

Cite this: *CrystEngComm*, 2012, **14**, 3012

www.rsc.org/crystengcomm

COMMUNICATION

Water adsorbing silver–adenine interpenetrated framework†

Jitendra Kumar,^a Prakash Kanoo,^b Tapas Kumar Maji^{*b} and Sandeep Verma^{*a}

Received 5th December 2011, Accepted 10th February 2012

DOI: 10.1039/c2ce06625d

We describe the synthesis and properties of a novel silver complex of an adenine derivative bearing a sulfonate group. Adenine and sulfonate coordination with silver ions eventually leads to the formation of entangled networks with an embedded catenated framework and double helical assemblies.

The rational design of inorganic–organic hybrid materials with entangled supramolecular architecture of individual motifs has attracted a great deal of attention because of the topological influences over the bulk properties of the material and their potential applications.¹ Diverse arrays of entangled supramolecular assemblies which include polycatenanes, polyrotaxanes, knots and Borromean rings have been documented.² Even in biomacromolecules, such entangled architectures have been observed *e.g.* catenated circular DNA³ and protein chainmail.⁴

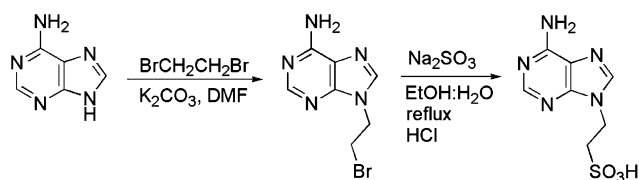
We have reported the formation of novel 3D silver–adenine frameworks with modified adenine derivatives owing to the presence of multiple metal-binding sites in their skeleton.⁵ Our investigation has revealed that N9-alkyl substituents generate metallaquartets,^{5a–c} a carboxyethyl substituent affords a silver–adenine hexameric framework^{5d} whereas a cyanoethyl substituent results in the formation of an interconnected metalated framework.^{5e} Thus, the N9-substituent has a significant influence over the structural outcome. As an extension, we decided to incorporate sulfonic group at the N9-position and synthesize 2-(N9-adeninyl)ethanesulfonic acid [9-SA] as shown in Scheme 1 for exploiting its coordination for generating more complex structures. The coordination aspects of sulfonate grouping with silver ions have been extensively studied due to the interesting functional properties imparted by the soft and flexible silver–sulfonate interactions.⁶ Silver(I) cation is known for having variable coordination spheres with distorted coordination geometries mainly due to its d^{10} electronic configuration.⁷ Hence it is expected

that adenine, containing a sulfonate group, will provide an interesting topology with the combination of ring imino nitrogen–Ag interactions and weaker Ag–sulfonate interactions.[‡]

The colorless crystals of **1** (9-SA: silver complex) were grown within two weeks by layering an acetonitrile solution of silver nitrate or silver triflate over an aqueous solution of 9-SA ligand. X-Ray crystallographic studies showed that the complex crystallized in monoclinic space group $C2/c$. The structure of the supramolecular lattice of **1** $[C_7H_{12}AgN_5O_5S]_\infty$ is a three-dimensional solid having entangled networks. The asymmetric unit consists of one silver ion neutralized by the monoanionic form of 9-SA ligand, along with two water molecules (Fig. 1). The geometry around the silver ion is distorted tetrahedral which comprises two ring imino nitrogens, one sulfonate oxygen and one water molecule with further weak Ag–O interaction of 2.824(6) Å with another oxygen of the sulfonate group as shown in Fig. 1b.

