8012 *Inorg. Chem.* **2010**, *49*, 8012–8016
DOI: 10.1021/ic1010902

Inorganic Chemistry
Article

Interconnected Trimeric, Pentameric, and Hexameric Metallacycles in a Singular Silver−Adenine Framework

Ashutosh Kumar Mishra and Sandeep Verma*

Department of Chemistry, Indian Institute of Technology (IIT) Kanpur, Kanpur 208016, India

Received May 31, 2010

This Article describes the synthesis and crystallographic investigation of a silver complex of a modified adenine derivative bearing a nitrile pendant at the N9 position. All three adenine ring nitrogen atoms coordinated to silver ions, while the fourth coordination was achieved at the nitrile functionality, thus resulting in the formation of silver-mediated interconnected trimeric, pentameric, and hexameric metallacyclic rings and helical signatures in two orthogonal directions.

Introduction

Nitrogenous nucleobases offer multiple metal binding possibilities for the generation of novel coordination motifs and architectures.[1] Such interactions could also be used to amend classical hydrogen-bonded base-pairing patterns with the help of metal-mediated base pairing to create unusual supramolecular architectures.[2] This effect can be further augmented by the deliberate introduction of metal-binding functional groups at specified sites, thus leading to interesting coordination patterns and unique architectures.[3]

9-Substituted adenine offers three main coordination sites, N1, N3, and N7, with N1 and N7 being predominantly used for metal ion complexation in the mono- or bidentate coordination mode.[4] However, several examples involving the coordination mode that employs all three nitrogen atoms in adenine analogues are known,[5] including several examples from our group.[6] Our focused investigation of silver−adenine interaction has afforded interesting supramolecular motifs suitable for patterned surface deposition, enhanced luminescence properties, and applications involving fluorescent sensing for silver ions.[6,7] We have designed suitably N9-substituted adenine ligands to achieve hierarchical architectures of increased complexity (Scheme 1a). In this connection, we recently reported the formation of a silver metallamacrocyclic hexamer, as a result of tetradentate coordination involving μ-(N1,N3,N7) interaction and an additional coordination via an N9 carboxylate group bearing a substituent.[6d] To broaden the scope of this approach, we prepared 3-(6-aminopurin-9-yl)propionitrile (Scheme 1b) containing an N9-nitrile pendant, and a detailed crystallographic investigation of its silver complex was performed.

Experimental Section

^{1}H and ^{13}C NMR spectra were obtained on a JEOL-DELTA2 500 model spectrometer operating at 500 MHz. The chemical shifts were referenced with respect to tetramethylsilane

---

*To whom correspondence should be addressed. E-mail: sverma@iitk.ac.in.

(1) (a) Sessler, J. L.; Lawrence, C. M.; Jayawickramarajah, J. *Chem. Soc. Rev.* **2007**, *36*, 314–325. (b) Sivakova, S.; Rowan, S. J. *Chem. Soc. Rev.* **2005**, *34*, 9–21.

(2) (a) Müller, J. *Eur. J. Inorg. Chem.* **2008**, *24*, 3749–3763. (b) Clever, G. H.; Kaul, C.; Carell, T. *Angew. Chem., Int. Ed.* **2007**, *46*, 6226–6236. (c) Polonius, F. A.; Müller, J. *Angew. Chem., Int. Ed.* **2007**, *46*, 5602–5604. (d) Tanaka, K.; Clever, G. H.; Takezawa, Y.; Yamada, Y.; Kaul, C.; Shionoya, M.; Carell, T. *Nat. Nanotechnol.* **2006**, *1*, 190–194. (e) Tanaka, K.; Tengeiji, A.; Kato, T.; Toyama, N.; Shionoya, M. *Science* **2003**, *299*, 1212–1213. (f) Shen, W. Z.; Lippert, B. *J. Inorg. Biochem.* **2008**, *102*, 1134–1140. (g) Zhu, X.; Rusanov, E.; Kluge, R.; Schmidt, H.; Steinborn, D. *Inorg. Chem.* **2002**, *41*, 2667–2671. (h) Amo-Ochoa, P.; Miguel, P. J. S.; Lax, P.; Alonso, I.; Roitzsch, M.; Zamora, F.; Lippert, B. *Angew. Chem., Int. Ed.* **2005**, *44*, 5670–5674. (i) Knobloch, B.; Sigel, R. K. O.; Lippert, B.; Sigel, H. *Angew. Chem., Int. Ed.* **2004**, *43*, 3793–3795.

