Synopsis of the thesis entitled

Novel Metallomacrocyclic Dithiocarbamate Complexes and Their Potential Applications in Host-Guest Binding Study

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By

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Synopsis of the Thesis

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Title of the Thesis: "Novel Metallomacrocyclic Dithiocarbamate Complexes and Their Potential Applications in Host-Guest Binding Study"

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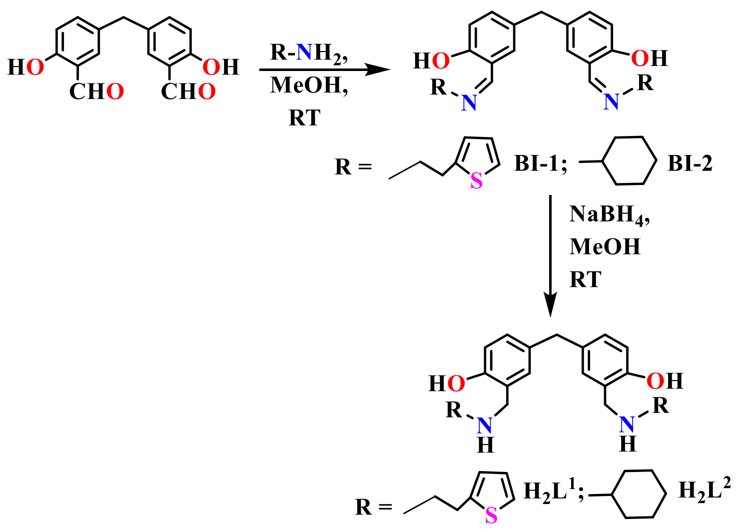
Thesis comprises of synthesis, spectral and crystallographic characterization of several diamine ligand precursors bearing either diphenylmethane, thiophene or piperazine moieties in the spacer and their ensuing bimetallic bis-dithiocarbamate macrocyclic complexes. These newly synthesized sulphur rich metallomacrocyclic compounds have been systematically investigated for their ability to bind/ sense various environmentally hazardous organic guests such as organic dyes (acid orange(II), bromocresol green, bromothymol blue, bromophenol blue, methylene blue, crystal violet) and heavy metal ions such as Hg^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+}, Ag^{+} by using NMR titration, UV-visible / fluorescence study. The effective and forthright methodologies have been employed in the synthesis of these compounds. A DFT level calculations have been performed to reinforce the experimental outcomes. The thesis is mainly divided into five chapters.

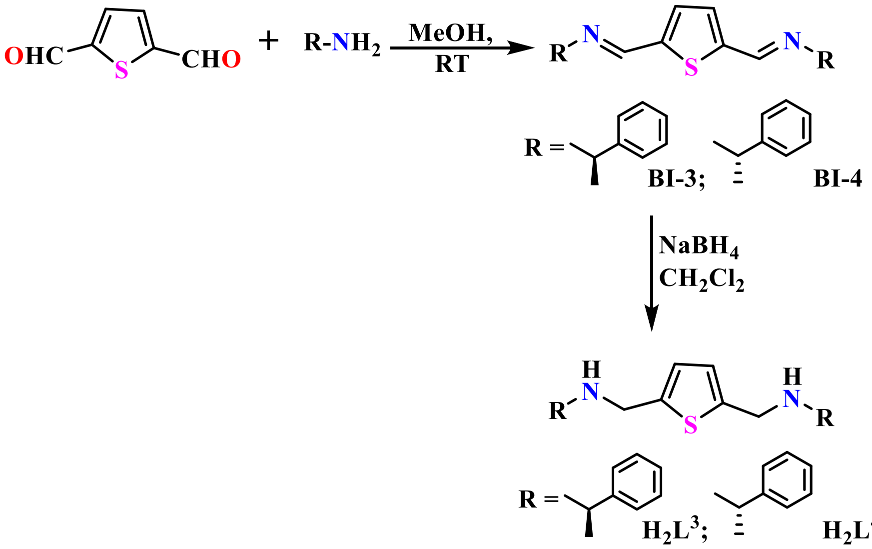
Chapter 1: A detailed literature review on functionalized diamine precursors holding varied spacers and their importance in the development of novel 1,1-dithiocarbamate ligand systems and their transition/ non-transition metal dithiocarbamate complexes that display an array of applications in the area of medicinal, material and in the supramolecular chemistry has been included in this chapter. The reactivity of newly synthesised metallomacrocyclic molecules towards various guest species have been further emphasised. The foremost objectives of the present investigation are also described in this chapter.

Chapter 2 includes the design and synthesis of several diamine ligand precursors (H_2L^1-H_2L^6) holding either diphenylmethane, thiophene or piperazine moieties in the spacers as per the **Scheme 1-3**. All of the functionalized organic diamines were characterized thoroughly by Elemental analysis, NMR (^{1}H and ^{13}C), UV-visible, FTIR and single crystal X-ray diffraction (SCXRD) techniques. The optical properties of these molecules have been further investigated by using UV-visible spectral data and the results are well supported by theoretical calculations.

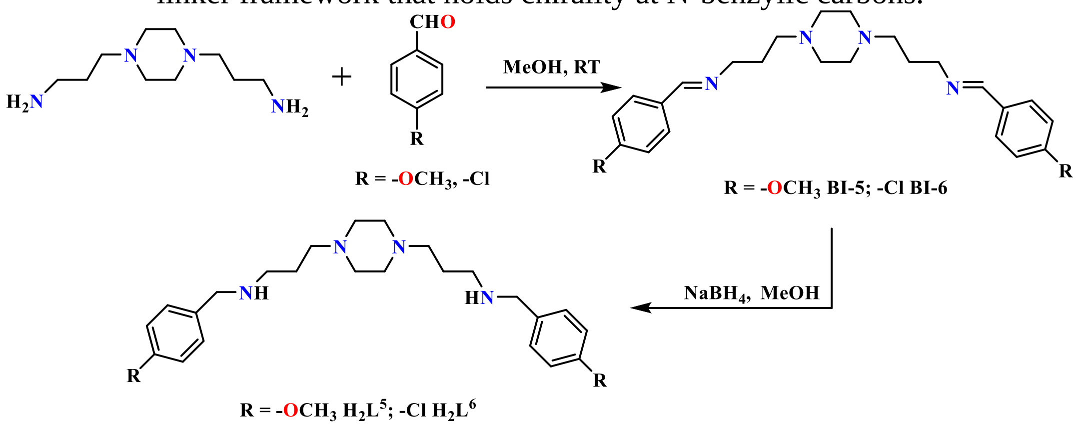
Single crystals of the organic precursors H_2L^1, BI-3 and BI-4 suitable for single crystal X-ray diffraction study were grown by slow evaporation of these compounds in CH_2Cl_2. The unprecedented molecular structures of H_2L^1, BI-3 and BI-4 are shown in Fig. 1, Fig. 2 and Fig. 3, respectively.