The 9-SA anion behaves as a tridentate ligand in which adenine renders bidentate coordination mode whereas pendant sulfonate grouping exhibits weak monodentate coordination mode to silver ions. The coordination of adenine nitrogens namely N1 and N7 to silver ions resulted in a 1D polymeric chain permeating this structure along the c -axis (Fig. 1c) which eventually replaces the complementary hydrogen bonding schemes found for the adenine nucleobase usually in the absence of metal ions where the H-bonding interaction between the Watson–Crick face and the Hoogsteen face results in adenine ribbons.⁸ Further confirmation of such polymeric assembly was evident from the analysis of HRMS data which clearly show the peaks of detectable intensity corresponding to $[M + Ag]^+$, $[2M + Ag]^+$, $[2M + 2Ag - H]^+$ and $[3M + 2Ag - H]^+$ in ES⁺ mode where ‘M’ denotes the neutral 9-SA molecule (see ESI[†]).

Interestingly, the lattice consists of two sets of such polymeric chains (rendered with different colours) which are interrelated with a center of inversion (as shown in Fig. 1c) and sulfonate grouping is projected in the opposite direction connecting other polymeric chains of the same orientation through weak Ag–O_{sulfonate} coordination (2.75 Å) which is in accordance with the reported literature.⁶ The



Scheme 1 Synthetic scheme for 9-SA.

^aDepartment of Chemistry, Indian Institute of Technology Kanpur, Kanpur-208016, UP, India. E-mail: sverma@iitk.ac.in; Tel: +91 512 259 7643

^bChemistry and Physics of Materials Unit (CPMU), Jawaharlal Nehru Center for Advanced Scientific Research (JNCASR), Bangalore 560064, India. E-mail: tmaji@jncasr.ac.in; Fax: +91 80 2208 2766; Tel: +91 80 2208 2826

† Electronic supplementary information (ESI) available: Summary of structural refinement parameters, crystallographic information in.cif format, a hydrogen bonding table and additional representations of the crystal lattice as figures for complex **1**. CCDC reference number 787582. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2ce06625d

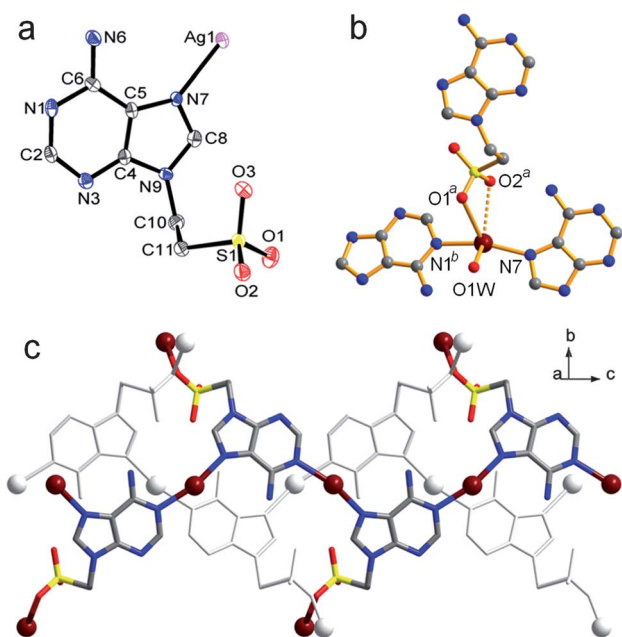


Fig. 1 (a) ORTEP diagram of **1** at 35% probability level; (b) coordination around silver ions in **1** ($\text{Ag-O1}^a = 2.753(7)$, $\text{Ag-O2}^a = 2.824(6)$, $\text{Ag-N1}^b = 2.205(6)$, $\text{Ag-N7} = 2.195(6)$, $\text{Ag-O1W} = 2.724(17)$ Å; symmetry code: $a = \frac{1}{2} + x$, $\frac{1}{2} + y$, z and $b = x$, $-y$, $\frac{1}{2} + z$); (c) two different sets of silver-mediated polymeric chains of opposite orientation running along the c -axis in **1** (hydrogen atoms and solvent molecules are removed for clarity, color code: C—grey; O—red; N—blue; S—yellow and Ag—dark brown).

