two phenyl groups from two different adjacent molecules and an acetone molecule of solvation. If the Mn-Cl direction corresponded with the normal to the plane of the nitrogens, the contact between PH44 and the chloride would be prohibitively close. Thus, the distortion of the square pyramidal symmetry appears to be the result of a compromise between molecular packing constraints. In fact, since three of the phenyl groups are inclined about 50° to the NLS plane while the one making the close contact with the chloride is inclined 77° would seem to indicate that the rotation of this phenyl group is also participating in the compromise.

The anisotropic temperature factors of the (Cl)Mn(TPP) (Table I) generally increase as the distance of the atoms increases from the center of the molecule. Such behavior has been observed previously with TPP[21] and $(H_2O)Mg(TPP)$[22] and is due to a small quasi-rigid body angular oscillation of the molecule. Thus, the peripheral atoms of the molecule have reduced peak heights and consequently, increased standard deviations in atomic parameters.

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Supplementary Material Available: A table of $|F_o|$ and $|F_c|$ (Table I), hydrogen atom coordinates (Table II), and parameters of least-squares planes (Table III) (9 pages). Ordering information is given on any current masthead page.

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Interaction of Metal Ions with 8-Azapurines. 3. Synthesis and Structure of Trichloro(8-azaadeninium)zinc(II)·

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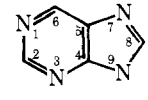
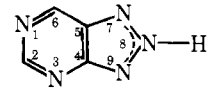
Abstract: The complex trichloro(8-azaadeninium)zinc(II), $[ZnCl_3(AAH)]$, $C_4H_5Cl_3N_6Zn$, has been synthesized, and its crystal and molecular structure have been determined from three-dimensional x-ray counter data. The complex crystallizes in the triclinic space group $P\bar{1}$ with two molecules in a cell of dimensions: a = 6.516 (16), b = 10.389 (25), c = 7.736 (17) Å; α = 107.13 (12), β = 86.01 (11), γ = 93.31 (11)°. The observed and calculated densities are 2.03 (3) and 2.056 g cm^{-3}, respectively. Least-squares refinement of 746 data obtained from a crystal of poor quality has led to a conventional R factor (on F) of 0.073. The structure consists of monomeric $[ZnCl_3(AAH)]$ units which are hydrogen bonded to each other. The zinc(II) ion coordinates to the azapurine cation through the N(3) atom only with a Zn-N bond length of 2.07 (1) Å. This type of coordination is unique for purines and their analogues. The geometry around the zinc(II) center is roughly tetrahedral, the three remaining sites being occupied by chloride ions at distances of 2.215 (5) to 2.267 (5) Å. The purine ring is protonated at N(1), C(2), and N(8) only. There is no intramolecular hydrogen bonding, but the intermolecular hydrogen bonding is extensive. The geometry of the azapurine ligand is consistent with that observed in other studies.

A recent review[1] of crystallographic studies of metal-purine complexes has revealed two basic trends concerning the site of metal coordination. In the majority of cases, if the purine (A) is substituted in the N(9) position, the metal will coordinate to N(7); the only known exception to this rule occurs[2] in the trichloro(9-methyladenine)zincate(II) ion, $[ZnCl_3(9MA)]^-$, where the metal coordinates to N(1). In unsubstituted purines, the metal will coordinate to the imidazole nitrogen which is protonated in the free neutral ligand (N(7) for theophylline and N(9) for all other naturally occurring purines[1]); the only known exception to this rule is[3] trichloro(adeninium)zinc(II), $[ZnCl_3(AH)]$, where the metal coordinates to N(7). The N(9) position in this compound is protonated.



A, purine



B, 8-azapurine

Since some of the 8-azapurines (B) are known to be of chemotherapeutic value,[4,5] metal interactions with these purine analogues have been of considerable interest in our laboratory. Crystallographic[6] and chemical[7,8] studies of 8-azapurine nu-

cleosides have shown that the orientation of the purine ring relative to the sugar is altered when a nitrogen atom is substituted into the 8-position of the purine; this change in orientation may lead to a disruption of the hydrogen bonding scheme of the nucleic acid into which the azapurine nucleoside is incorporated.[9,10] Metal coordination to the azapurines may also influence the resulting hydrogen-bonding interactions by further altering the electronic properties of the ring.

The results of our studies have indicated that the trends found in metal-purine interactions (vide supra) are not observed in metal-azapurine interactions. Thus, the reaction of Cu^{2+} and 8-azaadenine resulted in coordination to N(8) followed by hydrolysis of the azapurine at the C(2) position forming $[CuCl_4(HACT)_2]$, where HACT is (5-amino-4-carboxamidinium)[1,2,3]triazole.[11] Unfortunately, there are no crystallographic data concerning the site of protonation in the triazole portion of free, neutral 8-azaadenine. Pullman and Pullman, however, have calculated that the preferred site for the proton is N(7).[12] Moreover, the interaction of Cd^{2+} with 8-azahypoxanthine (AHX) forms[13] $[Cd(H_2O)_4(AHX)_2]$, in which the metal coordinates to N(7) of the azahypoxanthine anion. Crystallographic data reveal that the N(8) position is protonated in free, neutral 8-azahypoxanthine.[14] In addition, the N(9) and N(8) positions in $Cd(H_2O)_4(AHX)_2$ are unprotonated. Clearly, therefore, neither of these complexes fits the pattern established for the naturally occurring purines. The present study involves the interaction of Zn^{2+} with 8-azaadenine under acidic conditions. We report here the results of that interaction and the crystal structure of the product, trichloro(8-azaadeninium)zinc(II), in which the metal coordinates to N(3); this is the first reported case of unidentate metal-N(3) coordination in metal-purine or purine analogue complexes.

