CrystEngComm

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/crystengcomm

Crystal Engineering with a Purine Rare Tautomer: Structures and Luminescence Properties

Shruti Khanna[a] and Sandeep Verma[a,b]*

[a]Department of Chemistry, [b]Centre for Environmental Sciences and Engineering

Indian Institute of Technology Kanpur, Kanpur-208016 (UP), India

sverma@iitk.ac.in

Abstract:

Cadmium, a metal known to be toxic to living systems through unfavorable interactions with biomolecules, interacts with purine nucleobases through N7 imino nitrogen and induces modifications by altering amino-imino tautomeric equilibrium. Herein, we report unique crystallographic signatures of cadmium complexes of N9-benzyl N^6-methoxyadenine, a rare imino tautomer of adenine. These complexes exhibit a variety of coordination numbers and spatial geometries, highlighting the ability of nucleobases to form diverse supramolecular architectures, enabling better understanding of metal-DNA interactions. Cd^{2+} ion in complex **1** has a coordination number of four with distorted tetrahedral geometry, while **2** and **3** are hexa-coordinated, where **2** displays discrete distorted octahedron geometry and **3** appears as a dinuclear complex. On the other hand, complex **4** exhibits a less common hepta-coordination mode with distorted pentagonal bipyramidal geometry. The luminescence properties of these cadmium complexes are also reported.

Introduction

Cadmium is a toxic metal present in the environment and is recognized as being hazardous to living forms. It could serve a mitogenic role in order to stimulate cell proliferation, inhibit apoptosis, and facilitate formation of cancerous lesions in a number of tissue types. Cadmium is also implicated in renal damage by inducing cell death: low-to-moderate concentrations cause apoptosis, while exposure to higher concentrations may lead to tissue necrosis. While direct DNA damage by cadmium is not well established, it is known to induce

formation of reactive oxygen species resulting in DNA damage. Another significant pathway mediating cadmium toxicity concerns interference with DNA repair mechanisms, cell cycle and apoptosis. Thus, it is inevitable that cadmium-based inhibition of DNA repair and apoptosis, may lead to increased mutation rate. The ensuing genomic instability may lead to cancer and other diseases associated with an unstable genome.[1]

The significance of metal-nucleic acid interactions has spawned intensive studies concerning structural elucidation of metal-heterocyclic nucleobase interactions. Crystallographic studies of these systems have afforded interesting data on coordination geometry of complexes as well as insight into possible biological role of metal ions at the nucleic acid level. Newer avenues are also being sought to include synthesis of metal-mediated base pairs for nucleic acid functionalization. Replacement of conventional hydrogen bonds between complementary nucleobases by metal coordinated systems also affords entry into metal-modified nucleic acids, which could be used for sensing applications, for construction of DNA-based molecular machines and to synthesize charge conducting nucleic acids.[2]

Cd(II) preferably interacts with adenosine and guanosine through N7 imino nitrogen.[3-5] Its interaction with adenine is reported to result in irreversible structural changes by altering the propensity of amino-imino tautomeric equilibrium causing mispairing and mutations.[3,6] Covalent binding of Cd(II) to DNA nucleobases may cause redistribution in the electron density of the heterocyclic ring, thereby weakening the phosphodiester bonds resulting in DNA damage.[3] Wei *et al*. reported crystal structure of cadmium complex with adenine, wherein a binuclear complex was formed by treating monosodium salt of adenosine-5'-monophosphoric acid with cadmium nitrate.[7] Since then, several supramolecular architectures exploiting Cd-adenine interactions *via* ring nitrogens have been reported in literature.[8,9]

We became interested in determining the structural manifestations of cadmium with tautomerized bases, as binding of metal ions leads to stabilization of rare mutagenic tautomers.[10] Moreover, it has been shown that binding of Cd(II) to DNA results in the prevention of enzymatic digestion perhaps due to metal mediated structural modifications affecting amino–imino tautomeric forms and the shift in this equilibrium may be held responsible for mispairing and mutagenesis.[11] Given this background with cadmium ions and our ongoing interest in metal-

adenine interactions,[12] we decided to study N^6-methoxyadenine, which affords shift towards rare imino tautomer, to understand its interaction with Cd(II) ions.

Experimental Section:

1. Synthesis of ligand, L: The synthesis of N9-benzyl-N^6-methoxyadenine has been previously reported by us.[12m]

2. Synthesis of complex 1 [$C_{52}H_{52}F_{12}N_{20}O_4P_2Cd$]: The reaction of ligand **L** (1 eq) with freshly prepared $Cd(PF_6)_2$ (1 eq) solution in MeOH and subsequent slow evaporation afforded colorless block-shaped crystals of complex **1** (Yield: 52%). HRMS: $[L+H]^+$: 256.1039 (Calcd.: 256.1198), $[3L+Cd]^{2+}/2$: 439.6146 (Calcd.: 439.6197), $[2L+H]^+$: 511.2207 (Calcd.: 511.2318) and $[4L+Cd]^{2+}/2$: 567.1713 (Calcd.: 567.1757)

3. Synthesis of complex 2 [$C_{13.50}H_{16}N_{5.50}O_{3.50}Cd_{0.25}$]: The violet colored crystals of **2** were obtained by slow evaporation of methanolic solutions of ligand **L** (1 eq) and $Cd(NO_3)_2.4H_2O$ (1 eq.) (Yield: 58%). HRMS: $[L+H]^+$: 256.1115 (Calcd.: 256.1198), $[2L+H]^+$: 511.2300 (Calcd.: 511.2318), $[4L+Cd]^{2+}/2$: 567.1728 (Calcd.: 567.1757) and $[2L+Cd+NO_3]^+$: 686.1168 (Calcd.: 686.1152)

4. Synthesis of complex 3 [$C_{13}H_{13}Cl_{1.50}N_5O_{2.50}Cd_{0.50}$]: The equimolar reaction of ligand **L** (1 eq) and $CdCl_2.H_2O$ (1 eq) in MeOH afforded colorless crystal corresponding to **3** (Yield: 40%). HRMS: $[L+H]^+$: 256.1105 (Calcd.: 256.1198), $[2L+H]^+$: 511.2325 (Calcd.: 511.2318) and $[4L+Cd]^{2+}/2$: 567.1752 (Calcd.: 567.1757)

5. Synthesis of complex 4 [$C_{31}H_{38}N_{10}O_8Cd$]: The reaction of methanolic solutions of ligand **L** (1 eq) and $Cd(OAc)_2.2H_2O$ (1 eq) yielded colorless crystals of complex **4** under slow evaporation (Yield: 64%). HRMS: $[L+H]^+$: 256.1084 (Calcd.: 256.1198), $[3L+Cd]^{2+}/2$: 439.6145 (Calcd.: 439.6197), $[2L+H]^+$: 511.2302 (Calcd.: 511.2318) and $[4L+Cd]^{2+}/2$: 567.1713 (Calcd.: 567.1757)

Crystal structure determination and refinement

Crystals were coated with light hydrocarbon oil and mounted in the 100 K dinitrogen stream of a Bruker SMART APEX CCD diffractometer equipped with CRYO Industries low-temperature