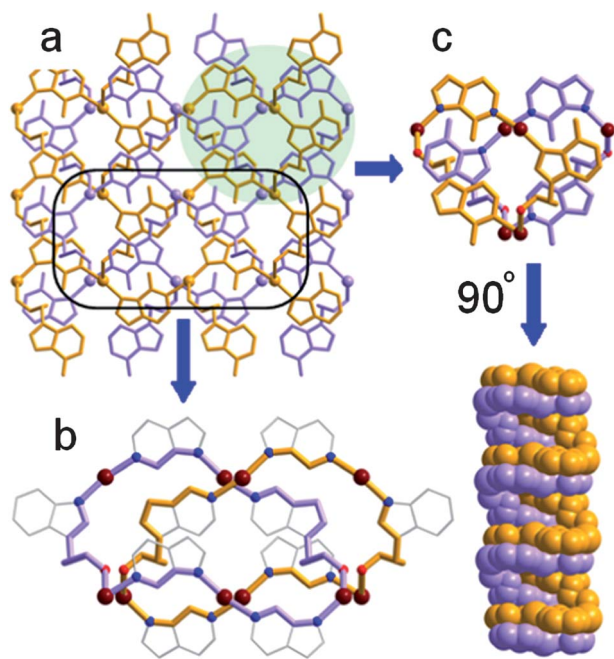


Fig. 2 (a) Interpenetrated networks in **1** (view along the a -axis); (b) part of the lattice as the catenated structure and (c) Highlighted portion in (a) revealed an embedded helical structure (view along a - and c -axes, respectively).

closest silver–silver distance between polymeric chains is found to be 3.62 Å.

The crystal lattice of **1** is shown in Fig. 2a. The opposite orientation of sulfonate grouping from the two sets of polymeric chains leads to a highly interesting entangled structure and the solvent water guest molecules sit inside the small cavities. The catenated segment of the lattice consists of two pentameric rings as represented with different color codes and each pentameric ring is contributed by two different polymeric chains of the same orientation and the ring closure was invoked by $\text{Ag-O}_{\text{sulfonate}}$ coordination as shown in Fig. 2b. The crystal lattice can also be dissected to visualize an embedded double helical structure running along the a -axis with a pitch length of 11.12 Å as a consequence of adenine and $\text{Ag-O}_{\text{sulfonate}}$ coordination (Fig. 2c). A schematic representation of the lattice is given in Fig. 3a which clearly shows the entangled structure due to the presence of two sets of networks in the lattice. Thus the incorporated sulfonate moiety plays an important role in giving an unusual supramolecular lattice apart from the adenine nucleobase.

The crystal lattice is further reinforced with significant hydrogen bonding interaction rendered by the exocyclic amino group and non-coordinated sulfonate oxygen atoms. Closer inspection revealed that one of the NH_2 hydrogen interacts with sulfonate oxygen O2 ($d = 2.01$ Å) belonging to the same set of polymeric chain whereas other hydrogen interacts with O3 of the sulfonate group (2.24 Å) belonging to the different set as represented in Fig. 3b. These interactions probably encourage network interpenetration and also interlinking of both independent frameworks together.

The dehydrated complex **1** was subjected to solvent vapour adsorption study at RT with different solvents of varying size and polarity. The profiles recorded for H_2O (kinetic diameter, 2.68 Å), MeOH (4.0 Å) and EtOH (4.3 Å) vapour using a BELSORP-aqua3 analyzer are shown in Fig. 4. It appears that **1** is highly selective towards H_2O as no uptake was noticed with MeOH and EtOH vapour. The H_2O adsorption isotherm shows a two-step profile with slow but gradual uptake at low pressures. The 1st step uptake, 54 mL g^{-1} up to $P/P_0 \approx 0.7$, corresponds to ~ 0.85 mol of H_2O per formula unit of **1**. This initial 1st step adsorption can be attributed to the central part of the pore where O2W water molecules are hydrogen bonded with $-\text{SO}_3$ group. After $P/P_0 \approx 0.7$ a sudden uptake was observed leading to a final uptake volume of 90 mL g^{-1} that