Scheme 1: Synthesis of new organic diamines (H_2L^1- H_2L^2) bearing diphenylmethane in the linker framework with N-thiophenylethyl-/ cyclohexyl substituents.



Scheme 2. Synthesis of new organic diamines (H_2L^3- H_2L^4) bearing thiophene in the linker framework that holds chirality at N-benzylic carbons.



Scheme 3: Preparation of diamines holding piperazine in the linker framework with *p*-methoxybenzyl/ *p*-chlorobenzyl *N*-substituents at peripheral positions.

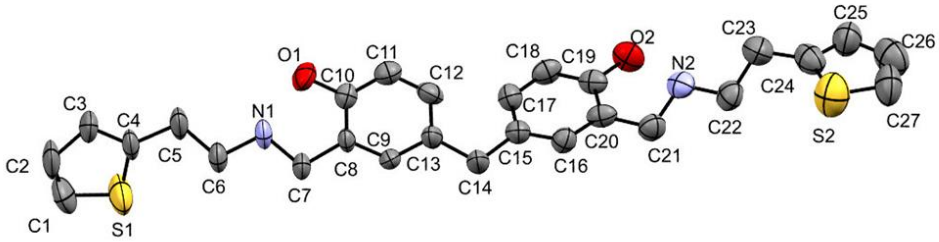


Fig. 1. Molecular structure of $\mathbf{H_2L^1}$ (hydrogens are omitted for clarity).

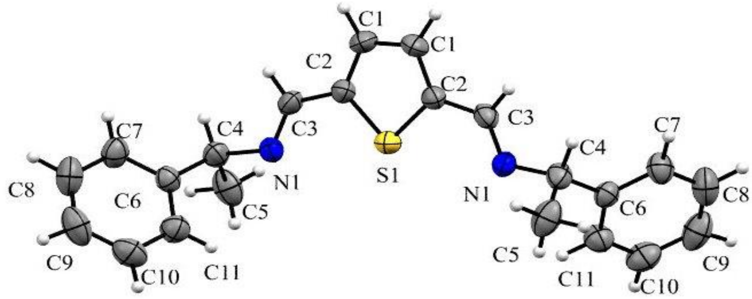


Fig. 2. Molecular structure of **BI-3**.

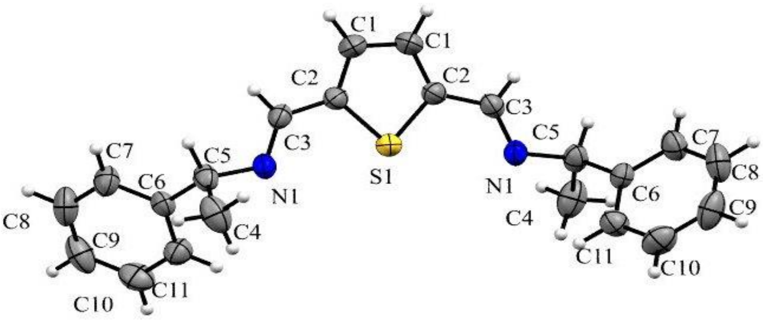
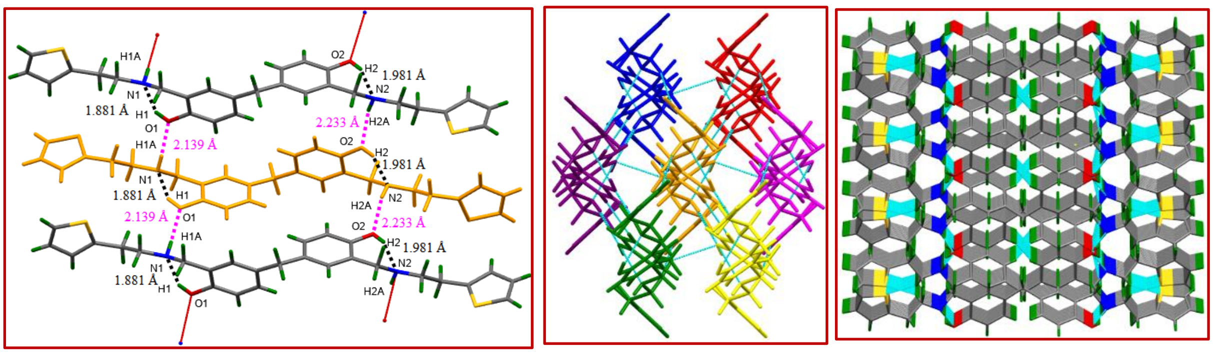


Fig. 3. Molecular structure of **BI-4**.

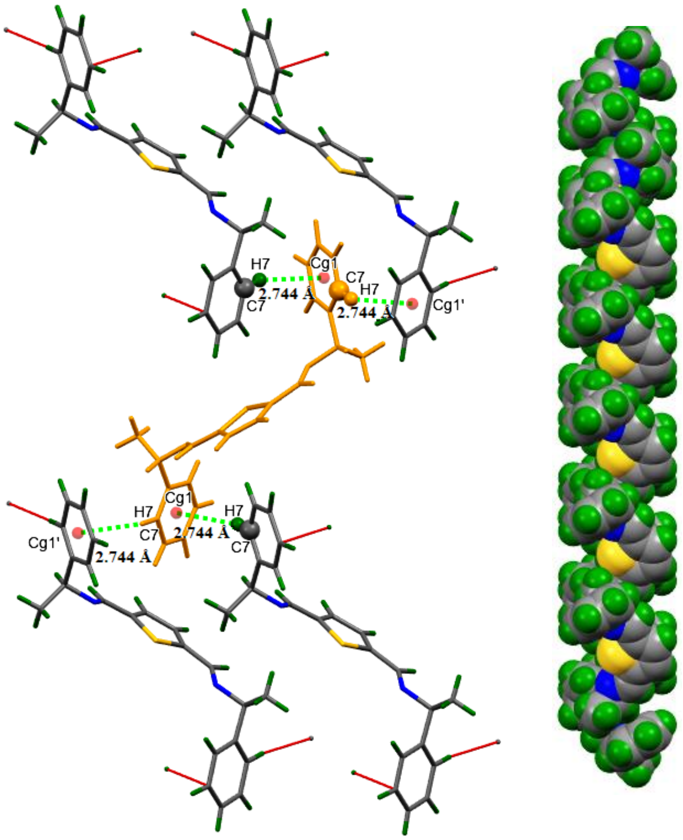
The molecules of $\mathbf{H_2L^1}$ have shown the propensity to form intra- and intermolecular H-bonding interactions O-H…N (1.881 Å) and N-H…O (2.139 Å) in the solid state, forming a 2D sheet like supramolecular structure in bc-plane as shown in Fig. 4.



