

Silver(I) based dinuclear metallacycles with free thiophenyl/thiomethyl units

SARITA YADAV^a, DEEPAK GUPTA^a and MALAICHAMY SATHIYENDIRAN^{a,b,*}

^aDepartment of Chemistry, University of Delhi, Delhi 110 007, India

^bSchool of Chemistry, University of Hyderabad, Hyderabad, 500 046 India

e-mail: msathi@uohyd.ac.in

MS received 1 October 2015; revised 8 December 2015; accepted 10 December 2015

Abstract. Three dinuclear, ionic and homoleptic metallacycles decorated with free thiophenyl or thiomethyl units were synthesized using AgOS(O₂)CF₃ and benzimidazole derived ditopic N-donor ligands at ambient condition. The complexes were characterized by analytical and spectroscopic (IR and ¹H NMR) techniques and two of the complexes were structurally characterised through single crystal X-ray diffraction.

Keywords. Metallacycle; benzimidazole; silver; supramolecule; thiophenyl; thiomethyl

1. Introduction

The coordination chemistry of silver(I) ion has been studied widely from the perspective of synthesis of molecular and supramolecular frameworks for materials and biological applications.¹ The property of diverse coordination numbers and geometries exhibited by silver ion when combined with a judicious choice of coordinating ligands facilitate the formation of several interesting one-, two- and three dimensional supramolecular architectures.² Among these supramolecules, discrete silver(I)-based supramolecular coordination complexes i.e., metallacycles are a notable class.^{3–14} Nitrogen donor ligands explored till now for the synthesis of silver-based metallacycles are mostly pyridyl-based motif³ and a countable pyrazole,^{4,5} pyrimidine,⁶ imidazole,⁷ benzimidazole,⁸ pyridylpyrimidine,⁹ benzotriazole,¹⁰ Schiff base,¹¹ thioquinoline,¹² adenine,¹³ and dipyrin¹⁴ derivatives. However, the design and synthesis of silver(I)-based metallacycles decorated with covalently bonded uncoordinated heterocycles/soft-donors is a challenge due to the high affinity of heterocyclic unit to silver(I) ion that is regarded as a soft acid which favours coordination to a soft base.^{5,12} We have recently reported considerable variety of rhenium based metallacycles utilizing furan/thiophene/thiomethyl functional units attached benzimidazolyl based ligands (figure 1) with interesting structural and photophysical properties.¹⁵ Herein, we report a new class of silver(I)-based metallacycles decorated with free thiophenyl and

thiomethyl units. Self-assembly of three dinuclear, ionic and homoleptic complexes was achieved using silver trifluoromethanesulfonate (AgOS(O₂)CF₃) and a ditopic N-donor ligand. The complexes were characterized by elemental analysis, FT-IR, mass spectrometry and nuclear magnetic resonance spectroscopic techniques. The molecular structures of two of the complexes were further confirmed by single-crystal X-ray diffraction analysis.

2. Experimental

2.1 Materials and general procedures

Ligands (L¹, L² and L³) were synthesized according to reported procedure and were stable in moisture and air.^{15g, 15j} AgOS(O₂)CF₃ was procured from Sigma Aldrich. Analytical grade CH₂Cl₂, and CH₃OH were purchased and used as received. Elemental analysis was performed on an Elementar Analysen systeme GmbH Vario EL-III instrument. FT-IR spectral data were obtained on a Shimadzu IR435 spectrometer using KBr pellet in the frequency range 400–4000 cm⁻¹. ¹H NMR spectra were recorded on a JEOL ECX 400 NMR spectrometer. The chemical shifts are reported in parts per million (ppm) relative to residual solvent signal.

2.2 Synthesis of the complexes 1-3: General procedure for synthesis of metallacycles

AgOS(O₂)CF₃ in CH₃OH was added dropwise to a ditopic ligand in CH₂Cl₂ in a round bottom flask

*For correspondence

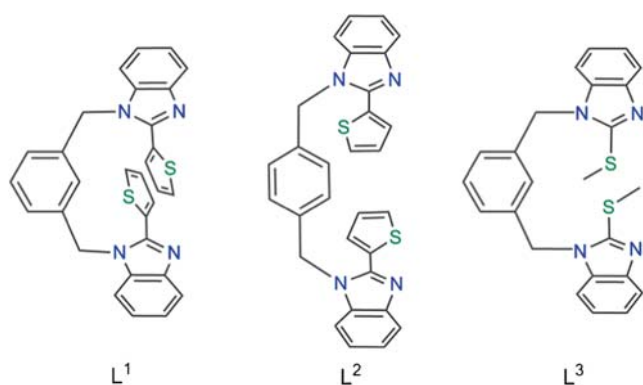


Figure 1. Ditopic ligands used for the synthesis of metallacycles.

with constant stirring at room temperature. Very fine precipitate was obtained immediately in the reaction mixture. It was stirred overnight. The resulting product as precipitate was filtered, and allowed to dry in the air. The filtrate was kept undisturbed. Crystals of metallacycle were obtained from the filtrate.