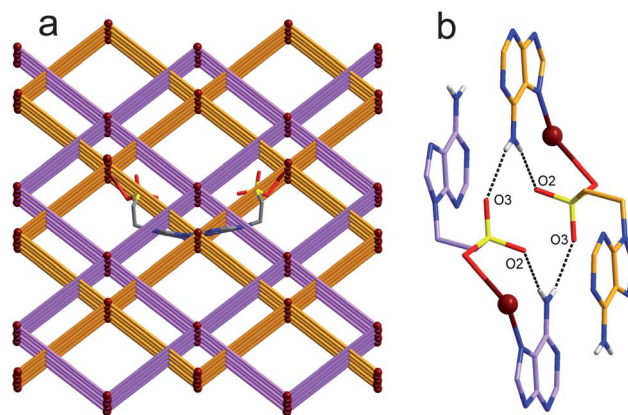


Fig. 3 (a) Schematic view of entanglement in **1** (view close to the c -axis) and (b) hydrogen bonding interaction in **1**, interconnecting two different sets of polymeric chains.

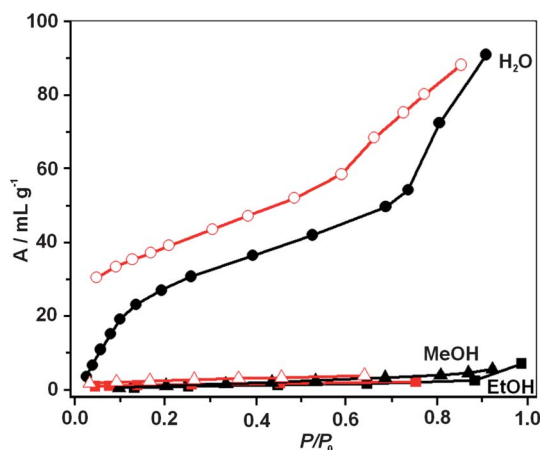


Fig. 4 Vapour sorption isotherms for **1**: H₂O (circles) at 298 K; MeOH (triangles) at 293 K and EtOH (squares) at 298 K. Closed symbols indicate adsorption and open symbols desorption. P_0 is the saturated vapour pressure of the adsorbates at the corresponding temperature.

corresponds to a total 1.4 mol of H₂O per formula unit of **1**. The desorption curve does not retrace the adsorption curve and a prominent hysteresis was observed which indicates strong interaction of the H₂O molecules with pore surfaces. The βE_0 value, which reflects adsorbate–adsorbent affinity, calculated using DR equation is found to be 5.8 kJ mol^{−1} and also suggests strong interaction of H₂O molecules with **1**. The exclusion of larger molecules like MeOH and EtOH is probably because of the smaller channel dimension compared to the kinetic diameter of the adsorbate molecules.

In conclusion, we have synthesized a silver-complex with entangled networks showing selective water vapour adsorption over methanol or ethanol. Thus, the notion of creating hierarchical structures with interesting topological preferences and properties as a result of minor chemical modification of the adenine nucleobase has been realized.

We thank Single Crystal CCD X-ray facility at IIT-Kanpur, CSIR, for S. P. Mukherjee Fellowship (J.K.). This work is supported by Council for Scientific and Industrial Research, India (SV).

Notes and references

† General: ¹H and ¹³C NMR spectra were obtained on a JEOL-DELTA2 500 model spectrometer operating at 500 MHz and 125 MHz, respectively. High resolution mass spectra were obtained on a WATERS HAB 213 machine, Department of Chemistry, IIT-Kanpur, India.

