mm; the distance between $(\bar{1}11)$ and $(1\bar{1}\bar{1})$ was 0.175 mm; and the distance between (100) and $(\bar{1}00)$ was 0.242 mm. Intensity data were collected with the crystal mounted on a glass fiber and oriented approximately perpendicularly to the (100) face. The narrow-source, open-counter ω-scan technique was used to test the mosaicity of the crystal; the crystal was determined to be acceptable for data collection. A basis for the least-squares refinement was obtained by centering 12 reflections at a takeoff angle of 1.5° through a narrow vertical slit; using the logic of Busing and Levy in the PDP-8/L computer.[38] the cell parameters and orientation matrix were refined.

The takeoff angle for collecting intensity data was 1.5° which was the angle at which the peak intensity of a strong reflection was approximately 85% of the maximum value as a function of takeoff angle. The counter aperture was 5.0 mm high and 5.0 mm wide and was positioned 32 cm from the crystal. The data were collected using the θ–2θ scan technique at a scan rate of 1.0°/min. To allow for the presence of both $K\alpha_1$ and $K\alpha_2$ radiations, the scan range was from 0.6° below the calculated $K\alpha_1$ peak position to 0.6° above the calculated $K\alpha_2$ position. After each scan, stationary-counter, stationary-crystal background counts of 10 sec were taken at both ends of the scan. The data were collected through a Ni filter of 0.5 mil thickness on a Picker four-circle automatic diffractometer using Cu $K\alpha$ radiation.

A unique data set having $2\theta \leq 123°$ was obtained, yielding 1461 independent intensities. After every 100 reflections, the intensities of three standard reflections were measured; these standards showed no deviations other than those predicted from counting statistics.

Data processing was carried out as described by Corfield et al.[39] The intensities were assigned standard deviations according to the formula

$$\sigma(I) = [C + 0.25(\mathrm{ts}/\mathrm{tb})^2(B_H + B_L) + (pI)^2]^{1/2}$$

after the data were corrected for background, and the value of p was selected to be 0.05. This term in the expression is used to prevent extremely high weight being given to very large reflections.[40] The values of I and $\sigma(I)$ were corrected for Lorentz and polarization effects and for absorption factors. The absorption coefficient for these atoms was found to be 76.64 cm^{-1} for Cu $K\alpha$ radiation, and the transmission coefficients evaluated for the chosen crystal ranged from 0.20 to 0.42. Of the 1461 independent reflections, 1131 were found to be greater than three times their estimated standard deviations. These 1131 reflections were the only ones used in the refinement of the structure.

Table I. Positional Parameters for $CuCl_4(HACT)_2 \cdot H_2O$

Atom	*X*	*Y*	*Z*
Cu	0.0	0.0	0.0
Cl(1)	0.07096 (8)	0.20551 (13)	0.11207 (6)
Cl(2)	0.16578 (8)	0.28300 (14)	−0.39666 (7)
N(1)	0.12650 (30)	0.42703 (55)	−0.24526 (24)
N(3)	0.16673 (32)	0.40802 (53)	0.43172 (26)
C(4)	0.13569 (28)	0.40997 (54)	−0.07622 (24)
C(5)	0.12573 (28)	0.26116 (53)	−0.13107 (26)
C(6)	0.14010 (27)	0.26494 (54)	−0.20382 (25)
N(6)	0.16319 (30)	0.10647 (54)	−0.22837 (26)
N(7)	0.08964 (25)	0.10131 (46)	−0.11230 (21)
N(8)	0.07494 (25)	0.14382 (47)	−0.04981 (21)
N(9)	0.10366 (27)	0.33053 (50)	−0.02751 (23)
O(1)	0.0	0.25112 (72)	0.25
HN(1)	0.0996 (46)	0.4734 (86)	0.2657 (39)
HN(1)′	0.1352 (41)	0.4225 (75)	−0.2841 (37)
HN(3)	0,2057 (42)	0.3801 (83)	0.4132 (36)
HN(3)′	0.1623 (37)	0.3288 (73)	0.4720 (34)
HN(6)	0.1638 (35)	0.1134 (72)	−0.2696 (34)
HN(6)′	0.1735 (42)	0.0083 (78)	−0.1944 (38)
HN(9)	0.1058 (39)	0.3667 (84)	0.0113 (34)
HO(1)	0.0044 (51)	0.1783 (80)	0.2827 (39)

