molecules. The mean W–W distances are equal, within the esd's, being 2.610 (3) Å for McCarley's molecule and 2.61 (1) Å for the present case.

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Registry No. $W_3O_3Cl_5(O_2CCH_3)(PBu_3)_3$, 73470-14-1.

Supplementary Material Available: Table IV (least-squares planes and dihedral angles) and tables of observed and calculated structure factors for the compound (26 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
The University of North Carolina, Chapel Hill, North Carolina 27514

Metal Ion Interactions with 8-Azapurines. Synthesis and Structure of Dichlorobis(8-azaadenine)mercury(II) and Tetraaquabis(8-azahypoxanthinato)mercury(II)

BRADFORD J. GRAVES and DEREK J. HODGSON*

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The crystal and molecular structures of dichlorobis(8-azaadenine)mercury(II), $Hg(C_4N_6H_4)_2Cl_2$, and tetraaquabis(8-azahypoxanthinato)mercury(II), $Hg(C_4N_5OH_2)_2(H_2O)_4$, have been determined from three-dimensional X-ray data collected on an automatic diffractometer. The mercury–8-azaadenine complex crystallizes in space group *Ima*2 of the orthorhombic system with four formula units in a cell of dimensions $a = 27.68$ (3) Å, $b = 6.97$ (1) Å, and $c = 7.21$ (1) Å. The observed and calculated densities are 2.57 (2) and 2.596 g cm^{-3}, respectively. Full-matrix, least-squares refinement of the structure using 587 independent intensities has converged to a final value of the conventional *R* factor (on *F*) of 0.082. The crystal structure contains sheets of a two-dimensional Hg–Cl lattice, which lie parallel to the crystallographic *bc* plane, with the 8-azaadenine ligands extending above and below. The mercury ion sits on the crystallographic twofold axis and is coordinated to two trans purines via N(3) (2.72 (2) Å) and to four chloride ions—two coordinating strongly (2.39 (1) Å) and two weakly (2.92 (1) Å)—resulting in an approximate (2 + 4) octahedral arrangement. The mercury–8-azahypoxanthinato complex crystallizes in space group *C*2/*c* of the monoclinic system with four formula units in a cell of dimensions $a = 6.459$ (5) Å, $b = 11.233$ (8) Å, $c = 20.276$ (17) Å, and $\beta = 94.97$ (5)°. The observed and calculated densities are 2.45 (2) and 2.469 g cm^{-3}, respectively. Refinement of 1522 independent data converged to a final value of *R* of 0.070. The crystallographic twofold axis generates a linear chain of the formula units parallel to the *c* axis. The monomers are linked together by strong base-stacking interactions, and adjacent chains are held together through extensive hydrogen bonding. The mercury atom sits on the crystallographic inversion center and is coordinated to two trans purines through N(9) (2.04 (1) Å) and four water molecules (2.68 (1) and 2.80 (1) Å). Again, the coordination geometry around mercury approximates the (2 + 4) octahedral arrangement but with a cis O–Hg–O angle of 65.0 (4)°.

Introduction

Nucleic acids are the basis on which cells exist, function, and reproduce. Consequently, a large amount of effort is being devoted to the study of these polymers. But because of the difficulty inherent with obtaining precise structural information about even the smallest of these (transfer RNAs),[1-3] a great deal of effort has also been put toward the study of nucleic acid constituents[4] —nucleotides, nucleosides, and bases. Much has been learned from these studies concerning the hydrogen-bonding and stacking interactions[5] that occur as well as the conformational effects that exist within all nucleic acids.

The study of metal ion interactions with these same nucleic acid constituents[6-12] is also of great importance due to the variety of metal ion–nucleic acid interactions observed in biological systems.[13-18] These range from simple interactions such as those with Mg^{2+} and Mn^{2+}, which primarily stabilize the highly anionic nucleic acids, to complex interactions involving metalloenzymes such as the polymerases. Indications are that all nucleotidyl transferases contain Zn^{2+} ions,[19-22]

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including the DNA and RNA polymerases, which function, in part, to synthesize new nucleic acids. In some cases, the zinc ions are thought to interact directly with the nucleic acid template and nascent polymer.[23]

A number of analogues of the nucleic acid constituents have been studied in the past because of their altered biological reactivity, which sometimes includes antineoplastic activity.[24] Such is the case with several azanucleosides (6-azapyrimidine and 8-azapurine nucleosides), the study of which was prompted by the discovery of the antineoplastic activity of 8-azaguanine.[25] The mode of action of these agents is not exactly known but may involve altered (1) sugar-base conformations, (2) hydrogen-bonding interactions, or (3) electronic structures or some combination of the three.[26] One way to study electronic structure is to observe metal ion interactions with the bases. Up until a few years ago, no structural information on metal ion interaction with 8-azapurines existed. The small amount of data[27-29] accumulated since then has shown that they are very different from the interactions with the natural purines.[8] Metal ion coordination to the natural purines will nearly always occur at the imidazole nitrogen atom, which is protonated in the free, neutral base (this is N(9) in most cases), but the 8-azapurines do not adhere to this rule. As part of a continuing study, we wish to report two metal ion–8-azapurine structures: Tetraaquabis(8-azahypoxanthinato)mercury(II) and dichlorobis(8-azaadenine)mercury(II).

Experimental Section

Synthesis of the Compounds. The dichlorobis(8-azaadenine)mercury(II) complex ($Hg(8\text{-}AAd)_2Cl_2$) was prepared by the addition of 25 mL of 40 mM aqueous mercury chloride to a 25-mL solution of 40 mM 8-azaadenine in 0.25 M HCl. This mixture was heated to 35 °C and then allowed to cool slowly, whereupon large aggregates of colorless, needlelike crystals formed, which were filtered and air-dried. Chemical analysis confirmed the $Hg(8\text{-}AAd)_2Cl_2$ formulation.[30] Anal. Calcd for $HgCl_2C_8H_8N_{12}$: C, 17.67; H, 1.48; N, 30.91. Found: C, 17.69; H, 1.46; N, 30.85.

