

# Conformation driven complexation of two analogous benzimidazole based tripodal ligands with Ag(I) resulting in a trigonal prism and a coordination polymer

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**Abstract.** Two analogous tripodal ligands, namely, 1,3,5-tris(benzimidazol-1-ylmethyl)-2,4,6-triethylbenzene (**1-Et**) and 1,3,5-tris(benzimidazol-1-ylmethyl)-2,4,6-trimethoxybenzene (**1-OMe**) have been used for complexation with silver(I) tetrafluoroborate. A trinuclear Ag(I) salt, formulated as  $[\text{Ag}_3(\mathbf{1-Et})_2]^{3+}(\text{BF}_4)_3 \cdot 7\text{CH}_3\text{CN} \cdot y\text{H}_2\text{O}$  was formed in the complexation reaction of **1-Et** with silver(I) tetrafluoroborate, which consists of a trigonal prismatic cation formed by three bicoordinated Ag(I) coordinated with two **1-Et** ligands. In case of the **1-OMe** ligand, however, a one dimensional ladder, formulated as  $[(\text{Ag}(\mathbf{1-OMe})\text{OH}_2)^+(\text{BF}_4)^-\cdot\text{MeOH}]_\infty$  was obtained which is constituted of a tetracoordinated Ag(I) center in a distorted tetrahedral environment. The crystal structures of the ligand hydrates namely **1-Et**•**H<sub>2</sub>O** and **1-OMe**•**3.6H<sub>2</sub>O** have been discussed along with the structure of methanol *solvate-hydrate* of **1-Et**. The imidazole rings of the **Bim** groups in **1-Et** in the crystal structures of the ligand as well as in its coordination complex with the Ag(I) are pointed inward with respect to the central ring, whereas it is pointed outwards in the crystal structures of **1-OMe** as well as its Ag(I) complex.

**Keywords.** Silver(I); coordination polymer; metallocycle; tripodal ligands; inclusion complexes.

## 1. Introduction

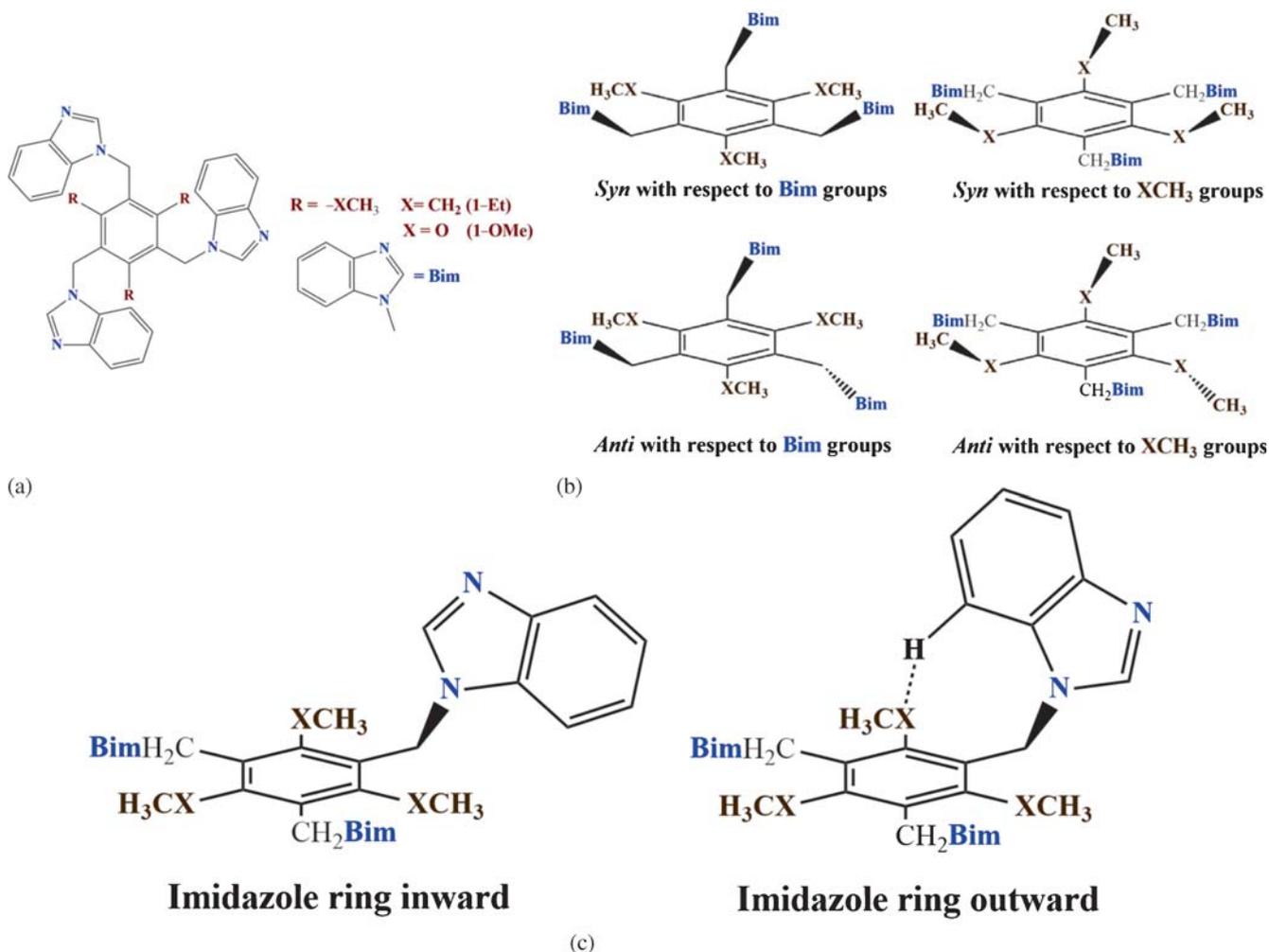
Supramolecular chemistry has witnessed a very systematic study in understanding the nature of coordinate bonds, hydrogen bonds and other non-covalent interactions and their further utilization in the construction of molecules and supramolecular systems, with desired structures and functions. In the synthesis of coordination complexes involving metals, the primary challenge is to understand the coordination capacity and the coordination geometry of the metal involved, followed by designing of suitable ligands in accordance to the coordination geometry. The ever-expanding library of coordination complexes,<sup>1–5</sup> metal-organic frameworks,<sup>6–10</sup> metal clusters,<sup>11–15</sup> coordination polymers<sup>16–22</sup> and intermetallic composites,<sup>23–27</sup> are evidences of the extent to which the phenomenon of metal-coordination could be exploited in order to synthesize complicated architectures with greater structural certainty.