2.2a Synthesis of metallacycle 1: Metallacycle **1** was obtained from $\text{AgOS(O)}_2\text{CF}_3$ (25.5 mg, 0.099 mmol), CH_3OH (5 mL), 1,3-bis((2-(thiophen-2-yl)-benzimidazol-1-yl)methyl)benzene (50 mg, 0.099 mmol), and CH_2Cl_2 (5 mL). Yield: 93% (70 mg, 0.046 mmol). Anal. Calcd. (%) for $\text{C}_{62}\text{H}_{44}\text{N}_8\text{O}_6\text{F}_6\text{S}_6\text{Ag}_2\cdot\text{H}_2\text{O}$ (M_r 1519.18 + 18.02): C, 48.44; H, 3.02; N, 7.29, S 12.52. Found: C, 48.18; H, 2.72; N, 7.41, S 12.56. FT-IR (KBr, cm^{-1}): $\nu(\text{C}=\text{N})$ 1565 (w, br). $^1\text{H NMR}$ (400 MHz, $\text{DMSO}-d_6$): δ 5.68 (s, 4H, H^8), 6.73 (s, 1H, H^{11}), 6.95 (d, $J = 7.3$ Hz, 2H, H^9), 7.06–7.08 (m, 2H, H^4), 7.21–7.30 (m, 5H, $\text{H}^{5,6,10}$), 7.36 (d, $J = 3.7$ Hz, 2H, H^3), 7.47 (d, $J = 8.2$ Hz, 2H, H^7), 7.71 (d, $J = 7.8$ Hz, 2H, H^4), 7.74 (dd, $J = 5.0, 0.9$ Hz, 2H, H^5). Crystals suitable for X-ray diffraction were obtained from $\text{CH}_2\text{Cl}_2:\text{CH}_3\text{OH}$ mixture.

2.2b Synthesis of metallacycle 2: Powder of **2** was obtained from 1,4-bis((2-(thiophen-2-yl)-benzimidazol-1-yl)methyl)benzene (50 mg, 0.099 mmol), CH_2Cl_2 (5 mL), $\text{AgOS(O)}_2\text{CF}_3$ (25.5 mg, 0.099 mmol), and CH_3OH (5 mL). Yield: 70% (53 mg, 0.0349 mmol). Anal. Calcd (%) for $\text{C}_{62}\text{H}_{44}\text{N}_8\text{O}_6\text{F}_6\text{S}_6\text{Ag}_2\cdot\text{CH}_2\text{Cl}_2$ (M_r 1519.18 + 84.93): C, 47.17; H, 2.89; N, 6.99, S 11.99. Found: C, 47.55; H, 3.08; N, 7.25, S 11.44. FT-IR (KBr, cm^{-1}): $\nu(\text{C}=\text{N})$ 1562 (w, br). $^1\text{H NMR}$ (400 MHz, $\text{DMSO}-d_6$): δ 5.71 (s, 4H, H^8), 7.01 (s, 4H, H^9), 7.15 (t, $J = 4.6$ Hz, 2H, H^4), 7.21–7.28 (m, 4H, $\text{H}^{5,6}$), 7.47 (d, $J = 3.6$ Hz, 2H, H^3), 7.52 (dd, $J = 6.7, 2.6$ Hz, 2H, H^7), 7.69–7.72 (m, 2H, H^4), 7.77 (d, $J = 5.0$ Hz, 2H, H^5).

2.2c Synthesis of metallacycle 3: Metallacycle **3** was obtained from 1,3-bis((2-(methylthio)-benzimidazol-1-yl)methyl)benzene (86 mg, 0.200 mmol), CH_2Cl_2 (5 mL), $\text{AgOS(O)}_2\text{CF}_3$ (51.5 mg, 0.200 mmol), and CH_3OH (5 mL). Yield: 83% (113.5 mg, 0.083 mmol). Anal. Calcd. (%) for $\text{C}_{50}\text{H}_{44}\text{N}_8\text{O}_6\text{F}_6\text{S}_6\text{Ag}_2\cdot 2\text{H}_2\text{O}$ (M_r 1375.05 + 36.03): C, 42.56; H, 3.43; N, 7.94, S 13.63. Found: C, 42.53; H, 3.10; N, 7.95, S 13.77. FT-IR (KBr, cm^{-1}): $\nu(\text{C}=\text{N})$ 1610 (w, br). $^1\text{H NMR}$ (400 MHz, $\text{DMSO}-d_6$): δ 2.63 (s, 6 H, CH_3), 5.32 (s, 4H, H^8), 7.02 (s, 1H, H^{11}), 7.12–7.20 (m, 6H, $\text{H}^{5,6,9}$), 7.29 (t, $J = 8.0$ Hz, 1H, H^{10}), 7.38 (d, $J = 8.0$ Hz, 2H, H^7), 7.58 (d, $J = 4.0$ Hz, 2H, H^4). Crystals suitable for X-ray diffraction were obtained from $\text{CH}_2\text{Cl}_2:\text{CH}_3\text{OH}$ mixture.