(3) (a) Galindo, M. A.; Houlton, A. *Inorg. Chim. Acta* **2009**, *362*, 625–633. (b) Meiser, C.; Song, B.; Freisinger, E.; Peilert, M.; Sigel, H.; Lippert, B. *Chem.—Eur. J.* **1997**, *3*, 388–398. (c) Price, C.; Elsegood, M. R. J.; Clegg, W.; Houlton, A. *J. Chem. Soc., Chem. Commun.* **1995**, 2285–2286. (d) Price, C.; Elsegood, M. R. J.; Clegg, W.; Rees, N. H.; Houlton, A. *Angew. Chem., Int. Ed.* **1997**, *36*, 1762–1764. (e) Shipman, M. A.; Price, C.; Elsegood, M. R. J.; Clegg, W.; Houlton, A. *Angew. Chem., Int. Ed.* **2000**, *39*, 2360–2362.

(4) Lippert, B. *Coord. Chem. Rev.* **2000**, *200−202*, 487–516.

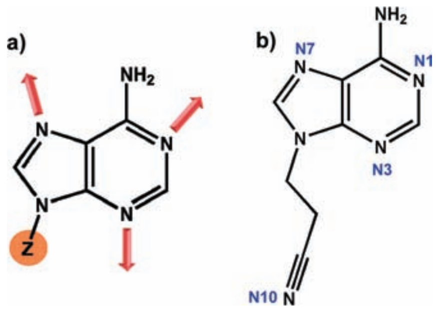
(5) (a) García-Teràn, J. P.; Castillo, O.; Luque, A.; García-Couceiro, U.; Romàn, P.; Lezama, L. *Inorg. Chem.* **2004**, *43*, 4549–4551. (b) Fish, R. H.; Jaouen, G. *Organometallics* **2003**, *22*, 2166–2177. (c) Rojas-Gonzàlez, P. X.; Castiñeiras, A.; Gonzàlez-Pérez, J. M.; Chóquesillo-Lazarte, D.; Niclós-Gutiérrez, J. *Inorg. Chem.* **2002**, *41*, 6190–6192. (d) Rother, I. B.; Freisinger, E.; Erxleben, A.; Lippert, B. *Inorg. Chim. Acta* **2000**, *300−302*, 339–352.

(6) (a) Purohit, C. S.; Verma, S. *J. Am. Chem. Soc.* **2006**, *128*, 400–401. (b) Purohit, C. S.; Mishra, A. K.; Verma, S. *Inorg. Chem.* **2007**, *46*, 8493–8495. (c) Purohit, C. S.; Verma, S. *J. Am. Chem. Soc.* **2007**, *129*, 3488–3489. (d) Kumar, J.; Verma, S. *Inorg. Chem.* **2009**, *48*, 6350–6352.

(7) (a) Verma, S.; Mishra, A. K.; Kumar, J. *Acc. Chem. Res.* **2010**, *43*, 79–91. (b) Mishra, A. K.; Purohit, C. S.; Kumar, J.; Verma, S. *Inorg. Chim. Acta* **2009**, *362*, 855–860. (c) Mishra, A. K.; Purohit, C. S.; Verma, S. *CrystEngComm* **2008**, *10*, 1296–1298. (d) Pandey, M. D.; Mishra, A. K.; Chandrasekhar, V.; Verma, S. *Inorg. Chem.* **2010**, *49*, 2020–2022. (e) Prajapati, R. K.; Kumar, J.; Verma, S. *Chem. Commun.* **2010**, *46*, 3312–3314. (f) Mishra, A. K.; Verma, S. *Inorg. Chem.* **2010**, *49*, 3691–3693.