The tetraaquabis(8-azahypoxanthinato)mercury(II) complex ($Hg(8\text{-}AHX^-)_2(H_2O)_4$) was formed in a similar manner, except that a 4 mM aqueous solution of $HgCl_2$ was used and 8-azahypoxanthine (4 mM) was dissolved in a slightly basic medium. The mixture was allowed to stand at room temperature, and after several weeks a number of colorless, rhombohedral crystals formed. These crystals were filtered and air-dried, and analysis confirmed the $Hg(8\text{-}AHX^-)_2(H_2O)_4$ formulation.[30] Anal. Calcd for $HgC_8H_{12}N_{10}O_6$: C, 17.64; H, 2.22; N, 25.71. Found: C, 17.64; H, 2.21; N, 25.59.

X-ray Data Collection. (a) $Hg(8\text{-}AAd)_2Cl_2$. Preliminary examination of crystals from the reaction mixture by precession and Weissenberg photography indicated that they belong to the orthorhombic crystal system. The systematic absences are $h + k + l = 2n + 1$ for hkl and $h = 2n + 1$ for $hk0$. Photographs also revealed that for a general reflection $k = 2n + 1$ is systematically weak. Thus, the photographs suggest space group *Imma* (No. 74) or, after reassigning the axes, *Ima*2 (No. 46). Successful solution and refinement in *Ima*2 confirmed that assignment. In space group *Ima*2 the systematic weakness of the h odd data suggested that Hg lies on the crystallographic twofold axis at $(0, 0, z)$. Accurate cell constants were obtained by least-squares[31] refinement of the diffractometer settings for 12 reflections. The cell constants and their esd's, obtained by this method, as well as additional crystal information, are listed in Table I.

Table I. Crystal Specifications for $Hg(8\text{-}AAd)_2Cl_2$ and $Hg(8\text{-}AHX^-)_2(H_2O)_4$

	$Hg(8\text{-}AAd)_2Cl_2$	$Hg(8\text{-}AHX^-)_2(H_2O)_4$
a, Å	27.68 (3)	6.459 (5)
b, Å	6.97 (1)	11.233 (8)
c, Å	7.21 (1)	20.276 (17)
α, deg	90.0	90.00
β, deg	90.0	94.97 (5)
γ, deg	90.0	90.00
V, Å^3	1390.95	1465.52
fw	543.73	544.84
Z	4	4
D_{obsd}, g mL^{-1} (in $CHBr_3$/CCl_4)	2.57	2.45
D_{calcd}, g mL^{-1}	2.596	2.469
μ, cm^{-1}	252.67 (Cu Kα) 114.59 (Mo Kα)	105.56 (Mo Kα)
space group	*Ima*2	*C*2/*c*

Table II. Data Collection Parameters

parameter	$Hg(8\text{-}AAd)_2Cl_2$		$Hg(8\text{-}AHX^-)_2$-$(H_2O)_4$
radiation	Cu Kα	Mo Kα	Mo Kα
takeoff angle, deg	1.5	1.8	1.8
scan mode	θ–2θ	θ–2θ	θ–2θ
scan range, deg	$2\theta \leqslant 122$	$2\theta \leqslant 60$	$2\theta \leqslant 65$
scan width, deg	1.60	1.70	1.90
scan speed (2θ), deg min^{-1}	1	0.5	1
bkgd, s	10	40	10
dispersion factor	0.285	0.692	0.692

Initial diffraction data were collected on an automatic diffractometer equipped with copper radiation [λ(Cu K$\bar{\alpha}$) is 1.5418 Å], a nickel filter, and a scintillation counter. The crystal used for data collection is bounded by the six crystallographic axial faces and was mounted along the a axis. The crystal dimensions are 0.56 × 0.10 × 0.05 mm in the a, b, and c directions, respectively. Data collection parameters for this data set are listed in Table II. Crystal stability and orientation were checked throughout data collection by monitoring the intensities of three standard reflections. No systematic deviation was detected.

Data reduction was carried out according to the method of Ibers and co-workers.[32] The intensities and their standard deviations were corrected for Lorentz–polarization effects and absorption. A total of 980 reflections was processed of which 361 had $I \geq 3\sigma(I)$.

A second data set was collected on $Hg(8\text{-}AAd)_2Cl_2$ that used molybdenum radiation [λ(Mo K$\bar{\alpha}$) is 0.71069 Å] and a graphite monochromator. A crystal with the same morphology but smaller size (0.80 × 0.08 × 0.03 mm) was used for data collection. The data collected in the same manner as before; data collection parameters are listed in Table II. Data reduction was carried out in a completely analogous manner. The value assigned to the correction factor, p, was 0.05. A total of 1028 reflections was processed of which 587 had $I \geq 3\sigma(I)$.

(b) $Hg(8\text{-}AHX^-)_2(H_2O)_4$. The crystal used for data collection is bounded by the faces (001), (00$\bar{1}$), (110), ($\bar{1}\bar{1}$0), (1$\bar{1}$0), and ($\bar{1}$10) and was mounted along the b axis, which is parallel to the long diagonal of the rhombic face. The distances separating the pairs of opposite faces listed above are 0.58, 0.48, and 0.51 mm, respectively. Additional crystal data are listed in Table I. Preliminary Weissenberg and precession photographs suggested that the crystals belong to the monoclinic system. The systematic absences are $h + k = 2n + 1$ for hkl and $l = 2n + 1$ for $h0l$. The photographs also revealed a systematic weakness of $l = 2n + 1$ for a general reflection. Thus, the space group could be either *Cc* (No. 12) or *C*2/*c* (No. 15), but the observed

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systematic weakness suggests $C2/c$. Eventual structural solution and refinement in $C2/c$ and failure to obtain significantly improved results in Cc confirms $C2/c$ as the correct space group. Accurate cell constants and their esd's were obtained as previously described and are listed in Table I.

Diffraction data were collected with use of molybdenum radiation and a graphite monochromator. All other pertinent parameters are listed in Table II. Crystal stability and orientation were checked as previously described with no systematic deviation detected. Data reduction was also very similar. The value assigned to the correction factor, p, was 0.05, and the linear absorption coefficient[33a] is listed in Table I. A total of 2374 reflections was processed of which 1522 had $I \geq 3\sigma(I)$. Only these latter data were considered observed and used in subsequent calculations.