Solution and Refinement of the Structure. All least-squares refinements in this analysis were carried out on F, the function minimized being $\Sigma w(|F_o| - |F_c|)^2$; the weights, w, were taken as $4F_o^2/\sigma^2(F_o)^2$. In all calculations of F_c, the atomic scattering factors for Cu and N were taken from Cromer and Waber,[41] those for C and O were from the tabulations of Ibers,[42] those of Cl were from Hanson et al.,[43] and those of H were from Stewart, Davidson, and Simpson.[44] The effects of the anomalous dispersion of copper were included in calculations of F_c,[45] the values of $\Delta f'$ and $\Delta f''$ being taken from the tabulations of Cromer and Liberman.[46]

The position of the copper atom was determined from a three-dimensional Patterson function;[47] the locations of the Cl, O, N, and C atoms were obtained from and refined in subsequent difference Fourier maps and least-squares calculations. The presence of the water molecule and the absence of the pyrimidine C(2) carbon atom were apparent from the structural results and were confirmed by the elemental analysis (vide supra). Isotropic refinement of all nonhydrogen atoms gave values of the conventional agreement factors $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$ of 0.108 and 0.159, respectively. Anisotropic refinement of these same atoms yielded R_1 = 0.050 and R_2 = 0.074. The hydrogen atoms were unambiguously located in a difference Fourier map; a subsequent least-squares calculation in which nonhydrogen atoms were refined anisotropically and hydrogen atoms were refined isotropically gave R_1 = 0.042 and R_2 = 0.057. Attempts to refine the structure in the noncentrosymmetric space group Cc gave no significant improvement in R_2 and eventually led to a structure which contained an inversion center at the metal.

The final values of F_o and F_c suggested to us that no correction for secondary extinction was necessary, and none was applied. In the final cycle of least-squares refinement, no atomic parameter experienced a shift of more than 0.8 times its estimated standard deviation, which is taken as evidence of convergence. A final difference Fourier showed peaks of approximately 1.8 e $Å^{-3}$ in the vicinity of the copper atom, which may be due to some small error in the absorption correction; no other peaks larger than 0.46 e $Å^{-3}$ were observed.

The positional and thermal parameters obtained from the last cycle of least-squares, along with their standard deviations as estimated from the inverse matrix, are presented in Tables I and II. The atomic numbering scheme used in Tables I and II and elsewhere in this paper is designed to show that the ligand is a deriva-

Table II. Thermal Parameters for $CuCl_4(HACT)_2 \cdot H_2O$

Atom	β_{11}[a] or B(Å^2)	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	0.00545 (6)	0.01221 (20)	0.00237 (4)	−0.00263 (8)	0.00274 (4)	−0.00127 (6)
Cl(1)	0.00575 (7)	0.01034 (23)	0.00196 (5)	−0.00213 (9)	0.00246 (5)	−0.00100 (7)
Cl(2)	0.00498 (7)	0.01283 (24)	0.00235 (5)	−0.00003 (9)	0.00249 (5)	−0.00022 (7)
N(1)	0.00626 (26)	0.01359 (84)	0.00258 (17)	0.00056 (35)	0.00313 (18)	0.00025 (29)
N(3)	0.00724 (28)	0.01455 (82)	0.00357 (18)	0.00363 (40)	0.00409 (21)	0.00233 (32)
C(4)	0.00343 (23)	0.01091 (82)	0.00201 (16)	−0.00102 (33)	0.00166 (17)	−0.00033 (29)
C(5)	0.00343 (23)	0.01024 (79)	0.00162 (16)	−0.00009 (33)	0.00145 (16)	0.00039 (28)
C(6)	0.00272 (21)	0.01088 (82)	0.00173 (16)	−0.00039 (31)	0.00129 (16)	−0.00039 (29)
N(6)	0.00605 (26)	0.01396 (85)	0.00239 (16)	0.00051 (36)	0.00279 (18)	−0.00009 (30)
N(7)	0.00464 (21)	0.01158 (69)	0.00242 (15)	0.00006 (30)	0.00231 (16)	−0.00053 (26)
N(8)	0.00466 (20)	0.01135 (70)	0.00244 (15)	−0.00077 (30)	0.00231 (15)	−0.00001 (26)
N(9)	0.00522 (23)	0.01226 (72)	0.00223 (16)	−0.00177 (32)	0.00253 (16)	−0.00175 (28)
O(1)	0.00820 (39)	0.01259 (96)	0.00300 (23)	0.0	0.00370 (27)	0.0
HN(1)	6 (2)					
HN(1)′	2 (1)					
HN(3)	4 (1)					
HN(3)′	3 (1)					
HN(6)	3 (1)					
HN(6)′	4 (1)					
HN(9)	1 (1)					
HO(1)	5 (1)					

