

Synthesis and Spectral Studies of Mercury (II) Complexes with S₄ Macrocyclic Ligands

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ABSTRACT

The synthesis and characterization of numerous macrocyclic polyoxaethers have been reported in last few decades [1-5] but a limited number of macrocyclic polythiaethers [6-11]; mixed azo-oxa-thia macrocyclic [1-5] and microbicyclic [12-13] polyethers containing four or more sulfur atoms in macrocyclic ring have been reported. A keen interest has been raised for macrocyclic polyoxaethers through stable complex formation with cations of the alkali and alkaline earths; ammonium and silver [14]. As model compounds these are used varying degrees of biological activity in the process of active ion transport [15-18]. The thia and mixed oxa-thia macrocyclic show lower selectivity and coordinatability of active metal ions [1-5]. A survey of literature reveals that very few macrocyclic polythiaethers have been synthesised and characterised [19]. In this paper 1, 4, 7, 10-Tetrathiacyclododecane i.e. [12]aneS₄ and 1, 4, 8, 11-Tetrathiacyclotetradecane i.e. [14]aneS₄ have been synthesised and interacted with HgX₂ in 1:1 molar ratio in methanol (Where X=Cl or Br or I or NO₃ or ClO₄ or CH₃COO) to form Hg(II) complexes.

EXPRIMENTAL

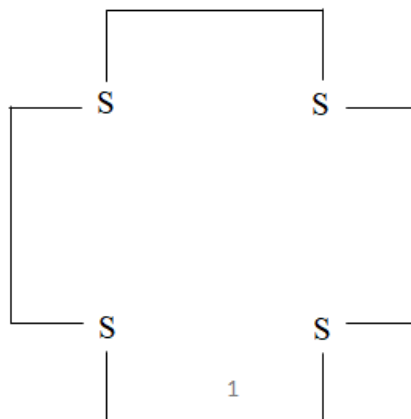
The ligands 1, 4, 7, 10-Tetrathiacyclodo-decane i.e. [12]aneS₄ and 1,4,8,11-Tetrathiacyclotetradecane i.e. [14]aneS₄ were synthesised by procedure as given in literature [19].

Preparation of [Hg[12]aneS₄X₂] and [Hg[14]aneS₄X₂]

1 mmol of [12]aneS₄ or [14]aneS₄ in methanol is mixed with 1 mmol of HgX₂ (where X = Cl or Br or I or NO₃ or ClO₄ or CH₃COO) and refluxed for 3 hrs. The orange red precipitate was obtained, filtered and recrystallised with benzene: pet-ether (9:1) and air-dried [Fig. I & II].

RESULTS AND DISCUSSION

All these prepared complexes [Hg[12]aneS₄X₂] and [Hg[14]aneS₄X₂] (where X = Cl or Br or I or NO₃ or ClO₄ or CH₃COO) were orange red solids. They were stable at room temperature. The elemental analysis for Hg, C, H, S, Cl or Br were found (for calculated and found values) within ± 0.5%.