Structure Solution and Refinement. All least-squares refinements in these analyses were carried out on F, the function minimized being $\sum w(|F_o| - |F_c|)^2$ where the weights, w, were taken as $w = 4F_o^2/\sigma^2(F_o^2)$. In the calculations of F_c, the atomic scattering factors for all atoms were taken from ref 33b. The effects of anomalous dispersion of Hg and Cl, if applicable, were also included in the calculations of F_c, the values of $\Delta f'$ and $\Delta f''$ being taken from ref 33c. The usual agreement factors are $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

(a) $Hg(8\text{-}AAd)_2Cl_2$. The structure was solved by the heavy-atom method[34] using the Cu Kα data. In space group $Ima2$ the mercury atom is constrained to lie on either the mirror plane or the twofold axis. The observed systematic weakness of the $h = 2n + 1$ data suggests the latter. Isotropic, least-squares refinement with Hg fixed at the origin gave values for R_1 and R_2 of 0.264 and 0.332, respectively. All remaining nonhydrogen atoms were located in subsequent difference Fourier maps. Anisotropic refinement of Hg and Cl atoms and isotropic refinement of all others converged with derived values of R_1 and R_2 of 0.132 and 0.166, respectively.

Structure refinement was completed by using the Mo Kα data. In the final cycle of least squares there were 587 observations and 55 variables (including two scale factors); no parameter shifted by more than 0.5σ, which is taken as evidence of convergence. The final values of R_1 and R_2 were calculated to be 0.082 and 0.112, respectively. Attempts to refine anisotropic thermal parameters for the purine atoms were unsuccessful, and no hydrogen atoms were ever revealed or included in the calculations. A final difference Fourier map contained several peaks in the vicinity of the mercury position. The highest of these was 4.7 e Å^{-3}, but beyond this residual density around mercury, the map was featureless.

(b) $Hg(8\text{-}AHX^-)_2(H_2O)_4$. This structure was solved by a combination of the heavy-atom method[34] and direct methods.[35] The mercury atom was located in a three-dimensional Patterson map, but we were unable to discern any other atom positions in a difference Fourier that followed refinement of the mercury atom position. Since mercury contributes only to data with even values of l, the data were separated on this basis and sets of normalized structure factors, E, with values greater than 1.80 were separately scaled and calculated. The two sets were recombined, and multiple solutions were generated by using symbolic addition methods. Seven of ten purine atoms were extracted from an E map of the third best solution. These atoms were refined, and all remaining nonhydrogen atoms were located in a subsequent difference Fourier map. Isotropic refinement of all nonhydrogen atoms gave values for R_1 and R_2 of 0.351 and 0.410, respectively. Absorption correction of the data lowered the R factors to 0.240 and 0.300, respectively. Anisotropic refinement of just the mercury atom further decreased the R factors to 0.079 and 0.112. A difference Fourier map revealed the positions of the two purine hydrogen atoms, but none of the water hydrogen atoms could be resolved. In the final cycle of least squares all nonhydrogen atoms were refined anisotropically and only the isotropic thermal parameters, B, were varied for the two hydrogen atoms. There were 1522 observations and 117 variables; no parameter shifted by more than 0.1σ, which is taken as evidence of convergence. The final derived values of R_1 and R_2 are 0.070 and 0.095, respectively. Refinement of the structure in space group Cc did not increase the quality of the results (R_1 = 0.104, R_2 = 0.138). Thus, $C2/c$ is confirmed. The final difference Fourier contained significant residual density in the vicinity of the mercury atom, but beyond these peaks the map was featureless. The high residual density around mercury is assumed to be due to some error in the absorption correction or in the anisotropic thermal model.

Table III. Atomic Positional Parameters for $Hg(8\text{-}AAd)_2Cl_2$ and $Hg(8\text{-}AHX^-)_2(H_2O)_4$

atom	x	y	z
	(a) $Hg(8\text{-}AAd)_2Cl_2$		
Hg[a]	0.0000	0.0000	0.0000
Cl	−0.032 (1)	−0.226 (1)	0.219 (2)
N(1)	−0.124 (1)	0.485 (4)	−0.053 (4)
C(2)	−0.085 (1)	0.376 (4)	−0.022 (5)
N(3)	−0.086 (1)	0.189 (3)	0.028 (6)
C(4)	−0.128 (1)	0.106 (4)	−0.056 (5)
C(5)	−0.166 (1)	0.206 (5)	−0.129 (6)
C(6)	−0.171 (1)	0.420 (6)	−0.126 (6)
N(6)	−0.203 (1)	0.503 (5)	−0.166 (6)
N(7)	−0.207 (1)	0.074 (5)	−0.179 (6)
N(8)	−0.186 (1)	−0.088 (4)	−0.161 (5)
N(9)	−0.137 (1)	−0.064 (5)	−0.085 (6)
	(b) $Hg(8\text{-}AHX^-)_2(H_2O)_4$		
Hg[a]	0.0000	0.0000	0.0000
N(1)	−0.250 (2)	0.193 (1)	0.235 (1)
C(2)	−0.196 (2)	0.242 (1)	0.178 (1)
N(3)	−0.148 (2)	0.183 (1)	0.126 (1)
C(4)	−0.157 (2)	0.065 (1)	0.135 (1)
C(5)	−0.211 (2)	0.005 (1)	0.190 (1)
C(6)	−0.262 (2)	0.072 (1)	0.247 (1)
O(6)	−0.305 (2)	0.032 (1)	0.301 (1)
N(7)	−0.195 (2)	−0.113 (1)	0.179 (1)
N(8)	−0.135 (2)	−0.128 (1)	0.119 (1)
N(9)	−0.112 (2)	−0.024 (1)	0.090 (1)
OW(1)	0.352 (2)	−0.121 (1)	0.032 (1)
OW(2)	0.326 (2)	0.136 (1)	0.061 (1)
H(1)[a]	−0.283	0.243	0.267
H(2)[a]	−0.199	0.326	0.174

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

The atomic positional parameters for both structures, which were obtained from the last cycle of least squares, along with their standard deviations as estimated from the inverse matrix, are presented in Table III. Lists of the atomic thermal parameters and the observed and calculated structure amplitudes are available (see paragraph at the end of the paper regarding supplementary material).