Published on Web 08/09/2010
© 2010 American Chemical Society

Scheme 1. (a) Schematic Representation of the Possible Mode of Metal Binding Sites in an N9-Adenine Analogue and (b) Chemical Structure of the Ligand



(TMS). High-resolution mass spectrometry (HRMS) spectra for the ligand and metalated complexes were recorded at IIT Kanpur, Kanpur, India, on a Waters Q-Tof Premier Micromass HAB 213 mass spectrometer. Solvents were evaporated using a rotary evaporator under reduced pressure. Adenine, acroylnitrile, and silver nitrate were purchased from Spectrochem Pvt. Ltd., Mumbai, India, and potassium carbonate was purchased from SD Fine Chemicals Pvt. Ltd., Mumbai, India, and used without further purification. All solvents were distilled prior to use using standard procedures. Fluorescence spectra were recorded on a Varian Luminescence Cary Eclipse with a 10 mm quartz cell at 25 ± 0.1 °C, and electronic spectra were recorded on a Perkin-Elmer-Lambda 20 UV−vis spectrometer with a 10 mm quartz cell at room temperature. A 10 μM stock solution of **1** in a water−dimethyl sulfoxide [DMSO; 1:1 (v/v)] system was used to perform the fluorescence experiment. The excitation wavelength was 320 nm.

X-ray Analysis and Structure Refinement. Data were collected on a Bruker SMART CCD4 X-ray diffraction instrument using graphite-monochromated Mo Kα radiation (α = 0.710 Å) at 100 K. The crystal was solved by direct methods using the *SIR92* program[8] and refined using full-matrix least squares on F^2 (*SHELX97*).[9] The structure was expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at geometrically idealized positions. Table 1 contains the final refinement parameters for **1**. All of these software packages were the integrated *WINGX* software package. CCDC 778346 contains 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).

Synthesis. Synthesis of 3-(6-Aminopurin-9-yl)propionitrile (1). In a round-bottomed flask, adenine (500 mg, 1 equiv) was dissolved in 5 mL of DMSO, followed by the addition of potassium carbonate (30 mg, 1.2 equiv), and the resulting solution was stirred for 30 min at room temperature. After acroylnitrile (1.22 mL, 0.95 equiv) was added, the reaction was stopped after 30 min. The compound was extracted with a water−ethyl acetate system and further purified by column chromatography (75.6% yield). HRMS [(M + H)$^+$]. Calcd: *m*/*z* 189.0889. Found: *m*/*z* 189.0856. ^{1}H NMR (500 MHz, DMSO-d_6, 20.9 °C, TMS): δ 3.15 (t, 2H), 4.40−4.43 (t, 2H), 7.25 (s, 1H), 8.14 (s, 1H), 8.15 (s, 1H). ^{13}C NMR (125 MHz, DMSO-d_6, 20.6 °C, TMS): δ 18.65, 40.86, 118.50, 119.21, 141.08, 149.15, 153.15, 156.55. Anal. Calcd for $C_8H_8N_6$: C, 51.06; H, 4.28; N, 44.66. Found: C, 51.21; H, 4.19; N, 44.60.

Synthesis of a Silver Complex of 1. In a 25 mL round-bottomed flask, wrapped with aluminum foil, the ligand was dissolved in methanol, and to this was added dropwise with stirring the corresponding silver salt solution in water (1 mol equiv). The complex started precipitating out with the addition of the silver salt solution. Stirring was continued for another 1 h. After that time, the precipitate was carefully filtered to avoid direct light and washed with water (4 × 5 mL) and methanol (4 × 5 mL) to remove any traces of unreacted metal salt and ligand. The product so obtained was dried under a high vacuum. The yields were almost quantative. HRMS (L + Ag$^+$). Calcd: *m*/*z* 294.9861. Found: *m*/*z* 294.9865. HRMS (L + 2Ag$^+$ + 1). Calcd: *m*/*z* 402.8991. Found: *m*/*z* 402.8940. HRMS (L + 3Ag$^+$). Calcd: *m*/*z* 508.7963. Found: *m*/*z* 508.9141. HRMS (L + 4Ag$^+$ + 2). Calcd: *m*/*z* 617.7171. Found: *m*/*z* 617.7957. ^{1}H NMR (500 MHz, DMSO-d_6, 22.8 °C, TMS): δ 3.13−3.16 (t, 2H), 4.49−4.55 (t, 2H), 7.77 (s, 1H), 8.32 (s, 1H), 8.42 (s, 1H). ^{13}C NMR (125 MHz, DMSO-d_6, 17.7 °C TMS): δ 18.71, 40.83, 118.63, 118.85, 142.67, 149.28, 154.09, 155.94.