(a) (b) (c)

Fig. 4. Asymmetric molecule of H_2L^1 forming (a) intra- and intermolecular H-bonding interactions, arranges the molecules along *c*-axis (tilted down), (b) supramolecular aggregate consists of **7** molecules in the *bc*-plane (c) 2D sheet like supramolecular structure in *bc*-plane.

However, the molecules of BI-3 and BI-4 holding *S*- and *R*-chirality at benzylic carbons are sustained primarily through intermolecular C-H…π (2.744 Å) interactions as shown in Fig. 5 (a).



(a) (b)

Fig. 5. Asymmetric molecule of **BI-3** primarily forms (a) C-H… π intermolecular contacts, arranges the molecules along *c*-axis, leading to a supramolecular aggregate consists of 5 molecules. (b) Spacefill model illustrating the formation of 2D drill screw like architecture (view along c-axis).

Each peripheral phenyl groups of **BI-3** offering C-H…π (2.774 Å; Cg1= Cg1' = C6C7C8C9C10C11) donor-acceptor contacts, connecting four molecules anti-parallelly along c-axis. These contacts are extended two dimensionally and forming a fascinating 2D drill screw like architecture as shown in Fig. 5(b).

Moreover, frontier molecular orbitals of bis-imine precursors BI-3-BI-6 and their reduced products H_2L^3-H_2L^6 were derived from DFT calculation at B3LYP/6-31G level (Fig. 6 and Fig. 7) which clearly suggests that Homo and Lumo molecular orbitals are mainly localized at central thiophenyl group in BI-3-BI-4 and H_2L^3-H_2L^4 (Fig. 6) whereas in BI-5-BI-6 and H_2L^5-H_2L^6 holding piperazine in the spacer, the highest occupied molecular orbitals (Homo) are mainly localized at the central piperazine but lowest occupied molecular orbitals (Lumo) are localized at one of the peripheral phenyl rings (Fig. 7).

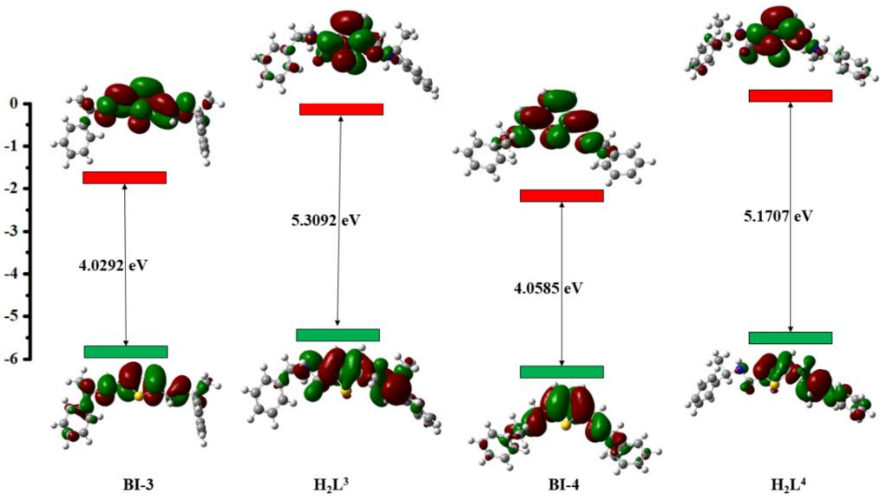


Fig. 6. Frontier molecular orbitals derived from DFT calculation at B3LYP/6-31G level.