Experimental Section

The complex was prepared using a method similar to that used by Weitzel and Spehr[15] to form the guanine analogue. After several days, colorless crystals of trichloro(8-azaadeninium)zinc(II), $[ZnCl_3(AAH)]$, precipitated from the acidic solution.

On the basis of Weissenberg and precession photographs, the crystal was assigned to the triclinic system with a space group of either $P1$ or $P\bar{1}$. Subsequent refinement of the structure suggests that the space group is probably $P\bar{1}$. Using the least-squares method of Busing and Levy,[16] the lattice constants were refined to be a = 6.516 (16) Å, b = 10.389 (25) Å, c = 7.736 (17) Å, α = 107.13 (12)°, β = 86.01 (11)°, and γ = 93.31 (11)°. The observed density, obtained by flotation in iodomethane and methylene chloride, is 2.03 (3) g cm^{-3}. The calculated density, using two formula units per unit cell, is 2.056 g cm^{-3}. Hence, in space group $P\bar{1}$, no crystallographic symmetry is imposed on the molecules.

A parallelepiped crystal was mounted in grease in a sealed capillary tube to avoid exposure to air, since earlier work with the crystals indicated that the compound was hygroscopic. Using the narrow-source, open-counter ω-scan technique to test the mosaicity of the crystal, it was found that the peaks were severely split, indicating a multiple crystal. However, since the remaining crystals were rapidly decomposing, we decided to use this crystal for data collection. Twelve reflections were centered at a takeoff angle of 1.0° through a narrow vertical slit; the most intense peak of the split reflections was used in each case. These 12 reflections were used as a basis for the least-squares refinement. The cell parameters and orientation matrix were refined using the logic of Busing and Levy[16] in the PDP-8/L computer.

Data were collected on an automatic four-circle Picker diffractometer using Mo Kα radiation and a graphite monochromator. The takeoff angle for collecting intensity data was 1.3°, which was the angle at which the peak intensity of a strong reflection was approximately 90% 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 at a scan rate of 1.0°/min using the θ-2θ scan technique. To allow for the presence of both Kα_1 and Kα_2 radiations and for the splitting of the peaks, the scan range was from 1.0° below the calculated Kα_1 peak position to 1.0° above the Kα_2 peak position. At both ends of the scan, stationary-counter, stationary-crystal background counts of 20 s were taken.

A unique data set having 2θ(Mo) $\leq$ 45° was obtained, yielding 885 intensities. After every 100 reflections, the intensities of three standard reflections were measured. The crystal moved several times during data collection and was recentered in the beam each time; data collection was resumed at a point before which the intensities of the standards showed sharp decreases. At this stage of the data collection, the crystal began to decompose in the x-ray beam; fortunately, it appeared that few data with 2θ(Mo) > 45° were greater than background, and so data collection was terminated at 2θ = 45° without severely reducing the number of available data. The crystal decomposition was quite sudden, since the standards had remained essentially constant for the first 885 data but then diminished in intensity by more than 50% while the next 100 data were gathered.

Data processing was carried out as described by Ibers and coworkers.[17] The intensities were assigned standard deviations according to the formula $\sigma(I) = [C + 0.25(t_s/t_b)^2(B_H + B_L) + (pI)^2]^{1/2}$ after the data were corrected for background. A value of 0.060 was given p, the term in the expression used to prevent extremely high weight being given to a very intense reflection.[18] The values of I and $\sigma(I)$ were corrected for Lorentz and polarization effects. Since the crystal dimensions were not obtained before decomposition occurred, no absorption correction was made. Of the 885 reflections, 746 independent intensities exceeded twice their estimated standard deviations. These 746 data were the only ones used in the refinement of the structure.

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 Zn and Cl were taken from Volume IV of "International Tables for X-Ray Crystallography",[19] those for N were from Cromer and Waber,[20] those for C from tabulation of Ibers,[21] and those for H from Stewart, Davidson, and Simpson.[22] The effects of the anomalous dispersion of zinc and chlorine were included in calculations of F_c,[23] the values of $\Delta f'$ and $\Delta f''$ being taken from the tabulation of Cromer and Liberman.[24]