[a] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

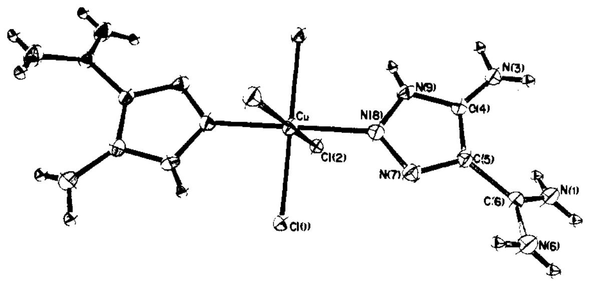

Figure 1. View of the $CuCl_4(HACT)_2$ molecule; the numbering scheme for the ligand atoms is chosen to correspond to the 8-azaadenine precursor. The thermal ellipsoids of the hydrogen atoms have been artificially reduced for clarity.

Table III. Intramolecular Distances in $CuCl_4(HACT)_2 \cdot H_2O$

Atoms	Distance, Å	Atoms	Distance, Å
Cu–N(8)	2.049 (3)	C(4)–C(5)	1.394 (5)
Cu–Cl(1)	2.258 (2)	C(5)–N(7)	1.361 (5)
Cu–Cl(2)	2.967 (2)	C(5)–C(6)	1.455 (6)
N(1)–HN(1)′	0.79 (6)	C(6)–N(6)	1.306 (5)
N(1)–HN(1)	0.88 (6)	N(6)–HN(6)	0.76 (5)
N(1)–C(6)	1.314 (5)	N(6)–HN(6)′	0.88 (6)
N(3)–HN(3)	0.84 (6)	N(7)–N(8)	1.306 (5)
N(3)–HN(3)′	0.95 (6)	N(8)–N(9)	1.364 (5)
N(3)–C(4)	1.333 (5)	N(9)–HN(9)	0.74 (5)
C(4)–N(9)	1.336 (5)	O(1)–HO(1)	0.76 (6)

Table IV. Bond Angles in $CuCl_4(HACT)_2 \cdot H_2O$

Atoms	Angle, deg	Atoms	Angle, deg
N(8)–Cu–Cl(1)	88.9 (1)	C(4)–C(5)–C(6)	129.2 (3)
N(8)–Cu–Cl(2)	97.2 (1)	N(6)–C(6)–N(1)	121.1 (4)
Cl(1)–Cu–Cl(2)	90.0 (1)	N(6)–C(6)–C(5)	119.6 (4)
HN(1)′–N(1)–HN(1)	124 (5)	N(1)–C(6)–C(5)	119.3 (3)
HN(1)′–N(1)–C(6)	116 (4)	HN(6)–N(6)–HN(6)′	131 (5)
HN(1)–N(1)–C(6)	120 (4)	HN(6)–N(6)–C(6)	116 (4)
HN(3)–N(3)–HN(3)′	122 (5)	HN(6)′–N(6)–C(6)	113 (4)
HN(3)–N(3)–C(4)	117 (4)	N(8)–N(7)–C(5)	108.0 (3)
HN(3)′–N(3)–C(4)	118 (3)	N(7)–N(8)–N(9)	107.7 (3)
N(3)–C(4)–N(9)	123.5 (4)	HN(9)–N(9)–C(4)	131 (4)
N(3)–C(4)–C(5)	133.2 (4)	HN(9)–N(9)–N(8)	117 (5)
N(9)–C(4)–C(5)	103.3 (3)	C(4)–N(9)–N(8)	111.5 (3)
N(7)–C(5)–C(4)	109.5 (3)	HO(1)–O(1)–HO(1)′	96 (9)
N(7)–C(5)–C(6)	121.1 (3)		