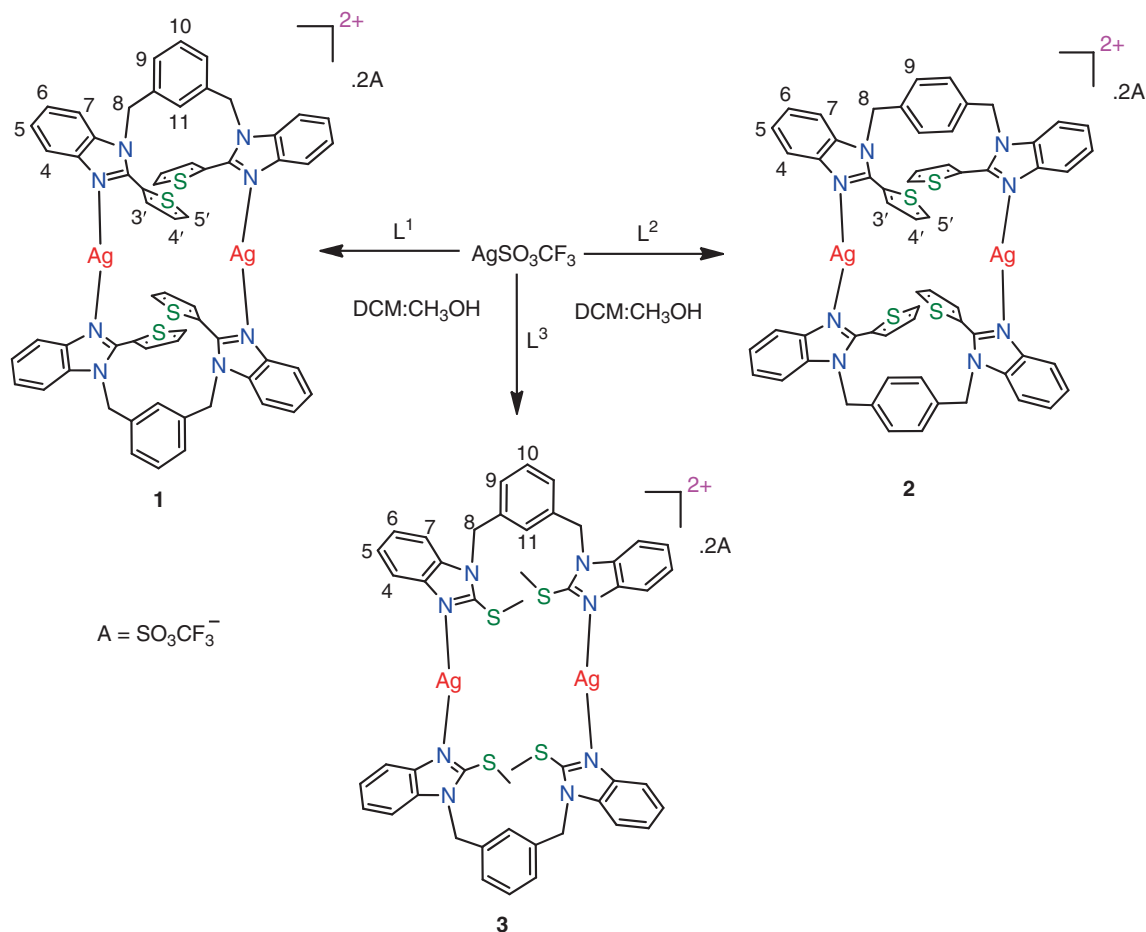
2.3 X-ray crystallography

Intensity data of suitably sized crystal of **1** was collected on an Oxford Xcalibur S diffractometer (4-circle κ goniometer, Sapphire-3 CCD detector, ω scans, graphite monochromator, and a single wavelength enhanced X-ray source with $\text{MoK}\alpha$ radiation).^{16a} Pre-experiment, data collection, data reduction, and absorption correction were performed with the CrysAlisPro software suite.^{16b} Intensity data of suitably sized crystal of **3** was collected on a Bruker AXS SMART-APEX diffractometer with a CCD area detector and graphite monochromator. The frames were collected by ω , ϕ and 2θ rotation at 10s per frame with SMART.^{16c} The measured intensities were reduced to F^2 and corrected for absorption with SADABS.^{16d} The structures were solved by direct methods using SIR 92 which revealed the atomic positions, and refined using the SHELX-97 program package and SHELXL97 (within the WinGX program package).^{16e–16g} Non-hydrogen atoms were refined anisotropically. C–H hydrogen atoms were placed in geometrically calculated positions by using a riding model. Table S1 for crystallographic data of **1** and **3** can be found in Supplementary Information

3. Results and Discussion

3.1 Characterization of 1–3

Metallacycles **1–3** were synthesized by self-assembly of benzimidazolyl derived ditopic ligands, L^1 – L^3 , with $\text{AgOS(O)}_2\text{CF}_3$ in 1:1 $\text{CH}_2\text{Cl}_2:\text{CH}_3\text{OH}$ in 93, 70 and 83% yields, respectively (scheme 1). The complexes are air and moisture stable solids and soluble in common organic solvents. The FT-IR spectra of **1–3** in KBr showed a band for $\nu_{\text{C}=\text{N}}$ at 1565, 1562 and 1610 cm^{-1} . These bands are shifted to lower frequencies compared



Scheme 1. Synthesis of metallacycles **1–3**.

to those for the free ligands which reflect the weakening of C=N bond due to bonding with silver ion.