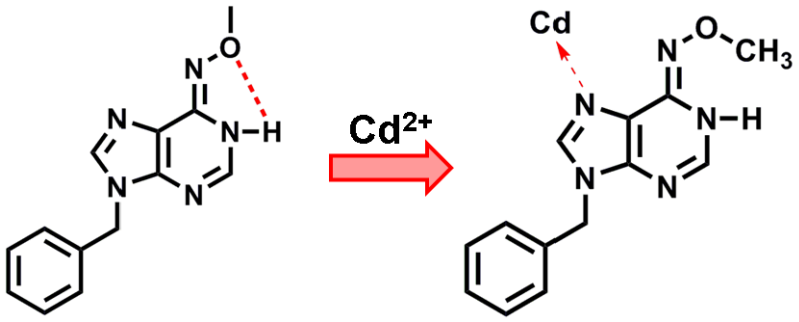
apparatus and intensity data were collected using graphite-monochromated Mo-Kα radiation. The data integration and reduction were processed with SAINT software.[13] An absorption correction was applied.[14] Structures were solved by the direct method using SHELXS-97 and refined on F^2 by a full-matrix least-squares technique using the SHELXL-97 program package.[15] Non-hydrogen atoms were refined anisotropically. In the refinement, hydrogens were treated as riding atoms using the SHELXL default parameters. Crystal structure refinement parameters are given in **Table 1**. All of these software packages were the integrated WINGX software package. CCDC Nos. **946756**, **946757**, **946758** and **946759** 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).

Results and discussion

Herein, we describe the interaction of N9-benzyl-N^6-methoxyadenine (**L**) with four different cadmium salts. It is interesting to note that these four complexes exhibit different coordination numbers thereby resulting in disparate geometries around cadmium ions. Complex **1** exhibits a coordination number of four, while complexes **2** and **3** are hexa-coordinated. Interestingly, complex **4** afforded less common hepta-coordinated cadmium geometry. These four complexes **1-4** are discussed in the order of increasing coordination numbers of Cd(II).

Crystal structure analysis of ligand, L

Crystal structure of **L** projects a *syn*-imino tautomeric form due to intramolecular hydrogen bonding between oxygen atom of the methoxy group and N1–H atom (Scheme 1), as previously reported by us.[12m] Upon complexation, Cd^{2+} ions coordinate selectively with the N7 nitrogen of purine derivative irrespective of the counteranions used, thus favoring and stabilizing *syn*-imino tautomeric form. This observation is in corroboration with literature reports, wherein the nature of cadmium binding to purines was explored with the help of DFT calculations and it was shown that Cd^{2+} ion binding alters the amino-imino tautomeric equilibrium, subsequently stabilizing the rare imino tautomeric form.[6]



Scheme 1: *syn*- imino tautomer of N9-benzyl N^6-methoxyadenine, **L**, stabilized by intramolecular hydrogen bonding interactions and its complexation with Cd^{2+} ion resulting in N7 coordination.

Crystal structure analysis of complex 1

Complexation behavior of ligand **L** with $Cd(PF_6)_2$, a cadmium salt having a bulky, non-coordinating counteranion, was probed by single X-ray crystallographic method. Colorless block-shaped crystals were grown in a week by mixing freshly prepared $Cd(PF_6)_2$ solution with methanolic solution of **L**. Refinement of the crystal data confirmed that **1** $[C_{52}H_{52}F_{12}N_{20}O_4P_2Cd]$ belonged to the triclinic system with '*P*1' space group. Complex **1** exhibited a distorted tetrahedral coordination environment around Cd^{2+} ions, where overall charge of the complex was neutralized by two non-coordinating PF_6^- counteranions (Figure 1). The asymmetric unit consisted of a discrete CdN_4 core where Cd^{2+} ion coordinated to four ligands through N7 nitrogen, in a monodentate coordination mode. The four angles in this polyhedron were 103.64°, 107.52°, 110.68° and 111.77°. The distances corresponding to Cd–N7A, Cd–N7B, Cd–N7C and Cd–N7D were 2.21 Å, 2.24 Å, 2.19 Å and 2.19 Å, respectively. The shorter bond lengths for Cd–N7C and Cd–N7D, than typically observed (Cd–N: 2.2 Å), could be attributed to the large bond angle of 111.76° between N7C–Cd–N7D in the distorted tetrahedral complex **1**.[16]