tive of 8-azaadenine; thus, the triazole atoms have been numbered C(4), C(5), N(7), N(8), and N(9) in the manner analogous to that used for the imidazole portion of purine, and the carboxamidine and amine ligand atoms bear numbers which relate to the pyrimidine portion of the purine from which they were formed. A compilation of observed and calculated structure amplitudes is available.[48]

Description of the Structure

The structure consists of monomeric, six-coordinate $CuCl_4(HACT)_2$ molecules (where $HACT^+$ is (5-amino-4-carboxamidinium)[1,2,3]triazole) which are hydrogen bonded to water molecules. A view of the complex is shown in Figure 1 (see note above concerning the numbering scheme for the ligand). The coordination around the copper(II) centers is the commonly observed axially elongated octahedral geometry.[49] The base plane is formed by the N(8) atoms of the two trans $HACT^+$ ligands and by the chlorine atoms Cl(1) and Cl(1)′, while the axial ligands are Cl(2) and Cl(2)′; the copper atom lies on an inversion center.

The intramolecular distances and angles observed in this complex are given in Tables III and IV, respectively. The Cu–N(8) distance of 2.049 (3) Å is slightly larger than the Cu–N distances of from 2.000 to 2.041 Å reported[5,9,50–52] for copper(II) complexes of adenine but is in the range of Cu–N distances normally observed for copper(II) complexes.[53] The in-plane Cu–Cl(1) separation of 2.258 (2) Å is also normal.[54,55] The axial Cu–Cl(2) length of 2.967 (2) Å is considerably longer than the equatorial Cu–Cl(1) distance, but is within the range observed for out-of-plane Cu–Cl distances in a variety of tetragonal pyramidal and octahedral chlorine-bridged copper dimers.[54–57]

The basal plane formed by Cu, N(8), N(8)′, Cl(1), and Cl(1)′ is strictly planar, since the copper atom lies on a crystallographic inversion center. The in-plane bond angles at copper are roughly 90°, with a Cl(1)–Cu–N(8) angle of 88.9 (1)° and a Cl(1)–Cu–N(8)′ angle of 91.1 (1)°. This small distortion from 90° may be due to the presence (vide infra) of an intramolecular N(9)–H(9)···Cl(1) hydrogen bond which draws Cl(1) closer to N(9) than to N(7)′ and thereby reduces the Cl(1)–Cu–N(8) angle. The Cu–Cl(2) out-of-plane vector is not perpendicular to the base plane, since the N(8)–Cu–Cl(2) angle is 97.2 (1)°; this may again be due to the complex intermolecular hydrogen bonding of Cl(2) (vide infra).

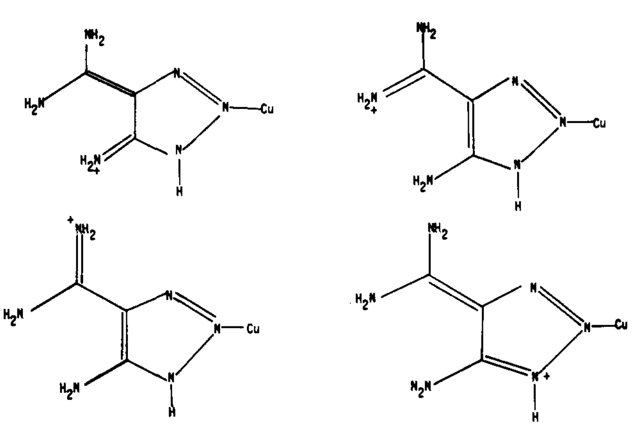

Figure 2. The four probable resonance contributors to the HACT$^+$ ligand.