1, 4, 7, 10-Tetrathiacyclodecane i.e. [12] aneS₄Ligand

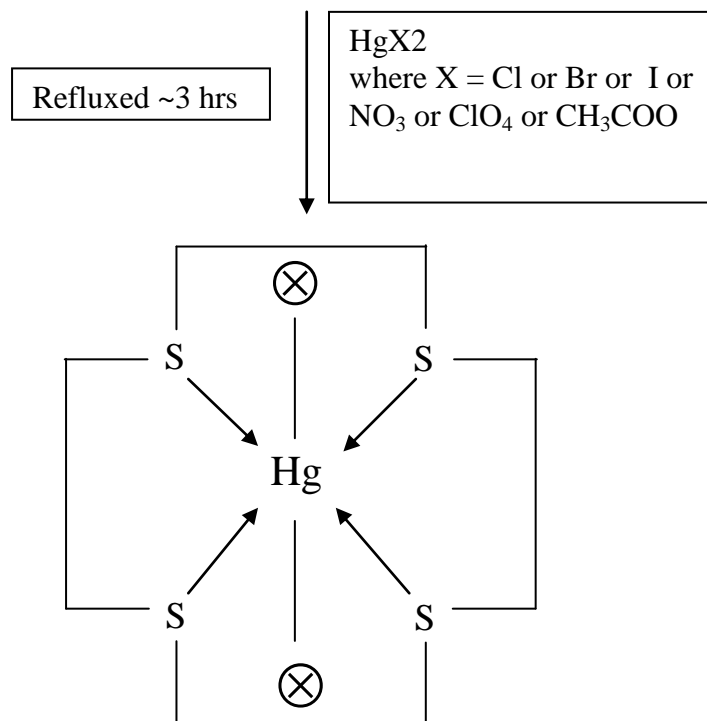
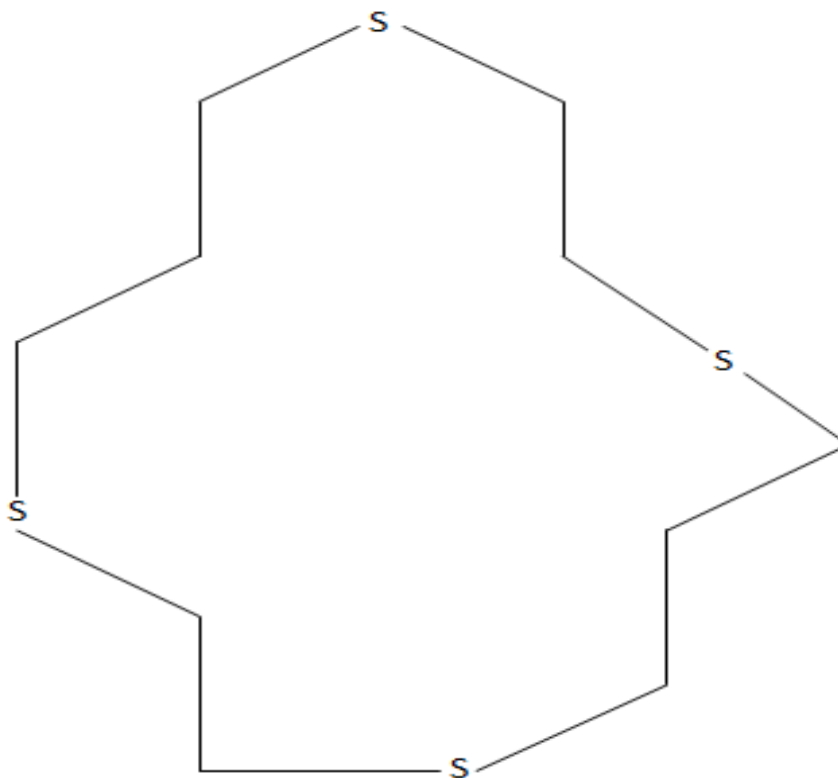