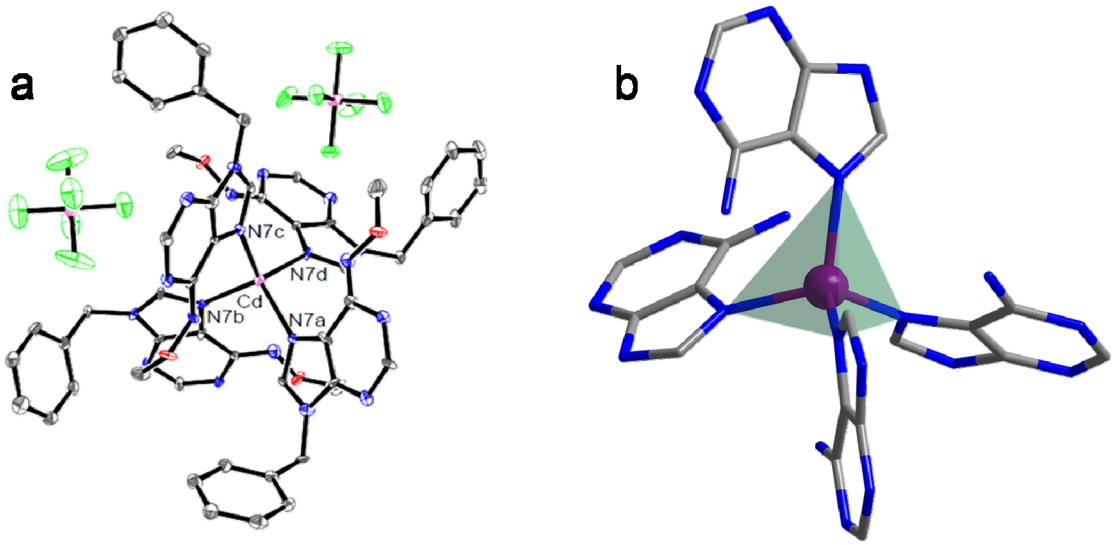
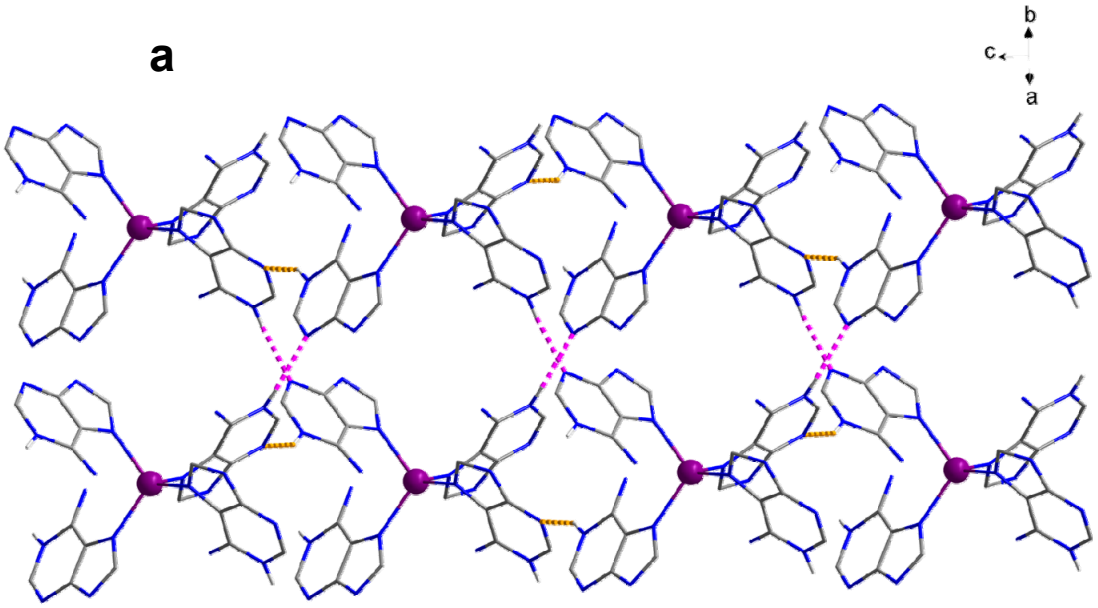
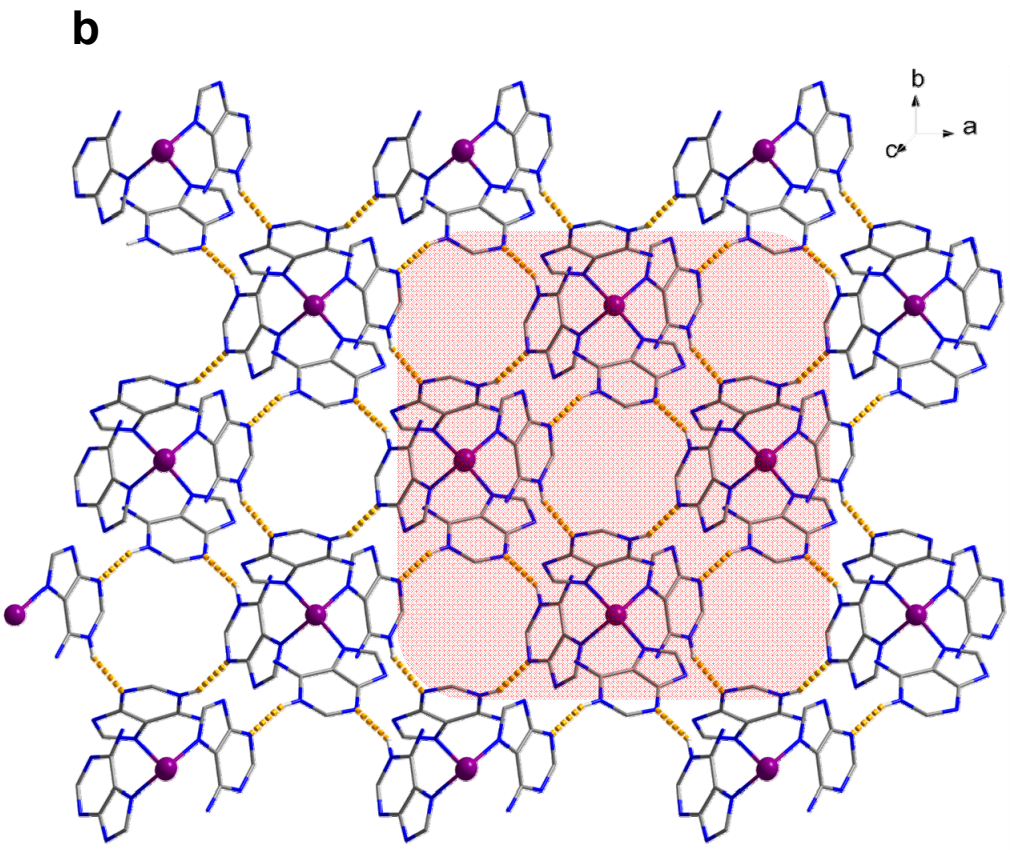


Figure 1. (a) ORTEP diagram of **1** showing asymmetric unit of the cell at 35% probability level; (b) Representation of distorted tetrahedral geometry of Cd(II) in complex **1**. (Benzyl rings, oxygen atoms and hydrogen atoms are removed for clarity).

Stability of the crystal lattice could be ascribed to extensive intermolecular hydrogen bonding interactions between N1–H and N3 nitrogen atoms of the purine ring. It was further observed that the hydrogen bonding interaction between N1–H with N3 atoms occurred at two different bond distances of 2.05 Å (orange) and 2.11 Å (pink) as depicted in Figure 2a, which interested us to probe the lattice further. This network of hydrogen bonding appears as a two-dimensional sheet when viewed along *c*-axis (Figure 2b). However, a tilted view of this two-dimensional sheet provided a rather interesting crystallographic insight into the coordination mode of the complex which can be clearly visualized from the magnified view of the hydrogen bonded lattice (Figure 2c). Unique pattern of hydrogen bonding in this complex enables an interesting three dimensional growth of the crystal lattice. As highlighted in Figure 2c, the lattice contains two parallel sets of complex units participating in multidirectional hydrogen bonding.





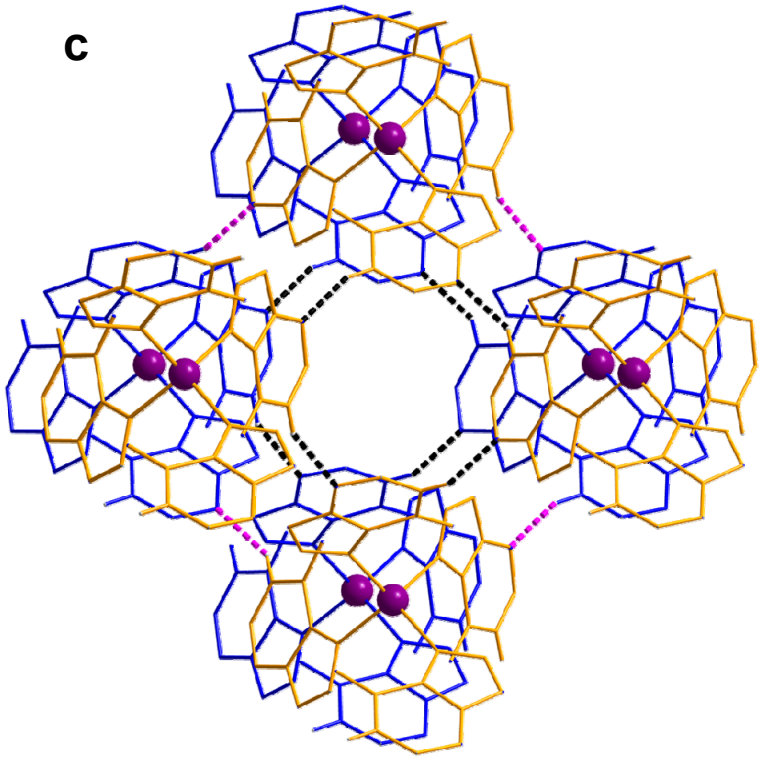


Figure 2. Part of crystal lattice of complex **1** illustrating (a) different extent of hydrogen bonding interactions between N1–H and N3 (pink: 2.11 Å and orange: 2.05 Å) (b) 2D-sheet-like structure formed by intermolecular hydrogen bonding interactions between N1–H and N3; (c) magnified view of (b) showing triple hydrogen bonding interactions between two parallel sets of complex units.