Synthesis of 2-(N9-adeninyl)ethanesulfonic acid: 9-(2-bromoethyl) adenine⁹ (1.5 g, 1.0 eq.) and Na₂SO₃ (940 mg, 1.2 eq.) were suspended in 15 mL of an ethanol : water (2 : 1) mixture and refluxed at 80 °C till the completion of reaction as monitored by TLC analysis. The solution was cooled down to room temperature and acidified with 1 N HCl to pH 5 and dried. The residue was dissolved in 10 mL of dimethyl formamide and stirred for 10 min and filtered to remove excess of NaCl. The DMF layer was evaporated and the residue was washed with 10 mL of methanol and dried which afforded the title compound as an off white powder (1.1 g, yield 73%). HRMS: [M + H]⁺ calculated: 244.0504, found: 244.0508; [M + Na]⁺ calculated: 266.0324, found 266.0327. mp > 275 °C; ¹H NMR (500 MHz, DMSO-*d*₆, 25 °C, TMS): δ (ppm) 2.97 (t, 2H, CH₂), 4.36 (t, 2H, CH₂), 7.16 (s, 2H, NH₂), 8.09 (s, 1H, C8-H), 8.10 (s, 1H, C2-H); ¹³C NMR (125 MHz, DMSO-*d*₆, 25 °C, TMS): δ (ppm) 50.86, 119.06, 141.85, 149.81, 152.73, 156.28.

Synthesis of 9-SA silver complex (1): The colorless crystals of **1** (9-SA: silver complex) were grown by layering an acetonitrile solution of silver nitrate over an aqueous solution of 9-SA and crystals were obtained within two weeks. The same complex was also obtained by using silver triflate and silver perchlorate as confirmed by X-ray crystallography. HRMS characterization of complex **1** was carried out in both ESI(+) and ESI(−) modes which shows the polymeric structure (Table S1†). Elemental analysis (C₇H₁₀AgN₅O₄S as monohydrate): calculated C, 22.84; H, 2.74; N, 19.02; found C, 22.78; H, 2.51; N, 18.33%.