The positions of the zinc atom and one of the chlorine atoms were determined from a three-dimensional Patterson function;[25] the locations of the other Cl, C, and N atoms were obtained from and refined in subsequent difference Fourier maps and least-squares calculations. 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 0.121 and 0.151, respectively. Anisotropic refinement of these atoms yielded R_1 = 0.070 and R_2 = 0.086. A difference Fourier map revealed the locations of the three ring hydrogen atoms and one of the amine protons. The ring hydrogen atoms were placed in positions calculated on the basis of sp^2 geometry at C or N and C–H or N–H bond lengths of 0.95 Å. The position of the remaining amine proton was similarly calculated, and all five protons were included in subsequent least-squares calculations. A final least-squares refinement, in which all nonhydrogen atoms were varied anisotropically and all hydrogen atoms were placed in calculated positions and not varied, yielded R_1 = 0.065 and R_2 = 0.080. The anisotropic thermal parameters for all of the carbon and nitrogen atoms of the pyrimidine portion of the azapurine ligand were nonpositive definite after this refinement. This is clearly in part a reflection of the poor quality of the data set which resulted from this crystal, but is also partly due to the low observation to variable ratio of 5.87:1. Consequently, two subsequent least-squares cycles were run in which the zinc and chlorine atoms were refined anisotropically while the carbon and nitrogen atoms were refined isotropically; the hydrogen atoms were treated as above. This refinement, involving 746 observations and 77 variables, converged to values of R_1 and R_2 of 0.073 and 0.095. The isotropic thermal parameters of the azapurine ring atoms were all reasonable, with all B values in the range 2.3–3.4 Å^2, and so this refinement was accepted as providing the best description of the structure available.

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 0.31σ, which is taken as evidence for convergence. A final difference Fourier map showed several peaks of approximately

Table I. Positional Parameters for $[ZnCl_3(AAH)]$

Atom	X	Y	Z
Zn	0.0292 (2)	−0.2005 (1)	0.1352 (2)
Cl(1)	0.2252 (4)	−0.0370 (2)	0.3203 (4)
Cl(2)	−0.0080 (4)	−0.3778 (3)	0.2447 (4)
Cl(3)	−0.2618 (4)	−0.1212 (3)	0.0843 (4)
N(1)	0.2549 (5)	−0.1911 (9)	−0.3887 (14)
C(2)	0.1393 (18)	−0.1890 (11)	−0.2359 (17)
N(3)	0.1819 (13)	−0.2490 (8)	−0.1184 (12)
C(4)	0.3609 (17)	−0.3207 (10)	−0.1686 (16)
C(5)	0.4885 (18)	−0.3264 (11)	−0.3196 (16)
C(6)	0.4343 (18)	−0.2565 (12)	−0.4413 (18)
N(6)	0.5402 (14)	−0.2523 (9)	−0.5902 (13)
N(7)	0.6507 (14)	−0.3993 (9)	−0.3243 (13)
N(8)	0.6086 (14)	−0.4363 (9)	−0.1746 (13)
N(9)	0.4368 (14)	−0.3927 (9)	−0.0693 (13)
HN(1)[a]	0.206	−0.142	−0.463
HC(2)	0.018	−0.134	−0.214
HN(6)	0.719	−0.249	−0.609
HN(6)′	0.476	−0.256	−0.701
HN(8)	0.698	−0.494	−0.141

[a] The positional parameters of hydrogen atoms were not varied.

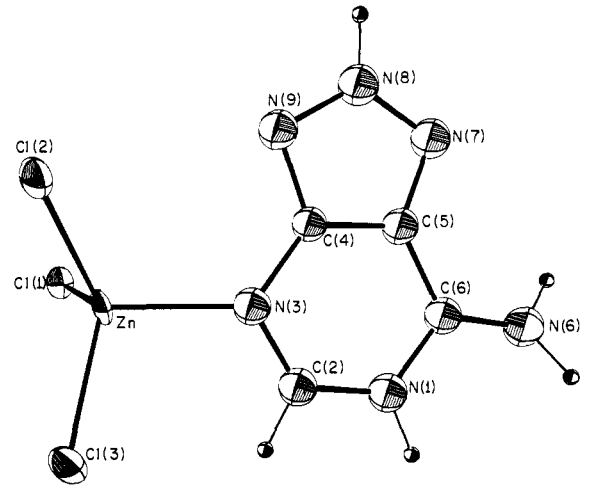


Figure 1. View of a single molecule of $[ZnCl_3(AAH)]$. Hydrogen atoms are shown as spheres of arbitrary size, other thermal ellipsoids are at the 40% probability level.

1.2 e Å^{-3} in the vicinity of the zinc atom and peaks of approximately 0.8 e Å^{-3} in the area of the chlorine atoms. This residual density is probably due to the lack of an absorption correction. No other peaks larger than 0.5 e Å^{-3} were observed.

Tables I and II contain the positional and thermal parameters obtained from the last least-squares cycle, along with their standard deviations as estimated from the inverse matrix. The numbering scheme is that commonly used in purine systems. A compilation of observed and calculated structure amplitudes is available.