The ‘*molecular library model*’ and the ‘*symmetry interaction model*’ are well-established synthetic approaches adopted widely for the synthesis of metal-centered systems.<sup>28</sup> In the context of the choice of the ligands, it is understood that the molecular library

approach relies on the rigidity associated with the non-chelating di/tritopic ligands, whereas in case of the symmetry interaction approach, the inherent flexibility associated with a ligand and symmetry of the coordination sphere around the metal is a primary requirement. Systematic application of both the approaches led to the successful synthesis of molecular squares,<sup>29–32</sup> rectangles<sup>33–37</sup> and other polyhedron<sup>38–43</sup> structures. Stang and coworkers adopted a *ligand directed approach*,<sup>44–46</sup> which involved designing of a multi-dentate ligand acting as a *molecular clip*. The ligand directed approach was successfully used by Su *et al.*, in the synthesis of metal-organic framework involving Ag(I) and a neutral, semirigid, tripodal ligand, 1,3,5-tris(benzimidazol-1-ylmethyl)-2,4,6-trimethylbenzene (**1-Me**).<sup>47</sup> This approach has been termed as *ligand-directed symmetry-interaction* model by the authors. The assembly forms a tricationic trigonal prism. Later on, this ligand has been explored by many authors for complexation with several other metals.

Herein, we report the complexation of the ethyl (**1-Et**) and methoxy (**1-OMe**) analogues of this tripodal ligand **1-Me** with Ag(I) (scheme 1a). In our approach, we have neither changed the overall symmetry of the molecule nor the coordinating group in the ligand but made a small change by replacing an apparently

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**Scheme 1.** (a) The ligands used for the study: 1,3,5-tris(benzimidazol-1-ylmethyl)-2,4,6-triethylbenzene (**1-Et**) and 1,3,5-tris(benzimidazol-1-ylmethyl)-2,4,6-trimethoxybenzene (**1-OMe**). (b) The possible *syn* and *anti* conformations in **1-Et** ( $X = CH_2$ ) and **1-OMe** ( $X = O$ ) with respect to the orientation of the **Bim** moiety or the ethyl ( $X = CH_2$ )/methoxy ( $X = O$ ) groups. (c) The outward and inward alignment of the **Bim** moiety resulting into two possible ligation modes. In case of  $R = OMe$ , the outward alignment may gain an extra stability because of a possible C–H...O interaction.

innocent group, *i.e.* methyl, by ethyl or methoxy group to study their influence on the network structure. As these groups are known as very weakly interacting in nature and are also located in the interior position of the molecule, they are not expected to influence the supramolecular interaction directly. But are they capable of changing the molecular conformation and hence control the network structures? In order to understand the influence of these apparently innocent groups on the conformation of ligands, we have studied the crystal structures of the ligands as well along with their Ag(I) complexes.

## 2. Experimental

Silver(I) tetrafluoroborate, 1,3,5-triethylbenzene and 1,3,5-trimethoxybenzene were purchased from Sigma Aldrich Ltd. and used as such. Benzimidazole was

purchased from Loba Chemie Ltd. All solvents were purchased from Qualigens Chemicals and used without further purification.

### 2.1 Synthesis of the ligands

1,3,5-tris(bromomethyl)-2,4,6-triethylbenzene<sup>48</sup> and 1,3,5-tris(bromomethyl)-2,4,6-trimethoxybenzene<sup>49</sup> were synthesized according to procedures reported in the literature.

**2.1a Preparation of 1,3,5-tris(benzimidazol-1-ylmethyl)-2,4,6-triethylbenzene (**1-Et**):** Potassium hydroxide (328.7 mg, 5 eq., 5.66 mmol) was added to a solution of benzimidazole (668.9 mg, 5 eq., 5.66 mmol) in THF (50 mL) at room temperature with constant stirring.

After about 1 h, a solution of 1,3,5-tris(bromomethyl)-2,4,6-triethylbenzene (500 mg, 1.13 mmol) in 50 mL of THF was added dropwise for two hours. The reaction mixture was stirred for 48 h under reflux. The solvent was removed under vacuo and the solid was extracted with  $3 \times 50$  mL of dichloromethane. The combined organic extracts were washed with water, dried with sodium sulfate. The compound was obtained as an off white solid by removing the dichloromethane under vacuo. M.p. 249–251°C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 0.87 (9H, t, 7.6 Hz), 2.58 (6H, q, 8.4 Hz), 5.31 (6H, s), 7.22 (6H, m), 7.26 (3H, d, 8.0 Hz), 7.37 (3H, d, 6.8 Hz), 7.53 (3H, s).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 15.3, 22.6, 42.9, 109.3, 120.6, 122.8, 123.4, 130.1, 133.9, 141.0, 143.8, 146.4.