The ^1H NMR spectra of **1–3** were recorded in d_6 -DMSO at room temperature (figures S1–S8). The correlations between the peaks in ^1H NMR spectra of **1–3** were made with the help of ^1H - ^1H COSY NMR spectra. The spectra of the complexes display one set of signals, suggesting the existence of a single species in solution. Another option is that the presence of conformers that undergo a rapid equilibrium in solution on the NMR time scale. The ^1H -NMR spectrum of powder of **1** is similar to that of the crystals of **1**. In the ^1H NMR spectrum of **1**, protons H^4 and H^9 show slight downfield shift whereas the signals for other protons remain almost unchanged as compared to the free ligand (figure S1). The downfield shift is indicative of the coordination with the metal ion. In addition, remarkable upfield shift is observed for H^{11} by 1.99 ppm in comparison to the free ligand, which is probably due to the ring current effect from the nearby benzimidazolyl units. In the solid-state structure of **1**, the conformation of L^1

allows the positioning of H^{11} proton between the two *face-to-face* arranged benzimidazolyl rings (figure S4). This further supports the stability of the metallacyclic framework of **1** in solution. A similar observation was made for **3** where the signal for H^{11} proton was shifted upfield by comparatively a lesser value (0.09 ppm), presumably due to the less aromatic clouds around the proton (figure S3). Similar effects have previously been observed for few silver metallacycles.^{8a} The H^{11} chemical resonance merged with $\text{H}^{5,6,9}$ protons chemical resonances in the powder sample of **3**. This may be due to the possibility of presence of various conformers due to rotation of the free functional units in the powder sample. The ^1H NMR spectrum of metallacycle **2** was largely similar to that of the free L^2 (figure S2). The composition of the complexes was further supported by ESI-MS data (figures S8–S15). The molecular ion peaks for metallacycles **2** and **3** were observed at $m/z = 1369.0192$ and 1225.0182 , respectively, which confirm the formation of monocationic metallocyclic species $[\text{Ag}(\text{L})_2(\text{OS}(\text{O})_2\text{CF}_3)]^+$ (figures S10 and S13). The base

peaks in the ESI-MS spectra of metallacycles **1**, **2** and **3** can be seen at $m/z = 1113.1631$, 1113.1635 and 969.1624 respectively (figures S8, S11, S14). These can be assigned to another monocationic $[\text{Ag}(\text{L})_2]^+$ species in solution. The identification of such a sub-unit in the MS spectra of all the three metallacycles leads to a generalization that monocationic species might be the key intermediate, that upon subsequent reaction with another silver ion, results in the final metallacycle.^{8c} Moreover, the dicationic metalocyclic species $[\text{Ag}_2\text{L}_2]^{2+}$ was also identified in the ESI-MS spectra of all the three metallacycles (figures S9, S12, S15).

3.2 X-Ray Diffraction Studies

Single crystal X-ray diffraction studies of **1** and **3** revealed binuclear dicationic metallacyclic $[\text{Ag}_2\text{L}_2]^{2+}$ motif and two triflate anions per formula unit (figure 2). Two ligands, act as molecular clip, coordinated with two silver ions using benzimidazolyl nitrogen atom (figure 2). The ligands take *anti*-conformation in both the complexes in such a way that both thiophenyl/thiomethyl units in each ligand motif point in opposite directions. The two thiophenyl rings are non-coplanar with the benzimidazolyl plane (dihedral angle = 45° and 71°) in **1** (figure 3). The Ag–N bond lengths are comparable in **1** (2.106(6), 2.099(5) Å), **3** (2.121(4), 2.111(4) Å) and known Ag–imidazolyl/Ag–benzimidazolyl-based metallacycles ($[\text{Ag}_2\text{L}_2]^{2+}$ (2.076–2.131 Å), where L = ditopic clip ligand).^{7,8} Slightly bent geometry is observed

around the metal center (N(1)–Ag–N(4) = 168° in **1** and 174.1° in **3**). The higher deviation from linearity for the N(1)–Ag–N(4) angle in **1** as compared to that in **3** is reflected in Ag...Ag distance (4.850 Å in **1** and 6.216 Å in **3**). The overall size of metallacyclic framework of **3** including van der Waals radii is 18.02 Å (length) \times 6.49 Å (width). The observed differences related to the metallacyclic core in **1** and **3** can be attributed to the inward orientation of one of the two S-Me groups on the ligand towards the metallacyclic core in **3**.

Both the metallacycles display a variety of non-covalent interactions. In the crystal lattice of **1**, the cationic metallacycle and triflate anion are connected through moderate to strong C–H...O contacts (2.59–2.62 Å) and moderate C–H...F interactions (2.64 Å). Further, metallacyclic units are connected with each other through moderate C–H... π interactions (2.89 Å) (figure 4). These interactions result in the formation of sheets which stack one over another resulting in a three-dimensional framework.

Metallacycle **3** displays similar type of non-covalent interactions. Molecules of **3** form a linear array through weak C–H... π interactions (2.85 Å). The triflate ions inter-connect the individual metallacyclic arrays to form a 3D-network through moderate to strong C–H...O (2.29–2.70 Å) interactions where one of the oxygens undergo a trifurcated H-bonding interaction with three hydrogen atoms simultaneously (figure 5).

