



Crystallographic Signatures of N⁶-Methoxyadenine Imino Tautomer–Silver Complexes

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(5) Supporting Information



ABSTRACT: Detailed crystallographic analysis of four silver complexes of N9-benzyl-N⁶-methoxyadenine, 1, on the basis of three different counteranions and silver ion stoichiometry, is discussed in this article. 1 is a rare tautomer of adenine, which exhibits promutagenic behavior as it partly mimics hydrogen bond donor and acceptor properties of guanine and mispairs with cytosine. Complexes 2 and 4 exhibit discrete Ag_2L_2 dimer, while complex 3 shows two AgL_2 units in addition to a Ag_2L_2 dimer, all in a head-to tail fashion. Complex 5, on the other hand, shows four AgL_2 units coordinated in a head-to-head fashion affording a three-dimensional lattice stabilized by CH···F interactions. Various noncovalent interactions such as hydrogen bonding, CH- π interactions, argentophilic interactions, and Ag- π interactions stabilize these complexes.

INTRODUCTION

Prototropic tautomerism in purine and pyrimidine nucleobases of DNA has relevance in understanding DNA mutations and ensuing phenotypic effects.¹ Such mutations are a critical area of concern for chemists, biochemists, and biologists alike as it is estimated that human cells may experience considerable DNA damage amounting to at least 2000-10000 times per day, but are quickly repaired by protective cellular mechanisms.² According to the Watson-Crick base pairing rules, it is well-known that adenine binds to thymine/uracil, while guanine pairs with cytosine through hydrogen bonding interactions;³ however, the formation of "rare tautomers" may cause deviation from the usual base pairing schemes.^{1b,4} X-ray crystal analysis of certain metalnucleobase complexes has revealed concerted intramolecular 1,3proton shift from exocylic N-atom to ring N-atoms. In addition, several physical and quantum mechanical studies have been reported in the literature investigating physicochemical properties such as acidity and basicity, stability, hydration, and ionization energies of nucleobase tautomeric forms resulting from metal ion coordination and substitutions.46,5

The choice of substitution at the adenine N^6 position may contribute to the formation of the rare imino tautomer. Electron-donating groups such as amino, hydroxyl, and methoxy at the exocyclic amino group shift the equilibrium toward a higher ratio of imino tautomer favoring this tautomerism.⁶ The N^6 -methoxyadenine derivative crystallizes out in its imino form, mimicking a guanine base, while maintaining an amino—imino equilibrium in solution. This change in structure explains its ambiguous base pairing capacity with thymine and cytosine leading to pyrimidine transition mutation, which incidentally is observed in DNA polymerase III readout when N^6 -methoxyadenine is present in the template strand during replication.⁷ These experiments also suggest that *anti*-imino tautomer of N^6 -methoxyadenine predominates in B-DNA. Moreover, studies of corresponding adenosine derivatives have also confirmed promutagenic behavior of such tautomers.⁸

We have extensively studied metalated purine nucleobases and explored their novel supramolecular architectural motifs, polymeric matrices and surface patterning using atomic force microscopy.⁹ Herein, we report a modified synthesis of N9-benzyl-N⁶-methoxyadenine (Scheme 1), structure of its imino tautomer in the solid state (Figure 1).¹⁰ This article presents crystallographic studies concerning Ag(I)-stabilized rare tautomer, where the multiple structures originate on the basis of the nature of counteranions and silver stoichiometry.

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Scheme 1. Synthesis of N9-Benzyl N^6 -Methoxyadenine (1)



Figure 1. Prototropic tautomerism of N^9 -benzyl- N^6 -methoxyadenine **1.** (a) Amino and imino tautomers; (b) *syn-* and *anti-*imino tautomers.



EXPERIMENTAL SECTION

1. Synthesis of N9-Benzyl-N⁶-methoxyadenine (1). Ligand **1** was synthesized in two steps starting from 6-chloropurine by the following procedure (Scheme 1).

Step 1: In a typical procedure, 6-chloropurine (2 g, 1 equiv) was dissolved in DMSO (25 mL), which was followed by the addition of K_2CO_3 (2.15 g, 1.2 equiv). To the reaction mixture, dropwise benzyl bromide (1.5 mL, 0.95 equiv) was added and stirred at room temperature for 10 h. Reaction mixture was then concentrated under *vacuum* and the crude reaction mass was purified by silica-gel column chromatography using 10–20% EtOAc: petroleum ether yielding 1.5 g (48%) of pure compound as white powder. HRMS: (M + H)⁺ = calculated: 245.0594, observed: 245.0953. ¹H NMR: (500 MHz, CDCl₃, 25 °C, TMS) δ (ppm) 5.45 (s, 2H, CH₂), 7.32 (d, 2H, Ar–H), 7.36 (t, 3H. Ar–H), 8.09 (s, 1H, C8–H), 8.79 (s, 1H, C2–H). ¹³C NMR (125 MHz, CDCl₃, 25 °C, TMS); δ (ppm) 47.86, 127.90, 128.86, 129.25, 131.46, 134.45, 144.93, 151.11, 151.81, 152.15.

