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Synthesis of Schiff base derived ligands 1-chloro-2 (2-chloroethoxy) ethane derived ligand (S1) and 1,2-bis(2-chloroethoxy)ethane derived ligand (S2)

Dr. Shital Joshi*

*Department of Chemistry, Govt. Arts and Science College, Ratlam (M.P.) INDIA

Abstract - The ligands (5E,15E)-7,8,9,10,11,12, 13,14,22,23,25, 26-dodecahydr odibenzo[h,v] [1,4,7] trioxa [11,14,17,20] tetraazacyclotricosine [1-chloro-2(2-chloroethoxy) ethane derived ligand (S_1)] and (5E,15E)-7,8,9,10,11,12,13, 14,22,23, 25,26,28,29-Tetradecahydrodibenzo[k,y][1,4,7,10]tetraoxa[14,17,20,23] tetraazacyclo hexacosine [1,2-bis(2-chloroethoxy)ethane derived ligand (S_2)] have been synthesized by nucleophilic aromatic substitution reaction of Schiff base 2,2'((1E,11E)-2,5,8,11-tetraazadodeca-1,1-diene-1,12-diyl)diphenol (TTS)/N,N'-bis[2-(salicylideneamino) ethane-1,2-diamine (TTS). The ligands S_1 and S_2 have been synthesized by condensation reaction of Schiff base (TTS) with dichloro derivatives of diethylene and triethylene glycol respectively and characterized by elemental analysis, IR, ^{1}H NMR, and Mass spectrometry method.

Keywords: Schiff base derived ligand, glycol derived ligand, 1-chloro-2(2-chloroethoxy) ethane derived ligand (S_1), 1,2-bis(2-chloroethoxy)ethane derived ligand (S_2).

Introduction - Schiff base is class of compounds which contains carbon nitrogen double bond. Schiff bases are easily prepared by the condensation reaction or microwave irradiation of primary amine with carbonyl compounds, these carbonyl compounds may be aldehydes, ketones and acids[1, 2]. Large no of compounds are prepared using Schiff base which are used to prepare their transition metal complexes which are of great interest due to their diverse reactivity and wide application in catalysis, pharmaceuticals, functional materials[3-8].

However despite extensive scientific reports on the synthesis, characterization, crystalline structure and application of the transition metal complex, there are limited report on the use of Schiff base as ionophore in supramolecular chemistry[9-12]. L. Mishra *et al.* studied tetradentate thioiminato Schiff base as carriers for transport of nickel ions through chloroform liquid membrane[13] and S. Dubey *et al.* synthesized mixed donor ionophore using Schiff base and studied liquid membrane transport of transition metal ions and the effect of donor site of ionophore on separation of metal ions[14, 15], still very little attention paid in this field.

In the present work a Schiff base derived ligands S_1 & S_2 have been synthesized and characterized by elemental analysis, IR, ^{1}H NMR, Mass and spectrometry method which can be used as ionophores.

Material And Methods:

1 **Chemicals:** All the chemicals used throughout the course of experimental work were of AR grade. The reagents used for synthesis of Schiff base are salicylaldehyde and TETA were purchased from Loba Chemie and S. D. Fine respectively. The Schiff base (TTS) is prepared by reported method[16]. The reagent used for synthesis of ligand S_1 is 1-chloro-2(2-chloroethoxy)ethane was obtained from Merck and for ligands S_2 are 1,2-bis(2-chloroethoxy)ethane was obtained from Sigma Aldrich. Sodium hydroxide (NaOH) was obtained from CDH. The solvents dichloromethane (DCM), dimethyl sulfoxide (DMSO), were obtained from Merck.

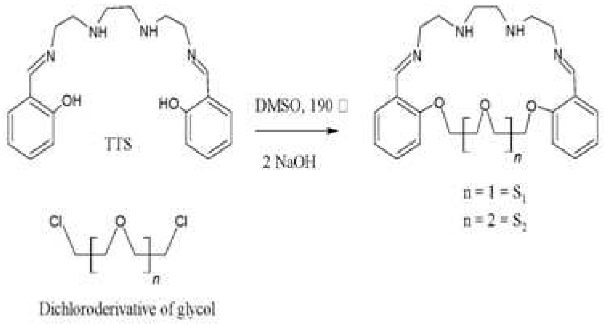
2 Instruments - Capillary melting point apparatus was used for determination of melting point of ligands, FTIR spectra were recorded on FTIR spectrophotometer at Central Analytical Laboratories, Indore, ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ using tetramethylsilane as an internal reference on Brucker Avance II 400 NMR spectrophotometer, SAIF, Punjab University, Chandigarh. Elemental analysis and Mass spectral analysis have been carried out using Eurovector EA 3000 elemental analyzer and Waters UPLC-TQD mass spectrometer respectively from CDRI, Sophisticated Analytical Instrumentation Facility (SAIF), Lucknow UP.