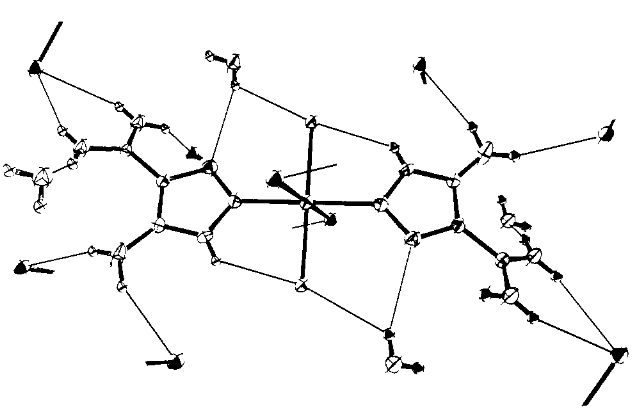

Figure 3. The hydrogen bonding in $CuCl_4(HACT)_2 \cdot H_2O$. The axial chlorine atoms Cl(2) are indicated by the solid segments.

The most surprising result of this study, of course, is the apparent hydrolysis which the 8-azaadenine ligand undergoes in this weakly acidic medium. While the hydrolysis at C(2) and C(8) of naturally occurring purines takes place under relatively mild conditions in basic solution,[58,59] adenine is not affected by boiling with hydrochloric acid, and its salts with mineral acids are stable.[60] Adenine can, however, be converted to the analogous amidine, 5-amino-4-carboxamidineimidazole (ACI), by heating the sulfate in a sealed tube at 150° for 2 hr;[61] these conditions are, of course, much more severe than those used in the present experiment.

The expulsion of C(2) from adenine *N*(1)-oxide at 100° in 1 *M* HCl has been reported,[62] and the structure of the perchlorate salt of the copper(II) complex of the resulting 4-aminoimidazole-5-carboxamidoxime ligand has been determined.[63] This ligand rearrangement is strikingly similar to that observed in the present case, but here again the conditions employed are much more severe than those used by us. Moreover, the addition of copper(II) ion has no effect on the rate of degradation of adenine *N*(1)-oxide,[64] which is not degraded by 0.01 *N* sulfuric acid in the presence or absence of copper(II).[65] We find that, under the conditions of our experiment, 8-azaadenine is also apparently not degraded in the absence of metal ion. While the interaction of 8-azaadenine with dilute acid has not previously been documented, 8-azaguanine can be recrystallized from 0.2 *M* HBr solution[24] and is merely protonated without ring opening by 6 *M* HCl or by concentrated HBr.[66] Hence, it appears that the ring opening at C(2) in 8-azaadenine is assisted by the metal coordination at N(8); it remains possible, however, that 8-azaadenine is less stable in weakly acidic solutions than are adenine and 8-azaguanine.

The amidine ACI has been postulated to be an intermediate in the formation of glycine from adenine,[61] and it has been shown by isotopic labeling that the amino group of the glycine originated from N(7) and that the carbon atoms originated from C(4) and C(5).[61,67] It is apparent, therefore, that 8-azaadenine could be degraded to glycine via ACT in an analogous fashion since the 8-atom is not incorporated into the product. Hence, it would appear that the presence of copper(II) may greatly facilitate the formation of glycine from 8-azaadenine since it may assist in the formation of ACT. This is of potential biological significance, since 8-azaadenine can be incorporated into nucleic acids.