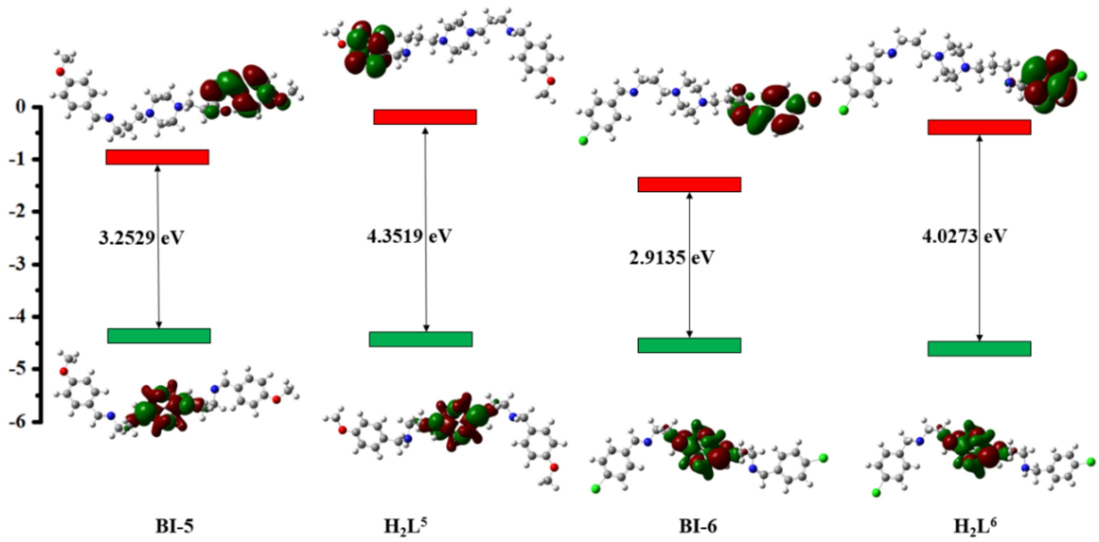


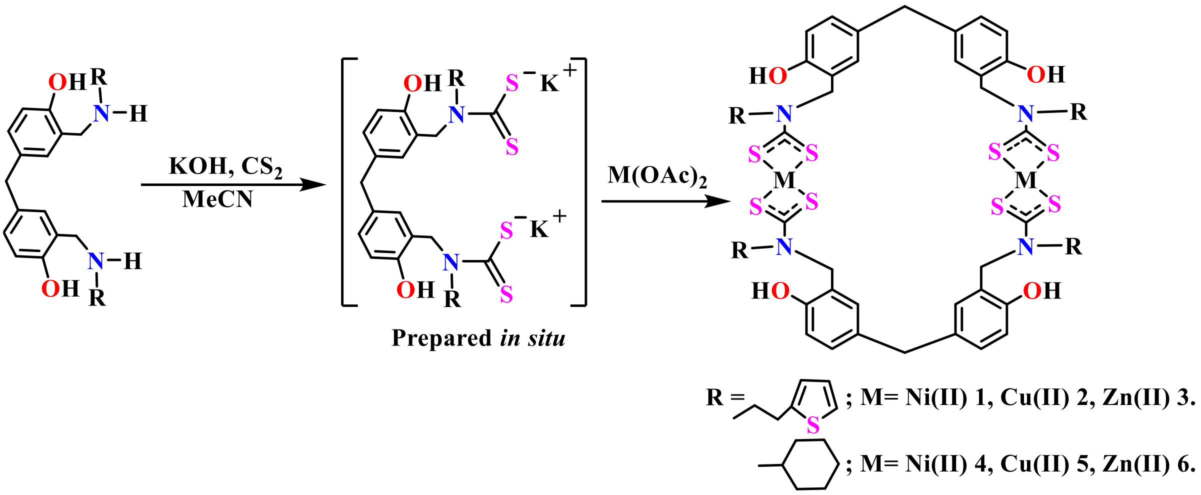
Fig. 7. Frontier molecular orbitals derived from DFT calculation at B3LYP/6-31G level.

Table.3. Summary of computational study

Entry	HOMO (eV)	LUMO (eV)	Band Gap (eV)	Entry	HOMO (eV)	LUMO (eV)	Band Gap (eV)
BI-3	-5.9658	-1.9366	3.4724	**BI-5**	-4.2458	-0.9929	3.2529
H_2L^3	-5.6518	-0.3426	5.3092	**H_2L^5**	-4.3707	-0.0188	4.3519
BI-4	-6.1378	-2.0792	4.0585	**BI-6**	-4.4512	-1.5377	2.9135
H_2L^4	-5.5470	-0.3763	5.1707	**H_2L^6**	-4.5288	-0.5015	4.0273

The calculated Homo-Lumo band gaps fall in the range of 2.9-5.3 eV suggesting non-semiconducting nature of these organic molecules which indeed well supported by experimentally. The diamine precursors H_2L^1-H_2L^6 have been further studied for their utility to form corresponding dithiocarbamate ligands and their ensuing metal complexes and the results are elaborated in the coming chapters.

Chapter 3: In this chapter, metal directed self-assembly of diamine precursors H_2L^1-H_2L^2 with CS_2 and Ni^{II}, Cu^{II} or Zn^{II} ions (**Scheme 4**) leading to a new series of binuclear metallomacrocyclic dithiocarbamate complexes **1-6** holding pendent phenolic and thiophenyl groups at the peripheral position of macrocycle is summarized. The compounds were characterized by microanalysis, NMR (^{1}H, ^{13}C), HRMS, UV-visible, FTIR, thermogravimetric and crystallographic techniques.



Scheme 4: Synthesis of binuclear metallomacrocyclic dithiocarbamate complexes **1-6** holding pendent phenolic and thiophenyl groups at the peripheral position of macrocycle.

The unambiguous structure of nickel(II) dithiocarbamate complex **1** (Fig. 8a) has been determined by means of SCXRD which is found to be consistent with its theoretically optimized structure (Fig. 8b)

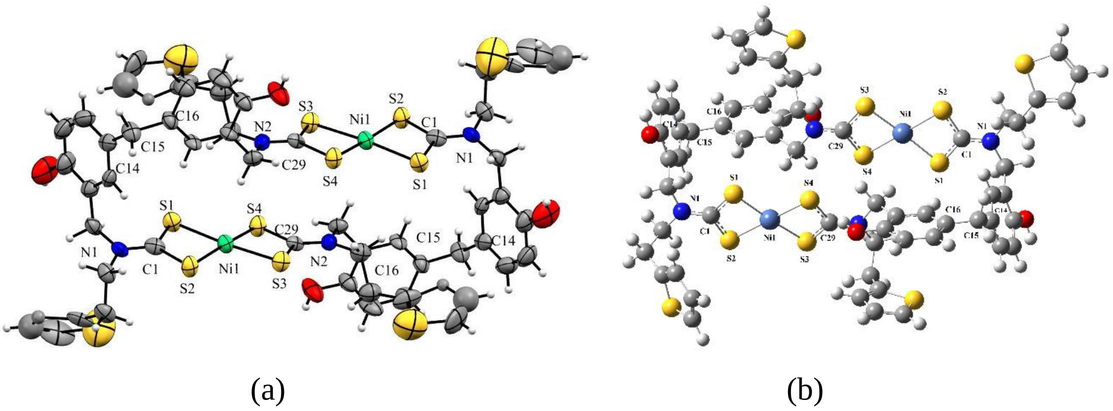


Fig.8. (a) X-ray structure (b) optimized structure of nickel(II) complex **1**.

The geometry of all the complexes 1-6 has been optimized by a DFT level calculations and the structural parameters obtained theoretically are well compared with experimentally determined structural parameters. Notably, the molecules of complex **1** are stabilized by a good number of C-H….S intermolecular contacts forming an attractive 3D multiple open tubular supramolecular assembly as shown by spacefill model (Fig. 9).