Description of the Structure

(a) $Hg(8\text{-}AAd)_2Cl_2$. We realized at the outset of this study that the extremely poor crystal quality, combined with the problems inherent in the study of complexes of the third-row metals, would prevent us from obtaining reliable atomic parameters for the azapurine atoms. Our principal interest in the structure, however, was in the mode of coordination of the mercury(II) atom to the azapurine, and this we have been able to establish.

The crystal structure of the complex consists of layers of a mercury–chlorine lattice, which are parallel to the crystallographic bc plane and are separated by 13.84 Å ($a/2$). A view of one layer is shown in Figure 1, and a listing of the bond distances and angles is given in Table IV. Above and below each layer sit loosely bound 8-azaadenine ligands. There are two extremely short interatomic distances between purines on adjacent layers (see Table V). The N(6)···N(6) contact (2.61 Å) and the N(7)···N(7) contact (2.41 Å) are both well below the sum of the van der Waals radii for two nitrogen atoms.[36] These interactions are similar to the N(9)···N(9) contact (2.80

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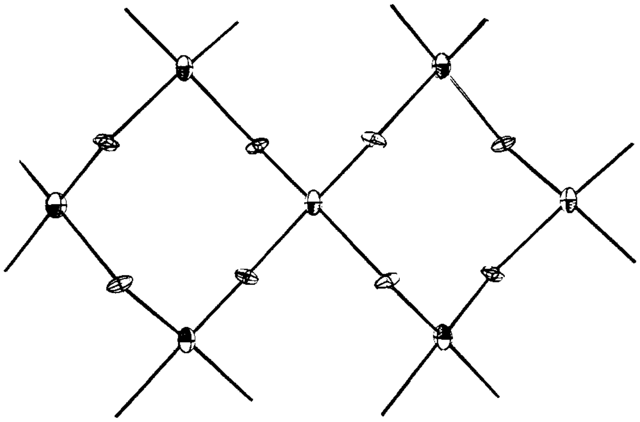

Figure 1. View of the mercury–chlorine lattice in Hg(8-AAd)$_2$Cl$_2$. The view is normal to the crystallographic *bc* plane.

Table IV. Distances (Å) and Angles (Deg) in Hg(8-AAd)$_2$Cl$_2$ and Hg(8-AHX$^-$)$_2$(H$_2$O)$_4$

Hg(8-AAd)$_2$Cl$_2$		Hg(8-AHX$^-$)$_2$(H$_2$O)$_4$	
Hg-Cl	2.39 (1)	Hg-OW(1)	2.68 (1)
Hg-Cl′	2.92 (1)	Hg-OW(2)	2.80 (1)
Hg-N(3)	2.72 (2)	Hg-N(9)	2.04 (1)
N(1)-C(2)	1.35 (3)	N(1)-C(2)	1.36 (1)
C(2)-N(3)	1.35 (3)	C(2)-N(3)	1.30 (1)
N(3)-C(4)	1.44 (4)	N(3)-C(4)	1.34 (1)
C(4)-C(5)	1.37 (4)	C(4)-C(5)	1.38 (2)
C(5)-C(6)	1.49 (5)	C(5)-C(6)	1.44 (2)
C(6)-N(6)	1.10 (5)	C(6)-O(6)	1.24 (1)
C(6)-N(1)	1.46 (4)	C(6)-N(1)	1.39 (1)
C(5)-N(7)	1.48 (5)	C(5)-N(7)	1.35 (1)
N(7)-N(8)	1.27 (4)	N(7)-N(8)	1.31 (1)
N(8)-N(9)	1.46 (4)	N(8)-N(9)	1.32 (1)
N(9)-C(4)	1.23 (5)	N(9)-C(4)	1.40 (1)
Cl-Hg-Cl	97.6 (7)	N(1)-H(1)	0.90
Cl-Hg-Cl′	85.3 (2)	C(2)-H(2)	0.95
Cl-Hg-Cl′	175.7 (3)	N(9)-Hg-OW(1)	94.3 (4)
Cl′-Hg-Cl′	91.9 (5)	N(9)-Hg-OW(2)	89.4 (4)
Cl-Hg-N(3)	87.3 (7)	OW(1)-Hg-OW(2)	65.0 (4)
Cl-Hg-N(3′)	87.2 (7)	Hg-N(9)-C(4)	127 (1)
Cl′-Hg-N(3)	89.7 (7)	Hg-N(9)-N(8)	125 (1)
Cl′-Hg-N(3′)	96.1 (7)	C(4)-N(9)-N(8)	108 (1)
N(3)-Hg-N(3′)	171.5 (3)	N(9)-N(8)-N(7)	110 (1)
Hg-Cl-Hg	141.2 (4)	N(8)-N(7)-C(5)	109 (1)
Hg-N(3)-C(4)	119 (2)	N(7)-C(5)-C(6)	133 (1)
Hg-N(3)-C(2)	115 (2)	N(7)-C(5)-C(4)	108 (1)
C(2)-N(3)-C(4)	107 (3)	C(6)-C(5)-C(4)	119 (1)
N(3)-C(4)-N(9)	129 (3)	C(5)-C(4)-N(9)	105 (1)
N(3)-C(4)-C(5)	126 (3)	C(5)-C(4)-N(3)	128 (1)
C(5)-C(4)-N(9)	105 (3)	N(9)-C(4)-N(3)	127 (1)
C(4)-N(9)-N(8)	112 (3)	C(4)-N(3)-C(2)	112 (1)
N(9)-N(8)-N(7)	111 (3)	N(3)-C(2)-N(1)	125 (1)
N(8)-N(7)-C(5)	101 (3)	C(2)-N(1)-C(6)	126 (1)
N(7)-C(5)-C(4)	111 (3)	N(1)-C(6)-C(5)	110 (1)
N(7)-C(5)-C(6)	124 (3)	N(1)-C(6)-O(6)	123 (1)
C(4)-C(5)-C(6)	124 (3)	C(5)-C(6)-O(6)	127 (1)
C(5)-C(6)-N(6)	125 (4)	C(6)-N(1)-H(1)	117
N(6)-C(6)-N(1)	130 (4)	C(2)-N(1)-H(1)	117
C(5)-C(6)-N(1)	105 (3)	N(1)-C(2)-H(2)	118
C(6)-N(1)-C(2)	126 (3)	N(3)-C(2)-H(2)	117
N(1)-C(2)-N(3)	125 (2)		

