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Water adsorbing silver-adenine interpenetrated framework[†]

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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 N9substituent has a significant influence over the structural outcome. As an extension, we decided to incorporate sulfonic group at the N9position 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(1) 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.

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Fig. 1 (a) ORTEP diagram of **1** at 35% probability level; (b) coordination around silver ions in **1** (Ag–O1^{*a*} = 2.753(7), Ag–O2^{*a*} = 2.824(6), Ag–N1^{*b*} = 2.205(6), Ag–N7 = 2.195(6), Ag1–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 Ag-O_{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 Ag-Osulfonate 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 noncoordinated sulfonate oxygen atoms. Closer inspection revealed that one of the NH₂ 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 H₂O (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 H₂O as no uptake was noticed with MeOH and EtOH vapour. The H₂O 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 H₂O 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 -SO₃ 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: H_2O (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.

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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: 266.0327. mp > 275 °C; ¹H NMR (500 MHz, DMSO-d₆, 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-d₆, 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 ($C_7H_{10}AgN_5O_4S$ as monohydrate): calculated C, 22.84; H, 2.74; N, 19.02; found C, 22.78; H, 2.51; N, 18.33%.

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