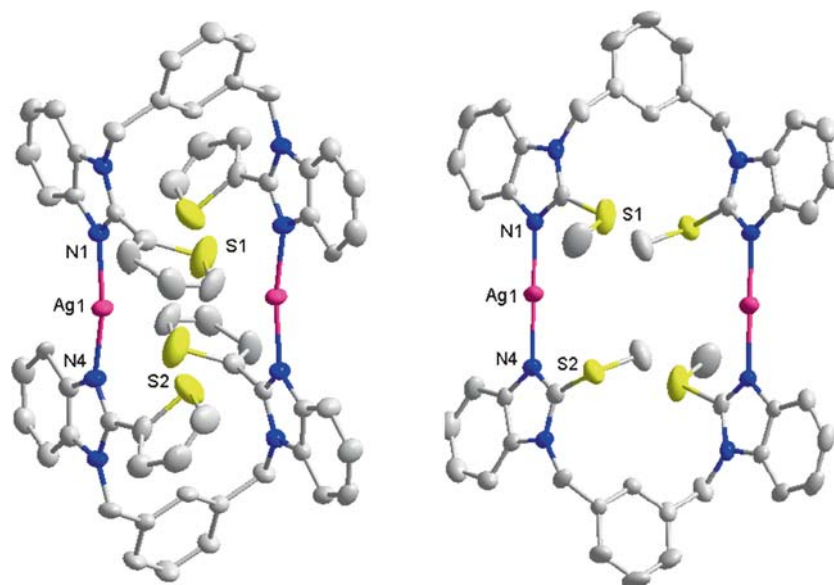


Figure 2. The ORTEP representations of **1** (left) and **3** (right) at 30% probability level. Hydrogen atoms and triflate ions have been removed for clarity. Selected bond distances (Å) and angles (degree) **1/3**: Ag1–N1 2.106(6)/2.121(4), Ag1–N4 2.099(5)/2.111(4), N1–Ag1–N4 168.1(2)/174.1(2).

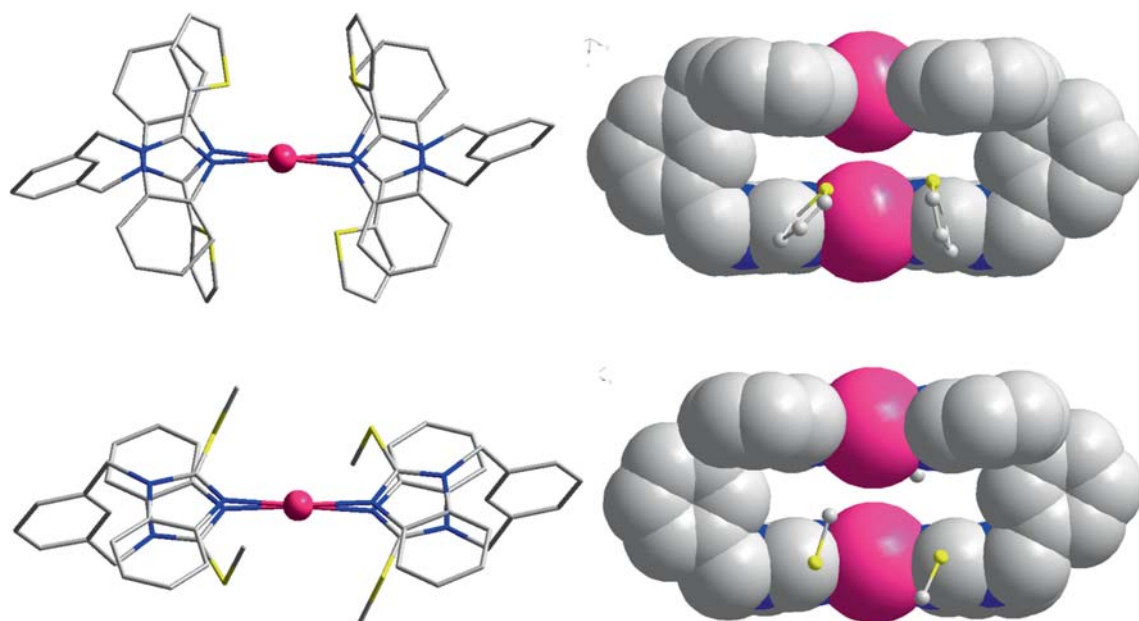


Figure 3. Two different views of molecular structures of **1** (top) and **3** (bottom). Hydrogen atoms and triflate ions have been removed for clarity. C – gray, N – blue, S – yellow, Ag – pink.