**2.1b Preparation of 1,3,5-tris(benzimidazol-1-ylmethyl)-2,4,6-trimethoxybenzene (1-OMe):** KOH (328.7 mg, 5 eq., 5.66 mmol) was added to a solution of benzimidazole (668.9 mg, 5 eq., 5.66 mmol) in THF (50 mL) at room temperature with constant stirring. After 1 h, a solution of 1,3,5-tris(bromomethyl)-2,4,6-trimethoxybenzene (500 mg, 1.13 mmol) in 50 mL of THF was added dropwise for 2 h. The reaction mixture was stirred for 48 h under reflux. The solvent was removed under vacuo and the solid was extracted with  $3 \times 50$  mL of dichloromethane. The combined organic extracts were washed with water, dried with sodium sulfate. The compound was obtained as a yellowish solid after removal of the dichloromethane under vacuo. M.p. 124–126°C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 2.84 (9H, s), 4.64 (6H, s), 7.13 (3H, m), 6.81 (3H, m), 6.62 (3H, d, 8.0 Hz), 6.59 (3H, d, 8.0 Hz), 7.26 (3H, s).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 33.17, 58.12, 104.58, 115.13, 117.16, 118.05, 128.33, 137.78, 138.25, 155.09.

## 2.2 Synthesis of the Ag(I) complexes

All complexation reactions and crystallizations of the complexes have been performed under minimum exposure to light.

**2.2a Preparation of bis( $\mu_3$ -1,3,5-tris((benzimidazol-1-yl)methyl)-2,4,6-trimethylbenzene)-tri-silver tetrakis(tetrafluoroborate acetonitrile solvate hydrate)  $[\text{Ag}_3(1\text{-Et})_2]^{3+}(\text{BF}_4)^- \cdot 7\text{CH}_3\text{CN} \cdot y\text{H}_2\text{O}$ :** 30 mg of silver(I) tetrafluoroborate (0.1546 mmol) was dissolved in 5 mL of methanol and 56.9 mg of the tripodal ligand **1-Et** (0.66 eq., 0.1030 mmol) was dissolved in 5 mL of dichloromethane. The two solutions were mixed and stirred for 30 min during which a white precipitate was formed. The precipitate was filtered, dried and further dissolved

in 5 mL of acetonitrile to form a clear solution. Diffraction quality single crystals of the complex, suitable for single crystal diffraction experiments, were obtained by slow evaporation of the acetonitrile solution within a period of 24 h. The solid was characterized by single crystal x-ray diffraction.

**2.2b Preparation of (1,3,5-tris(benzimidazol-1-ylmethyl)-2,4,6-trimethoxybenzene)silver(I) tetrafluoroborate methanol solvate monohydrate  $[(\text{Ag}(1\text{-OMe})\text{OH}_2)^+(\text{BF}_4)^- \cdot \text{MeOH}]_\infty$ :** 30 mg. of silver(I) tetrafluoroborate (0.1546 mmol) and 90 mg of **1-OMe** (1 eq.) were dissolved in 5 mL of methanol in a 25 mL erlenmeyer flask, leading to the formation of a dirty white precipitate. This precipitate was found to be insoluble in methanol even after heating. Dropwise addition of dimethylsulphoxide (15 drops) to the methanol suspension with constant heating, led to the dissolution of the precipitate resulting in a clear dark brown solution. The flask containing the solution was kept in dark for slow cooling and further evaporation of the solvent. After 2 days, very small crystalline materials were formed. A very small crystal was selected for the characterization of the material using single crystal diffraction. Crystallization experiments from pure dimethylsulphoxide and *N,N'*-dimethylformamide solutions resulted in the polycrystalline solid materials not suitable for diffraction experiments.

## 2.3 X-Ray Crystallography

X-ray crystal data were collected on Xcalibur Eos Oxford Diffraction Ltd. with Mo- $\text{K}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm were applied.<sup>50</sup> Structure solution and refinement were performed with SHELXS and SHELXL<sup>51</sup> respectively in Olex 2 version 1.2.6 package.<sup>52</sup> In the **1-Et**•**H<sub>2</sub>O** structure, all carbon bonded hydrogens are placed at calculated positions. The water molecule is disordered over two positions and has been modelled with occupancy of 0.5 for each part. The ADPs of the disordered O atoms have been constrained to be same using EADP and the hydrogen atoms have been placed at calculated positions. ISOR has been applied to make the water oxygens isotropic to achieve satisfactory convergence in the refinement. In the **1-Et**•**2MeOH**•**H<sub>2</sub>O** structure, all hydrogens are placed at calculated positions. EADP has been used to constrain the ADP of the methanol carbon atoms to be same. In case of the **1-OMe**•**3.6H<sub>2</sub>O** structure, all carbon bonded hydrogens are placed in calculated positions. One of the water molecules is disordered over two positions

and has been refined with occupancies 0.25 and 0.75, respectively. The other water molecule has been refined with occupancy of 0.6. In  $[\text{Ag}_3(\mathbf{1-Et})_2]^{3+}(\text{BF}_4)_3 \bullet 7\text{CH}_3\text{CN} \bullet y\text{H}_2\text{O}$  structure, the tetrafluoroborate anions, acetonitrile solvent and water molecules could not be located from refinement. The highly diffused electron densities have been treated using SQUEEZE<sup>53</sup> routine of PLATON.<sup>54</sup> All hydrogens have been placed at calculated positions. The number of acetonitrile molecules in the lattice has been estimated from NMR of the crystals. In the  $[(\text{Ag}(\mathbf{1-OMe})\text{OH}_2)^+(\text{BF}_4)^- \bullet \text{MeOH}]_\infty$  structure, all carbon bonded hydrogens are placed at calculated positions. The tetrafluoroborate anion is disordered over two orientations and has been modelled with 0.52 and 0.48 occupancies, respectively. The ADPS of the disordered fluorine atoms (F1A, F1B, F2A, F2B, F3A, F3B) and the boron atom (B1) were made equal by using EADP. In one of the methoxy groups, the carbon atom C33 is disordered over two positions and has been modelled with occupancies 0.48 and 0.52. The ADPs of C33A and C33B have been constrained to be same using EADP. The hydrogen atoms of the water molecule have been fixed using DFIX (0.86 (2) Å). The methanol molecule is disordered over three positions and has been modelled with 0.53, 0.24 and 0.23 occupancies. The C–O bond distances have been restrained to 1.40(2) Å using DFIX. The methanol carbon and the oxygen atoms have been refined isotropically. Addition of hydrogens to the modelled methanol molecules led to non-converging refinement cycles hence disordered methanol moieties were kept without hydrogens.