Crystal structure analysis of complex 2

We carried out an equimolar reaction of ligand **L** with $Cd(NO_3)_2.4H_2O$ in methanol, resulting in a violet colored solution, which yielded crystals of **2** on slow evaporation for two weeks. Complex **2** [$C_{13.50}H_{16}N_{5.50}O_{3.50}Cd_{0.25}$] crystallized in a triclinic system in '*P*-1' space group. The asymmetric unit of complex **2** revealed that the metal ion is coordinated to two purine rings and a water molecule. The lattice consisted of a nitrate counteranion and a methanol molecule (Figure 3a). This asymmetric unit when grown further developed into a discrete distorted octahedron where a Cd^{2+} ion was found coordinated to four purine rings *via* N7 nitrogen. The latter occupied equatorial positions, while two coordinated water molecules occupied apical positions (Figure 3b). The cadmium ion, given its half occupancy in the asymmetric unit, was neutralized by only one nitrate ion. Some selected bond lengths in **3** are Cd–N7: 2.412 Å, Cd–N7′: 2.409 Å and Cd–O1W: 2.252 Å.

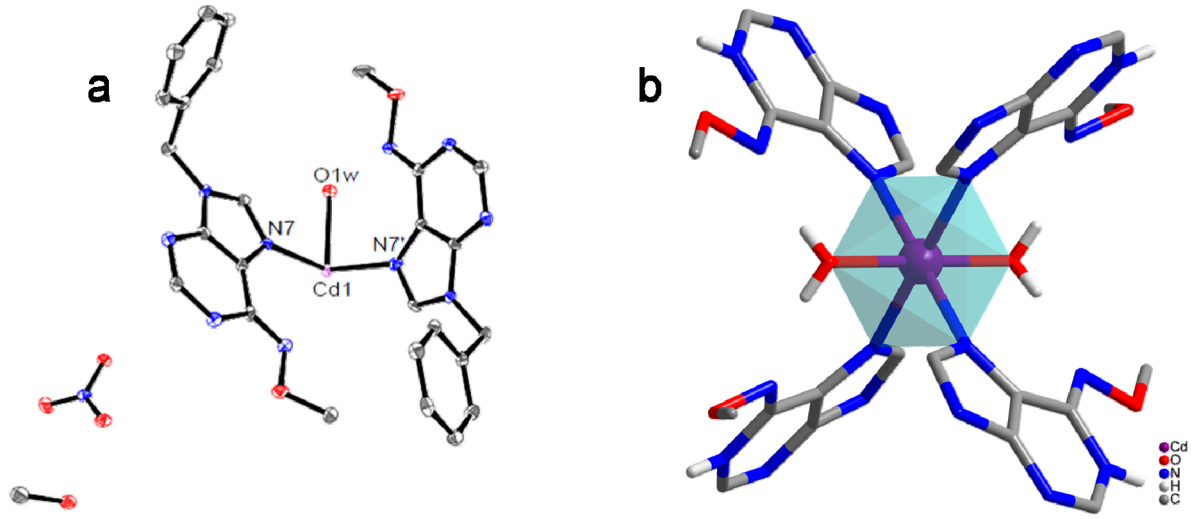


Figure 3. (a) ORTEP diagram of complex **2** showing the asymmetric unit at 35% probability level; (b) Distorted octahedral geometry of Cd(II) in complex **2**. (Benzyl rings are removed for clarity)

The crystal lattice is stabilized by strong intramolecular hydrogen bonding interactions between the apical water molecules, O1W and N^6 nitrogen atoms with distances 1.903 Å and 1.942 Å (Figure 4a). The isolated methanol molecule and nitrate ion further support intermolecular hydrogen bonding interactions by mediating connection between two octahedral units (Figure 4b). The corresponding hydrogen bonding distances are: N1–H···ONO_2: 2.328 Å, N1–H···$OHCH_3$: 1.952 Å and CH_3O–H···ONO_2: 1.938 Å.

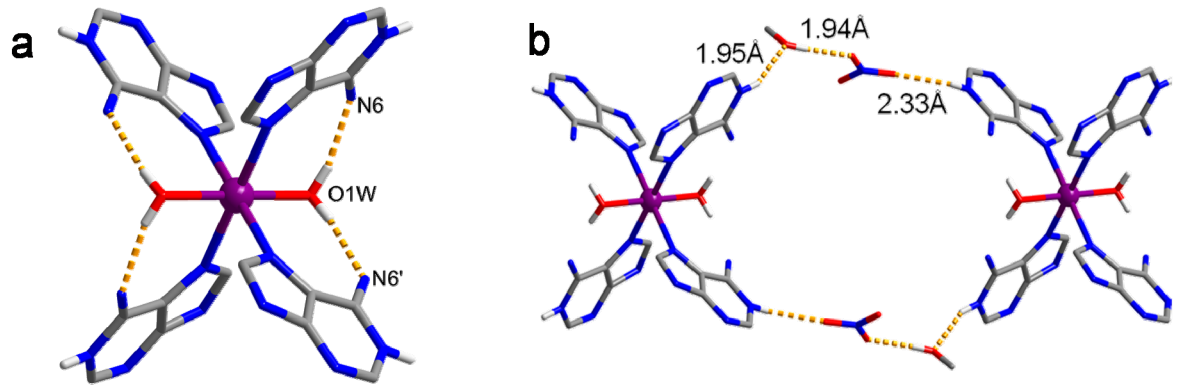


Figure 4. Part of crystal lattice of **2** illustrating (a) intramolecular hydrogen bonding between O1W and N^6 nitrogen atoms; (b) intermolecular hydrogen bonding interactions between octahedral units through mediating nitrate ion and isolated methanol molecule.

Interestingly, coordination of a water molecule to cadmium ion resulted in a geometrical transformation of the complex from a tetra-coordinated cadmium to hexa-coordinated octahedral structure.

Crystal structure analysis of complex 3

Synthesis of complex **3** was carried out by mixing methanolic solutions of **L** (1 eq.) and $CdCl_2.H_2O$ (1 eq.). Crystal data refinement confirmed that **3** [$C_{13}H_{13}Cl_{1.50}N_5O_{2.50}Cd_{0.50}$] crystallized in a triclinic system with '*P*-1'space group. The asymmetric unit of crystal lattice consisted of four ligand molecules coordinated *via* N7 to two Cd^{2+} ions, two bridging chlorine atoms connecting two Cd(II) centers, and four terminal chloride ions maintaining overall neutrality of the complex. The overall coordination geometry around each Cd^{2+} ion was judged to be distorted octahedral, where two purine N7 nitrogens were coordinated in a *trans* fashion and the equatorial plane consisted of a bridged chloride ion and two terminal chloride ions. Interestingly, each of these two octahedrons from two Cd^{2+} ions were shared across the edge of two bridging chlorides, resulting in a dinuclear dimeric Cd(II) complex (Figure 5a).