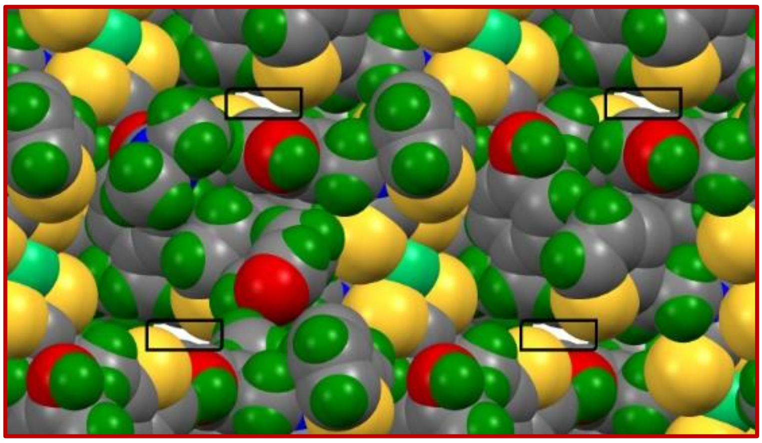
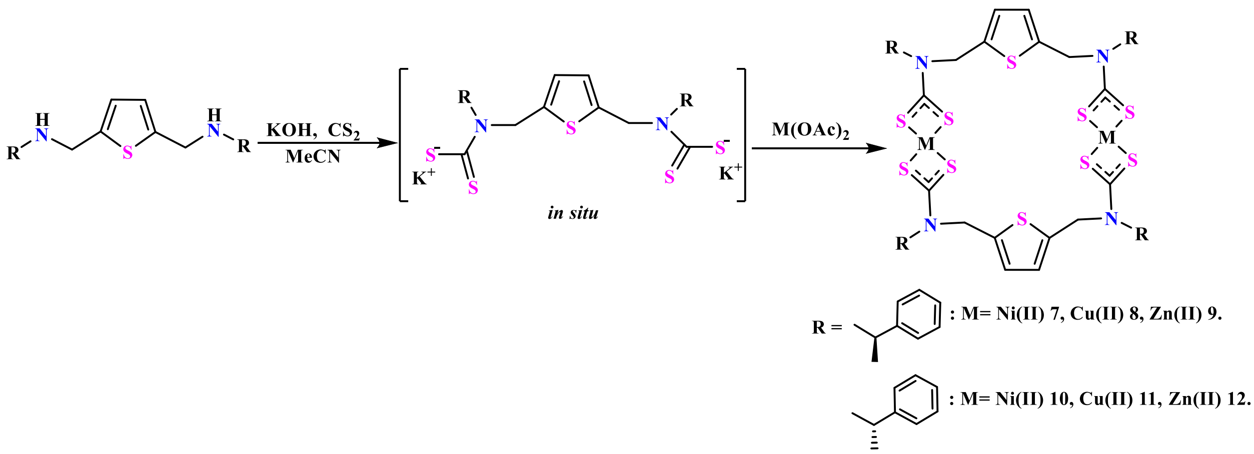


Fig. 9. Molecules of complex **1** forming an attractive 3D multiple open tubular supramolecular assembly through a number of C-H….S intermolecular contacts.

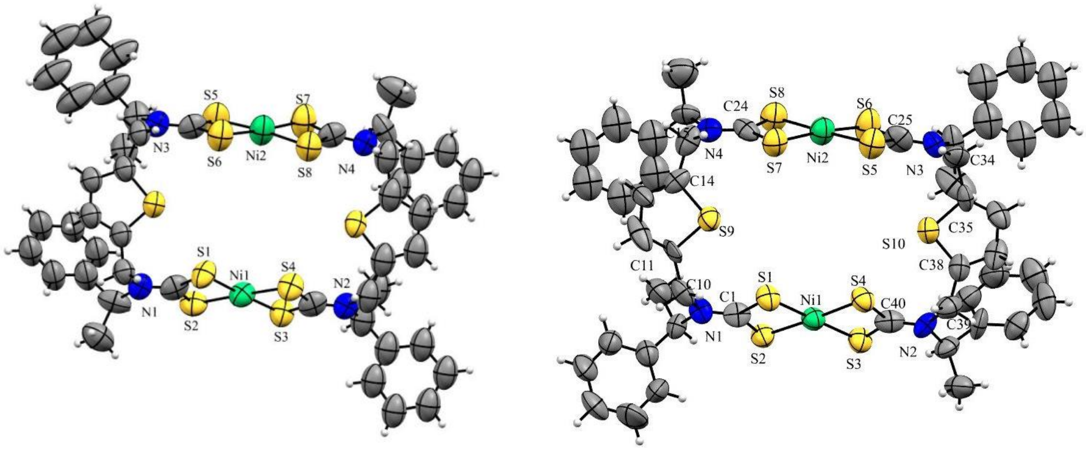
Complexes holding thiophenyl groups are found to be thermally more stable as their degradation start at ~200°C which is much higher than the degradation temperature of other complexes **4-6** holding cyclohexyl groups. Interestingly, the band gaps calculated theoretically for all the complexes 1-6 suggests that copper (II) dithiocarbamate complexes with band gaps of 1.86 eV (for **2**) and 1.89 eV (for **5**) are semiconducting in nature. Further, binuclear metallomacrocyclic dithiocarbamate Ni^{II} complex **1** and Zn^{II} complex **3** have shown the ability to bind environmentally hazardous organic dyes "Acid orange (II)" and "Bromocresol green" in 3:1 and 1:2 stoichiometric ratio, respectively.

In Chapter 4, the chiral secondary amines (H_2L^3-H_2L^4) holding thiophene spacer synthesized in the previous chapter, were taken for the development of new binuclear dithiocarbamates macrocyclic complexes of Ni^{II}, Cu^{II} and Zn^{II} (7-12) as per the following Scheme 5.



Scheme 5: Synthesis of binuclear dithiocarbamate macrocyclic complexes **7-12** holding thiophene in the spacer.

The compounds were characterized by microanalysis, NMR (^{1}H, ^{13}C), HRMS, UV-visible, magnetic moment, FTIR, thermogravimetric and crystallographic techniques. The UV-visible data along with magnetic moment data reveals square planar geometry around Ni^{II}, Cu^{II} ions and tetrahedral geometry around Zn^{II} ions in their respective compounds. Further, the geometry around these metal centres were confirmed by SCXRD study.



(a) (b)

Fig. 10. Molecular structure of (a) complex **7** and (b) complex **10**.

The structural parameters obtained experimentally are well supported by theoretical calculations.

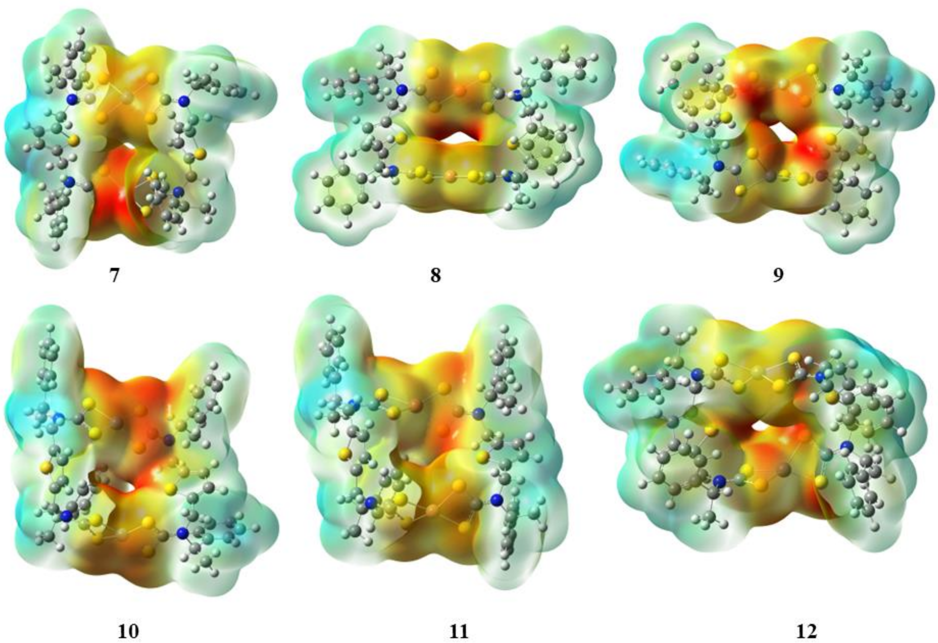


Fig. 11. *MESP* diagrams for the metallomacrocyclic complexes **7-12**.