Step 2: N9-benzyl-6-chloropurine (4 g, 1 equiv) was suspended in butanol (50 mL). To this were then added *O*-methyl hydroxylamine hydrochloride (6.82 g, 5 equiv) and triethyl amine (13 mL, 5.75 equiv).



Figure 2. ¹H NMR of ligand 1. Inset displaying the imino-amino ratio difference for the chemical shift values of 5.23 and 5.37.

Table 1. Crystal Structure Refinement Parameters for 1-5

identification code	ligand 1	complex 2	complex 3	complex 4	complex 5
empirical formula	C ₁₃ H ₁₃ N ₅ O	$C_{26}H_{26}Ag_2N_{12}O_8$	$C_{78}H_{86}Ag_4N_{34}O_{22}$	$C_{26}H_{26}Ag_2Cl_2N_{10}O_{10}$	C ₂₆ H ₂₈ AgF ₆ N ₁₀ O ₃ P
$M_{ m r}$	255.28	850.33	2281.27	925.21	781.42
crystal system	triclinic	triclinic	monoclinic	triclinic	tetragonal
space group	$P\overline{1}$	$P\overline{1}$	P1 21/n1	$P\overline{1}$	P42/n
a (Å)	10.0702(19)	7.2331(10)	22.321(4)	9.915(2)	30.163(5)
b (Å)	11.277(2)	7.9989(11)	12.638(3)	9.942(2)	30.163(5)
c (Å)	11.358(2)	13.7505(18)	31.194(4)	16.461(3)	6.574(5)
α (deg)	88.658(4)	79.317(2)	90	101.292(5)	90
β (deg)	87.650(4)	78.741(2)	95.07(4)	98.813(4)	90
γ (deg)	77.547(3)	71.096(2)	90	93.590(3)	90
volume (Å ³)	1259.2(4)	731.74(17)	8765.2(29)	1565.4(6)	5981(5)
Ζ	4	1	4	2	8
$D_x (Mg m^{-3})$	1.347	1.930	1.729	1.963	1.736
F(000)	536	424	4616	920	3152
$\mu (\mathrm{mm}^{-1})$	0.092	1.412	0.975	1.496	0.814
θ range for data collection (deg)	2.47-26.0	2.72-28.38	4.09-25.03	2.09-28.34	4.11-25.03
limiting indices	$\begin{array}{c} -12 \rightarrow h \rightarrow 12, -13 \rightarrow k \\ \rightarrow 12, -14 \rightarrow l \rightarrow 11 \end{array}$	$\begin{array}{c} -9 \rightarrow h \rightarrow 9, -10 \rightarrow k \\ \rightarrow 6, -18 \rightarrow l \rightarrow 15 \end{array}$	$\begin{array}{c} -25 \rightarrow h \rightarrow 26, -14 \rightarrow k \\ \rightarrow 15, -37 \rightarrow l \rightarrow 28 \end{array}$	$ \begin{array}{c} -13 \rightarrow h \rightarrow 12, -13 \rightarrow k \\ \rightarrow 12, -18 \rightarrow l \rightarrow 21 \end{array} $	$\begin{array}{c} -24 \rightarrow h \rightarrow 35, -35 \rightarrow k \\ \rightarrow 35, -7 \rightarrow l \rightarrow 7 \end{array}$
reflections collected	6999	4752	44855	10296	29846
unique reflections	4787	3430	15396	7354	5250
R(int)	0.0219	0.0178	0.0772	0.0311	0.1342
completeness to θ	= 25.00, 97.8	= 25.00, 97.5	= 25.00, 99.5	= 28.34, 94.0	= 25.00, 99.4
$T_{\rm max}/T_{\rm min}$	0.9855/0.9819	0.7752/0.7372	0.8440/0.8068	0.7745/0.7247	0.8673/0.8348
data/restraints/ parameters	4787/0/345	3430/0/218	15396/9/1273	7354/0/429	5250/3/432
GOF on F^2	1.172	1.260	1.024	1.116	1.033
$\begin{bmatrix} R_1 \text{ and } R_2 \\ [I > 2\sigma(I)] \end{bmatrix}$	0.0518, 0.1392	0.0484, 0.1037	0.0589, 0.1296	0.0667, 0.1594	0.0704, 0.1735
R_1 and R_2 (all data)	0.0684, 0.1740	0.0749, 0.1725	0.0935, 0.1514	0.1096, 0.2420	0.1161, 0.2075
largest diff peak and hole $(e \cdot A^{-3})$	0.489 and -0.506	2.184 and -2.900	2.299 and -0.762	2.015 and -2.009	1.928 and -0.693

The reaction mixture was refluxed at 120 °C and the progress of the reaction was monitored. Heating was stopped after 6 h and solvent was removed under a vacuum. The solid so obtained was washed with water (2 × 50 mL) and extracted into ethyl acetate (3 × 100 mL). The organic layer was collected, dried, and concentrated for further purification using silica-gel column chromatography with CHCl₃. Pure compound 1 was obtained as a white powder. Yield: 3.5 g (84%). HRMS: $(M + H)^+$ = calculated: 256.1198, observed: 256.1196. m.p.: Decomposes with melting at 227–229 °C.