Fig. 1: Preparation of [Hg[12]aneS₄X₂] Complex



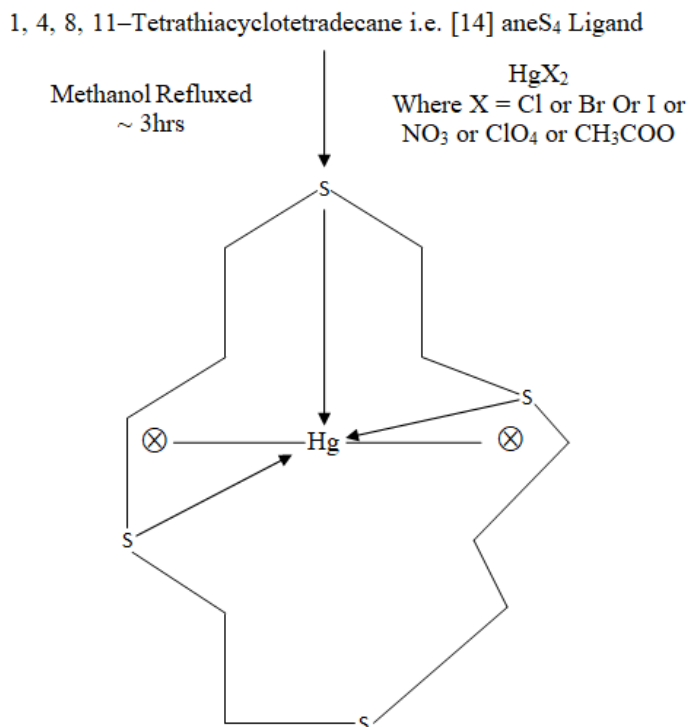


Fig II: Preparation of [Hg[14]aneS₄X₂] Complexes

Hg³P_{1/2} Photoelectron Peak

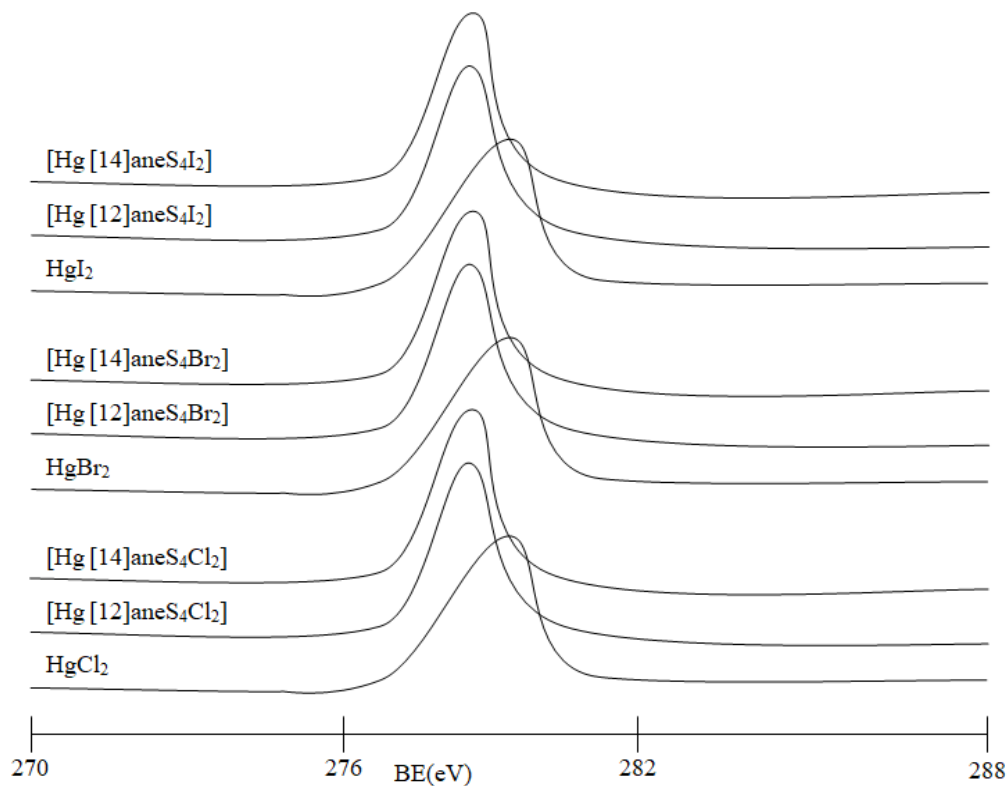


Fig.3: Hg³P_{1/2} binding energies (eV) in HgX₂; [Hg[12]aneS₄X₂] and [Hg[14]aneS₄X₂] Complexes