The molecular electrostatic potentials of **7-12** were determined theoretically, suggesting localisation of negative potential around chelate rings and positive potentials around C-H groups and confirms the ability of these molecules to offer donor-acceptors intermolecular contacts in the solid state which is indeed verified experimentally. For instance, molecules of complex **7** evidently offer intermolecular CH….S, $\pi_{aromatic}$… $\pi_{chelate}$ and CH…pi contacts, arranges the molecules three dimensionally and forming a fascinating supramolecular assembly displaying 3D pores of (5 × 18) Å^2 dimensions in the solid state as shown in Fig. 12.

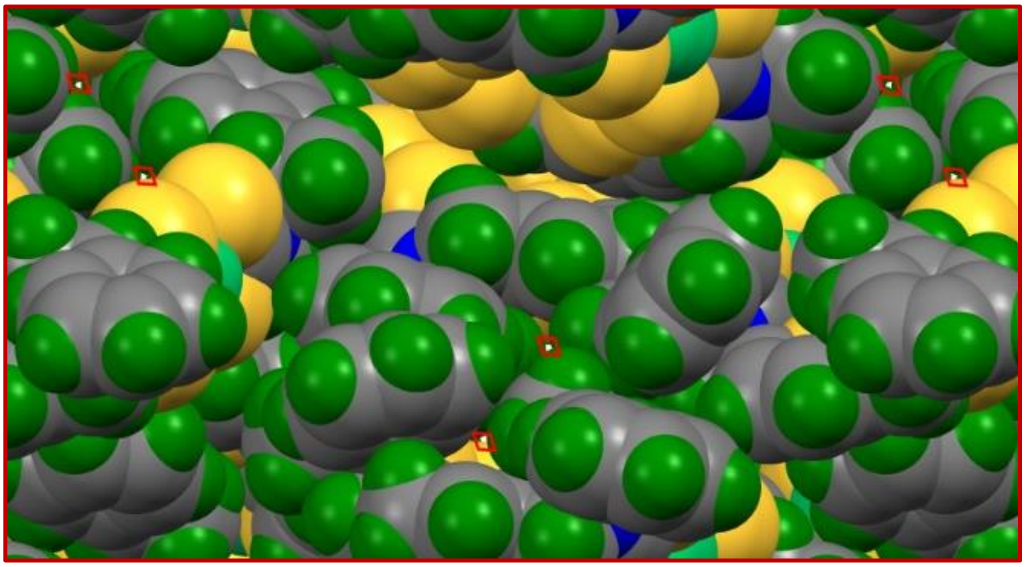
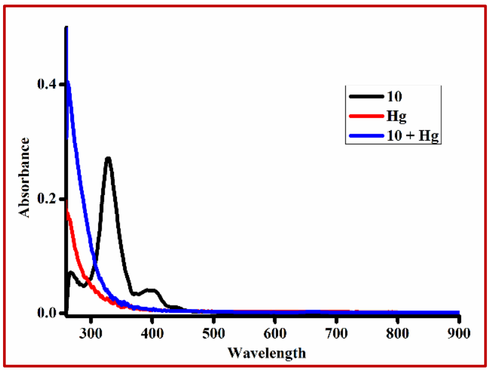
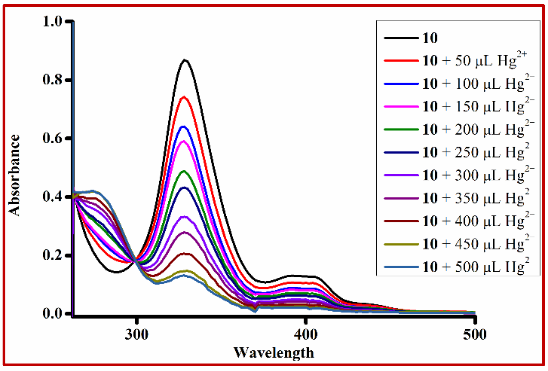


Fig. 12. Supramolecular assembly formed by complex **7** displaying 3D pores of dimension (5 × 18) Å^2 shown by the spacefill model.

Similar to the nature of copper(II) complexes **2** and **5** included in chapter 4, the band gaps calculated theoretically for all the complexes **7-12** suggests that copper(II) dithiocarbamate complexes with band gaps of 2.08 eV (for **8**) and 1.84 eV (for **11**) are semiconducting in nature. Further, binuclear metallomacrocyclic dithiocarbamate complexes **10-12** were further investigated for their ability to bind with environmentally hazardous heavy metal ions viz.