NMR. Solution state amino-imino tautomerism in N9-substituted N^{6} -alkoxyadenines has been studied previously by proton nuclear magnetic resonance, ^{6,10,14} and ultraviolet and infrared spectroscopy, ^{14c} clearly indicating domination of imino tautomer in polar solvents such as DMSO or water.^{6,14c} Such observations were also made in the case of 1 by determining differences in chemical shift values and integrals of the two tautomeric forms (Figure 2). The peak ratio of 4:1 for the protons of the imino tautomer with respect to the amino tautomer as observed in ¹H NMR spectra indicates its greater stability and predominance. ¹H NMR (DMSO-*d*₆) 11.16 (br s, 0.95 H, H_i-N1), 10.90 (br s, 0.23 H, H_a-N6), 8.34 (s, H_a-2), 8.28 (s, H_a-8), 7.92 (s, 1.0 H, H_i8), 7.53 (br s, 1.1 H, H_i2), 7.28 (m, 6.83 H, Ar–H), 5.37 (s, 0.5 H, *a*-CH₂), 5.23 (s, 2.03 H, *i*-CH₂), 3.73 (s, 0.85 H, *a*-OMe), 3.71 (s, 3.08 H, *i*-OMe) (i: imino, a: amino).

2. Synthesis of Complex 2 $[C_{26}H_{26}Ag_2N_{12}O_8]$. Block-shaped violet color crystals of the complex were obtained in a week's time from their methanolic solution by dissolving stoichiometric amounts of AgNO₃ (1 equiv) and ligand 1 in methanol (yield: 63%). HRMS: $[L + H]^+$: 256.1173 (Calcd.: 256.1198), $[L + Ag]^+$: 362.0120 (Calcd.: 362.0171) and $[2 L + Ag]^+$: 617.1165 (Calcd.: 617.1291).

3. Synthesis of Complex 3 $[C_{78}H_{86}Ag_4N_{34}O_{22}]$. The complex was grown by slow evaporation of ligand 1 (1 equiv) and AgNO₃ (2 equiv) solutions in methanol. Violet colored crystals were obtained in a month's time (yield: 30%). HRMS: $[L + H]^+$: 256.1226 (Calcd.: 256.1198), $[L + Ag]^+$: 362.0172 (Calcd.: 362.0171) and $[2 L + Ag]^+$: 617.1243 (Calcd.: 617.1291).

4. Synthesis of Complex 4 $[C_{26}H_{26}Ag_2Cl_2N_{10}O_{10}]$. The equimolar reaction of $AgClO_4$ (1 equiv) and ligand 1 (1 equiv) in MeOH gave the violet colored solution which under slow evaporation for 2–3 weeks gave crystals of complex 4 (yield: 50%). HRMS: $[L + H]^+$: 256.1191 (Calcd.: 256.1198), $[L + Ag]^+$: 362.0191 (Calcd.: 362.0171) and $[2L + Ag]^+$: 617.1299 (Calcd.: 617.1291).

5. Synthesis of Complex 5 $[C_{26}H_{28}AgF_6N_{10}O_3P]$. The reaction of freshly prepared AgPF₆ (1 equiv) solution with ligand 1 (1 equiv) in MeOH and subsequent slow evaporation afforded brown crystals of complex 5 (yield: 42%). HRMS: $[L + H]^+$: 256.1118 (Calcd.: 256.1198) and $[2L + Ag]^+$: 617.1293 (Calcd.: 617.1291).

CRYSTAL STRUCTURE DETERMINATION AND REFINEMENT

There was distinct color in most of the crystals of complexes **2–5**. This observed coloration could be attributed to silver ion complexation of neutral imino tautomer. UV–vis titrations were conducted using 10^{-4} M solution of ligand **1** in methanol against Ag⁺ ions. An increase in absorbance ($\lambda = \sim 465$ nm) was noted with the addition of increasing equivalents of Ag⁺ ions (Figure S1, Supporting Information).

Crystals were coated with light hydrocarbon oil and mounted in the 100 K dinitrogen stream of a Bruker SMART APEX



Figure 3. (a) ORTEP diagram of 1 at 30% probability level; (b) syn-imino tautomer; (c) ribbon formation in 1 as viewed along the *a*-axis showing two crystallographically independent units.



Figure 4. (a) ORTEP diagram of 2 showing the asymmetric unit of the cell at 30% probability level; (b) representation of tetracoordinated geometry around silver ion and Ag…Ag interaction with a distance of 2.92 Å.