S2p Photoelectron Peak

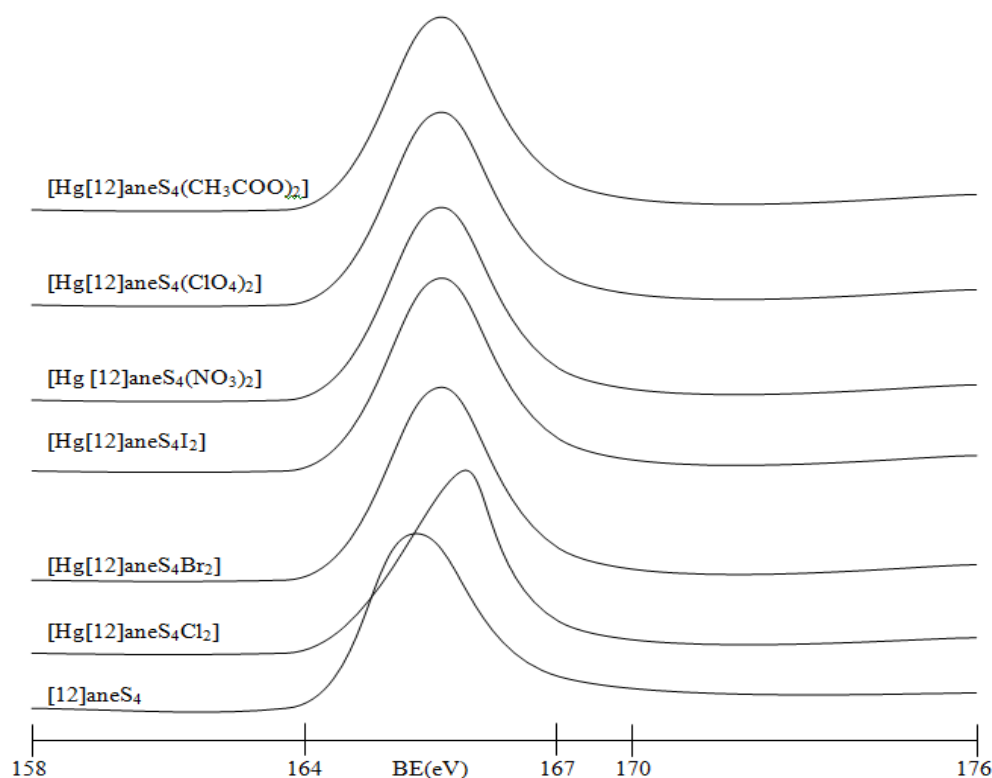


Fig.4: S2p binding energies (eV) in ligand [14]aneS₄ and [Hg(14)aneS₄X₂] where X=Cl or Br or I

Table I: Hg^{3p} 1/2, 3/2; S2p and X binding energies (eV) in ligands, HgX₂ and [Hg(n)aneS₄X₂] Complexes

Sr. No.	Ligand & Complex	Hg		S2p	X		
		Hg ^{3p} 1/2	Hg ^{3p} 3/2		Cl _{2p}	Br _{3p} 1/2	N1s from NO ₃
1	[12]aneS ₄	-	-	166.2	-	-	-
2	[14]aneS ₄	-	-	166.2	-	-	-
3	HgCl ₂	279.8	847.8	-	201.8	-	-
4	[Hg[12]aneS ₄ Cl ₂]	278.8	846.8	167.2	202.2	-	-
5	[Hg[14]aneS ₄ Cl ₂]	278.8	846.8	166.2-167.4	202.2	-	-
6	HgBr ₂	279.6	847.6	-	-	189.6	-
7	[Hg[12]aneS ₄ Br ₂]	278.6	846.6	167.0	-	190.0	-
8	[Hg[14]aneS ₄ Br ₂]	278.6	846.6	166.2-167.2	-	190.0	-
9	HgI ₂	279.4	847.4	-	-	-	-
10	[Hg[12]aneS ₄ I ₂]	278.4	846.4	167.0	-	-	-
11	[Hg[14]aneS ₄ I ₂]	278.4	846.4	166.2-167.2	-	-	-
12	Hg(NO ₃) ₂	279.4	847.4	-	-	-	404.4
13	[Hg[12]aneS ₄ (NO ₃) ₂]	278.4	846.4	167	-	-	405.2
14	[Hg[14]aneS ₄ (NO ₃) ₂]	278.2	846.2	166.2-167.2	-	-	405.2
15	Hg(ClO ₄) ₂	279.2	847.2	-	-	-	-
16	[Hg[12]aneS ₄ (ClO ₄) ₂]	278.0	846.2	167.2	-	-	-
17	[Hg[14]aneS ₄ (ClO ₄) ₂]	278.0	846.2	166.2-167.2	-	-	-
18	Hg(CH ₃ COO) ₂	279.0	847.0	-	-	-	-
19	[Hg[12]aneS ₄ (CH ₃ COO) ₂]	278.0	846.0	167.0	-	-	-
20	[Hg[14]aneS ₄ (CH ₃ COO) ₂]	278.0	846.0	166.2-167.2	-	-	-

The molar conductance of all these complexes were obtained below $38 \text{ Ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ in acetone 10^{-3} molar solution at room temperature, suggested all these complexes are no electrolyte with composition of $[\text{Hg}[12]\text{aneS}_4\text{X}_2]$ and $[\text{Hg}[14]\text{aneS}_4\text{X}_2]$ [20].