Selected bond lengths for this complex are: Cd–N7: 2.378 Å, Cd–N7′: 2.389 Å, Cd–Cl_t: 2.53 Å; while chloride bridges were found to be asymmetric (Cd–Cl_b: 2.356 Å and Cd–$Cl_{b'}$: 2.455 Å) and could be accounted to the structural distortions arising from the dimeric nature of the complex. Due to this dissimilarity in the bond lengths of bridging chlorine atoms, the angles in the Cd_2Cl_2 ring are considerably different (Cd1–Cl_b–Cd2: 74.23° and Cl_b–Cd–$Cl_{b'}$: 105.76°) (b: bridged, t: terminal). It is also interesting to note here that Cd-Cl_b distances were found significantly smaller than Cd-Cl_t distances, which is contrary for such complexes.[17] Two terminal chlorides were found interacting with N1–H atoms through intermolecular hydrogen bonding interactions with distances of ~2.415 Å (Figure 5b). Such intermolecular interactions result in a 1D coordination polymer along *c*-axis enhancing overall stability of the crystal lattice.

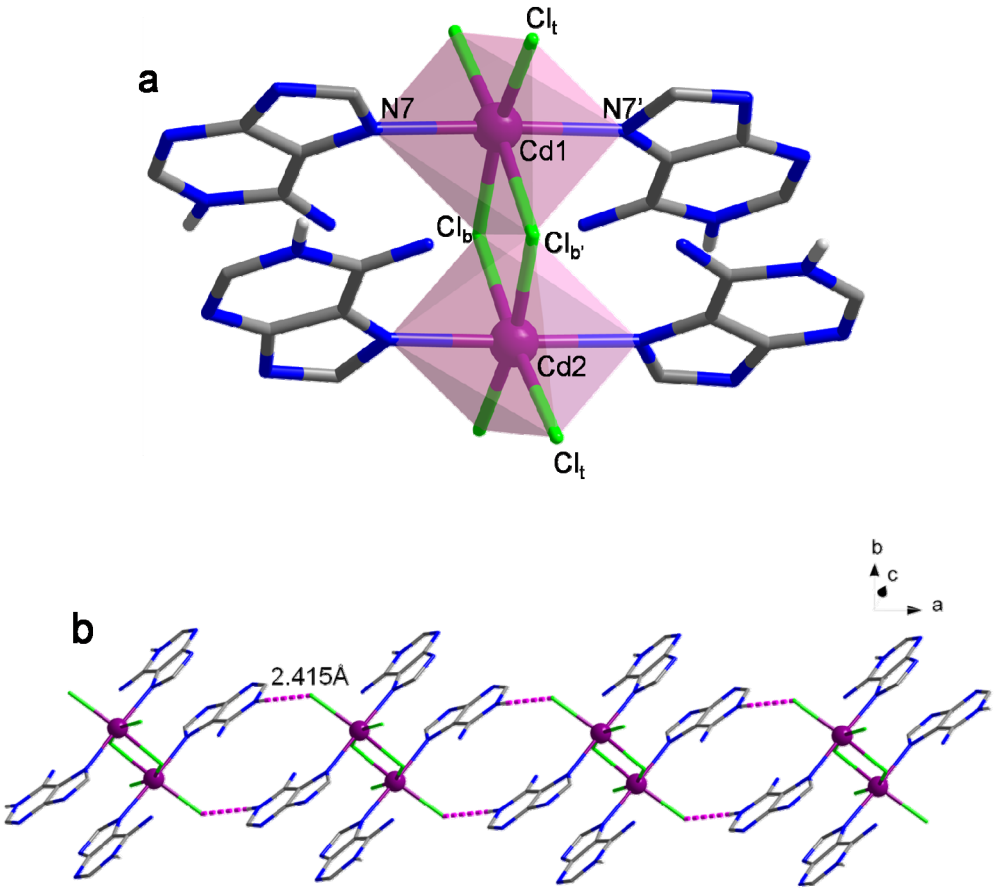


Figure 5. (a) Distorted octahedral geometry of Cd^{2+} ions in complex, **3**; (b) part of crystal lattice highlighting intermolecular hydrogen bonding interactions between N1–H and Cl_t atoms.

Crystal structure analysis of complex 4

Methanolic solution of **L** (1 eq.) and $Cd(OAc)_2.2H_2O$ (1 eq.) were reacted together to yield crystals suitable for X-ray diffraction for complex **4**. The complex $[C_{31}H_{38}N_{10}O_8Cd]$ crystallized in a triclinic system with '*P -1*' space group, where a closer inspection of crystal lattice revealed that purine rings support monodentate N7 coordination in a head-to-head fashion, resulting in a discrete complex (Figure 6a). Cd(II) ion exhibited a hepta-coordinated polyhedron where Cd atom coordinated to two N7 nitrogens from the purine ring, four chelating carboxylate oxygen atoms from two acetate anions and a water molecule. The geometry around Cd(II) ion could be described as distorted pentagonal bipyramidal as shown in Figure 6b.[18] The polyhedron

is composed of two chelating acetate ions and a water molecule occupying the equatorial positions, whilst both N7 nitrogens from the purine rings were positioned at the apices. Due to chelated acetate groups, the corresponding coordinated oxygen atoms (O2, O3, O4 and O5) were slightly altered resulting in a angular deviation from the theoretical value of 72° observed for a regular pentagon (O2–Cd–O3: 52.89° and O4–Cd–O5: 54.45°).[18b] The angle between apical N7 nitrogens and Cd^{2+} ion, N7–Cd–N7' was 178.38°, also deviated slightly from a perfect linear angle.

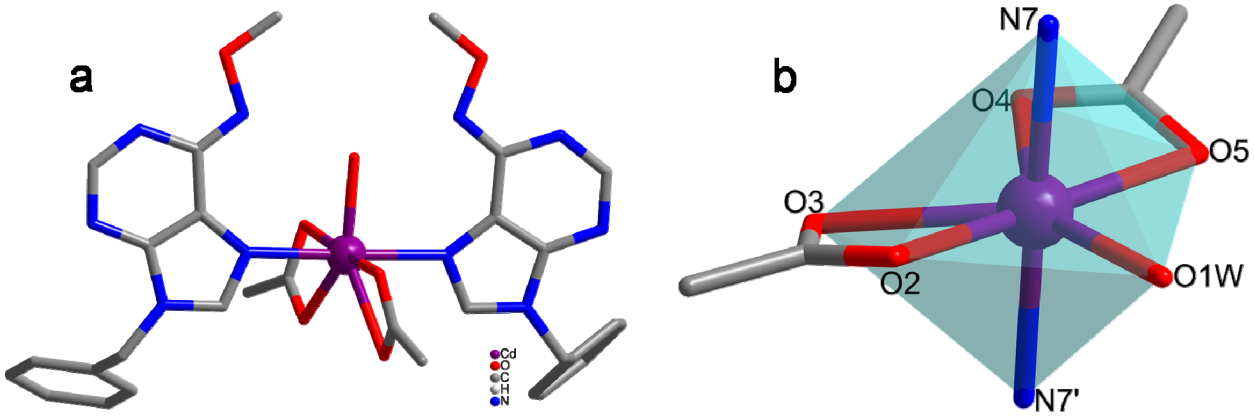


Figure 6. (a) Illustration of asymmetric unit of complex **4**; (b) Distorted pentagonal bipyramidal geometry of Cd(II) in complex **4**.