CCD diffractometer equipped with CRYO Industries lowtemperature apparatus and intensity data were collected using graphite-monochromated Mo–K α radiation. The data integration and reduction were processed with SAINT software.¹¹ An absorption correction was applied.¹² Structures were solved by the direct method using SHELXS-97 and refined on F^2 by a full-matrix least-squares technique using the SHELXL-97 program package.¹³ Non-hydrogen atoms were refined anisotropically. In the refinement, hydrogens were treated as riding atoms using the SHELXL default parameters. In the case of 3 and 5, water molecules were found trapped in the lattice and the hydrogen atoms of these water molecules are located on the Fourier map and constraints were applied to fix the O–H distance and H–O–H angle. Crystal structure refinement parameters are given in Table 1. All of these software packages were the integrated WINGX software package. CCDC Nos. 856027, 856028, 856029, 856030 contain the supplementary crystallographic data for this paper. Copies of this information can be obtained free of charge upon application to CCDC, 12 Union Road, Cambridge CB21EZ, U.K. (fax +44–1223/ 336–033; e-mail deposit@ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Crystal Structure Analysis of 1. The crystal structure of ligand 1 has already been reported in the literature;¹⁰ however, a brief description of its solid state structure is discussed here to provide a background of the present work. Crystals suitable for X-ray crystallographic analysis were obtained by slow evaporation of methanolic solution of 1. Refinement data suggest that 1 crystallized in a triclinic unit cell ($P\overline{1}$) consisting of two crystallographically independent molecules (Figure 3a). The distinction between these two molecules lies in the difference of orientation of the benzyl rings at the N9 position (Figure 3c).¹⁰ The crystal structure of 1 clearly reveals the occurrence of the *syn*-imino tautomer stabilized by the



Figure 5. (a) Hydrogen bonded lattice of 2, also depicting $\pi - \pi$ interactions (benzyl rings are removed for clarity); (b) part of crystal lattice depicting CH··· π stacking interactions (nitrate ions are omitted for clarity).



Figure 6. ORTEP diagram of the asymmetric unit of complex **3** at 20% probability illustrating six ligand molecules coordinated to four silver ions neutralized by four nitrate counteranions and four unbound water molecules.



Figure 7. Part of crystal lattice of 3 illustrating the weak out-of-plane coordination of Ag1 and Ag2 to N7C and N7B in AgL_2 unit thereby resulting in a distorted tetrahedral geometry around these silver ions as shown in the highlighted region. Linear coordination of Ag3 and Ag4 is also shown.

intramolecular hydrogen bonding between N⁶–OMe and N1–H (Figure 3b). The bond distances of 1.39 Å between N1 and C6 and 1.29 Å between N⁶ and C6 suggest a single bond character for N1–C6 and a double bond character for the N⁶–C6 bond. It is known that *syn* orientation of imino tautomer dominates in N9-substitued-N⁶-alkoxyadenines.^{6,10,15}

The crystal lattice of 1 is composed of neatly packed adenine ribbons with alternately arranged two crystallographically independent molecules, which are stabilized by three hydrogen bonds through both Watson–Crick and Hoogsteen faces. These unusual hydrogen bonding interactions result from prototropic tautomerism where N⁶–H shifts to the N1 ring nitrogen, thereby creating altered donor and acceptor sites. This anomalous hydrogen bonding scheme causes slight differences in the H-bond distances between atoms (Table 3). Interestingly, the orientation of the *syn*-imino tautomer remains intact even in metal complexes, where the coordinating silver ion is positioned in an *anti*orientation in four crystal structures.

The preponderance of amino to imino tautomer, in the neutral form of adenine nucleobase, estimated in the range of 10^4-10^5 , could be modulated in the presence of coordinating metal ions.¹⁶ So far, there have been a limited number of reports concerning solution or solid state structure of neutral adenine tautomer exhibiting interaction with metal ions.¹⁷ On the basis of prior observations and our ongoing work on adenine—silver interactions, we decided to elucidate solid state structures of N9-benzyl-N⁶-methoxyadenine (1) in the presence of silver ions. These studies were also intended to provide evidence for the importance of N⁶, N7 coordination in stabilizing the adenine neutral imino tautomer.^{4a}

Crystal Structure Analysis of Complex 2. Block-shaped violet colored crystals, suitable for single crystal X-ray analysis, were grown in a week by slow evaporation from the methanolic solution of ligand 1 (1 equiv) and AgNO₃ (1 equiv). Crystal data refinement suggested that 2 $[C_{26}H_{26}Ag_2N_{12}O_8]$ crystallizes in a triclinic space group " $P\overline{1}$ ". The asymmetric unit of the cell is composed of one ligand coordinated to a silver ion which is neutralized by a nitrate ion (Figure 4a). A closer inspection of crystal lattice revealed that the ligand 1 supports a bidentate coordination mode, where N⁶ and N7 ring nitrogens coordinate to silver ions in a head-to-tail fashion resulting in a dinuclear dimeric species (Figure 4b).