Description of the Structure

Figure 1 shows a view of the structure, which consists of monomeric, four-coordinate $[ZnCl_3(AAH)]$ molecules (where AAH is protonated 8-azaadenine). The coordination around the zinc(II) atom is distorted tetrahedral and involves the three chlorine atoms and the N(3) atom of the azapurine ring. Tables III and IV contain the intramolecular distances and bond angles, respectively. The zinc-chlorine distances of 2.267 (5), 2.238 (6), and 2.215 (5) Å are in the normal range of tetrahedral Zn-Cl distances,[2,3,26] as is the Zn-N distance of 2.073 (11) for Zn-N distances.[2,3,27] The bond lengths associated with the ring are within the range of bond lengths seen in other 8-azapurine compounds.[6,14,28-33]

The angles associated with these five atoms are Cl(1)-Zn-Cl(2), 109.1 (2)°; Cl(2)-Zn-Cl(3), 115.1 (2)°; Cl(1)-Zn-Cl(3), 111.4 (2)°; Cl(1)-Zn-N(3), 106.5 (3)°; Cl(2)-Zn-N(3), 111.8 (3)°; and Cl(3)-Zn-N(3), 102.3 (3)°. The variations among these Cl-Zn-Cl angles may be due to the extensive intermolecular hydrogen bonding associated with the crystal (vide infra).

The most unusual aspect of this interaction is the metal coordination at N(3). Although there have been several reports of bridged bidentate N(3)-N(9) coordination in metal-purine compounds,[34-38] this is the first case of unidentate coordination to N(3). As previously noted, the Zn-N(3) bond distance of 2.073 (11) Å is comparable to other Zn-N distances (notably, the Zn-N(7) distance of 2.094 Å in $[ZnCl_3(AH)]^3$ and the Zn-N(1) distance[2] of 2.05 Å in $[ZnCl_3(9MA)]^-$); therefore, these three interactions are of similar strength. Moreover, coordination to N(3) supports the suggestion that there is considerable basicity associated with the N(3) atom in 8-

Table II. Thermal Parameters for $[ZnCl_3(AAH)]$

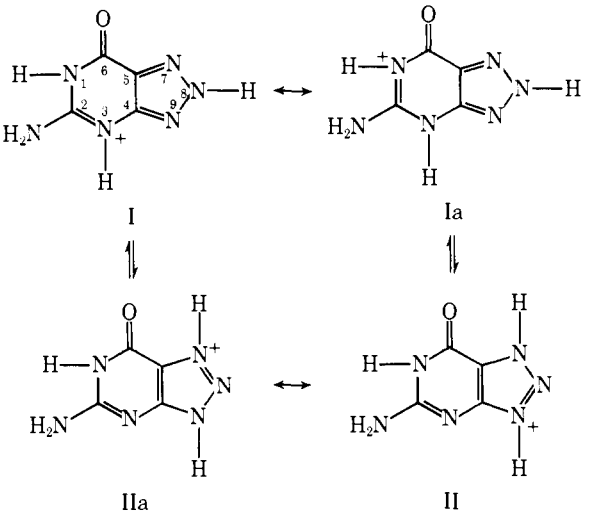
Atom	β_{11}[a] or B (Å^2)	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Zn	0.0111 (5)	0.0081 (2)	0.0093 (5)	0.0044 (2)	0.0081 (4)	0.0033 (2)
Cl(1)	0.0156 (8)	0.0077 (4)	0.0111 (8)	0.0030 (4)	0.0039 (7)	0.0034 (4)
Cl(2)	0.0183 (9)	0.0083 (4)	0.0163 (9)	0.0048 (4)	0.0100 (8)	0.0058 (5)
Cl(3)	0.0123 (8)	0.0096 (4)	0.0165 (9)	0.0039 (4)	0.0039 (7)	0.0042 (5)
N(1)	3.1 (2)					
C(2)	2.9 (2)					
N(3)	2.7 (2)					
C(4)	2.3 (2)					
C(5)	2.7 (2)					
C(6)	2.8 (2)					
N(6)	3.4 (2)					
N(7)	3.3 (2)					
N(8)	3.3 (2)					
N(9)	3.0 (2)					
HN(1)[b]	5.0					
HC(2)	5.0					
HN(6)	5.0					
HN(6)′	5.0					
HN(8)	5.0					

[a] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] The thermal parameters of the hydrogen atoms were not varied in the least-squares process.

Table III. Intramolecular Distances in [$ZnCl_3$(AAH)]

Atoms	Distance, Å	Atoms	Distance, Å
Zn-Cl(1)	2.267 (5)	C(5)-C(6)	1.420 (14)
Zn-Cl(2)	2.238 (6)	C(6)-N(1)	1.363 (15)
Zn-Cl(3)	2.215 (5)	C(6)-N(6)	1.311 (14)
Zn-N(3)	2.073 (11)	C(4)-N(9)	1.352 (12)
N(1)-C(2)	1.352 (14)	N(9)-N(8)	1.355 (13)
C(2)-N(3)	1.296 (13)	N(8)-N(7)	1.330 (12)
N(3)-C(4)	1.391 (14)	N(7)-C(5)	1.328 (14)
C(4)-C(5)	1.374 (15)		