Å) in the crystal structure of 8-azahypoxanthine,[37] though more severe. Within a layer, chlorine atoms act as asymmetric bridges between two mercury atoms. The two Hg–Cl distances in the bridge are 2.39 (1) and 2.92 (1) Å. This type of arrangement is very common in crystal structures that basically consist of a mercury–chlorine lattice[38-48] (see Table VI). The short bridging distance is, in fact, only slightly longer than the two terminal Hg–Cl bonds[39,40] listed in Table VI. The long bridging distance of 2.92 Å is considerably longer than the symmetric bridging distances listed in Table VI, but it is also significantly shorter than the long bridging distances of 3.07–3.19 Å reported for a variety of other mercury structures (see Table VI). The 8-azapurine acts as a monodentate ligand. The coordination geometry around mercury is, therefore, distorted octahedral with two strong and two weak bonds to chlorine atoms and two weak bonds to N(3) of the two 8-azaadenines. This (2 + 4) mode of octahedral coordination

Table V. Probable A-H···B Hydrogen Bonds and Close Interatomic Contacts in Hg(8-AAd)$_2$Cl$_2$ and Hg(8-AHX$^-$)$_2$(H$_2$O)$_4$

(a) Hg(8-AHX$^-$)$_2$(H$_2$O)$_4$

A	H	B	A···B, Å	H···B, Å	A-H···B, deg
N(1)	H(1)	N(7)^a	2.85	1.97	162.4
OW(1)		N(3)^b	2.91		
OW(2)		N(8)^c	2.91		
OW(1)		OW(2)^d	2.93		
OW(2)		O(6)^e	3.04		

(b) Hg(8-AAd)$_2$Cl$_2$

A	B	A···B, Å	A	B	A···B, Å
N(1)	N(9)^f	3.17	N(7)	N(7)^g	2.41
N(6)	N(8)^f	2.89	N(9)	Cl^h	3.57
N(6)	N(6)^g	2.61			

^{a} $-{}^1/_2 - x, {}^1/_2 + y, {}^1/_2 - z$. ^{b} ${}^1/_2 + x, -{}^1/_2 + y, z$. ^{c} ${}^1/_2 + x, {}^1/_2 + y, z$. ^{d} $1 - x, -y, -z$. ^{e} $-x, y, {}^1/_2 - z$. ^{f} $x, 1 + y, z$. ^{g} $-{}^1/_2 - x, y, z$. ^{h} $x, -{}^1/_2 - y, -{}^1/_2 + z$.

Table VI. Comparative Mercury Bonding Distances (Å)

compd	Hg-N	Hg-O	Hg-Cl	ref
Hg(8-AAd)$_2$Cl$_2$	2.72		2.39, 2.92	this work
Hg(8-AHX$^-$)$_2$(H$_2$O)$_4$	2.04	2.68, 2.80		this work
Hg(Guo)Cl$_2$	2.16		2.34 (terminal) 2.68, 2.76	39
Hg(1-MeCyd)Cl$_2$	2.17		2.32 (terminal) 2.72, 2.75	40
Hg(Ura)Cl$_2$		2.71	2.30, 3.07	41
Hg(1-MeThy)$_2$	2.04			42
Hg(MeOH)$_2$Cl$_2$		2.82	2.31, 3.07	43
Hg(py-*N*-O)Cl$_2$		2.59, 2.60	2.32, 3.19 2.34, 3.19	44
Hg(Nap)$_3$ClO$_4$•	2.14, 2.87 2.20, 2.84 2.30, 2.64	2.93		45
Hg(CH$_3$)(9-MeGua)$^+$	2.09	2.75, 2.99		46
(Hg(CH$_3$))$_2$(Ad)$^+$	2.09, 2.08			47
(Hg(CH$_3$))$_2$(9-MeAd)$^+$	2.09, 2.08			47
Hg(AdH)Cl$_3$			2.34, 3.26 2.38, 3.25 2.76, 2.82	48

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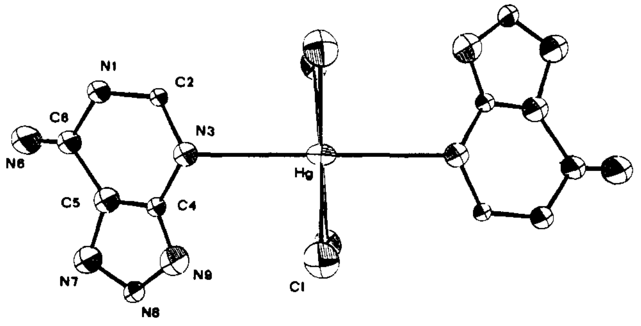

Figure 2. View of the coordination around mercury in $Hg(8\text{-}AAd)_2Cl_2$. Hydrogen atoms, which were not located in this analysis, are omitted.

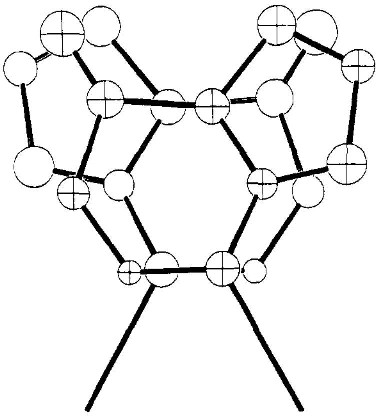

Figure 3. Base stacking in $Hg(8\text{-}AAd)_2Cl_2$. The top (darker) molecule is related to the bottom molecule by a combination of the *a* glide and *I* centering. The view is normal to the crystallographic *ab* plane.

is very common among Hg(II) complexes.[38] The cis bond angles range from 85.3 (2) to 97.6 (7)°, and the smallest trans angle is 171.5 (3)° (Table IV). The deviation from ideal octahedral geometry is probably due to the coordination ambivalence of mercury, which is generated by its polarizability. The Hg-N(3) distance is 2.72 (2)°, which is rather long compared to most Hg-N separations listed in Table VI. The only similar contacts are the secondary Hg-N interactions in the naphthyridine complex $[Hg(Nap)_3ClO_4]^+$. The complete coordination, including all Hg-Cl interactions, is shown in Figure 2.