The coordination geometry around the tetra-coordinated silver ions may be described as distorted tetrahedron wherein Ag(I) was found coordinated to N⁶ of one ligand (2.216 Å), N7 of other ligand (2.295 Å), and to the two oxygen atoms of nitrate counteranion (2.527 Å, 2.546 Å respectively). However,

Bond Lengths (Å)								
Ag(1)-N(6A)	2.21(48)	Ag(2)-N(6C)	2.22(48)					
Ag(1)-N(6B)	2.19(47)	Ag(2)-N(6D)	2.22(48)					
Ag(1)-N(7B)	2.85(47)	Ag(2)-N(7B)	2.70(46)					
Ag(1)-N(7C)	2.81(48)	Ag(2)-N(7C)	2.73(48)					
Bond Angles (deg)								
Ag(1)-N(7B)-Ag(2)	81.37(137)	N(6B)-Ag(1)-N(7B)	72.14(155)					
Ag(1)-N(7C)-Ag(2)	81.53(137)	N(6C)-Ag(2)-N(7C)	73.62(161)					
N(6A)-Ag(1)-N(7C)	84.36(156)	N(6D) - Ag(2) - N(7B)	87.15(161)					

Table 2. Selected Bond Lengths (Å) and Bond Angles (°) for Complex 3



Figure 8. Part of the crystal lattice of 3 displaying a columnar structure arising out of extensive hydrogen bonding network between N1 hydrogens of purine and nitrate ions and water molecules (black dotted line), C8 hydrogens with nitrate ions only (pink dotted line) and between nitrate ions and water molecules.

the presence of strong Ag…Ag interactions with a distance of 2.919 Å, much less than the sum of their van der Waals radii (3.40 Å), results in an interesting argentophilic $(Ag_2)^{2+}$ dimers formed by the two silver ions.¹⁸

The crystal lattice is further stabilized due to intermolecular hydrogen bonding interactions between N1H and O2 of the nitrate counteranion and C8H and O3 of the nitrate counteranion, as confirmed by hydrogen-bonding parameters given in Table 3. Significant π interactions are also implicated for the reinforcement and overall stability of the crystal lattice. Complex **2** exhibits face-to-face $\pi-\pi$ interactions between modified adenine rings with a centroid-to-centroid distance of 3.341 Å (Figure 5a). Additionally, the presence of intermolecular CH… π interaction (2.59 Å), via methyl in the methoxy group of one unit to the phenyl rings of the other unit, is observed within acceptable interacting distances with a C–H– X angle of 174.46°, where X is the centroid of the phenyl ring (Figure 5b).¹⁹

Crystal Structure Analysis of Complex 3. Role of the metal-to-ligand ratio on the coordination behavior of the ligand was probed by varying the M:L stoichiometry. Complex 3 was prepared by employing 2:1 stoichiometry of 1:AgNO₃ and violet-colored crystals were obtained through a slow evaporation process in few weeks' time. X-ray crystallographic analysis revealed that complex 3 $[C_{78}H_{86}Ag_4N_{34}O_{22}]$ crystallizes in a monoclinic space group "P1 21/n1". The asymmetric unit consists of six ligand molecules coordinated to four Ag(I) ions, neutralized by four nitrate ions, and four non-coordinated

water molecules (Figure 6). However, as seen in the ORTEP diagram, hydrogens for O2W have not been assigned as they are not unequivocally located on the Fourier map due to weakly diffracting crystal. Detailed crystal structure analysis of complex 3 revealed an unusual coordination of nitrogen atoms to silver ions as described below.

The remarkable feature of complex **3** is the presence of two sets of crystallographically unique silver ions (Ag1, Ag2 and Ag3, Ag4). ORTEP diagram reveals an interesting coordination pattern: two discrete AgL₂ units are present, coordinated in a head-to-tail fashion via N⁶ purine nitrogen, in addition to an Ag₂L₂ unit. The latter resembles complex **2**; however, geometry around the silver ions is slightly different with the presence of non-interacting nitrate ions, resulting in a linear geometry. This discrete dimer is defined by distance parameters of Ag(3)–N^{6F}: 2.112 Å, Ag(3)–N7E: 2.121 Å, Ag(4)–N^{6E}: 2.108 Å and Ag(4)–N7F: 2.110 Å, and angle parameters of N^{6F}–Ag(3)–N7E: 169.7° and N^{6E}–Ag(4)–N7F: 171.1°. Further, the observed Ag…Ag interaction at 2.809 Å is stronger compared to complex **2** at 2.919 Å.

Two AgL₂ units coordinate each other through weak, out-ofplane interactions of silver ions to N7 nitrogens of purine (shown in dotted lines in Figure 7). These silver ions can be assumed to adopt a linear geometry with angles N^{6A} –Ag(1)– N^{6B} : 169.33° and N^{6C} –Ag(2)– N^{6D} : 166.14°, while the bonding distances are Ag(1)– N^{6A} : 2.207 Å, Ag(1)– N^{6B} : 2.188 Å, Ag(2)– N^{6C} : 2.222 Å, and Ag(2)– N^{6D} : 2.221 Å. However, two N7 nitrogens, N7B and N7C, found in proximity to silver ions, are able to establish weak interactions with the distances Ag(1)–N7B: 2.850 Å, Ag(1)–N7C: 2.810 Å, Ag(2)–N7B: 2.699 Å, and Ag(2)–N7C: 2.732 Å, which are shorter than the sum of their van der Waals radii of 3.27 Å. This results in a long-range, out-of-plane coordination leading to a distorted tetrahedral geometry around silver ions.²⁰ Selected bond distances and bond angles of complex 3 are given in Table 2.