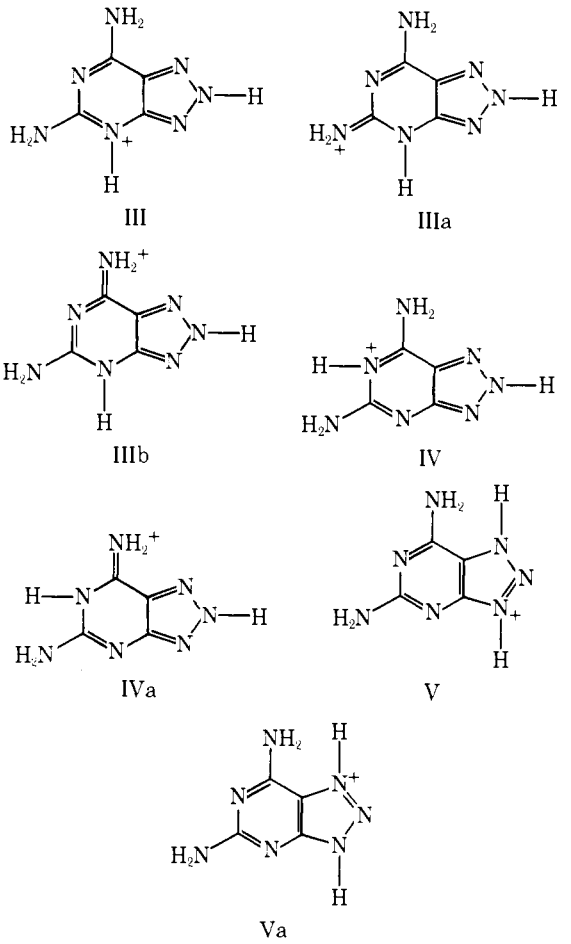
azapurine systems.[31] In 8-azaguanine hydrochloride[31] and hydrobromide,[32] the protons are located on N(1), N(8), and N(3) (I). This tautomer has two resonance contributors, with



I Ia IIa II

the positive charge delocalized over N(3) and N(1) (I, Ia). An equally plausible tautomer is one in which the protons are located on N(1), N(7), and N(9) (II); this tautomer would also have two resonance contributors with the positive charge delocalized over N(9) and N(7) (II, IIa).

A similar result is found in 8-aza-2,6-diaminopurine sulfate monohydrate.[29] In this structure, the protons are located on N(3) and N(8), and there is no proton on N(1) (III). There are three resonance contributors to this tautomer (III, IIIa,b) and two other reasonable tautomers of this compound, one with protons on N(8) and N(1) (IV) and one with protons on N(7) and N(9) (V). Both of these tautomers have two resonance contributors (IV, IVa and V, Va, respectively). In both of these 8-azapurine cations, the N(3)-N(8) tautomer is the observed



III IIIa IIIb IV IVa V Va

tautomer in the solid state. In contrast, the N(3) atom does not appear to have the same basicity in purines, and examination[1] of the structures of purine cations and their metal complexes demonstrates that N(3) is the least-readily protonated nitrogen atom, so that in complexes or cations in which only one nitrogen atom is unprotonated (or uncoordinated) that atom is invariably N(3). This does not imply that, in 8-azapurines, atom N(3) is more basic than N(1); it merely suggests that N(3) does exhibit more basicity than in the purines.

As far as the present ligand [8-azaadenine] is concerned, we find that in 8-azaadenine hydrochloride,[39] hydrogen bonding interactions with chlorine atoms indicate that the extra proton is on N(1) rather than on N(3). The metal coordination to N(3) may be attributed, in part, to the relative softness of the metal. It is noteworthy that Cu^{2+} coordinates to N(9) of

Table IV. Bond Angles in [$ZnCl_3$(AAH)]

Atoms	Angle, deg	Atoms	Angle, deg
Cl(1)-Zn-Cl(2)	109.1 (2)	C(5)-C(6)-N(1)	112.9 (12)
Cl(2)-Zn-Cl(3)	115.2 (2)	C(5)-C(6)-N(6)	125.7 (11)
Cl(1)-Zn-Cl(3)	111.4 (2)	N(1)-C(6)-N(6)	121.4 (11)
Cl(1)-Zn-N(3)	106.5 (3)	C(5)-N(7)-N(8)	100.2 (10)
Cl(2)-Zn-N(3)	111.8 (3)	N(7)-N(8)-N(9)	119.6 (9)
Cl(3)-Zn-N(3)	102.3 (3)	N(8)-N(9)-C(4)	98.9 (9)
C(6)-N(1)-C(2)	124.8 (10)	HN(1)-N(1)-C(6)	118.6
N(1)-C(2)-N(3)	125.2 (10)	HN(1)-N(1)-C(2)	116.7
C(2)-N(3)-C(4)	112.3 (10)	HC(2)-C(2)-N(1)	115.0
N(3)-C(4)-C(5)	126.1 (10)	HC(2)-C(2)-N(3)	119.7
N(3)-C(4)-N(9)	123.6 (12)	HN(6)-N(6)-C(6)	125.2
C(5)-C(4)-N(9)	110.3 (10)	HN(6)'-N(6)-C(6)	122.9
C(4)-C(5)-C(6)	118.6 (11)	HN(6)'-N(6)-HN(6)	111.9
C(4)-C(5)-N(7)	111.1 (10)	HN(8)-N(8)-N(7)	120.7
C(6)-C(5)-N(7)	130.3 (13)	HN(8)-N(8)-N(9)	119.7