- (a) C. P. Collier, G. Mattersteig, E. W. Wong, Y. Luo, K. Beverly, J. Sampaio, F. M. Raymo, J. F. Stoddart and J. R. Heath, *Science*, 2000, **289**, 1172; (b) Y. Luo, C. P. Collier, J. O. Jeppesen, K. A. Nielsen, E. DeLonno, G. Ho, J. Perkins, H.-R. Tseng, T. Yamamoto, J. F. Stoddart and J. R. Heath, *ChemPhysChem*, 2002, **3**, 519; (c) A. H. Flood, J. F. Stoddart, D. W. Steuerman and J. R. Heath, *Science*, 2004, **306**, 2055; (d) J. E. Green, J. W. Choi, A. Boukai, Y. Bunimovich, E. Johnston-Halperin, E. DeLonno, Y. Luo, B. A. Sheriff, K. Xu, Y. S. Shin, H.-R. Tseng, J. F. Stoddart and J. R. Heath, *Nature*, 2007, **445**, 414; (e) J. Berná, D. A. Leigh, M. Lubomska, S. M. Mendoza, E. M. Pérez, P. Rudolf, G. Teobaldi and F. Zerbetto, *Nat. Mater.*, 2005, **4**, 704; (f) Y. Liu, A. H. Flood, P. A. Bonvallet, S. A. Vignon, B. H. Northrop, H.-R. Tseng, J. O. Jeppesen, T. J. Huang, B. Brough, M. Baller, S. Maganov, S. D. Solares, W. A. Goddard, C.-M. Ho and J. F. Stoddart, *J. Am. Chem. Soc.*, 2005, **127**, 9745; (g) B. K. Juluri, A. S. Kumar, Y. Liu, T. Ye, Y.-W. Yang, A. H. Flood, L. Fang, J. F. Stoddart, P. S. Weiss and T. J. Huang, *ACS Nano*, 2009, **3**, 291.
- (a) *Molecular Catenanes, Rotaxanes and Knots: a Journey Through the World of Molecular Topology*, ed. J.-P. Sauvage and C. Dietrich-Buchecker, Wiley-VCH, Weinheim, 1999; (b) L. Fang, M. A. Olson, D. Benítez, E. Tkatchouk, W. A. Goddard, III and J. F. Stoddart, *Chem. Soc. Rev.*, 2010, **39**, 17 and references are therein; (c) G. A. Breault, C. A. Hunter and P. C. Mayers, *Tetrahedron*, 1999, **55**, 5265; (d) T. J. Hubin and D. H. Busch, *Coord. Chem. Rev.*, 2000, **200–202**, 5; (e) L. Raehm, D. G. Hamilton and J. K. M. Sanders, *Synlett*, 2002, 1743; (f) E. R. Kay, D. A. Leigh and F. Zerbetto, *Angew. Chem., Int. Ed.*, 2007, **46**, 72; (g) J. F. Stoddart, *Chem. Soc. Rev.*, 2009, **38**, 1802.
- B. Hudson and J. Vinograd, *Nature*, 1967, **216**, 647.
- W. R. Wikoff, L. Liljas, R. L. Duda, H. Tsuruta, R. W. Hendrix and J. E. Johnson, *Science*, 2000, **289**, 2129.
- (a) S. Verma, A. K. Mishra and J. Kumar, *Acc. Chem. Res.*, 2010, **43**, 79; (b) C. S. Purohit, A. K. Mishra and S. Verma, *Inorg. Chem.*, 2007, **46**, 8493; (c) C. S. Purohit and S. Verma, *J. Am. Chem. Soc.*, 2006, **128**, 400; (d) J. Kumar and S. Verma, *Inorg. Chem.*, 2009, **48**, 6350; (e) A. K. Mishra and S. Verma, *Inorg. Chem.*, 2010, **49**, 8012; (f) C. S. Purohit and S. Verma, *J. Am. Chem. Soc.*, 2007, **129**, 3488; (g) M. D. Pandey, A. K. Mishra, V. Chandrasekhar and S. Verma, *Inorg. Chem.*, 2010, **49**, 2020; (h) A. K. Mishra, C. S. Purohit and S. Verma, *CrystEngComm*, 2008, **10**, 1296.
- (a) P. Adrien Côté and G. K. H. Shimizu, *Coord. Chem. Rev.*, 2003, **245**, 49; (b) D. J. Hoffart, S. A. Dalrymple and G. K. H. Shimizu, *Inorg. Chem.*, 2005, **44**, 8868; (c) F.-F. Li, J.-F. Ma, S.-Y. Song and J. Yang, *Cryst. Growth Des.*, 2006, **6**, 209; (d) H. Wu, X.-W. Dong, H.-Y. Liu, J.-F. Ma, S.-L. Li, J. Yang, Y.-Y. Liu and Z.-M. Su, *Dalton Trans.*, 2008, 5331; (e) H.-Y. Liu, H. Wu, J.-F. Ma, J. Yang and Y.-Y. Liua, *Dalton Trans.*, 2009, 7957; (f) Z.-P. Deng, Z.-B. Zhu, S. Gao, L.-H. Huo, H. Zhao and S. W. Ng, *Dalton Trans.*, 2009, 6552.
- D. Venkataraman, Y. Du, S. R. Wilson, P. Zhang, K. Hirsch and J. S. Moore, *J. Chem. Educ.*, 1997, **74**, 915.
- (a) J. P. García-Teran, O. Castillo, A. Luque, U. García-Couceiro, G. Beobide and P. Roman, *Inorg. Chem.*, 2007, **46**, 3593; (b) D. Dobrzyńska and L. B. Jerzykiewicz, *J. Am. Chem. Soc.*, 2004, **126**, 11118.
- A. Fkyerat, M. Demeunynck, J. F. Constant, P. Michon and J. Lhomme, *J. Am. Chem. Soc.*, 1993, **115**, 9952.