### 3. Results and Discussion

Both the ligands **1-Et** and **1-OMe** (scheme 1a) have an inherent flexibility arising from different possible conformations of the **Bim** and ethyl/methoxy moieties around the central aromatic ring due to the presence of freely rotatable (Ar)C–CH<sub>2</sub>–N(bim) and (Ar)C–CH<sub>2</sub>CH<sub>3</sub>/(Ar)C–OMe single bond linkages. Due to free rotation around these bonds, molecules can attain different conformations (scheme 1b) which might lead to different crystal structures.

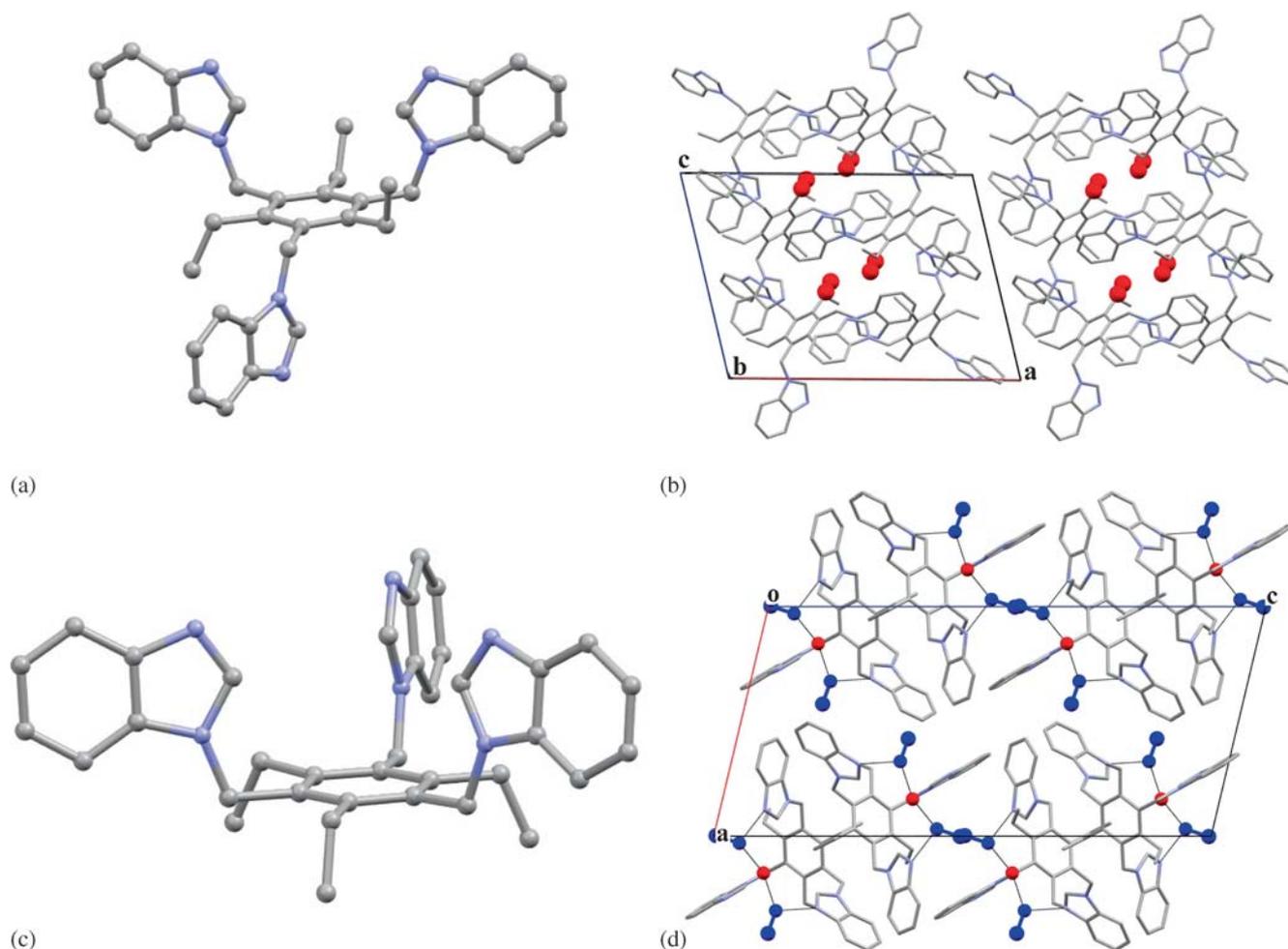
#### 3.1 Structure of **1-Et**•H<sub>2</sub>O, **1-Et**•2MeOH•H<sub>2</sub>O and **1-OMe**•3.6H<sub>2</sub>O

Crystallization of **1-Et** from various organic solvents *viz.*, chloroform, ethyl acetate, ethanol, benzene, toluene *etc.*, resulted in the formation of a crystalline monohydrate of the compound (**1-Et**•H<sub>2</sub>O). The system crystallizes in *P2<sub>1</sub>/c* space group with one

molecule, each of **1-Et** and water in the asymmetric unit (Figure S1 in Supplementary Information). The water molecule is disordered over two positions. The **Bim** groups in the molecule are found to adopt an *anti* conformation (scheme 1b), similar to the structure of **1-Me**<sup>55</sup> (CCDC ref. code UFEMAT), where two of the **Bim** moieties are directed above and the third one is directed below the central aromatic ring (figure 1a). The conformation of the ethyl groups in this system is in the *anti* conformation too. The three ∠(Ar)C–CH<sub>2</sub>–N–CH dihedral angles are 10.0(4), 12.8(5) and 29.6(4)° in this structure which provides a conformation where the imidazole ring of the benzimidazole moiety is pointed inwards (scheme 1c). The water molecule, residing in the channel which is running along the *b* axis, is involved in bridging two molecular units of **1-Et** *via* O–H···N hydrogen bonds (figure 1b, table 1).