Table V. 8-Azapurine Angular Dependence (deg) on Extraannular Substitution

Purine ring atom	Substitution			Complex		
	None	H	C	$CuCl_4(HACT)_2$[11]	$Cd(H_2O)_4(AHX)_2$[13]	$ZnCl_3(AAH)$
N(1)	120.3 (3)	127.2 (5)			124.3 (9)	124.8 (10)
	119.6-120.7	125.9-128.9			protonated	protonated
N(3)	111.9 (3)	117.7 (5)			113.9 (8)	112.3 (10)
	110.7-112.5	116.9-119.2			none	metalated
N(7)	102.9 (5)					
	102.4-103.3					
	H on N(8)			108.0 (3)	106.2 (7)	100.2 (10)
	108.4 (3)			H on N(9)	triazole ring	H at N(8)
	108.2-108.6			metalated at N(8)	has no proton	
	H or C on N(9)					
N(8)	108.2 (3)	116.8 (5)		107.7 (3)	111.9 (8)	119.6 (9)
	108.0-108.3	116.1-117.6		H on N(9)	triazole ring	protonated
	H or C on N(9)			metalated	has no proton	
N(9)	101.9 (5)	110.1 (2)	109.8	111.5 (3)	106.6 (7)	98.9 (9)
	101.4-102.5	110.4-109.7		protonated	triazole ring	H at N(8)
	H on N(8)			metalated at N(8)	has no proton	

protonated adenine[40] while Zn^{2+} coordinates to N(7) of the same ligand.[3] Also, the soft metal Cd^{2+} coordinates to N(7) of 8-azahypoxanthine[13] rather than to the more basic N(8) or N(9). In $[ZnCl_3(9MA)]^-$, however, Zn^{2+} coordinates[2] to N(1).

All three of these apparent anomalies (which were also noted in the introductory section, above) may be caused by intramolecular hydrogen bonding. Thus, in $[ZnCl_3(AH)]$[3] and $[ZnCl_3(9MA)]^-$,[2] there is a hydrogen bond formed between the N(6) proton and a coordinated chlorine atom; there is also a hydrogen bond formed between the O(6) atom and a coordinated water molecule in $[Cd(AHX)_2(H_2O)_4]$.[13] However, no such intramolecular hydrogen bond is observed in $[ZnCl_3(AAH)]$, suggesting that the N(3) coordination in $[ZnCl_3(AAH)]$ is preferred even to an N(1) coordination which would allow the N(6)-chlorine intramolecular hydrogen-bonding interaction.

The sites of protonation are not unusual. As previously noted, hydrogen bonding in 8-azaadenine hydrochloride[39] indicated that the N(1) atom is protonated; unfortunately, the triazole proton could not be located in 8AA·HCl. In $[CuCl_4(HACT)_2]$,[11] the Cu^{2+} atom is coordinated to N(8), suggesting that this position has considerable basicity; the location of the triazole proton at N(8) in the present structure offers further evidence for the basicity of this nitrogen atom.

Another interesting aspect of the reaction is the lack of degradation of the 8-azaadenine ligand. Albert[41] has reported the degradation in boiling, dilute acid of many 8-azapurines, including 8-azaadenine. This hydrolysis at C(2) is also seen in adenine N(1)-oxide with 1 M HCl at 100 °C.[42] When Cu^{2+} reacts with 8-azaadenine in 0.36 M HCl warmed to less than 50 °C, coordination occurs at N(8) and the ring is hydrolyzed at C(2) forming $[CuCl_4(HACT)_2]$.[11] The formation of 8-azaadenine hydrochloride[39] under identical conditions without the addition of Cu^{2+} ions suggested that it was the interaction of the Cu^{2+} with the ring at N(8) that encouraged the degradation rather than the presence of the acid. The conditions of the present experiment included lowering the pH of the solution to approximately pH 1 through the addition of concentrated hydrochloric acid but did not include heating the solution. Under these conditions the ring was not hydrolyzed; whether the cause of this lack of degradation is due to the absence of heating or to some increased stability from the Zn^{2+} interaction at N(3) cannot be discerned. However, the present result offers further compelling evidence that the degradation[11] in $[CuCl_4(HACT)_2]$ was brought about by the copper coordination at N(8).

A review of the ring geometries of all reported 8-azapurine compounds[6,14,28-33] shows several interesting trends. Table V contains angular values found in these 8-azapurines and in the three metal-8-azapurine complexes. Each entry in the substitution section contains the average angle, the number of compounds included in the average in parentheses, and the range of values observed. The N(7) entry is divided into two classes according to the protonation site in the triazole ring. In the complex section, the type of substitution pertinent to the angle is described. Only the triazole nitrogen atoms are listed for the copper complex since the parent 8-azaadenine ligand was hydrolyzed at C(2).[11]

Ringertz[43] has found that in purine compounds, protonation or substitution at a nitrogen atom increases the angle associated with that nitrogen. As can be seen in Table V, this trend is also found in the 8-azapurines. For example, the C(6)-N(1)-C(2) angle in compounds where the N(1) atom is unprotonated has an average value of 120.3°; protonation at this site increases the angle to an average value of 127.2°. The average unprotonated angle at N(3) is 111.9° while the average protonated angle is 117.7°. This increase in angle is also seen at the triazole nitrogen atoms.