Acetate anions offer a significant role in intermolecular hydrogen bonding interactions stabilizing the crystal lattice. O2 and O5 oxygen atoms of acetate ions were hydrogen bonded to N1–H atoms of two different purine rings with bonding lengths of 1.99 Å and 1.97 Å, respectively. In addition, C2–H and N3 were also involved in intermolecular hydrogen bonding interactions increasing overall stability of crystal lattice. The resulting hydrogen bonded lattice when viewed along *c*-axis showed a 2D–sheet like structure (Figure 7a), whereas when viewed along *a*-axis it displayed 1D helicate pattern showing O2 and O5 interactions with N1–H atoms (Figure 7b). Figure 7b illustrates that two interwoven helices, highlighted in blue and green, are made of discrete units of this distorted pentagonal bipyramidal complex and intersect at the metal center. The imaginary axis passing through this network allows unambiguous visualization of the crystallographic pattern where the cadmium atom coils around the axis. The green strand represented a right-handed screw axis where as blue strand depicted a left-handed screw axis.

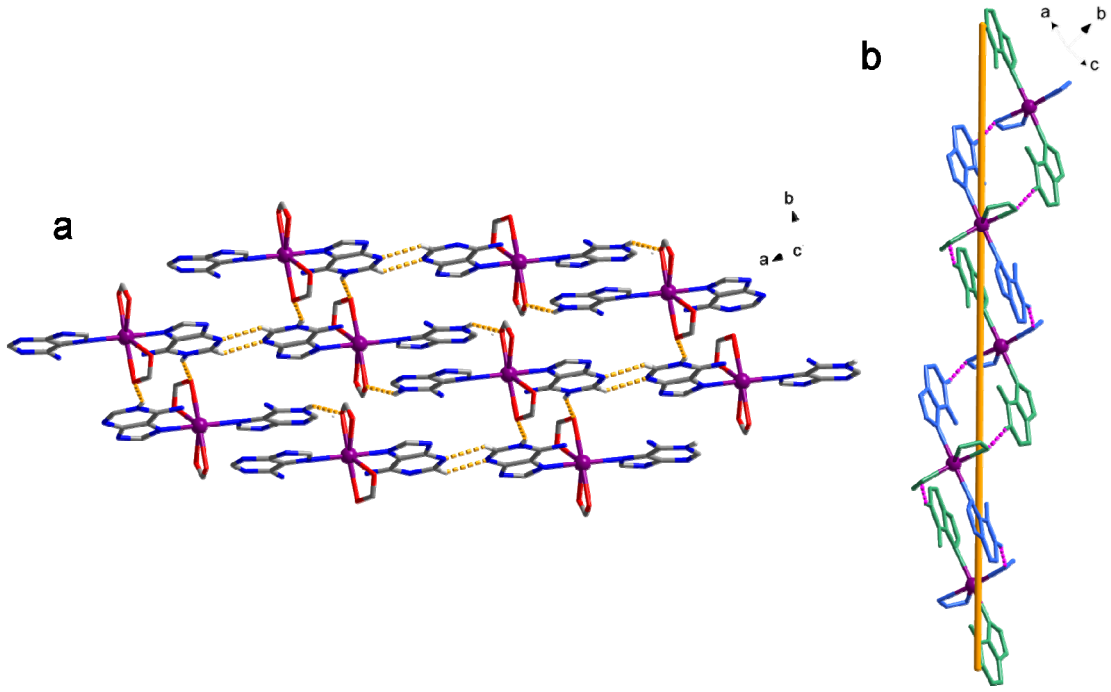


Figure 7. Part of the crystal lattice of **4** showing intermolecular hydrogen bonding interactions: (a) 2D-sheet like network along *c*-axis; (b) helical representation of the 1D-polymer.

Table 1: Crystal structure refinement parameters for **1─4**

Identification code	**Complex 1**	**Complex 2**	**Complex 3**	**Complex 4**
Empirical formula	$C_{52}H_{52}F_{12}N_{20}O_4P_2Cd$	$C_{13.50}H_{16}N_{5.50}O_{3.50}Cd_{0.25}$	$C_{13}H_{13}Cl_{1.50}N_5O_{2.50}Cd_{0.50}$	$C_{31}H_{38}N_{10}O_8Cd$
*M*r	1423.48	339.42	388.66	791.11
crystal system	Triclinic	Triclinic	Triclinic	Triclinic
space group	*P1*	*P-1*	*P-1*	*P-1*
a(Å)	12.4067(9)	10.1946(14)	10.1883(6)	9.8188(12)
b(Å)	12.7587(10)	11.9620(17)	10.9694(7)	11.2793(13)
c(Å)	12.7752(10)	12.8764(18)	15.1248(9)	16.186(2)
α (deg)	119.5380(10)	91.286(2)	70.4550(10)	109.391(2)
β (deg)	118.7600(9)	90.548(2)	75.2480(10)	92.323(2)
γ (deg)	90.3130(10)	109.725(5)	89.5710(10)	97.053(2)
Volume ($Å^3$)	1462.21(19)	1477.5(4)	1534.82(16)	1671.8(3)
Z	1	4	4	2
Dx (Mg m^{-3})	1.617	1.524	1.682	1.572
F(000)	722	700	782	812
μ (mm^{-1})	0.531	0.455	1.028	0.720
θ range for data collection(deg)	1.94-28.33	2.12-28.38	4.09-25.02	4.09-25.03
Limiting indices	-7→h→16, -16→k→15, -16→l→16	-13→h→6 -15→k→15 -16→l→17	-12→h→12, -13→k→12, -17→l→13	-11→h→11, -13→k→10, -10→l→19
Reflections collected	9384	9798	7936	8746
unique reflections	7787	6993	5278	5755
R(int)	0.0291	0.0229	0.0265	0.0226
Completeness to θ	= 28.33, 91.2	= 28.38, 94.6	= 25.02, 97.6	= 25.03, 97.3
T_{max} / T_{min}	0.9104 / 0.8875	0.9225/ 0.9025	0.8366 / 0.7979	0.8754 / 0.8577

Data / restraints / parameters	7787 / 3 / 761	6993 / 2 / 423	5278 / 0 / 401	5755 / 0 / 459
GOF on F^2	1.166	1.206	1.058	1.188
$R1$ and $R2$ [$I>2\sigma(I)$]	0.0604, 0.1291	0.0524, 0.1117	0.0570, 0.1575	0.0394, 0.0960
$R1$ and $R2$ (all data)	0.0833, 0.1893	0.0797, 0.1815	0.0675, 0.1727	0.0478, 0.1288
Largest diff. peak and hole(e.A^{-3})	2.130 and -3.315	2.168 and -3.347	1.267 and -1.705	0.812 and -0.863

PXRD Patterns

The crystal structures for complexes **1-4** were confirmed by PXRD patterns. It was observed that experimental PXRD patterns were in good agreement with corresponding simulated ones, confirming similarity of synthesized bulk materials to single crystals (ESI, Figure S1).