Table 1. Crystallographic Data for Complex **1**

identification code	**1**
empirical formula	$C_{16}H_{16}Ag_3N_{15}O_{12}$
fw	934.05
cryst color	colorless
cryst size (mm)	0.28 × 0.24 × 0.20
cryst syst	tetragonal
space group	$P4_32_12$ (No. 96)
a (Å)	9.6180(18)
b (Å)	9.6180(18)
c (Å)	29.490(8)
α (deg)	90
β (deg)	90
λ (deg)	90
V (Å^3)	2728.0(10)
D_{calcd} (mg m^{-3})	2.274
Z	4
μ(Mo Kα) (mm^{-1})	2.223
F(000)	1816
2θ range	2.2−26.0
reflns measd	15104
indep reflns	2478 [R(int) = 0.0441]
reflns obsd [$I > 2\sigma(I)$]	2685
no. of param	206
final R1, wR2 (obsd data)	R1 = 0.0432, wR2 = 0.1118
GOF (obsd data)	1.160
CCDC no.	778346

Results and Discussion

NMR Studies. Favorable interaction between the ligand and silver ions was evident in ^{1}H NMR titration experiments. It was observed that the addition of silver ions caused a downfield shift in the exocyclic amino protons from 7.25 to 7.82 ppm, while the C2H and C8H proton singlets were downfield-shifted from 8.14 and 8.16 to 8.34 and 8.46 ppm, respectively (Figure 1). These observations reflect significant interaction of modified silver−adenine complex, which results in substantial chemical shift values. After encouraging solution-phase studies, crystals of the silver−ligand complex were grown to investigate the solid-state interactions.

Crystallographic Studies. Crystals suitable for single-crystal analysis were grown by a slow evaporation technique from an acetonitrile solution of the ligand and silver nitrate. Colorless crystals were formed after 1 week. Refinement of the collected data suggested that the silver complex crystallized in the tetragonal system, space group $P4_32_12$ (No. 96). A closer inspection of the crystal lattice revealed a tetradentate coordination mode, where the three ring nitrogen atoms (N1, N3, and N7) and the nitrogen atom from the pendant nitrile group were coordinated

---

(8) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr*. **1993**, *26*, 343.

(9) Sheldrick, G. M. *SHELX97*; University of Goettingen: Goettingen, Germany, 1997.

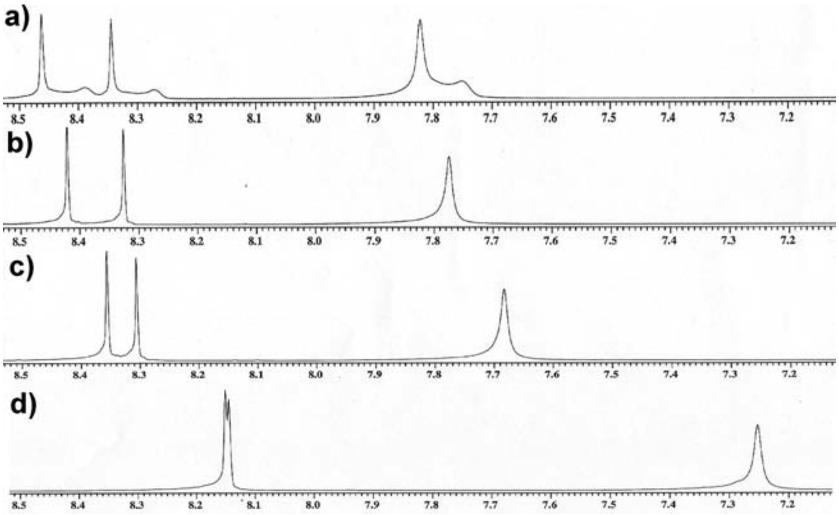


Figure 1. Representation of NMR titration data with added amounts of silver nitrate: (a) with 5 equiv of Ag^+; (b) with 1 equiv of Ag^+; (c) with 0.5 equiv of Ag^+; (d) ligand alone.