The crystal structure of complex 3 illustrates the critical role played by hydrogen bonding in stabilizing overall crystal packing. The two units in the lattice, AgL_2 and Ag_2L_2 , are represented in two different color codes for distinct visualization of hydrogen bonding patterns (Figure 8). These interactions mainly occur via purine N1-H and C8-H hydrogens with nitrate ions and water molecules. N1 hydrogens of all six purines are involved in hydrogen bonding with both nitrate ions and water molecules (black dotted line), and C8 hydrogens are exclusively involved in hydrogen bonding interactions with nitrate ions (pink dotted line) (Figure 8). Both nitrate ions and water molecules in turn also indulge in hydrogen bonding among themselves. Isolated oxygen atom also shows short contact with the nitrate ion (2.57-3.04 Å). Such myriad network of hydrogen bonding interactions across the crystal lattice could be visualized as a columnar structure,

Table 3. Hydrogen Bonding Table for Ligand 1^a and Complexes $2-5^a$

D-H…A	symmetry of A	D-H	H···A	D–A	∠D–H…A
	Ligand	11			
$N(1)-H(1)\cdots N(7')$	1 - x, -y, 1 - z	0.86	2.10	2.935	165
$N(1')-H(1')\cdots N(7)$	1-x, -y, -z	0.86	2.07	2.884	159
$C(2)-H(2)\cdots N(6')$	1 - x, -y, 1 - z	0.93	2.51	3.380	156
$C(2')-H(2')\cdots N(6)$	1 - x, -y, -z	0.93	2.50	3.351	152
	Comple	ex 2			
$N(1)-H(1)\cdots O(2)$	1 - x, 1 - y, -z	0.86	2.19	2.854	133
C(8) - H(8) - O(3)	-1 + x, y, z	0.93	2.51	3.232	135
	Comple	ex 3			
N(1A)-H(1A)-O(1W)	1 - x, 1 - y, -z	0.86	1.94	2.746	157
N(1B)-H(1B)-O(21)	1/2 - x, $-1/2 + y$, $1/2 - z$	0.86	1.96	2.762	156
$N(1C)-H(1C)\cdots O(14)$	-x, 1 - y, 1 - z	0.86	2.00	2.802	155
$N(1D)-H(1D)\cdots O(3W)$	1/2 - x, $1/2 + y$, $1/2 - z$	0.86	2.03	2.826	153
N(1E) - H(1E) - O(2W)	-1/2 + x, $1/2 - y$, $1/2 + z$	0.86	1.97	2.648	134
N(1F) - H(1F) - O(4W)	1/2 - x, $-1/2 + y$, $1/2 - z$	0.86	1.92	2.695	149
O(1W) - H(1W1) - O(13)		0.84	2.01	2.826	165
O(1W) - H(1W1) - O(23)		0.84	2.50	3.125	132
$O(1W) - H(2W1) \cdots O(34)$	1/2 - x, $1/2 + y$, $1/2 - z$	0.85	2.03	2.853	164
$O(4W) - H(1W4) \cdots O(12)$	1/2 - x, $1/2 + y$, $1/2 - z$	0.84	2.19	2.976	156
$O(4W) - H(1W4) \cdots O(22)$	1/2 - x, $1/2 + y$, $1/2 - z$	0.84	2.42	3,109	140
O(4W) - H(2W4) O(31)	1/2 - x - 1/2 + y - 1/2 - z	0.83	2.09	2 918	170
O(3W) H(1W3) O(22)	1/2 - x - 1/2 + y + 1/2 - z	0.83	2.09	2.910	130
O(3W) - H(1W3) - O(22)	1/2 - x, -1/2 + y, 1/2 - z 1/2 - x - 1/2 + y, 1/2 - z	0.83	2.20	2.004	162
O(3W) = H(1W3) = O(22)	$1/2 - x_{1} - 1/2 + y_{1} - 1/2 - z_{2}$	0.85	2.24	3.030	102
C(84) = H(84) = O(22)	1/2 - x, -1/2 + y, 1/2 - z	0.83	2.04	2.870	170
$C(\delta A) = H(\delta A) \cdots O(52)$	-1/2 + x, $3/2 - y$, $-1/2 + 2$	0.93	2.52	3.203	137
$C(8B) = H(8B) \cdots O(13)$		0.93	2.57	3.248	130
$C(8B) = H(8B) \cdots O(33)$		0.93	2.32	3.189	155
$C(8C) = H(8C) \cdots O(31)$	1 - x, 2 - y, 1 - z	0.93	2.33	3.18/	154
$C(8D) - H(8D) \cdots O(24)$		0.93	2.30	3.159	152
$C(8E) - H(8E) \cdots O(12)$	1 - x, 1 - y, 1 - z	0.93	2.23	3.108	157
$C(8F) - H(8F) \cdots O(34)$		0.93	2.52	3.364	151
	Comple	ex 4	2.20	2 2 4 2	105
N(1) - H(1) - O(2)	1 - x, 1 - y, -z	0.86	2.28	2.963	13/
N(1) - H(1) - O(2)	1 - x, -y, 1 - z	0.86	2.08	2.890	156
$C(2^{2}) - H(2^{2}) \cdots O(4)$	1 - x, -y, 1 - z	0.93	2.58	3.364	142
C(8) - H(8) - O(3)		0.93	2.35	3.206	153
$C(8') - H(8') \cdots O(4')$	-1 + x, y, z	0.93	2.44	3.124	130
	Comple	ex 5	2.20	2 002	100
$N(1) - H(1) \cdots F(3)$	-y, -1/2 + x, 1/2 + z	0.86	2.30	2.993	138
$N(1) - H(1) \cdots O(1W)$	x, y, -1 + z	0.86	1.98	2.794	156
$O(1W) - H(1W) \cdots F(2)$	y, 1/2 - x, 1/2 - z	0.86	2.01	2.857	165
$O(1W) - H(2W) \cdots N(6')$		0.86	2.09	2.952	177
$C(8)-H(8)\cdots F(1)$	1/2 - x, 1/2 - y, z	0.93	2.50	3.286	143
$C(8) - H(8) \cdots F(4)$	1/2 - x, 1/2 - y, z	0.93	2.41	3.157	137
$C(8')-H(8')\cdots F(1)$	1/2 - x, $1/2 - y$, z	0.93	2.30	3.195	161
$C(16')-H(16B)\cdots F(3)$	-y, -1/2 + x, -1/2 + z	0.96	2.46	3.375	160
^a Where D is donor and A is accept	tor, the bond lengths are in Å and angl	es are in deg.			