Thermal Analyses

Thermal stabilities of ligand and the four cadmium complexes (**1**-**4**) were examined by thermogravimetric analysis (TGA) (ESI, Figure S2). It is observed from TGA curves that ligand, **L** is stable up to ~ 226°C decomposing on further heating. This observation corroborates with the melting point of the ligand which is 227-229°C. Complexes **1** and **3** were found to be thermally stable up to ~ 238°C and ~ 250°C, respectively. However, complex **2** shows a weight loss of ~ 10.07% (expected 10.02%) up to 128°C owing to the loss of a free methanol molecule and two coordinated water molecules. The desolvated complex then began to decompose gradually. Complex **4** exhibits a weight loss of ~ 6.66% (expected 6.33%) up to 126°C corresponding to loss of a coordinated water molecule and a methanol molecule followed by a gradual collapse of the complex.

Luminescence Studies

Complexes exhibiting luminescent properties find applications as chemical sensors, in electrochemical displays, in photochemistry, to name a few.[19] The solution state UV-visible absorbance and photoluminescence spectra for free ligand, **L** and complexes **1**–**4** were recorded at room temperature at a concentration of 10^{-5} M in DMF (Figure 8, S3). The ligand exhibits λ_{max}

at 270 nm and a small broad peak at 333 nm. On complexation with cadmium ions, the absorbance intensity of both these peaks increases in all the four complexes. Surprisingly, a new broad peak was also observed in **2** in 400-450 nm region, which perhaps explains the violet color of this complex in solution (ESI, Figure S3). Upon excitation at 333 nm, emission at 430 nm was observed for free ligand, which could be ascribed to imidazole based π–π* transitions. Similar spectral profiles have also been reported for polyadenine where π–π* transitions of stacked purine rings were invoked for such emission.[20] The emission intensity was significantly enhanced upon Cd^{2+} complexation for all the four complexes **1**-**4**. These observations are in consistence with literature reports where complexes of d^{10} systems offer enhanced luminescence properties without introducing low-energy metal-centered or charge-separated excited states into a molecule.[12f,21] It is interesting to note that different emission intensities of the four complexes studied is perhaps also due to variation in anions. This anion-dependent disparity in emission intensities has been reported and ascribed to altered metal-ligand charge transfer transitions.[22]

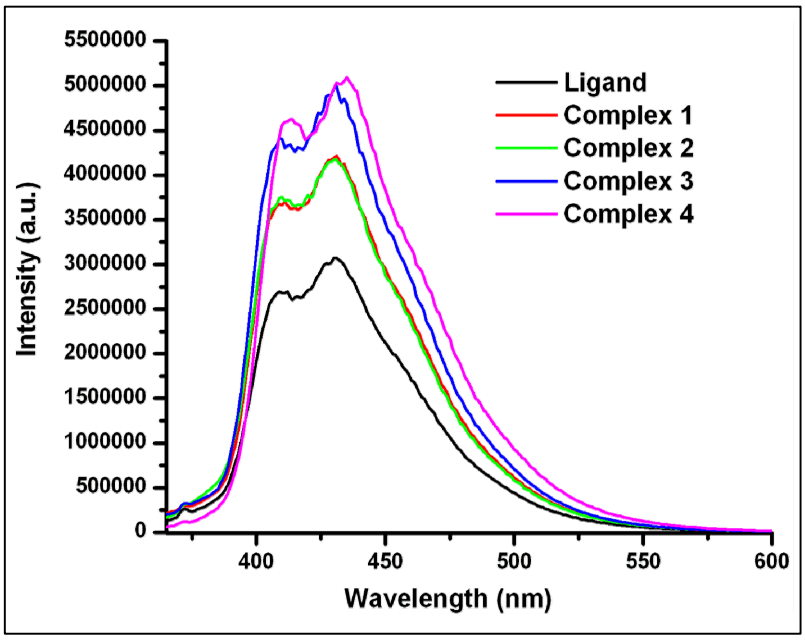


Figure 8. Emission spectra illustrating photoluminescent intensities of ligand, **L** and cadmium complexes, **1**-**4** recorded at room temperature in DMF.

Conclusion

In summary, the complexation behavior of N9-benzyl N^6-methoxyadenine with cadmium ions was studied by X-ray crystallography. The complexes exhibited various coordination numbers and corresponding disparate geometries with different cadmium salts. The thermal analyses and fluorescent behavior were also investigated for these complexes. Such extensive variety in the coordination behavior of cadmium ion to a rare tautomer would further open up new avenues towards the understanding of cadmium-induced mutagenesis.

Acknowledgments. We thank Single Crystal CCD X-ray facility (CESE) at IIT-Kanpur. CSIR, for senior pre-doctoral research fellowship to SK. SV acknowledges DAE-SRC for an Outstanding Investigator Award and DST for J C Bose National Fellowship.

Supporting information available: X-ray crystallographic data in CIF format are given. CCDC contains the supplementary crystallographic data for this paper with a deposition number of CCDC **946756** (complex **1**), **946757** (complex **2**), **946758** (complex **3**) & **946759** (complex **4**). 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].

References:

1. (a) B. A. Fowler, *Toxicology and Applied Pharmacology*, 2009, **238**, 294; (b) D. M. Templeton and Y. Liu, *Chemico-Biological Interactions,* 2010, **188**, 267; (c) M. Filipic, *Mutation Research/ Fundamental and Molecular Mechanisms of Mutagenesis*, 2012, **733**, 69; (d) R. K. Sigel, M. Skilandat, A. Sigel, B. P. Operschall and H. Sigel, *Metal Ions in Life Sciences*, 2013, **11**, 191.

2. P. Scharf and J. Müller, *ChemPlusChem*, 2013, **78**, 20.

3. Z. Hossain and F. Huq, *J. Inorg. Biochem.* 2002, **90**, 97.

4. V. A. Sorokin, V. A. Valeev, G. O. Gladchenko and I. V. Sysa, *Biofizika*, 1997, **42***,* 105.

5. (a) H. Sigel, *Chem. Soc. Rev.* 1993, 255; (b) A. S. Prakash, K. S. Rao and C. T. Dameron, *Biochem. Biophy. Res. Comm.* 1998, **244**, 198.

6. Y. Wu, R. Sa, Q. Li, Y. Wei and K. Wu, *Chem. Phy. Letters,* 2009, **467**, 387.

7. C. H. Wei and K. B. Jacobson, *Inorg. Chem*. 1981, **20**, 356.

8. (a) E. A. H. Griffith, N. G. Charles and E. L. Amma, *Acta Cryst.* 1982, **B-38**, 942; (b) M. A. Shipman, C. Price, A. E. Gibson, M. R. J. Elsegood, W. Clegg and A. Houlton, *Chem. Eur. J.* 2000, **6**, 4371; (c) N. Stanley, P. T. Muthiah, P. Luger, M. Weber and S. J. Geib, *Inorg. Chem. Comm.* 2005, **8**, 1056; (d) F. Wang and Y. Kang, *Inorg. Chem. Comm.* 2012, **20**, 266.

9. E. -C. Yang, H. –K. Zhao, B. Ding, X. –G. Wang and X. –J. Zhao, *New J Chem.* 2007, **31**, 1887.

10. (a) B. Lippert and D. Gupta, *Dalton Trans.* 2009, 4619; (b) B. Lippert, H. Schöllhorn and U. Thewalt. *Inorg. Chim. Acta*, 1992, **198-200**, 723; (c) F. Pichierri, D. Holthenrich, E. Zangrando, B. Lippert and L. Randaccio. *J. Biol. Inorg. Chem.* 1996, **1,** 439; (d) F. Zamora, M. Kunsman, M. Sabat and B. Lippert. *Inorg. Chem.* 1997, **36**, 1583; (e) W. Brüning, I. Ascaso, E. Freisinger, M. Sabat and Lippert. B. *Inorg. Chim. Acta*, 2002, **339**, 400; (f) O. Renn, B. Lippert and A. Albinati, *Inorg. Chim. Acta*, 1991, **190**, 285.