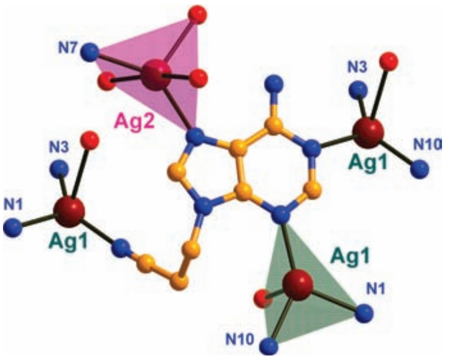


Figure 2. Representation of the tetradentate coordination mode in **1**. Crystallographically unique silver ions are highlighted by colored polyhedra.

to the silver ions. Interestingly, the coordination environment around the silver ions confirmed the presence of two crystallographically unique silver ions, labeled as Ag1 and Ag2, as represented by polyhedra of two different colors (Figure 2).

Ag1 was found to exhibit a tetracoordinated mode via participation of N1, N3, and N10 nitrogen atoms, from three different modified adenine–ligand molecules, and a nitrate counteranion (Figure 2). This arrangement leads to a distorted trigonal-pyramidal coordination geometry in which the counteranion occupies the axial position. The Ag–N bond distances were in the range of 2.23–2.35 Å, whereas the N1–Ag–N10, N1–Ag–N3, and N3–Ag–N10 bond angles were 97.63(6)°, 121.72(7)°, and 140.62(7)°, respectively.

On the other hand, Ag2 was stabilized in a rare pentacoordinated environment, displaying a distorted square-pyramidal geometry, via coordination from two N7 nitrogen atoms from two different molecules and three nitrate counteranions (Figure 2). The two N7 nitrogen atoms and two counteranions occupy the planar position in a trans fashion, while the third counteranion occupies the apical position, with a shorter bond length compared to the corresponding equatorial bond lengths [2.38(3) and 2.85(4) Å, respectively].

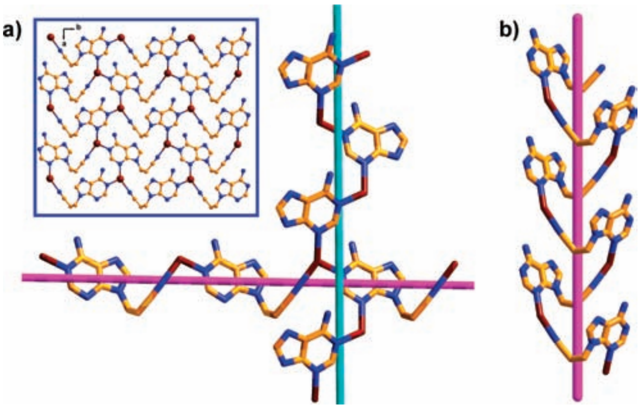


Figure 3. (a) 1D coordination polymeric helices in **1**, which run perpendicular to each other along the *a* and *b* axes (inset shows the view of the crystal lattice along the *c* axis). (b) 1D coordination polymeric helices in **1** along the *b* axis involving N3 and N10 nitrogen atoms.

The crystal lattice, when viewed along the *c* axis, reveals the formation of two different types of infinite 1D coordination polymeric helices tethered by intervening Ag1 ions and running in directions orthogonal to each other (Figure 3a). It is possible to identify one silver-tethered supramolecular helix along the *a* axis through the participation of N1 and N3 adenine nitrogen atoms possessing a right-handed screw axis, while the other one involves N1 and N10 (of nitrile group) nitrogen atoms and runs along the direction of the *b* axis, possessing a left-handed screw axis. There are other interesting helical features present in the crystal lattice involving N3 and N10 nitrogen atoms (Figure 3b). The emergence of such a framework could be ascribed to three fixed nitrogen centers in the heterocyclic ring, with another coordinating nitrogen center being contributed by the nitrile group (designated as N10) at adenine N9 position.