As we noted above, the geometry of the 8-azapurine ligand as determined from these data is unreliable and not deserving of much comment. Within the precision of this analysis, the base is approximately planar; the average deviation for the nine-atom, least-squares plane is 0.07 Å. Least-squares planes for the pyrimidine, triazole, and azapurine rings are tabulated in Table VII. The pyrimidine and triazole planes are inclined to each other by 3.6°, which is about 3 times the amount that is normally found in purines, but is only slightly larger than the 3.2° bend observed in the 9-ethylguaninium cation.[49] The 8-azaadenine ligands are oriented within each layer to form infinite, base-stacked chains. Base overlap is quite extensive as is shown in Figure 3. Adjacent purines in the chain are nearly parallel, forming an angle between them of only 0.35°, and are separated by 3.34 Å.

Proton positions and, hence, hydrogen-bonding interactions were impossible to unambiguously discern. Potentially, there are four sites at which the proton may attach to the 8-azaadenine ligand: N(1) or any of the three triazole nitrogen atoms. The N(7) site is most unlikely due to the already severe steric proximity of N(7) atoms on adjacent layers. Inspection of Table V indicates that there are two potential hydrogen-bonding interactions involving the three remaining sites. One of these is a N(6)···N(8) interaction for which the hydrogen atom is most certainly provided by N(6). Of the two remaining possibilities, the calculated basicities[50] of N(1) and N(9) show that N(9) is more basic and, hence, more likely to be protonated. Furthermore, a proton at this position allows the presence of a weak interaction to a bound chloride ion, which is not available if the proton were on N(1). Finally, the endocyclic angle at N(9) is considerably larger than it is at N(7), and it has been observed that protonation induces a sizable enlargement (of approximately 5°) of the internal angle.[51] In view of the large difference in the internal angles at N(7) and N(9) (11°), we feel that this effect is observable in spite of the large standard deviations associated with these angles. Therefore, it seems likely that the proton is attached to N(9) and that there are two major hydrogen bonds: N(6)-H···N(8) and N(9)-H···N(1).

Table VII. Planes in $Hg(8\text{-}AAd)_2Cl_2$ and $Hg(8\text{-}AHX^-)_2(H_2O)_4$[a]

atom	*x*	*y*	*z*	Δ, Å	Δ, Å	Δ, Å
			$Hg(8\text{-}AHX^-)_2(H_2O)_4$			
Hg	0.0000	0.0000	0.0000		−0.137	−0.155
N(1)	−2.0257	2.1633	4.7413	0.000*		−0.010*
C(2)	−1.5778	2.7179	3.5865	0.001*		−0.009*
N(3)	−1.1779	2.0557	2.5393	0.002*	−0.026	0.005*
C(4)	−1.2494	0.7292	2.7287	−0.006*	−0.007*	0.009*
C(5)	−1.6962	0.0568	3.8439	0.006*	0.004*	0.022*
C(6)	−2.1284	0.8064	4.9971	−0.003*	−0.037	0.000*
O(6)	−2.4986	0.3559	6.0879	−0.053		−0.057
N(7)	−1.5710	−1.2687	3.6075	−0.032	0.000*	0.001*
N(8)	−1.0789	−1.4399	2.4010		−0.004*	−0.019*
N(9)	−0.8817	−0.2684	1.8233	−0.027	0.007*	0.002*
			$Hg(8\text{-}AAd)_2Cl_2$			
Hg	0.0000	0.0000	0.0000	1.004		0.927
N(1)	−3.4339	3.3820	−0.3846	−0.069*		−0.030*
C(2)	−2.3402	2.6163	−0.1594	0.166*		0.179*
N(3)	−2.3745	1.3169	0.2007	−0.129*	−0.159	−0.164*
C(4)	−3.5456	0.7400	−0.4026	0.010*	−0.052*	−0.048*
C(5)	−4.6074	1.4342	−0.9320	0.072*	0.058*	0.037*
C(6)	−4.7201	2.9240	−0.9114	−0.049*	0.032	−0.030*
N(6)	−5.6153	3.4019	−1.1939	−0.148		−0.110
N(7)	−5.7180	0.5189	−1.2933	0.023	−0.045*	−0.048*
N(8)	−5.1454	−0.6117	−1.1586		0.018*	0.049*
N(9)	−3.8025	−0.4449	−0.6163	0.157	0.022*	0.056*

[a] The asterisks denote the atoms used in the plane calculation.

(b) $Hg(8\text{-}AHX^-)_2(H_2O)_4$. The crystal structure consists of complex monomers that are linked via pairwise base-stacking interactions to form infinite chains parallel to the *c* axis. The 8-azahypoxanthinato ligand coordinates to mercury only through N(9), and, hence, Hg is six-coordinated and approximately octahedral. The two independent Hg-O(water) distances are 2.68 (1) and 2.80 (1) Å. These interactions are weak and similar to all Hg-O interactions listed in Table VI. In contrast to the Hg-8-AAd structure, the 8-azapurine is bound very tightly to the mercury atom. The bonding distance (2.04 (1) Å) is the shortest Hg-N distance listed in Table VI and is equaled only by the strictly two-coordinated, linear complex of $Hg(1\text{-methylthymine})_2$.[42] The Hg-N(9) bond is nearly perpendicular to the base plane of the four water molecules—forming bond angles of 94.3 (4) and 89.4 (4)° with Hg-OW(1) and Hg-OW(2), respectively. However, the OW(1)-Hg-OW(2) angle is only 65.0 (4)°—showing again the extreme coordination geometry flexibility of mercury(II). A view of the coordination complex is shown in Figure 4. The geometry of the present complex, therefore, is in marked