11. Z. Hossain and F. Huq. *J. Inorg. Biochem.* 2002, **90**, 85.

12. (a) S. Verma, A. K. Mishra and J. Kumar, *Acc. Chem. Res*. 2010, **43**, 79; (b) C. S. Purohit and S.Verma, *J. Am. Chem. Soc*. 2006, **128**, 400; (c) C. S. Purohit, A. K. Mishra and S. Verma, *Inorg. Chem*. 2007, **46**, 8493; (d). C. S. Purohit and S. Verma, *J. Am. Chem. Soc.* 2007, **129**, 3488; (e). J. Kumar and S.Verma, *Inorg.Chem*. 2009, **48**, 6350; (f) A. K. Mishra and S. Verma, *Inorg. Chem.* 2010, **49**, 8012; (g) J. Kumar, S. Awasthi and S. Verma, *Cryst. Growth Des*. 2010, **10**, 3555; (h) A. K. Mishra, C. S. Purohit, J. Kumar and S. Verma, *Inorg. Chim. Acta*, 2009, **362**, 855; (i) A. K. Mishra, C. S. Purohit and S. Verma, *Cryst. Eng. Comm*. 2008, **10**, 1296; (j) A. K. Mishra, R. K. Prajapati and S. Verma, *Dalton Trans*. 2010, **39**, 10034; (k) V. Venkatesh, J. Kumar and S. Verma, *Cryst. Eng. Comm*. 2011, **13**, 6030; (l) A. K. Mishra, J. Kumar, S. Khanna and S. Verma, *Cryst. Growth Des.* 2011, **11**, 1623; (m) S. Khanna and S. Verma, *Cryst. Growth Des.* 2012, **12**, 3025.

13. SAINT+, 6.02 ed.; Bruker AXS, Madison, WI, **1999**.

14. Sheldrick, G. M. SADABS 2.0; University of Göttingen: Göttingen, Germany, **2000**.

15. Sheldrick, G. M. SHELXL-97: *Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, **1997**.

16. D. L. Reger, S. S. Mason and A. L. Rheingold, *Inorg. Chim. Acta*, 1995, **240**, 669.

17. (a) R. Iwamoto and H. Wakano, *J. Am. Chem. Soc.* 1976, 3764; (b) A. Benalte-García, M. A. Díaz-Díez, F. J. García-Barros, F. J. Higes-Rolando, A. M. Pizarro-Galán, J. D. Martín-Ramos and C. Valenzuela-Calahorro, *Polyhedron*, 1997,**16**, 297; (c) Y. Kang, S. -H. Moon, J. C. Byun and K. -M. Park, *Bull. Korean Chem. Soc.* 2010, **31**, 3017.

18. (a) G. Mendoza-Díaz, G. Rigotti, O. E. Piro and E. E. Sileo, *Polyhedron*, 2005, **24***,* 777; (b) J. Granifo, M. T. Garland and R. Baggio, *Inorg. Chem. Comm.* 2004, **7**, 77; (c) J. -R. Li, M. Du, X. -H. Bu and R. -H. Zhang, *J. Solid State Chem.* 2003, **173**, 20; (d) P. Arranz-Mascarós, R. López-Garzón, M. D. Gutierrez-Valero, M. L. Godino-Salido and J. M. Moreno, *Inorg. Chim. Acta*, 2000, **304***,*137.

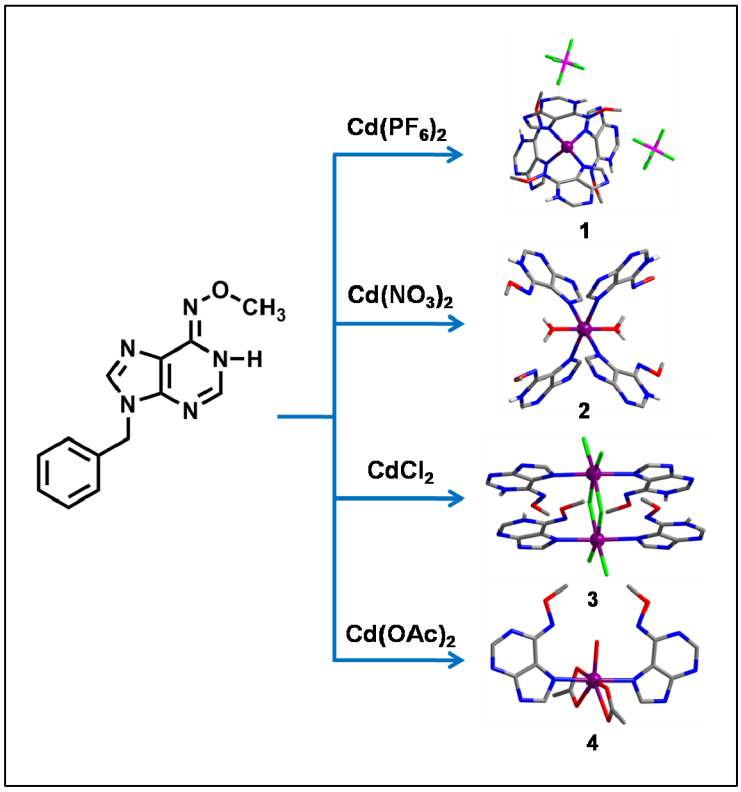
19. (a) J. E. McGarrah, Y. J. Kim, M. Hissler and R. Eisenberg, *Inorg. Chem*. 2001, **40**, 4510; (b) Q. Wu, M. Esteghamatian, N. X. Hu, Z. Popovic, G. Enright, Y. Tao, M. D'Iorio and S. Wang, *Chem. Mater*. 2000, **12**, 79.

20. A. I. Kononov and M. N. Bukina, *J. Biomol. Struc. Dynamics,* 2002, **20**, 465.

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

22. P. Lama and P. K. Bharadwaj, *Cryst. Growth Des.* 2011, **11**, 5434.

TOC:



Cadmium, a metal known to be toxic to living systems through unfavorable interactions with biomolecules, interacts with purine nucleobases through N7 imino nitrogen and induces modifications by altering amino-imino tautomeric equilibrium. Herein, we report unique crystallographic signatures of cadmium complexes of N9-benzyl N^6-methoxyadenine, a rare imino tautomer of adenine. These complexes exhibit a variety of coordination numbers and spatial geometries, highlighting the ability of nucleobases to form diverse supramolecular architectures, enabling better understanding of metal-DNA interactions. Cd^{2+} ion in complex **1** has a coordination number of four with distorted tetrahedral geometry, while **2** and **3** are hexa-coordinated, where **2** displays discrete distorted octahedron geometry and **3** appears as a dinuclear complex. On the other hand, complex **4** exhibits a less common hepta-coordination mode with distorted pentagonal bipyramidal geometry. The luminescence properties of these cadmium complexes are also reported.