A closer inspection of the lattice organization reveals a highly unusual occurrence of the formation of three different types of interconnected metallacyclic rings (Figure 4). The pentameric and hexameric rings are formed with the help of adenine rings and intervening silver ions, where a single interaction between silver and N10 nitrile nitrogen is invoked to achieve closure of the ring. However, the

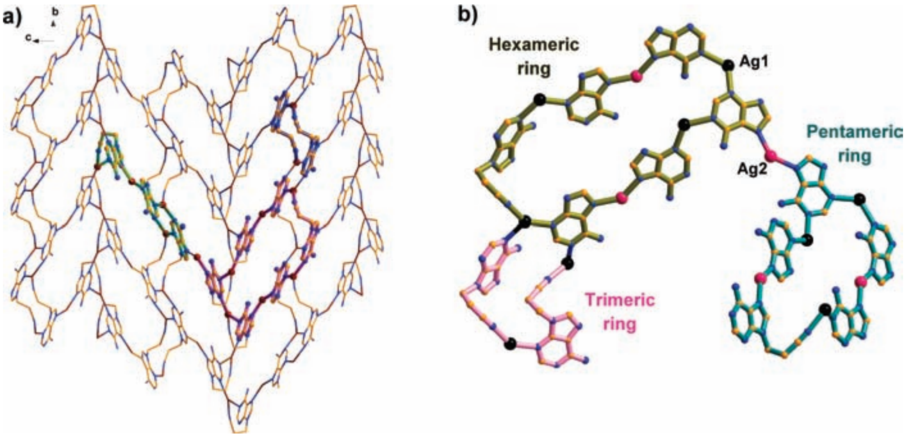


Figure 4. (a) Part of the crystal lattice viewed along the *a* axis showing embedded and interconnected 3-, 5-, and 6-membered metallacycles in **1**. (b) Representation of three different types (trimeric, pentameric, and hexameric) of interconnected rings, shown in different colors. Parts of the complex and hydrogen atoms are omitted for clarity.

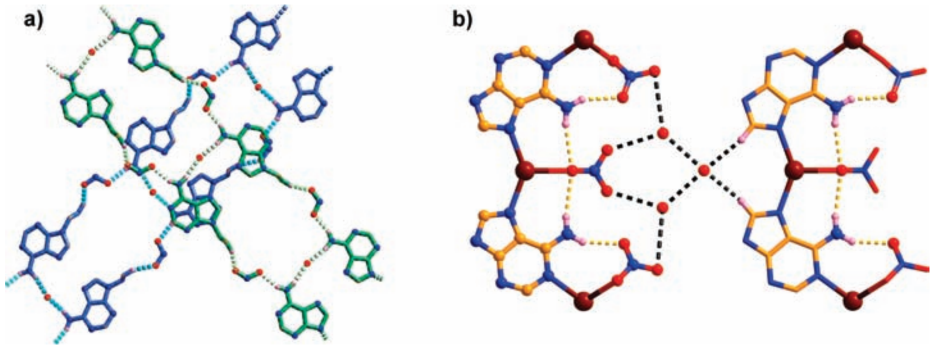


Figure 5. (a) Hydrogen-bonding interaction between the modified adenine and nitrate counteranions, leading to two polymeric chains running in different directions. (b) Representation of probable hydrogen-bonding interactions between water molecules present in the crystal lattice with an adjacent nitrate and the C8H hydrogen atom of the adenine moiety (shown with black dotted lines). Attempts to assign hydrogen atoms on the water molecules were unsuccessful during solution of the crystal.

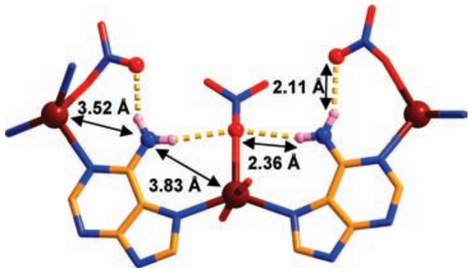


Figure 6. Close proximity of exocyclic amino groups to coordinated silver ions. Dotted lines shows hydrogen bonding between the N6 hydrogen atom and the nitrate anion. Other hydrogen atoms are omitted for clarity.