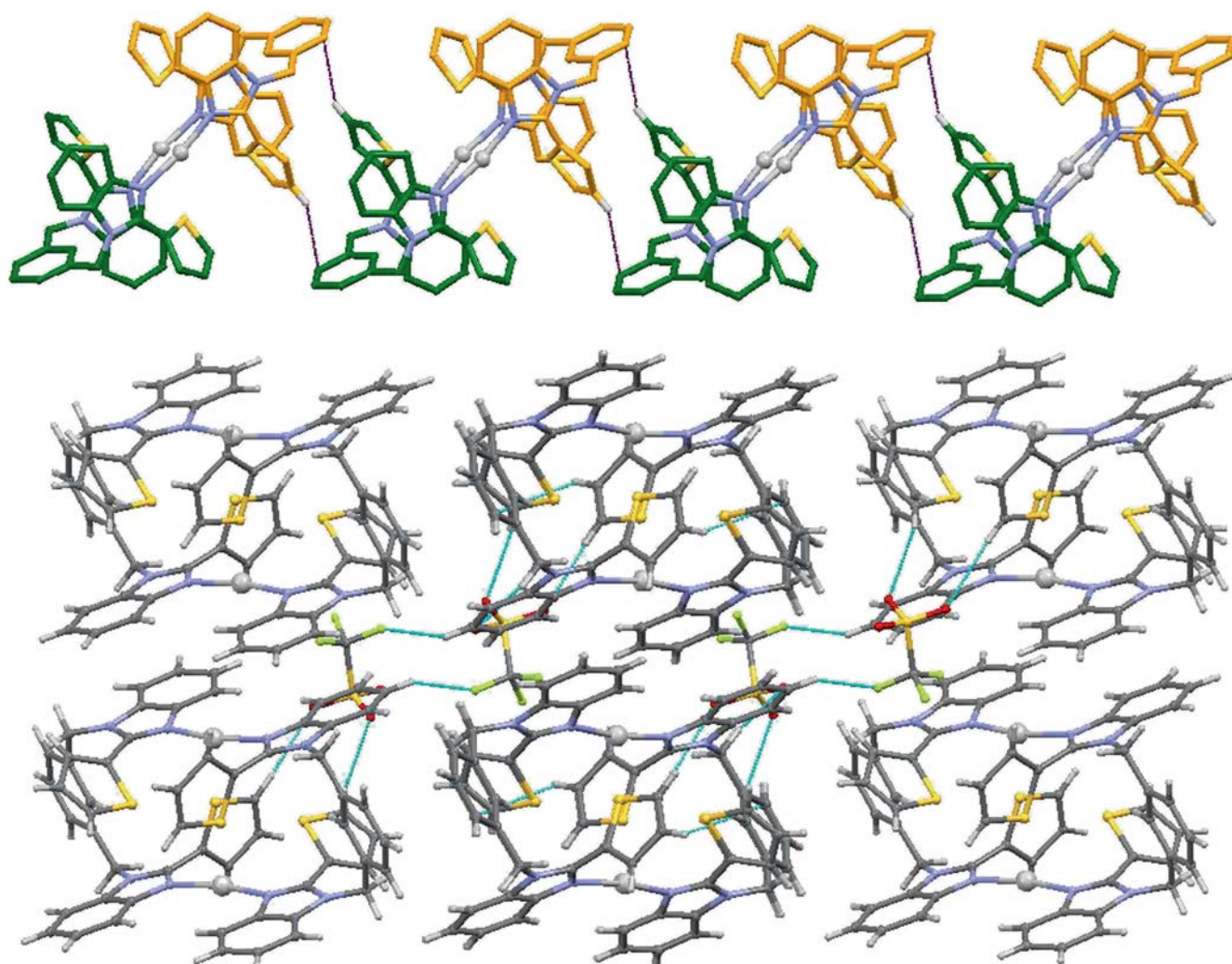


Figure 4. The C–H... π (top) interactions in crystal structure of metallacycle **1**. C–H...O, C–H... π and C–H...F interactions present in the crystal lattice of **1** leading to the formation of sheets in the *bc*-plane.