In an attempt to explore **1-Et** for its possible polymorphic forms and its lattice inclusion complexes, the compound was crystallized from different laboratory solvents. Whereas most of the crystallization experiments resulted in the formation of the same monohydrate form discussed above, a very unstable *solvate hydrate*<sup>56–58</sup> of **1-Et** was obtained from methanol (**1-Et**•2MeOH•H<sub>2</sub>O). The system crystallizes in *P2<sub>1</sub>/c* space group with one molecule of **1-Et**, two molecules of methanol and a water molecule in the asymmetric unit (Figure S1). A *syn* type of conformation (scheme 1b) is found with respect to the **Bim** as well as the ethyl groups in this crystal structure (figure 1c). The three ∠(Ar)C–CH<sub>2</sub>–N–CH dihedral angles in this structure are found to be as 0.3(5), 2.7(5) and 4.5(5)°. The two methanol molecules are hydrogen bonded to the free N atoms of two **Bim** moieties in a molecule and are interlinked to each other by hydrogen bonds (table 1) mediated by the water molecule. The inclusion system is highly unstable and was found to lose solvent of crystallization even at room temperature. In this structure, one methanol is residing in the channel, running parallel to the *b* axis, and the other one is in a cage type of cavity (figure 1d). In the **1-Et** hydrate structures, discussed above, certain features were found to be common for both systems in context of conformation of the **Bim** moiety – **a.** the benzimidazole planes are approximately perpendicular to the central ring; **b.** for each benzimidazole moiety, the imidazole rings are pointed inwards and the benzene rings are pointed outwards (∠(Ar)C–CH<sub>2</sub>–N–CH dihedral angles are <90°); **c.** the free N lone pairs are pointed along the perpendicular direction of the central aryl ring plane.

Crystallization of **1-OMe** from ethanol resulted in the formation of a crystalline hydrate, formulated as **1-OMe**•3.6H<sub>2</sub>O (Figure S1c in SI). The system



**Figure 1.** (a) The *anti* conformation of the **Bim** moieties and the ethyl groups in the structure of **1-Et** molecule in **1-Et·H<sub>2</sub>O** system. (b) The three dimensional packing of the **1-Et·H<sub>2</sub>O** system showing the incorporated water molecules in channels along *b* axis. (c) The *syn* conformation of the **Bim** moieties and the ethyl groups in **1-Et** in **1-Et·2MeOH·H<sub>2</sub>O**. (d) The three dimensional packing of the **1-Et·2MeOH·H<sub>2</sub>O** showing the incorporated methanol (shown as blue ball and stick) and water molecules (shown as red balls) along the *b* axis.

crystallizes in *P31c* space group with one third molecule of **1-OMe** in the asymmetric unit along with occupancy of one and 0.2 molecules of water. The water molecule, with full occupancy, is disordered over two positions. The conformation of the **Bim** and the methoxy moieties are of the *syn* type (scheme 1b), similar to that of **1-Et** in **1-Et·2MeOH·H<sub>2</sub>O** structure. However, unlike **1-Et** in **1-Et·2MeOH·H<sub>2</sub>O**, the imidazole ring is pointed outwards with respect to the central aryl group ( $\angle(\text{Ar})\text{C}-\text{CH}_2-\text{N}-\text{CH}$  dihedral angle is  $121.7(3)^\circ$  i.e.  $>90^\circ$ ) which renders a weak  $\text{C}-\text{H}\cdots\text{O}$  interaction ( $2.815 \text{ \AA}$ ,  $3.642(3) \text{ \AA}$ ,  $148.7^\circ$ ) between the benzene moiety of benzimidazole group and the OMe group (scheme 1c). As a result of this conformation, the lone pairs of the free N atoms are directed outwards and parallel to the plane of central ring (figure 2a). The water molecules occupy the channel, running along the crystallographic *c* axis (figure 2b).

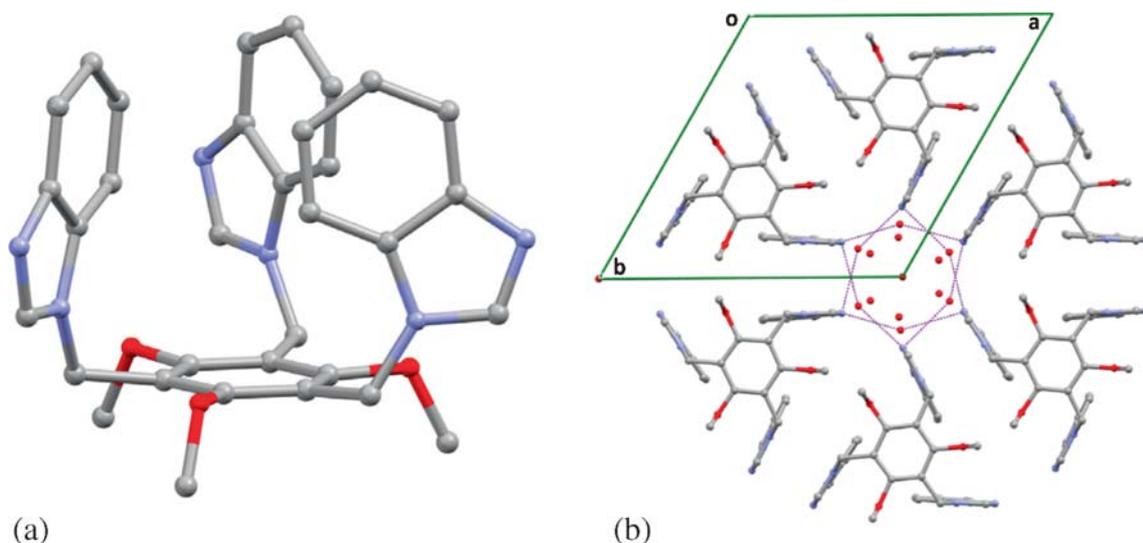
We were interested to investigate which of these conformational features of the ligands in their respective crystal structures are prevailed in and hence control the structure of their coordination complexes of these ligands with Ag(I).