An additional observation concerning the triazole nitrogen atoms was suggested by Sletten et al.[28] early in the crystallographic work on 8-azapurines and is supported by the accumulated data. In their discussion of 8-azaguanine,[28] they observe that when the angles associated with N(7) and N(9) are approximately equal, the triazole proton is located on N(8); when the two angles differ significantly, the proton is located on the nitrogen atom of the pair that possesses the larger angle. According to our table, the 8-azapurine compounds studied to date follow this trend. When, for example, the proton is on N(8), the angles associated with N(7) and N(9) are approximately 102°. When the N(7) angle is an average of 108.4° and the N(9) angle is an average of 110°, the proton is on N(9). Moreover, the average N(8) angle of 108.2° in this latter case is approximately equal to the N(7) angle.

In the review of metal purine complexes,[1] it was shown that metalation at the nitrogen atoms did not alter the geometries of the coordinated purines; this is also true in the 8-azapurine complexes. In $[CuCl_4(HACT)_2]$,[11] metal coordination occurs at N(8) and protonation is at N(9). The angle of 107.7 (3)° associated with N(8) is comparable to the 108.2° average angle of 8-azapurines with a proton on N(9); thus, it is the protonation and not the metalation which is governing the angle at this position. In $[Cd(H_2O)_4(AHX)_2]$,[13] the metal is coordinated at N(7), and there is no triazole proton. The angle at N(7) is 106.2 (7)°, and it is most interesting to note that this

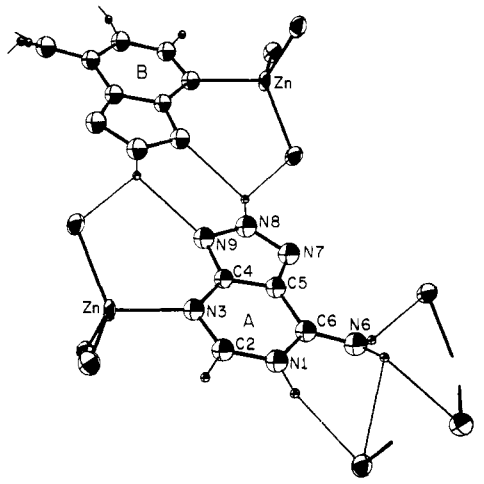


Figure 2. The intermolecular hydrogen bonding in $[ZnCl_3(AAH)]$. The chlorine atoms are represented by partially shaded ellipsoids, and the zinc atoms by completely shaded ellipsoids. The top molecule is related to the lower molecule by inversion.

angle is midway between the average angle of N(7) when N(9) is protonated and the average angle of N(7) when N(8) is protonated. The angles at N(7) and N(9) are once again very symmetric. Metalation at N(3) in $[ZnCl_3(AAH)]$ leaves the angle at N(3) virtually unchanged with respect to the angular range observed for azapurines which are unprotonated at N(3).

The angles associated with protonation follow the trends in extraannular substitution noted by Ringertz.[43] N(1) is protonated in both $[Cd(H_2O)_4(AHX)_2]$[13] and $[ZnCl_3(AAH)]$; the associated angles of 124.3 (9)° and 127.5 (10)°, respectively, correspond well with the angular range of protonated N(1) atoms. Likewise, the N(3) angle in $[Cd(H_2O)_4(AHX)_2]$[13] of 113.9 (8)° corresponds to the range of angles of unprotonated N(3) atoms.

The difference in the N(7) and N(9) angles in $[CuCl_4(HACT)_2]$[11] would correctly suggest that the proton is located on N(9), as would the similarity of the two angles in $[ZnCl_3(AAH)]$ suggest that the proton is on N(8). The angle at N(8) in this complex is the largest reported; in order to maintain planarity, the N(7) and N(9) angles are correspondingly small.

The azapurine ring is approximately planar, with no atom deviating from the best nine-atom least-squares plane by more than 0.02 Å, and the extracyclic N(6) atom is also in this plane; N(3) and N(7) show the greatest deviations from the plane being 0.018 and 0.019 Å below the plane, respectively. Evaluations of the deviations of the hydrogen atoms would be misleading since these atoms are in calculated positions. The azapurine could also be viewed as being comprised of two approximately planar rings with an angle of 55′ between them. The triazole portion has no atom deviating from the best five-atom least-squares plane by more than 0.01 Å, and the pyrimidine plane has no atom deviating by more than 0.015 Å from the best six-atom least-squares plane.