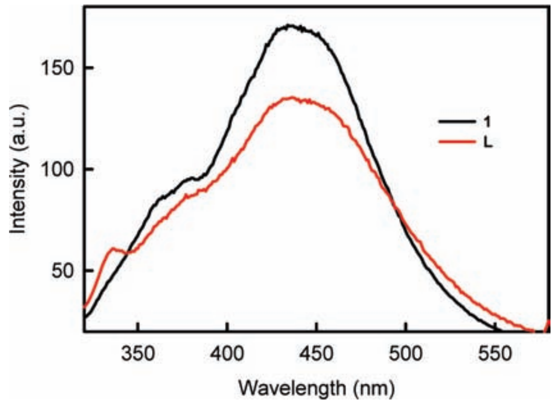


Figure 7. Fluorescence spectra of the ligand alone (red line) and in the presence of Ag^+ (black) in a 1:1 water−DMSO solution.

trimeric ring is composed of two silver−nitrile interactions, in addition to a N1−Ag−N3 interaction.

Significant hydrogen-bonding interactions between N6H and CH_2 (C11) of modified adenine with oxygen atoms of the nitrate group could be implicated in the reinforcement of the overall stability to the crystal lattice (Figure 5a). It is interesting to observe how these hydrogen-bonding interactions afford a boxlike arrangement, leading to a 1D polymeric chain. The hydrogen-bonding distances and the angles between N6−H···O and C−H···O were in the range of 2.11−2.36 and 2.38 Å and 156.12−167.63° and 139.95°, respectively. Favorable interactions between the water molecules present in the crystal lattice with adjacent nitrate and the C8H hydrogen atom of the adenine moiety are evident (Figure 5b), thereby further stabilizing the crystal lattice. Selected hydrogen-bonding distances and angles are given in Table 2.

As is evident from the solid-state analysis of **1**, there is visible proximity of the silver ions to the exocyclic amino groups of coordinated adenine moieties (Figure 6). Thus, the observed prominent NMR shift of an exocyclic amino group could be attributed to the polarizing effects resulting

Table 2. Selected Hydrogen-Bonding Distances and Angles for Complex **1**

D−H···A[#]	$d_{H\cdots A}$	$d_{D\cdots A}$	angle
N6−H6A···O2	2.11	2.92(9)	156
N6−H6B···O4[i]	2.36	3.20(9)	168
C8−H8···O6	2.45	3.36(11)	166
C11−H11A···O1	2.36	3.32(10)	174
C11−H11B···O3[ii]	2.39	3.19(9)	140

[#] Symmetry of A: (i) $^1/_2 - y$, $-^3/_2 + x$, $-^1/_4 + z$; (ii) $-^1/_2 + x$, $^1/_2 - y$, $^1/_4 - z$.

from metal ion coordination,[10] in addition to support from the hydrogen-bonding interaction with nitrate anions, further reinforcing the downfield shift.

Fluorescence Studies. 1 also exhibited weak fluorescence when compared to the ligand alone. When excited at 320 nm, it showed an enhanced emission maximum at ~450 nm, which could be ascribed to the known phenomenon of d^{10} metal complexes exhibiting enhanced fluorescence without introducing low-energy metal-centered or charge-separated excited states into the molecule (Figure 7).[11]

Conclusions

We have synthesized and investigated the solid-state structural analysis of silver complex of N9-adenine and its fluorescence behavior. The presence of two supramolecular helices running orthogonal to each other and the interconnection of three different types of metallacyclic rings are the salient features of the crystal lattice. The possibility of minor chemical modifications in nucleobases for the generation of complex hierarchical structures will be further evaluated.

Acknowledgment. DST, India, is gratefully acknowledged for financial support (to S.V.). A.K.M. acknowledges CSIR, India, for a Senior Research Fellowship.

Supporting Information Available: X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

---

(10) (a) Lüth, M. S.; Willermann, M.; Lippert, B. *Chem. Commun.* **2001**, 2058–2059. (b) Szabo, Z. *Coord. Chem. Rev.* **2008**, *252*, 2362–2380.

(11) (a) Prodi, L.; Bolletta, F.; Montalti, M.; Zaccheroni, N. *Eur. J. Inorg. Chem.* **1999**, 455–460. (b) Guo, X.; Qian, X.; Jia, L. *J. Am. Chem. Soc.* **2004**, *126*, 2272–2273. (c) Feng, L.; Chen, Z. *Sensors Actuat. B* **2007**, *120*, 665–668. (d) Yam, V. V.-W.; Lo, K. K.-W. *Chem. Soc. Rev.* **1999**, *28*, 323–334.