### 3.2 Crystal structure of $[\text{Ag}_3(\text{I-Et})_2]^{3+}(\text{BF}_4)_3^- \cdot 7\text{CH}_3\text{CN} \cdot y\text{H}_2\text{O}$

When silver(I) tetrafluoroborate and **1-Et** were allowed to react in a 3:2 ratio, a metallocyclic Ag(I) salt was obtained which could be characterized as  $[\text{Ag}_3(\text{1-Et})_2]^{3+}(\text{BF}_4)_3^- \cdot 7\text{CH}_3\text{CN} \cdot y\text{H}_2\text{O}$  by single crystal x-ray diffraction (Figure S1 in SI). The number of acetonitrile and water molecules in the lattice could not be identified because of highly diffused electron densities arose from disordered molecules. The presence of acetonitrile molecules in the lattice and its stoichiometry

**Table 1.** Parameters for the hydrogen bonds in the structures.

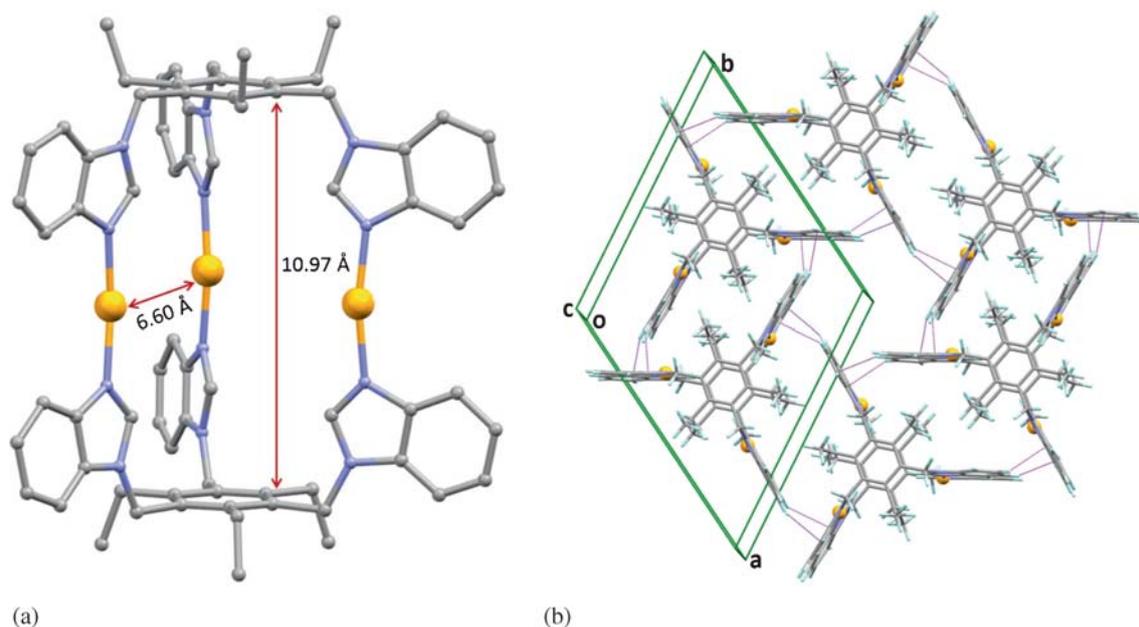
	$d(\text{\AA})$	$D(\text{\AA})$	$D-H\cdots A$ ( $^\circ$ )
1-Et•H <sub>2</sub> O			
C8–H8B $\cdots$ N1	2.61	3.363(4)	135
1-Et•2MeOH•H <sub>2</sub> O			
O1–H1A $\cdots$ O2	2.02	2.869(5)	175
O1–H1B $\cdots$ O3	2.51	2.863(6)	106
O2–H2 $\cdots$ N2	1.97	2.782(5)	169
O3–H3 $\cdots$ N4	1.88	2.692(6)	171
C16–H16 $\cdots$ O1	2.48	3.247(6)	140
C26–H26 $\cdots$ O1	2.55	3.314(6)	140
C36–H36 $\cdots$ O1	2.59	3.423(6)	149
1-OMe•3.6H <sub>2</sub> O			
O2B–H2BA $\cdots$ N2	2.07	2.862(10)	156
C5–H5A $\cdots$ O1	2.39	2.853(3)	109
C6–H6 $\cdots$ O2B	2.37	3.253(9)	158
[(Ag(1-OMe)OH <sub>2</sub> ) <sup>+</sup> (BF <sub>4</sub> ) <sup>-</sup> •MeOH] $_{\infty}$			
O4–H4B $\cdots$ F2A	2.32(10)	2.953(19)	132(9)
C4–H4 $\cdots$ O4	2.53	3.383(13)	152
C7–H7 $\cdots$ O1	2.38	3.228(11)	152
C8–H8A $\cdots$ O1	2.42	2.851(9)	107
C13–H13B $\cdots$ O1	2.39	2.852(8)	109
C24–H24B $\cdots$ O2	2.36	2.834(9)	109



**Figure 2.** (a) The *syn* conformations of the **Bim** as well as the methoxy groups in the structure of **1-OMe•3.6H<sub>2</sub>O** (hydrogen atoms and the water molecules have not been shown for clarity). (b) The three dimensional packing of **1-OMe•3.6H<sub>2</sub>O** showing the channel along *c* axis occupied by hydrogen bonded water molecules.

were confirmed by correlating the NMR spectrum of the crystals of the complex. It forms a trigonal prism like structure, similar to the coordination complex of **1-Me** with Ag(I)<sup>47</sup> but in a high symmetry space group. This metallocyclic salt<sup>59,60</sup> is crystallized in  $P6_3/m$  space group with one-sixth of the cationic cage framework in the asymmetric unit. The overall cationic metallocycle, constituted of three Ag(I) ions ligated to the neutral **Bim** moieties of two **1-Et** ligands, is forming a