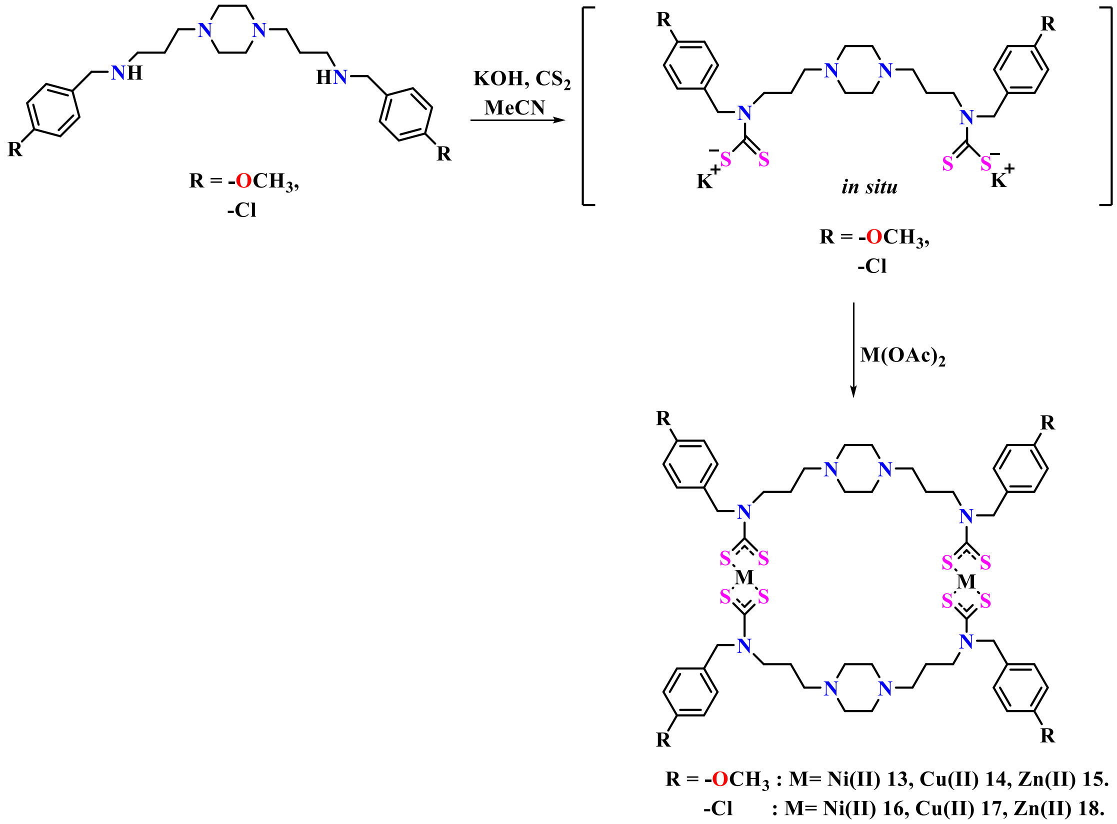


(a) **(b)**

Fig. 13. (a) Sensing study of complex **10** with Hg^{2+} (b) UV-visible titration of complex **10** with Hg^{2+}.

Cd^{2+}, Pb^{2+}, As^{3+}, As^{5+}, Hg^{2+}, Ag^{+} and the results suggests that binuclear metallomacrocyclic dithiocarbamate complexes **10-12** can sense Hg^{2+} and Pb^{2+} invariably as intra-ligand n→π* transition apparently associated with thiophene disappears in the presence of Hg^{2+} (Fig. 13). However, the effort to find out the exact stoichiometry of Host-Guest interaction and to establish the exact mode of binding of these metal ions are on the way.

Chapter 5: In this chapter, piperazine based diamine precursors **H_2L^5** and **H_2L^6** have been successfully utilized in the synthesis of a new series of bimetallic bis-dithiocarbamate complexes **13-18** holding functionalized linker framework. All the compounds have been characterized by elemental analysis, relevant spectroscopic (NMR, IR, UV-visible, HRMS), thermogravimetric techniques.



Scheme 6: Synthesis of Piperazine Based Metallomacrocyclic Dithiocarbamate Complexes **13-18**.

The appearance of expected number of sharp NMR signals (*ca* Fig. 14), macroanalysis and HRMS data (ca Fig. 15) confirmed the purity and composition of these complexes. The magnetic moment data along with UV-visible spectral data indicates square planar geometry around Ni^{II} and Cu^{II} centers and tetrahedral environment around Zn^{II} centers in their respective homo bimetallic dithiocarbamate complexes 13-18.