The HACT$^+$ ligand can be viewed as being comprised of the four resonance structures depicted in Figure 2; hence, the positive charge is formally delocalized over the four nitrogen atoms N(1), N(3), N(6), and N(9). The bond lengths observed in the ligand support this view. The N(7)-N(8) length of 1.306 (5) Å is the shortest interatomic distance in the molecule and is shorter than the corresponding bond in the 8-aza-2,6-diaminopurine cation[68] (HADP) or that in the 8-azaguaninium cation[65] (HAG), both of which are protonated at N(8) and not protonated at N(7); in the present case, therefore, this bond clearly contains much double bond character. The N(8)-N(9) separation of 1.364 (5) Å is, however, longer than the value of 1.345 Å found in these two analogs and is clearly largely a single bond in the present case. Similarly, the C(4)-N(9) separation of 1.336 (5) Å is considerably shorter than the C(5)-N(7) distance of 1.361 (5) Å, which suggests that the former contains some double bond character while the latter, which is longer than the C(5)-N(7) bonds in HADP (1.350 Å) and HAG (1.334 Å), contains very little. The terminal C-N bonds C(4)-N(3), C(6)-N(1), and C(6)-N(6), with lengths 1.333 (5), 1.314 (5), and 1.306 (5) Å, respectively, are all shorter than the value of 1.43 Å suggested by Kitaigorodskii[69] for a C-N single bond involving an aromatic carbon atom; the relative lengths of these three bonds suggest that the positive charge is localized more on the amidine atoms N(1) and N(6) than on the amine atom N(3).

The triazole portion of the ligand is approximately planar, with no atom deviating from the best five-atom least-squares plane by more than 0.006 Å. The amine nitrogen atom, N(3), also lies approximately in this plane, but Cu, C(6), and N(1) lie above the plane by 0.32, 0.13, and 0.75 Å, respectively, while N(6) lies 0.34 Å below it. Hence, the ring opening at C(2) and subsequent protonation at N(1) and N(3) have evidently been followed by a rotation around the C(5)-C(6) bond; it is apparent, therefore, that we are unable to decide with certainty whether the atom which we have labeled N(1) corresponds to N(1) or to N(6) in the 8-azaadenine precursor.

The hydrogen bonding scheme in this complex is quite complicated. The ligand contains seven potential donors and one potential acceptor, the water molecule provides two additional donors and one additional acceptor, and the chlorine ligands are potential hydrogen bond acceptors. As is shown in Figure 3, all of these potential hydrogen bond donors and acceptors appear to participate in hydrogen bond formation in this complex; the distances and angles associated with these probable hydrogen bonds are listed in Table V. The criterion used for inclusion of an interaction in Table V is that of Hamilton and Ibers,[70] who note that an A-H···B hydrogen bond probably exists if both the A-H and H···B separations are less than the sum of the van der Waals' radii of the two atoms (i.e., H and A or H and B) even if the A···B separation exceeds the sum of the van der Waals' radii of A and B; the values for the atomic van der Waals' radii used are from the tabulation of Pauling.[71]

The intramolecular hydrogen bonding is relatively sim-

Table V. Possible A–H···B Hydrogen Bonds in $CuCl_4(HACT)_2 \cdot H_2O$

A	B	A···B, Å	A–H···B angle, deg
N(3)	Cl(2)	3.262	160.5
N(6)	Cl(2)	3.331	156.9
N(1)	O(1)	2.921	161.4
N(9)	Cl(1)	2.971	130.6
N(1)	Cl(2)	3.276	159.6
N(6)	Cl(2)	3.331	132.4
N(3)	Cl(2)	3.262	151.7
O(1)	Cl(1)	3.231	128.0
O(1)	N(7)	3.260	154.2

ple, consisting only of possible N(9)-H(9)···Cl(1) hydrogen bonds with an N(9)···Cl(1) separation of 2.971 and an N(9)-H(9)···Cl(1) angle of 130°; as was noted earlier, it is possible that this interaction is responsible for the slight reduction from 90° of the N(8)-Cu-Cl(1) angle.

The unprotonated triazole atom N(7) apparently accepts a hydrogen bond from the water molecule, with an O(1)···N(7) separation of 3.26 Å and an O(1)-HO(1)···N(7) angle of 154°. This may be a bifurcated hydrogen bond, since there is also an O(1)···Cl(1) separation of 3.23 Å with an associated O(1)-HO(1)···Cl(1) angle of 128°; this latter angle indicates that, at best, the HO(1)···Cl(1) interaction is very weak. The amine and amidine protons all form probable intermolecular hydrogen bonds with the axial chlorine atoms of neighboring molecules with the exception of HN(1), which interacts with the water oxygen atom O(1).

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Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number JACS-75-2376.

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