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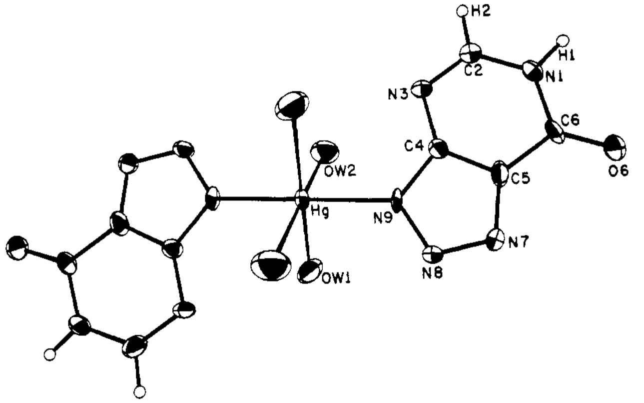

Figure 4. View of the coordination around mercury in Hg(8-AHX$^-$)$_2$(H$_2$O)$_4$.

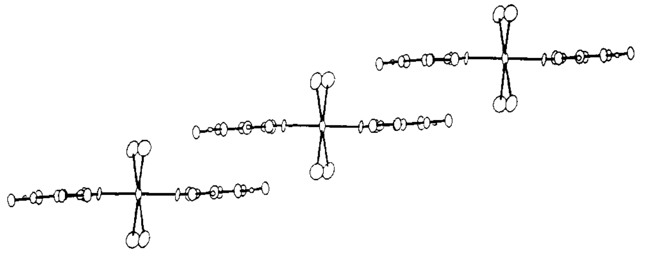

Figure 5. Base stacking in Hg(8-AHX$^-$)$_2$(H$_2$O)$_4$ viewed parallel to the base planes.

contrast to that observed for the analogous cadmium complex Cd(8-AHX$^-$)$_2$(H$_2$O)$_4$.[29] In the cadmium complex the metal coordinates to atom N(7) of the azapurine, presumably to allow an intramolecular hydrogen bond between atom O(6) and a coordinated water molecule. More significantly, the geometry at cadmium is much more nearly octahedral, with Cd–N and Cd–O distances in the narrow range of 2.30–2.33 Å. This contrast is due to the enhanced "softness" of mercury(II) over that of cadmium(II), which causes the former to bind very weakly to oxygen donors.

The molecular geometry of the azapurine ligand conforms with those of 8-azahypoxanthine[37] and several of its derivatives such as 2-(*o*-propoxyphenyl)-8-azahypoxanthine,[52] 9-(diethylcarbamoyl)-2-(2-propoxyphenyl)-8-azahypoxanthine,[53] and 2-phenyl-7-methyl-8-azahypoxanthine.[54] The geometry is also very similar to that of the same ligand in the cadmium complex.[29] When the standard deviations derived for the present structure are used, almost all dimensions are within 3σ of these related molecules. The only large, consistent difference occurs in the length of the C(4)–N(9) bond. This distance (1.40 (1) Å) is $(4-6)\sigma$ longer in Hg(8-AHX$^-$) than it is in the other structures. This lengthening is uncharacteristic but is probably due to the flow of electron density from the triazole ring system into the Hg–N(9) π system. The length of N(8)–N(9) has not changed because the anionic charge and the N(7)–N(8) π bond have flowed into N(8)–N(9) to compensate for the loss of π-electron density. Structural evidence of this lies in the near equality of the N(8)–N(9) and N(7)–N(8) (which formally is a double bond) bond lengths and of all the internal bond angles, except at C(4).

As mentioned above, the azapurine bases stack in a pairwise fashion. A view of the resulting infinite chain and pairwise stacking is shown in Figure 5. The two interacting purines are nearly parallel—forming an angle of 0.62° between them—and the average stacking distance is only 3.182 Å. The degree of overlap in the stacked pair is shown in Figure 6, and, as is usual for purines,[5] the overlap is limited. The very polar atom O(6) is situated over the middle of the adjacent azapurine. The azapurine ligand is reasonably planar (Table VII). The pyrimidine and triazole rings are planar, with maximum deviations of less than 0.01 Å, and they are inclined to each other by 1.49°. Finally, the azapurine plane is nearly perpendicular to the base of the coordinated water molecules—the angle between them is 92.2°.

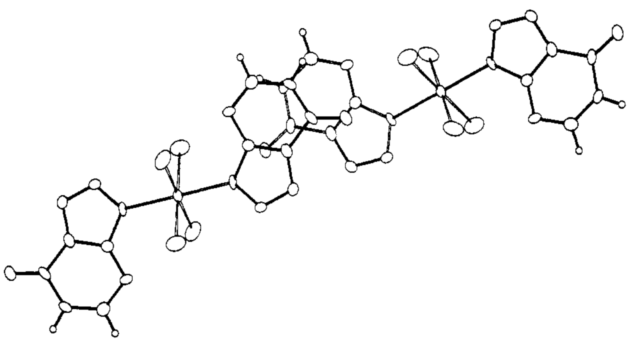

Figure 6. Base stacking in Hg(8-AHX$^-$)$_2$(H$_2$O)$_4$ viewed normal to the base planes. The lower molecule is related to the upper (dark) molecule by the twofold axis along *b*.

Due to our inability to unequivocally locate the water hydrogen atoms, it is impossible to make many definitive statements concerning hydrogen bonding. Water molecules would be the proton donors in four of the five probable hydrogen bonds listed in Table V. The postulation of these hydrogen bonds is based on highly favorable heavy-atom contacts that range from 2.91–3.04 Å, and from our experience these atoms have a propensity to hydrogen bond. Furthermore, this scheme utilizes all possible donors and acceptors.