$M_3L_2$ <sup>61–64</sup> type of system (figure 3a). The conformation of the ligand is found to be similar to that found in **1-Et•2MeOH•H<sub>2</sub>O**. The  $\angle(\text{Ar})\text{C}-\text{CH}_2-\text{N}-\text{CH}$  dihedral angle is  $14(1)^\circ$  in this conformation. A CSD search (CSD version 5.36, update May 2015, 3D coordinates determined) on the conformation of **1-Me** suggests that out of 23 structures reported with this molecule (table 2), in 20 cases the **Bim** moiety is found to adopt the *syn* conformation. Among these 20 structures,



**Figure 3.** (a) The  $M_3L_2$  ligation in the  $[Ag_3(1-Et)_2]^{3+}(BF_4)_3^- \cdot 7CH_3CN \cdot yH_2O$  metalocycle resembling a high symmetry prismatic cage with the dimensions of the cage. (b) Formation of the channel aided by the C–H $\cdots\pi$  interactions between the ligands of the prismatic cations.

exhibiting *syn* conformation, in sixteen cases the imidazole ring of the **Bim** moiety is pointed inwards facing the central aromatic ring, whereas only in two structures, NASQIJ and SIJJAJ, the imidazole ring of the **Bim** moiety is pointed outwards, similar to the structure of **1-OMe** in **1-OMe**•**3.6H<sub>2</sub>O**. In case of the other two structures, SURLOH and TIPZIC, the imidazole ring is

found to adopt both of the above mentioned conformations in the same molecule. On the other hand, in three cases, the **Bim** moieties are in *anti*-conformation. Based on the diffused electron densities observed inside the cage, generated within the metalocycle, one tetrafluoroborate anion is expected to be present there, and therefore, the other two tetrafluoroborate anions are

**Table 2.** CSD hits for the **1-Me** analogue based structures with different possible conformations of the **Bim** moieties within them. (CSD version 5.36, update May 2015, 3D coordinates determined).

<b>Bim</b> moiety directed inward	Syn Conformation		<i>Anti</i> Conformation
	<b>Bim</b> moiety directed outward	Both inward and outward directed <b>Bim</b> moiety	
GODFIQ	NASQIJ	SURLOH	SURLUN
GODFOW	SUJJAJ	TIPZIC	TIPZOI
EKOVAB			TIPZUO
HEFNIR			
LUDROR			
LUDRUX			
LUDSAE			
LUDSEI			
RAVNEJ			
RAVNIN			
RAVPEL			
RAVPIP			
RAKVIK			
SURMAU			
GULCAT			
UFEMAT			

residing outside the cage, similar to the case found in **1-Me** Ag complex.<sup>47</sup> The channel, along the *c* axis, is formed by the self-assembly of the prismatic moieties aided by C–H·· $\pi$  interactions among the benzene moieties of the **Bim** groups (figure 3b). The bicoordinated Ag(I) ion forms coordination bond with the free N (Ag–N = 2.09(2) Å, N–Ag–N = 169(1)°) of the **Bim** group. The length of the cavity is 10.97(5) Å (distance between two central rings) whereas the breadth of the cavity as could be concluded from the Ag··Ag separation within the cavity, is 6.60(2) Å (figure 3a).

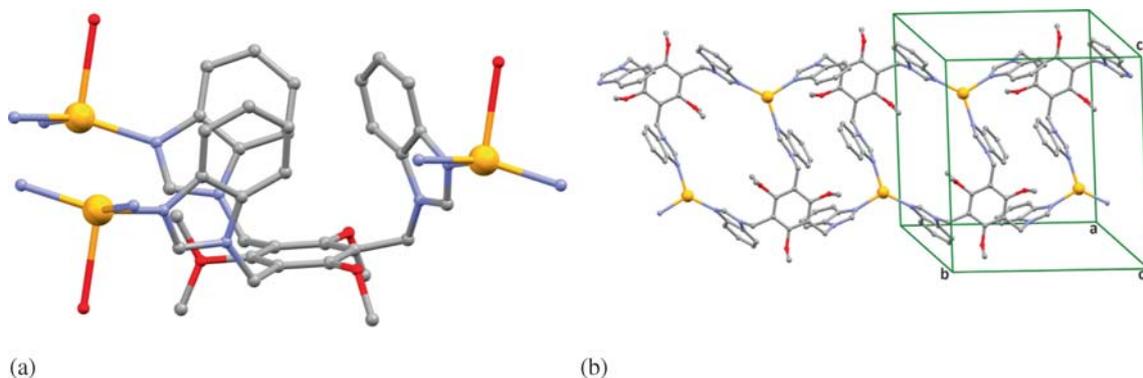
### 3.3 Structure of $[(\text{Ag}(\text{1-OMe})\text{OH}_2)^+(\text{BF}_4)^-\bullet\text{MeOH}]_\infty$

The reaction of silver(I) tetrafluoroborate with **1-OMe** in a 1:1 molar ratio results in the formation of a coordination polymer which could be characterized as  $[(\text{Ag}(\text{1-OMe})\text{OH}_2)^+(\text{BF}_4)^-\bullet\text{MeOH}]_\infty$  by single crystal x-ray diffraction (Figure S1 in SI). The solid is crystallized in  $P\bar{1}$  space group with one Ag(I) coordinated to a **Bim** wing of the ligand molecule of **1-OMe**, one tetrafluoroborate anion, a water molecule and a disordered methanol molecule forming the asymmetric unit. The methanol molecule is disordered over three positions whereas the tetrafluoroborate moiety is disordered over two positions. Similar to the conformation of **1-OMe** found in **1-OMe**·**3.6H<sub>2</sub>O**, the imidazole ring is directed outwards and the **bim** moieties are in *syn* conformation in the structure of the coordination polymer  $[(\text{Ag}(\text{1-OMe})\text{OH}_2)^+(\text{BF}_4)^-\bullet\text{MeOH}]_\infty$  (figure 4a). Due to the outward orientation of the imidazole rings, the benzene rings form C–H··O interactions (scheme 1c, table 1) with the OMe groups. The methoxy groups are also found in *syn* conformation except that one of the methoxy groups is disordered over two positions