The hydrogen bonding interactions, shown in Figure 2, are considerable. The azapurine ligands provide four potential donor sites and two potential acceptor sites, and the chlorine ligands provide three additional acceptor sites. All but one of these sites are involved in a hydrogen-bond interaction. The distances and angles associated with these possible hydrogen bonds are listed in Table VI. The criterion used for inclusion of an interaction in Table VI is that of Hamilton and Ibers,[44] 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.[45]

Table VI. Possible A—H···B Bonds in $ZnCl_3(AAH)$

A	B	A···B, Å	H···B, Å	A—H···B angle, deg
N(1)	Cl(1)	3.151	2.246	157
N(6)	Cl(2)	3.285	2.312	142
N(6)	Cl(1)	3.368	2.833	116
N(6)	Cl(3)	3.327	2.886	110
N(8)	Cl(2)	3.254	2.441	142
N(8)	N(9)	2.949	2.370	118

All of the hydrogen bonds are intermolecular. The azapurine rings are linked in space through an N(8)···N(9) hydrogen bond at a distance of 2.949 Å. This N(8) proton may be involved in a bifurcated hydrogen bond since there is also a N(8)···Cl(2) separation of 3.254 Å; analysis of the two angles associated with these interactions suggests that the N(9)···N(8) interaction may be the weaker of the two. All of the chlorine atoms are involved in hydrogen bonds with either amine hydrogen atoms or ring hydrogen atoms; these interactions may be responsible for the distortion of the tetrahedral angles around the Zn^{2+} atom.

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Supplementary Material Available: A listing of observed and calculated structure amplitudes (5 pages). For ordering information, consult any current masthead page.

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The Chemical Evolution of a Nitrogenase Model. 14. Stoichiometric Reactions of Complexes of Molybdenum(V), Molybdenum(IV), and Molybdenum(III) with Acetylene and Nitrogen

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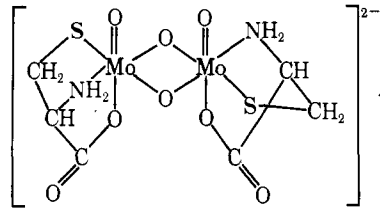
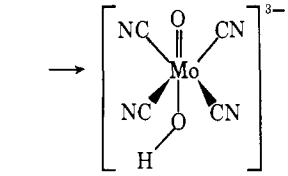
Abstract: The binuclear complex of oxomolybdate(V) with L-(+)-cysteine and related complexes with other ligands disproportionate in alkaline solutions into derivatives of oxomolybdate(IV) and -(VI). The Mo(IV) complexes generated in this fashion act as two-electron reductants with respect to acetylene and nitrogen. Acetylene is reduced exclusively to ethylene at low Mo(IV) concentrations. At higher concentrations of Mo(IV), ethane, 1,3-butadiene, and 1-butene are formed in addition to ethylene. Under the alkaline reaction conditions employed, nitrogen is not reduced to ammonia or hydrazine. However, diimide is formed as evidenced by a marked stimulation of hydrogen evolution, which is inhibited by allyl alcohol; both reactions are characteristic of diimide in strongly alkaline aqueous solution. Reactions of Mo(IV) species generated by the alkali decomposition of the ion $[Mo(O)_2(CN)_4]^{4-}$ with acetylene and nitrogen produced similar results. Reactions of complexes of Mo(III) with acetylene occur with low efficiency and are accompanied by the evolution of copious amounts of hydrogen, in contrast to the behavior of nitrogenase. Hence, the substrate reducing site of nitrogenase more likely contains a mononuclear Mo(IV) rather than a Mo(III) species in the active reduced form.

In recent papers of this series[1,2] we have demonstrated that mononuclear cyano complexes of oxomolybdate(IV) act as two-electron reductants in reactions with acetylene or nitrogen in mildly acidic and alkaline solutions. Because little is known about the behavior of complexes of oxomolybdate(IV), and in view of the continuing discussions concerning the valence changes of molybdenum in functional nitrogenase (N_2-ase), we have continued our studies to include reactions of Mo(IV) species generated in alkaline media, covering base concentrations up to 11 M (NaOH). It is realized that these conditions are no longer "biological", nor does this paper describe further improvements in the development of functional models of N_2-ase. However, since we have previously postulated that Mo(IV) complexes are the active catalysis in the molybdothiol model systems,[3] while other authors have suggested that Mo(III) derivatives are involved,[4] it seemed necessary to further reaffirm our original conclusions. In addition, we also decided to investigate some reactions of Mo(III) complexes to test their behavior under conditions of substrate reduction. The starting point of the present study was our observation[2] that the binuclear complex of oxomolybdate(V) with L-(+)-cysteine ("complex I")[5] reacts with alkaline cyanide to yield salts of the mononuclear cyanocomplexes of oxomolybdate(IV) ["complex II"][6,7] according to reaction eq 1. It thus seemed reasonable to expect that complex I would undergo disproportionation in alkaline solution also in the absence of added cyanide, giving rise to the formation of equilibrium



anion of complex I



anion of the hydroxo form of complex II

amounts of Mo(IV) complexes whose reactions with substrates of N_2-ase could thus be investigated under stoichiometric conditions. We also studied the reactivity of fragments of the ion $[Mo(O)_2(CN)_4]^{4-}$ generated in strongly alkaline solutions with respect to reducible substrates. Although this ion does not disproportionate, it decomposes in alkali with displacement of coordinated cyanide.[6] Hence, Mo(IV) species from different