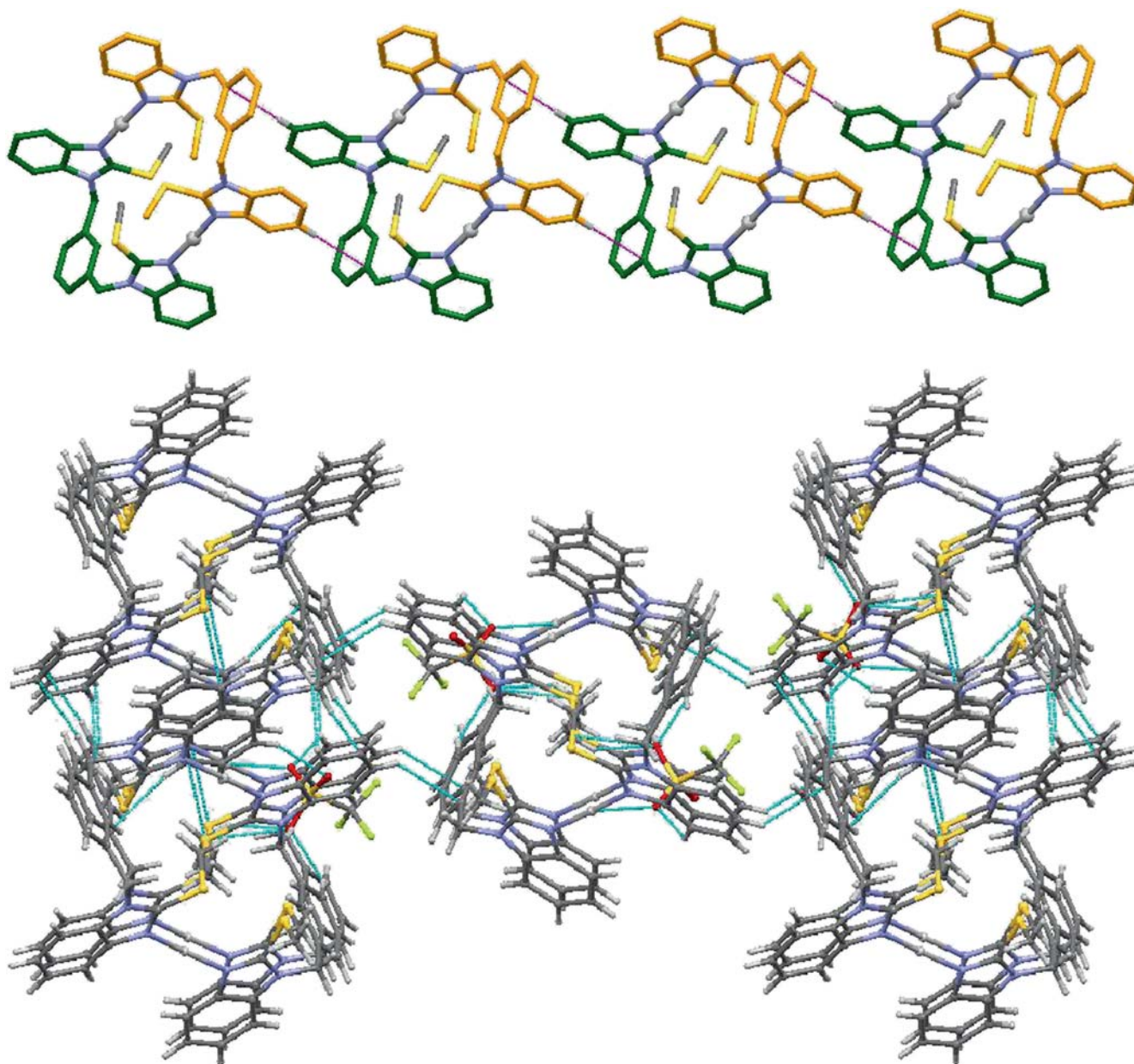


Figure 5. The C–H··· π interactions (top) in crystal structure of metallacycle **3**. The C–H···O and C–H··· π interactions present in the crystal lattice of **3** leading to the formation of sheets in the *ab*-plane.

4. Conclusions

A new family of metallacycles with covalently attached free thiophenyl/thiomethyl units was synthesized using AgOS(O)₂CF₃ and ditopic ligands and characterized by using crystallographic and spectroscopic techniques. Influence of substituents on the metallacyclic core upon the size of the metallacyclic framework is observed which can be helpful in designing the metallacycles with desired cavity size for host-guest activity for practical utilities. Moreover, the uncoordinated free thiophenyl/thiomethyl units on the metallacyclic

framework will be utilized for further coordination. We plan to explore this aspect in our future work.

Supplementary Information

Copies of NMR, mass spectra and crystallographic data table are available at www.ias.ac.in/chemsci. CCDC 1400518 and 1400519, contain the supplementary crystallographic data for **1** and **3**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge

CB2 1EZ, UK; fax: (+44) 1223-336 033; or e-mail: deposit@ccdc.cam.ac.uk.

Acknowledgements

We thank USIC & Department of Chemistry, University of Delhi, and School of Chemistry, University of Hyderabad for financial support and instrumentation facilities. SY thanks UGC for Junior Research fellowship.