where the outer periphery is composed of water molecules and nitrate anion, while the inner core comprises of silvercoordinated hydrophobic purine bases (Figure 8). The significant hydrogen bonding parameters are given in Table 3.

The stability of crystal lattice is further enhanced by remarkable $Ag \cdots \pi$ interactions encountered in the complex (Figure 9a).²¹ These interactions bring two crystallographically different subunits, AgL_2 and Ag_2L_2 , close to each other thereby reinforcing lattice stability. It is observed that Ag2 and Ag3 are in proximity to the adjacent purine imidazole rings, at respective distances of 3.66 Å and 3.46 Å, as can be seen in Figure 9a. It is also worth mentioning here that the planes

containing AgL_2 and Ag_2L_2 units show an interplanar separation of 3.36 Å (yellow and orange plane) and 2.99 Å (orange and purple plane), suggesting close contact and lattice stabilization (Figure 9b).

Crystal Structure Analysis of Complex 4. Replacement of counteranion was probed for its effect on the coordination behavior of ligand 1 in this complex. Mixing equimolar methanolic solution of AgClO₄ (1 equiv) and 1 (1 equiv) resulted in a violet-colored solution, which under slow evaporation for a few weeks afforded crystals of complex 4 $[C_{26}H_{26}Ag_2Cl_2N_{10}O_{10}]$. Careful inspection of the crystal data confirmed triclinic space group " $P\overline{1}$ ". The asymmetric unit of



Figure 9. Part of the crystal lattice of 3 depicting (a) Ag $\cdot \cdot \pi$ interactions; (b) interplanar separation.



Figure 10. (a) ORTEP diagram of 4 showing asymmetric unit of the cell at 30% probability level; (b) linear geometry of silver ions with a Ag...Ag distance 2.803 Å.



Figure 11. Part of crystal lattice of 4 depicting (a) hydrogen bonding interactions forming a 1D-polymeric sheet (benzyl groups are omitted for clarity); (b) π - π stacking interactions between centroids of adenine rings and also between benzyl rings and six-membered ring of the adenine moiety.

the lattice comprises of two crystallographically unique units wherein two ligand molecules coordinate to two silver ions, neutralized by perchlorate anions (Figure 10a). Crystallographic analysis revealed a bidentate coordination mode via purine N⁶ and N7 nitrogens, leading to Ag_2L_2 dimeric units similar to complex **2**. However, unlike complex **2**, complex **4** exhibited stronger argentophilic interactions with an unusually shorter Ag...Ag interaction distance of 2.803 Å. The silver ions in complex **4** display linear coordination, similar to the Ag_2L_2 subunit in complex **3**, through N7' (2.114 Å) and N⁶ nitrogen (2.130 Å), without participation of perchlorate counteranions (Figure 10b). The stability of the crystal lattice is enhanced due to intermolecular hydrogen bonding interactions of purine N1, C8, and C2 hydrogens. These interactions, mediated through bridging perchlorate ions, result in a one-dimensional polymeric sheet along the *a*-axis (Figure 11a). Moreover, extensive $\pi - \pi$ stacking interactions are observed between adjacent purines with a centroid distance of 3.59 Å and between the benzyl substituent and six-membered ring of the purine, with a centroid distance of 3.51 Å (Figure 11b). The important H-bond parameters are summarized in Table 3.