(*syn* and *anti*). The Ag(I) is found to be tetracoordinated, three with **Bim** moieties from three ligand molecules and one with water molecule which is found to be very weak (Ag–O 2.759 Å) (figure 4a). There are only 9 reports found in the CSD (CSD version 5.36, update May 2015, 3D coordinates determined, Ag–OH<sub>2</sub> > 2.759 Å) where Ag–OH<sub>2</sub> bond is greater than 2.759 Å (table 3). The Ag(I) ion is located slightly above (by 0.302 Å) the plane containing the three coordinating N atoms. The three Ag–N distances are 2.313(2) Å, 2.214(1) Å and 2.261(2) Å, whereas the N–Ag–N angles are respectively 117.73°(2), 133.03°(3) and 103.74°(3). Two Ag(I) ions and two **1-OMe** ligands form cyclic network which are further connected to each other *via* coordination bonds to form a 1D ladder like polymer, running along the *b* axis (figure 4b). The tetrafluoroborate anion and the water molecule occupy the space generated between the layers. We performed a CSD search (CSD version 5.36, update May 2015, 3D coordinates determined, only one Ag(I) per asymmetric unit) in order to find out the frequency of different coordination numbers observed in Ag(I) systems. Result suggests that out of 5111 data, there are 2135 crystal structures where Ag(I) forms bicoordinated coordination bonds which is followed by tetracoordinated (1417)

**Table 3.** CSD hits with Ag–OH<sub>2</sub> bond distances greater than 2.759 Å. (CSD version 5.36, update May 2015, 3D coordinates determined,  $d_{(\text{Ag}-\text{OH}_2)} > 2.759$  Å).

Hits	Ag–OH <sub>2</sub> (Å)	Hits	Ag–OH <sub>2</sub> (Å)
EKOYIN	2.826(2)	LOSNEM	2.615(2)
IMOZEQ	2.798(2)	MARHEU	2.805(2)
JAXVUA	2.696(2)	NUMZIF	2.773(2)
KIBVIB	2.855(2)	XIWLAR	2.776(2)
KOHWEK	2.790(2)		



**Figure 4.** (a) The *syn* conformation and the bridging coordination mode of **1-OMe** as observed in the  $[(\text{Ag}(\text{1-OMe})\text{OH}_2)^+(\text{BF}_4)^-\bullet\text{MeOH}]_\infty$  coordination polymer (disordered tetrafluoroborate anion and the disordered methanol molecule are not shown). (b) The one dimensional polymeric ladder formed along the crystallographic *b* axis (only the metal coordinated part is shown).

**Table 4.** Frequency of different coordination modes for Ag(I) in crystal structure database (CSD version 5.36, update May 2015, 3D coordinates determined, only one Ag(I) in asymmetric unit).

2 or more	5111	No. of hits with coordination no. 2 = 2135
3 or more	2976	No. of hits with coordination no. 3 = 1044
4 or more	1932	No. of hits with coordination no. 4 = 1417
5 or more	515	No. of hits with coordination no. 5 = 226
6 or more	289	No. of hits with coordination no. 6 = 216

and tricoordinated (1044) metal centres. Reports on even higher coordinated modes of Ag(I) are comparatively less in number (table 4).

#### 4. Conclusions

The syntheses and crystal structures of Ag(I) based metallocyclic salt and a coordination polymeric salt of Ag(I) respectively with the two tripodal ligands **1-Et** and **1-OMe** have been discussed along with the structures of **1-Et•H<sub>2</sub>O**, **1-Et•2MeOH•H<sub>2</sub>O** and **1-OMe•3.6H<sub>2</sub>O**. Two very similar ligands produce very different coordination complexes with Ag(I). Some of the conformational features, which also control the coordination mode and hence the overall crystal structures, have been transferred from the ligand to the complex. The *syn* and *anti* conformations of the **Bim** moieties in the **1-Et•H<sub>2</sub>O** and **1-Et•2MeOH•H<sub>2</sub>O** structures suggest that these two conformations are easily interconvertible at room temperature in solution state. The **Bim** moieties, in both the ligands in the respective structures of the complexes, are found to adopt the *syn* conformation. Along with the *syn* conformation of the **Bim** moieties, the imidazole rings are pointed inwards which enables the **1-Et** ligand to form a M<sub>3</sub>L<sub>2</sub> type of prismatic metallocycle with Ag(I), whereas in spite of *syn* conformation of the **Bim** moieties in **1-OMe**, the imidazole ring is directed outwards and hence it produces a 1D ladder type of polymer. Weak C–H···O interaction between the benzene ring of the benzimidazole moiety and the OMe group favors the conformation where the benzene ring is pointed inwards and imidazole ring is pointed outwards. On the other hand, when this methoxy group is replaced by an ethyl (**1-Et**) or methyl (**1-Me**) group, this favorable interaction is absent, rather the CH<sub>2</sub> (in **1-Et**) or the CH<sub>3</sub> (in **1-Me**) groups cause some steric hindrance to the benzene moiety in this conformational arrangement. This unfavorable situation is avoided in the other conformation where the benzene ring is directed outwards. In continuation of this work we are studying the complexation of these tripodal ligands with other transition metals.

#### Supplementary Information (SI)

Thermal ellipsoid plots at 30% probability, Tables for bond angles and bond lengths, Crystallographic table are given in the supporting information available at [www.ias.ac.in/chemsci](http://www.ias.ac.in/chemsci). CIF files containing complete information on the studied structures were deposited with CCDC, deposition number 1429072-1429076, and are freely available upon request from the following web site: [www.ccdc.cam.ac.Uk/data\\_request/cif](http://www.ccdc.cam.ac.Uk/data_request/cif).

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