Discussion

The general rule that has emerged from numerous crystal structures of metal complexes[8] with the naturally occurring purines is that the metal ion will coordinate to the imidazole nitrogen atom that is protonated in the free, neutral base. For most purines (all except theophylline) this is N(9); if N(9) is blocked, then N(7) is the secondary choice. In the case of bidentate coordination, the second linkage may involve any of the other nitrogen atoms, but N(9), N(3) binding is the most common. The present study, together with previous reports,[27-29] demonstrates that metal ion interactions with the 8-azapurines are not as easily categorized. The only two ligands that have been employed so far are 8-azaadenine and 8-azahypoxanthine. The two complexes with 8-azahypoxanthine are the most conventional in the sense that the metal ions coordinate to N(7) or N(9). The reason for this is that in both cases the ligand is deprotonated at the triazole moiety, and although the anionic charge is distributed over the entire ring (as indicated by the bond lengths and angles), coordination to the triazole ring is virtually a certainty. However, the binding of cadmium to N(7) is unusual because it leaves N(9) both uncoordinated and unprotonated.[29] Additional complexities are realized when one observes that the triazole proton is on N(8) in the solid-state structure of 8-azahypoxanthine.[37]

The complexes with 8-azaadenine are even more diverse. The interaction with Cu(II), for example, not only results in coordination to neither N(9) nor N(7) but also catalyzes the hydrolysis of the ligand at C(2). Also, zinc(II) interacts with the protonated base only at N(3) while the triazole hydrogen is on N(8), and N(9) is merely involved in a weak hydrogen bond. Finally, in the present study, mercury(II) barely interacts with 8-azaadenine at all—the coordination to N(3) is weak and may be governed more by hydrogen bonding and

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crystal-packing forces than by the basicities of the various sites. A precise crystal structure of free, neutral 8-azaadenine is not available at this time, but the details of the above structures suggest that the site of protonation will be either N(8) or N(9). Nevertheless, all three structures are anomalies according to the rules established for the natural purines, and they do not seem to lend themselves to the creation of a new set of rules for all 8-azapurines.

The 8-aza substitution achieves at least two changes in the purine ring system. First, it provides an additional basic site for potential proton attachment and hydrogen bonding. Second, as a basic site, it is bound to reduce the basicity of the two adjacent sites. This is confirmed by electron density calculations using the CNDO/2 approximation[55] on adenosine[56,57] and 8-azaadenosine.[57] It is this second effect that most likely is responsible for the unruly behavior of metal ion interactions with 8-azapurines. The reduction of basicity at N(9) and N(7) may be sufficient to allow the basic sites on the pyrimidine portion to compete favorably for metal ion coordination. The extent to which 8-aza substitution evens out the basicities of the triazole and pyrimidine nitrogen atoms will vary from purine to purine. Thus, it is unknown whether all 8-azapurines will exhibit similar anomalous behavior with respect to metal ion coordination, and, therefore, it is necessary to study these systems before the utility of their interactions can be evaluated.

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Registry No. $Hg(8\text{-}AAd)_2Cl_2$, 77495-61-5; $Hg(8\text{-}AHx^-)_2(H_2O)_4$, 77495-59-1.

Supplementary Material Available: Listings of atomic thermal parameters and of observed and calculated structure amplitudes (15 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry, The University of North Carolina, Chapel Hill, North Carolina 27514,
and Chemistry Department I, Inorganic Chemistry, H. C. Ørsted Institute,
University of Copenhagen, DK-2100 Copenhagen Ø, Denmark

Synthesis and Structural and Magnetic Characterization of *trans*-Aquatetraamminechromium(III)-μ-hydroxo-pentaamminechromium(III) Chloride Trihydrate $[[(NH_3)_4(H_2O)Cr(OH)Cr(NH_3)_5]Cl_5\cdot 3H_2O]$

SUSAN J. CLINE,[1a,b] JØRGEN GLERUP,*[1b] DEREK J. HODGSON,*[1a] GUNNAR S. JENSEN,[1b]
and ERIK PEDERSEN*[1b]

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The crystal and molecular structure of the dinuclear chromium(III) complex *trans*-aquatetraamminechromium(III)-μ-hydroxo-pentaamminechromium(III) chloride trihydrate (*trans*-$[(NH_3)_4(H_2O)Cr(OH)Cr(NH_3)_5]Cl_5\cdot 3H_2O$) has been determined from three-dimensional single-crystal counter X-ray data. The complex crystallizes in the monoclinic space group $C2/c$ with four formula units in a cell of dimensions a = 23.855 (7) Å, b = 7.387 (3) Å, c = 16.763 (7) Å, and β = 129.8 (1)°. The structure has been refined by full-matrix least-squares methods to a final value of the conventional R factor (on F) of 0.049 on the basis of 1638 independent intensities. The bridging hydroxo group lies on a crystallographic twofold axis, giving rise to a 50/50 disorder of the trans OH_2 and NH_3 ligand positions. The dinuclear cation is symmetrically bridged by the OH group, with Cr–O distances of 1.983 (1) Å and a bridging Cr–O–Cr angle of 155.1 (3)°. The geometry at each chromium(III) center is roughly octahedral, the ligating atoms being four cis ammine groups (Cr–N distances 2.062 (4)–2.084 (4) Å), the hydroxo bridge, and the disordered trans ligand. The magnetic susceptibility of the complex indicates antiferromagnetic coupling. The susceptibility data were fitted to a model assuming independent triplet, quintet, and septet energies; the results are almost consistent with the Van Vleck expression corrected for biquadratic exchange and lead to a triplet energy of 34.6 cm^{-1}. This triplet–singlet separation is much larger than that found in the related cis complex *cis*-$[(NH_3)_5Cr(OH)Cr(NH_3)_4(OH)]^{4+}$.

Introduction

The magnetic properties of dimeric transition-metal complexes have been shown to be dependent upon their structures. For the cases of complexes of the formulation $[M(L)OH]_2^{n+}$, where M is Cu(II) and L is a bidentate ligand, the magnetic exchange parameter, J, varies linearly[2] with the Cu–O–Cu bridging angle, Φ. In the case where M is Cr(III), the correlation between the structural and magnetic properties of the analogous complexes $[M(L)_2OH]_2^{n+}$ still exists,[3-8] but the exact nature of the variation of J with Φ is more difficult to discern.[7,8] So that a larger range in the bridging angle, Φ, can be obtained, the singly bridged rhodo and erythro chromium dimers, first reported by Jørgensen in 1882, are being examined structurally, magnetically, and spectroscopically.[9-21]

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(1) (a) The University of North Carolina. (b) H. C. Ørsted Institute, University of Copenhagen.

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