References

- (a) Khlobystov A N, Blake A J, Champness N R, Lemenovskii D A, Majouga A G, Zyk N V and Schröder M 2001 *Coord. Chem. Rev.* **222** 155; (b) Steel P J and Fitchett C M 2008 *Coord. Chem. Rev.* **252** 990; (c) Young A G and Hanton L R 2008 *Coord. Chem. Rev.* **252** 1346; (d) Slenters T V, Sagué J L, Brunetto P S, Zuber S, Fleury A, Mirolo L, Robin A Y, Meuwly M, Gordon O, Landmann R, Daniels A U and Fromm K M 2010 *Materials* **3** 3407; (e) Burgess J and Steel P J 2011 *Coord. Chem. Rev.* **255** 2094; (f) Fromm K M 2013 *Appl. Organomet. Chem.* **27** 683
- (a) Grapperhaus C A, Li M and Mashuta M S 2002 *Chem. Commun.* 1792; (b) Hannon M J, Painting C L, Plummer E A, Childs L J and Alcock N W 2002 *Chem. Eur. J.* **8** 2225; (c) Steel P J and Sumby C J 2002 *Chem. Commun.* 322; (d) Bu X-H, Xie Y-B, Li J-R and Zhang R-H 2003 *Inorg. Chem.* **42** 7422; (e) Dong Y-B, Zhang H-Q, Ma J-P, Huang R-Q and Su C-Y 2005 *Cryst. Growth Des.* **5** 1857; (f) Li X-P, Zhang J-Y, Pan M, Zheng S-R, Liu Y and Su C-Y 2007 *Inorg. Chem.* **46** 4617
- (a) Caradoc-Davies P L and Hanton L R 2003 *Dalton Trans.* 1754; (b) Sague J L, Meuwly M and Fromm K M 2008 *Cryst. Eng. Commun.* **10** 1542; (c) Deng Z-P, Zhu L-N, Gao S, Huo L-H and Ng S W 2008 *Cryst. Growth Des.* **8** 3277; (d) Wei W, Wu M, Huang Y, Gao Q, Zhang Q, Jiang F and Hong M 2009 *Cryst. Eng. Commun.* **11** 576; (e) Kilpin K J, Gower M L, Telfer S G, Jameson G B and Crowley J D 2011 *Inorg. Chem.* **50** 1123; (f) Kim C W, Noh T H and Jung O-S 2011 *Inorg. Chim. Acta* **365** 496; (g) Lee H, Kim E J, Ahn J, Noh T H and Jung O-S 2012 *J. Mol. Struct.* **1010** 111; (h) Wei W, Yu H, Jiang F, Liu B, Ma J and Hong M 2012 *Cryst. Eng. Commun.* **14** 1693; (i) Wan C-Q, Al-Thabaiti S A, Chen X-D and Mak T C W 2013 *Eur. J. Inorg. Chem.* 5265; (j) Joardar S, Roy, Samanta S and Dutta A M 2015 *J. Chem. Sci.* **127** 1819; (k) Li Y, Zhang W L, Du H J, Wang C H, Lu Y B and Niu Y Y 2015 *J. Chem. Sci.* **127** 1513; (l) Gupta A, Srivastava A K and Boomishankar R 2015 *J. Chem. Sci.* **127** 619
- (a) Dias H V R, Diyabalanage H V K and Gamage C S P 2005 *Chem. Commun.* 1619; (b) Hettiarachchi C V, Rawashdeh-Omary M A, Korir D, Kohistani J, Yousufuddin M and Dias H V R 2013 *Inorg. Chem.* **52** 13576
- (a) Reger D L, Foley E A and Smith M D 2010 *Inorg. Chem.* **49** 234; (b) Gardinier J R, Tatlock H M, Hewage J S and Lindeman S V 2013 *Cryst. Growth Des.* **13** 3864
- (a) Song R-F, Xie Y-B and Bu X-H 2003 *J. Mol. Struct.* **657** 311; (b) Wu C-J, Lin C-Y, Cheng P-C, Yeh C-W, Chen J-D and Wang J-C 2011 *Polyhedron* **30** 2260
- du Plessis M, Smith V J and Barbour L J 2014 *Cryst. Eng. Commun.* **16** 4126
- (a) Su C-Y, Cai Y-P, Chen C-L, Smith M D, Kaim W and zur Loye H-C 2003 *J. Am. Chem. Soc.* **125** 8595; (b) Chen C-L, Tan H-Y, Yao J-H, Wan Y-Q and Su C-Y 2005 *Inorg. Chem.* **44** 8510; (c) Raehm L, Mimassi L, Guyard-Duhayon C, Amouri H and Rager M N 2003 *Inorg. Chem.* **42** 5654
- (a) Maekawa M, Kitagawa S, Kuroda-Sowa T and Munakata M 2006 *Chem. Commun.* 2161; (b) Dash C, Mobin S M and Ghosh P 2011 *J. Chem. Sci.* **123** 97
- Zhou J, Liu X, Zhang Y, Li B and Zhang Y 2006 *Inorg. Chem. Commun.* **9** 216
- Laye R H 2007 *Inorg. Chim. Acta* **360** 439
- (a) Chen C-L, Yu Z-Q, Zhang Q, Pan M, Zhang J-Y, Zhao C-Y and Su C-Y 2008 *Cryst. Growth Des.* **8** 897; (b) Mudsainiyan R, Jassal A K, Arora M and Chawla S K 2015 *J. Chem. Sci.* **127** 849; (c) Murugavel R, Anantharaman G, Krishnamurthy D, Sathiyendiran M and Walawalkar M G 2000 *Proc. Indian Acad. Sci. (J. Chem. Sci.)* **112** 273
- Purohit C S and Verma S 2007 *J. Am. Chem. Soc.* **129** 3488
- Pogozhev D, Baudron S A and Hosseini M W 2011 *Dalton Trans.* **40** 437
- (a) Shankar B, Rajakannu P, Kumar S, Gupta D, Kannan T and Sathiyendiran M 2011 *Inorg. Chem. Commun.* **14** 374; (b) Gupta D, Rajakannu P, Shankar B, Shanmugam R, Hussain F, Sarkar B and Sathiyendiran M 2011 *Dalton Trans.* **40** 5433; (c) Shankar B, Hussain F and Sathiyendiran M 2012 *J. Organomet. Chem.* **719** 26; (d) Rajakannu P, Hussain F, Shankar B and Sathiyendiran M 2012 *Inorg. Chem. Commun.* **26** 46; (e) Shankar B, Elumalai P, Jackmil P J, Kumar P, Singh S and Sathiyendiran M 2013 *J. Organomet. Chem.* **743** 109; (f) Shankar B, Elumalai P, Hussain F and Sathiyendiran M 2013 *J. Organomet. Chem.* **732** 130; (g) Rajakannu P, Elumalai P, Mobin S M, Lu K-L and Sathiyendiran M 2013 *J. Organomet. Chem.* **743** 17; (h) Shankar B, Sahu S, Deibel, N, Schweinfurth D, Sarkar B, Elumalai P, Gupta D, Hussain F, Krishnamoorthy G and Sathiyendiran M 2014 *Inorg. Chem.* **53** 922; (i) Gupta D, Rajakannu P, Shankar B, Hussain F and Sathiyendiran M 2014 *J. Chem. Sci.* **126** 1501; (j) Rajakannu P, Mobin S M and Sathiyendiran M 2014 *J. Organomet. Chem.* **771** 68; (k) Shankar B, Elumalai P, Sathiyashivan D and Sathiyendiran M 2014 *Inorg. Chem.* **53** 10018; (l) Shankar B, Elumalai P, Shanmugam R, Singh V, Masram D T and Sathiyendiran M 2013 *Inorg. Chem.* **52** 10217; (m) Elumali P, Kanagaraj R, Marimuthu R, Shankar B, Kalita A C and Sathiyendiran M 2015 *Dalton Trans.* **44** 11274
- (a) ENHANCE, Oxford Xcalibur Single Crystal Diffractometer, version 1.171.34.40, Oxford Diffraction Ltd, Oxford, U.K., 2006; (b) CrysAlisPro, version 1.171.34.40, Oxford Diffraction Ltd, Oxford, U.K., 2006; (c) SMART, Bruker Molecular Analysis Research Tool, version 5.0, Bruker Analytical X-ray Systems,

Madison, WI 2000; (d) SAINT-NT, version 6.04, Bruker Analytical X-ray Systems, Madison, WI 2001; (e) Altomare A, Cascarano G, Giacovazzo C, Guagliardi A, Burla M C, Polidori G and Camalli M 1994 *J. Appl.*

Crystallogr. **27** 435; (f) Sheldrick G M SHELXL-97, Program for crystal structure refinement, University of Gottingen, Gottingen, Germany 1997; (g) Farrugia L J 1999 *J. Appl. Crystallogr.* **32** 837