Crystal Structure Analysis of Complex 5. Complex 5, containing PF_6^- , differs from the above complexes in terms of

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Figure 12. (a) Part of the 3-D crystal lattice of complex 5; (b) enlarged view of (a) illustrating hydrogen bonding and $\pi - \pi$ interactions (color code: P: pink, F: green).



Figure 13. (a) Part of the crystal lattice of complex **5** showing 1Dcoordination band through H-bonds between N1–H···OH₂ and HOH···N⁶ and π – π interactions; (b) Ag··· π interactions between Ag and six-membered rings of purine framework in two AgL₂ units (benzyl rings are removed for clarity).

non-coordinating behavior of its counteranion. 5 $[C_{26}H_{28}AgF_{6}\text{-}$ $N_{10}O_3P$] belonged to the tetragonal system in "P42/n" space group and exists as a AgL₂ complex in the crystalline state. Silver ions bridge two ligand molecules through linear N6 -Ag-N7 connectivity, in a head-to-head fashion exhibiting a two-coordinated linear geometry around the silver ion. The asymmetric unit of lattice consists of an unbound PF₆⁻ counterion and a free water molecule, both playing an important role in determining overall stability of the crystal lattice. The extensive hydrogen bonding interactions due to the presence of strong donor and acceptor groups in the purine ring, PF₆⁻ and water molecules, give rise to a complex threedimensional (3-D) framework (Figure 12a). Further analysis of the lattice revealed that AgL₂ units are held together in the crystal lattice by CH…F interactions between inorganic fluoride ions of PF₆⁻ and the purine C8 and methoxy group hydrogens, within the acceptable limit of 2.6 Å for CH---F interactions (see Table 3).²² Interestingly, C8-H also exhibits bifurcated hydrogen bonding with two different fluorine atoms of a $PF_6^$ group, while one of these fluorine atoms in turn displays a

bifurcated hydrogen bonding with C8H of the other ligand (Figure 12b). Purine N1 hydrogens and water also participate in intermolecular hydrogen bonding interactions through fluoride ions of PF_6^- . Moreover, π -interactions between the benzyl ring and six-membered ring of the adjacent purine also contribute to lattice stability (Figure 12b).

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Each discrete AgL₂ unit further extends along the *c*-axis forming an infinite 1D-coordination polymeric chain via N1H…OH₂ and HOH…N⁶ hydrogen bonding. Additionally, $\pi-\pi$ interactions between five-membered rings of the purine framework stabilize the polymeric chain as shown in Figure 13a. Interestingly, like in complex **3**, these polymeric chains display unique intermolecular Ag… π interactions but with six-membered rings of the purine framework with distances 3.48 and 3.84 Å (Figure 13b).^{21,22a} These noncovalent interactions cumulatively reinforce the overall supramolecular organization of **5**.

These crystallographic studies highlight the absolute preference of silver complexes toward N⁶-Ag-N7 bidentate coordination over the N⁶-Ag-N1 case. In an exhaustive computational study, Schreiber and González described that the affinity of silver ions for N7 coordination in terms of gas phase energy calculations. It was found that silver ion affinity for the N^6 , N^9 -unsustituted neutral adenine imino tautomer is ~75 kcal/mol, which is ~24 kcal/mol higher compared to other possible canonical tautomeric complexes.^{5b} Notably, the Ag–N7 distance in all four cases (2-5), described in this paper, was longer compared to Ag-N⁶ distances, suggesting that the latter is a highly stable coordination. This variance matches well with the calculated distances for silver-neutral adenine imino complexes,^{Sb} and, more importantly, it could be inferred that a stable bidentate N⁶-Ag-N7 coordination augments stability of imino tautomer upon silver ion complexation.

CONCLUSION

In summary, affinity of N9-benzyl-N⁶-methoxyadenine toward tautomerization and its complexation with silver were studied by X-ray crystallography. Diverse crystallographic patterns were obtained by varying the stoichiometry and counteranions of the corresponding silver salt. We have presented a detailed analysis of these complexes and the significant role played by

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noncovalent interactions such as hydrogen bonding, π -stacking, and argentophilic interactions. An interesting complexation behavior was also observed in complex 3, where six ligand molecules coordinated to four silver ions to give Ag₂L₂ and two AgL₂ structures. Such a complexation behavior when translated in a biological scenario may provide valuable insights into the mutagenic behavior of these rare tautomers.

ASSOCIATED CONTENT

S Supporting Information

X-ray crystallographic data in CIF format and additional experimental data for the complexes. This information is available free of charge via the Internet at http://pubs.acs.org/. CCDC contains the supplementary crystallographic data for this paper with a deposition number of CCDC 856027 (complex 2), 856030 (complex 3), 856028 (complex 4) and 856029 (complex 5). Copies of this information can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK. [Fax: +44–1223/336–033; E-mail: deposit@ccdc.cam.ac.uk].

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Notes

The authors declare no competing financial interest.

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