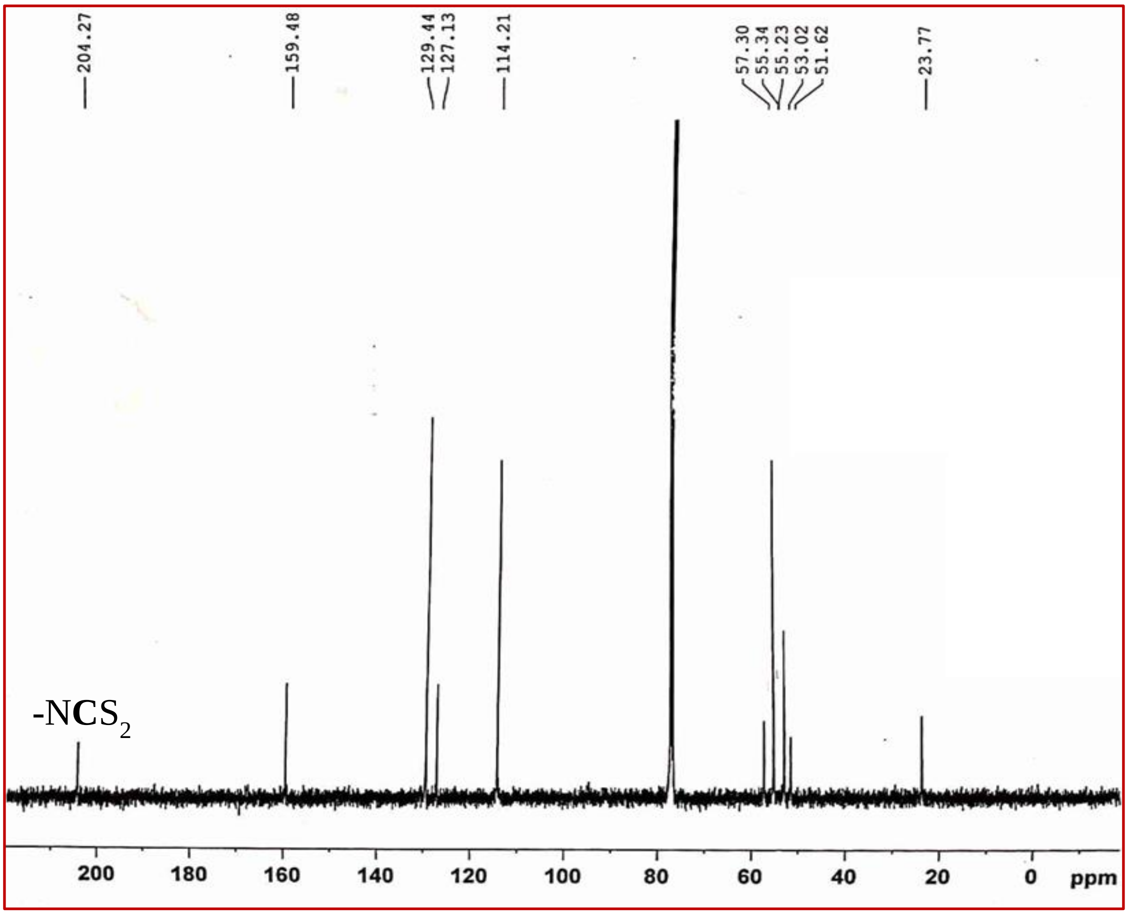


Fig.14. ^{13}C NMR specrun of Zn^{II} dithiocarbamate complex **15.**

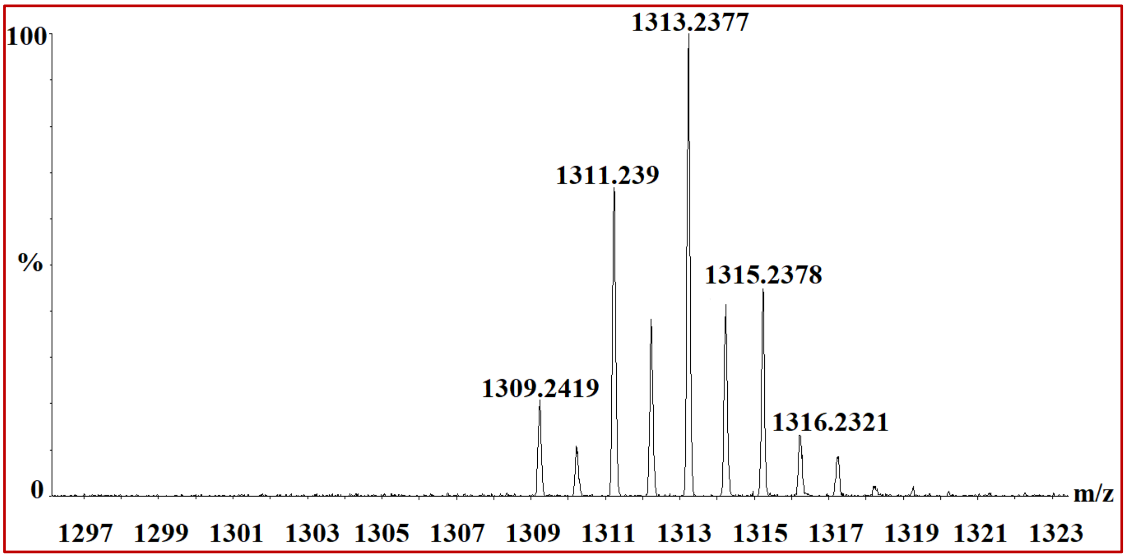
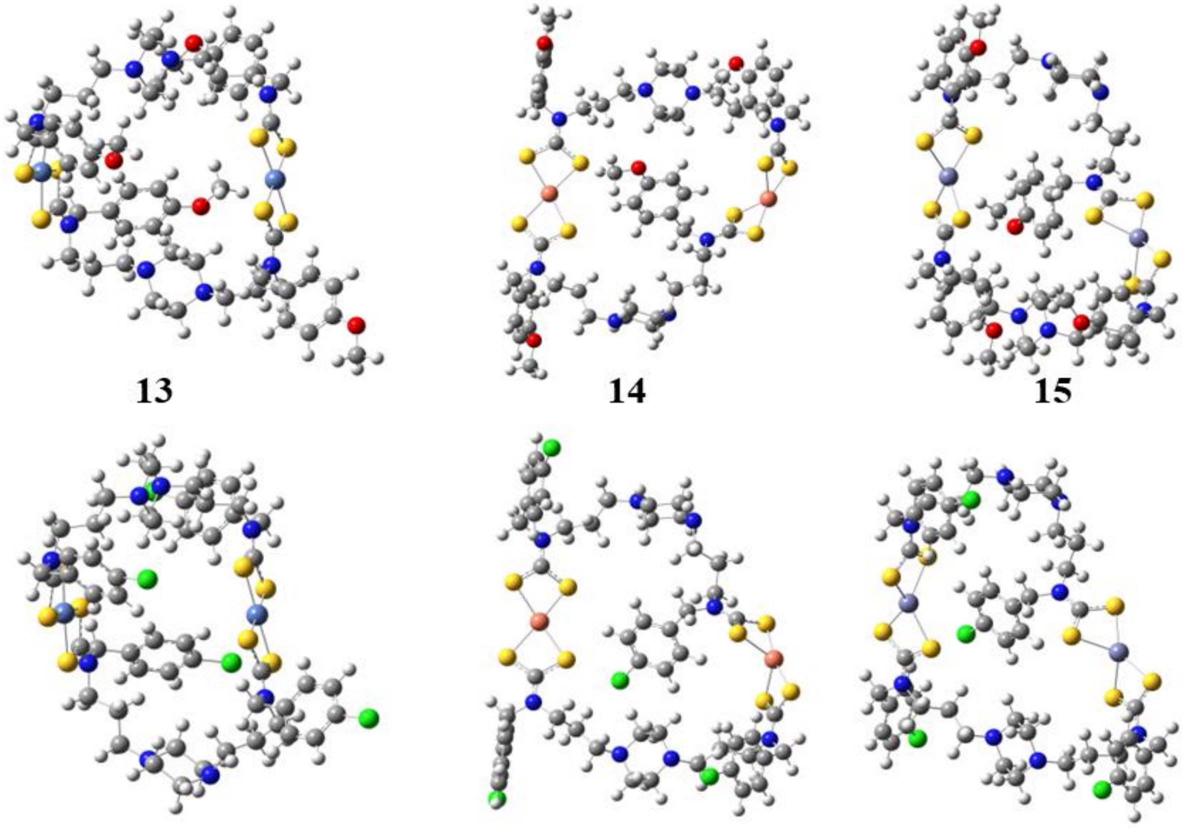


Fig.15. HRMS specrun of Zn^{II} dithiocarbamate complex **15.**



13 14 15 16 17 18

Fig.16. Optimized geometry for the minimum energy conformation of macrocyclic dithiocarbamate complexes **13-18** at B3LYP/LanL2DZ basis set.

The HOMO-LUMO band gaps obtained theoretically for Ni^{II} (**13** and **16**) and Cu^{II} (**14** and **17**) complexes falls in the range of 1.0-2.8 eV (Table 4) and suggests the semiconducting nature of these complexes.

Table.4: Energy of Homo-Lumo and energy band gaps

Entry	**HOMO (eV)**	**LUMO (eV)**	**Band gap (eV)**	**Entry**	**HOMO (eV)**	**LUMO (eV)**	**Band gap (eV)**
13	-4.7073	-1.8541	2.8532	**16**	-4.8107	-2.0501	2.7606
14	-4.7040	-3.3693	1.3347	**17**	-4.8929	-3.7013	1.1916
15	-4.6447	-0.9483	3.6964	**18**	-4.8472	-1.2754	3.5718

The potentials of all these complexes as a Host for a range of guest species including environmentally hazardous heavy metal ions are yet to be examined.

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