Far IR spectra have shown $\nu_{\text{Hg-Cl}}$ frequency in range of $260\text{-}280 \text{ cm}^{-1}$ in $[\text{Hg}[12]\text{aneS}_4\text{Cl}_2]$ and $[\text{Hg}[14]\text{aneS}_4\text{Cl}_2]$ complexes [21]; $\nu_{\text{Hg-Br}}$ in range of $280\text{-}293 \text{ cm}^{-1}$ in $[\text{Hg}[12]\text{aneS}_4\text{Br}_2]$ and $[\text{Hg}[14]\text{aneS}_4\text{Br}_2]$ complexes [21]; $\nu_{\text{Hg-I}}$ in the range of $100\text{-}123 \text{ cm}^{-1}$ in $[\text{Hg}[12]\text{aneS}_4\text{I}_2]$ and $[\text{Hg}[14]\text{aneS}_4\text{I}_2]$ complexes [21]; $\nu_{\text{Hg-NO}_3}$ in the range $1384\text{-}1306 \text{ cm}^{-1}$ in $[\text{Hg}[12]\text{aneS}_4(\text{NO}_3)_2]$ and $[\text{Hg}[14]\text{aneS}_4(\text{NO}_3)_2]$ complexes [22]; $\nu_{\text{Hg-ClO}_4}$ in the range of $610\text{-}624 \text{ cm}^{-1}$ in $[\text{Hg}[12]\text{aneS}_4(\text{ClO}_4)_2]$ and $[\text{Hg}[14]\text{aneS}_4(\text{ClO}_4)_2]$ complexes [23] and $\nu_{\text{Hg-CH}_3\text{COO}}$ IR frequency in the range $1448\text{-}1405 \text{ cm}^{-1}$ in $[\text{Hg}[12]\text{aneS}_4(\text{CH}_3\text{COO})_2]$ and $[\text{Hg}[14]\text{aneS}_4(\text{CH}_3\text{COO})_2]$ complexes [24].

The binding energies (eV) of prepared ligands $[12]\text{aneS}_4$ and $[14]\text{aneS}_4$; HgX_2 and prepared complexes $[\text{Hg}[12]\text{aneS}_4\text{X}_2]$ and $[\text{Hg}[14]\text{aneS}_4\text{X}_2]$ for $\text{Hg}^3p^{1/2,3/2}$, S2p and Xnp (where X= Cl or Br or I or NO_3 or ClO_4 or CH_3COO) are listed in Table I. It was observed that the binding energies (eV) of $\text{Hg}^3p^{1/2,3/2}$ in the starting material HgX_2 (where X= Cl or Br or I or NO_3 or ClO_4 or CH_3COO) were more than in prepared complex. $[\text{Hg}[12]\text{aneS}_4\text{X}_2]$ or $[\text{Hg}[14]\text{aneS}_4\text{X}_2]$ (Table I). These XPS data suggested that the electron density in mercury metal ion is more in prepared complexes than in HgX_2 due to coordination (Fig. 3) [25].

CONCLUSION

The Sp photoelectron spectra of all $[\text{Hg}[12]\text{aneS}_4\text{X}_2]$ complexes have shown only one single high intensity symmetrical photoelectron peak towards higher binding energy side [BE~167.2-167.4eV] than S2p photoelectron peak of ligand i.e. $[12]\text{aneS}_4$ but in all $[\text{Hg}[14]\text{aneS}_4\text{X}_2]$ complexes have shown two S2p photoelectron peak in intensity ratio 3:1; one high intensity energy side and other lower intensity at same position as in ligand $[14]\text{aneS}_4$. These S2p binding energies (eV) data suggested that all four sulfur atoms are coordinated to metal mercury ion in $[\text{Hg}[12]\text{aneS}_4\text{X}_2]$ complexes but in $[\text{Hg}[14]\text{aneS}_4\text{X}_2]$ complexes only three sulfur atoms are coordinated to metal mercury ion; one sulfur is uncoordinated (Table I)(Fig4). The Hg3s photoelectron peaks in all these metal complexes i.e. $[\text{Hg}[12]\text{aneS}_4\text{X}_2]$ and $[\text{Hg}[14]\text{aneS}_4\text{X}_2]$ have not shown multiple splitting, suggested diamagnetic nature [25].

On the basis of above physicochemical data of $[\text{Hg}[12]\text{aneS}_4\text{X}_2]$ and $[\text{Hg}[14]\text{aneS}_4\text{X}_2]$ complexes i.e. on the basis of elemental analysis, molar conductivity, IR and X-Ray photoelectron (XPS) data; it may be propose structure of all these complexes as shown in Fig.I and II and an octohedral geometry for $[\text{Hg}[12]\text{aneS}_4\text{X}_2]$ and trigonal bipyramidal geometry for $[\text{Hg}[14]\text{aneS}_4\text{X}_2]$ may be established.

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