Preparation of Ligands:

1 Synthesis of (5E,15E)-7,8,9,10,11,12,13,14,22,23,25,26-dodecahydro dibenzo [h,v] [1,4,7] trioxa [11,14,17,20] tetraazacyclotricosine (S_1) - The ligand S_1 has been synthesized by the reaction of Schiff base (TTS) with 1-

chloro-2(2-chloroethoxy)ethane and sodium hydroxide in 1:1:2 molar ratio using DMSO as solvent[17-22].

3.54 g of Schiff base (TTS) (0.01 mol) was dissolved in 50 mL DMSO in a round bottom flask then 5 mL aqueous solution of 0.80 g sodium hydroxide (0.02 mol) was added. The reaction mixture was stirred for 30 minutes at room temperature then 1.20 mL 1-chloro-2(2-chloroethoxy) ethane (0.01 mol) was added and refluxed for 12 h at 190^{0}C The product was neutralized by 1M HCl, mixed with DCM and washed by distilled water (twice) then with brine. The organic phase (DCM) was separated, dried (over anhydrous $MgSO_4$), filtered, concentrated and recrystallized with ethanol gave 45% of S_1 as dark brown solid. (Scheme 1)



Scheme 1 Synthesis of ligands S_1 and S_2

2 Synthesis of (5E,15E)-7,8,9,10,11,12,13,14, 22,23,25, 26,28, 29-Tetradecahydro dibenzo[k,y][1,4,7,10]tetraoxa [14,17,20,23]tetraazacyclohexacosine (S_2) - The cyclic ligand S_2 has been synthesized by reaction of Schiff base (TTS) with 1,2-bis(2-chloroethoxy)ethane and sodium hydroxide in 1:1:2 molar ratio using DMSO as solvent[17-22]. 3.54 g of Schiff base (TTS) (0.01 mol) was dissolved in 50 mL DMSO in a round bottom flask then 5 mL aqueous solution of 0.80 g sodium hydroxide (0.02 mol) was added. The reaction mixture was stirred for 30 minutes at room temperature then 1.55 mL of 1,2-bis(2-chloroethoxy)ethane (0.01 mol) was added and refluxed for 12 h at 190^{0}C The product was neutralized by 1M HCl, mixed with DCM and washed with distilled water (twice) then with brine. The organic phase (DCM) was separated, dried (over anhydrous $MgSO_4$), filtered, concentrated and recrystallized with ethanol gave 55% of S_2 as dark brown solid. (Scheme 1)

Results and discussion:

1 Characterization of ligands (S_1 & S_2) - The confirmation of synthesized ligands were carried out by melting point determination and TLC, while characterization has been done by FTIR, ^{1}H and ^{13}C NMR, ESI mass spectral and elemental analysis.

Table 1 (see in last page)

Table 1 shows the physical properties and elemental analysis of ligands (S.)

2 The FTIR spectral analysis of ligands - The characteristic FTIR spectral data of ligands are shown in table 2. Fig. 1 & 2 are FTIR spectra of ligands S_1 & S_2 respectively . The presence of absorption bands for imine (C=N), ether ($-CH_2-O-CH_2-$/Ar-O-Ar) groups in FTIR spectra of ligands confirm the condensation of Schiff base with dichloro derivative of polyethylene glycol[18-22].

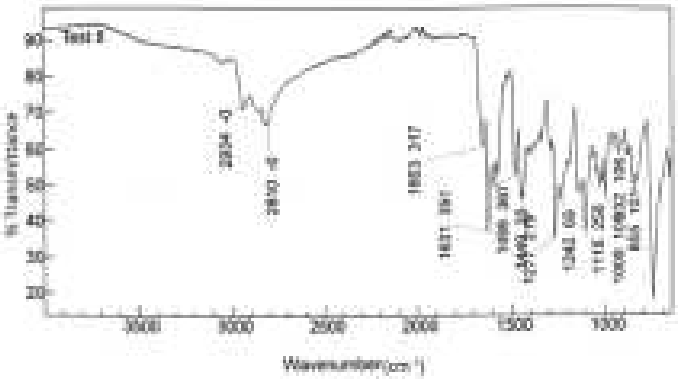


Fig. 1 FTIR spectrum of ligand S_1

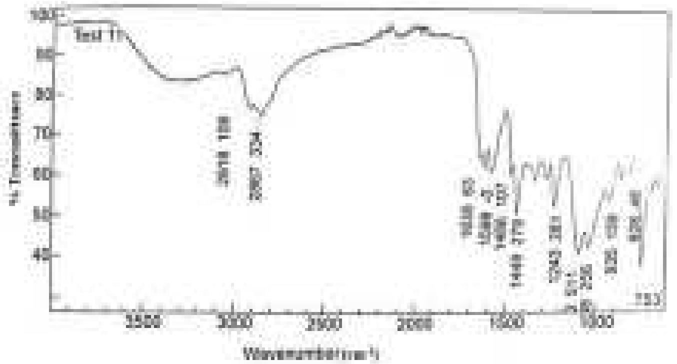


Fig. 2 FTIR spectrum of ligand S_2

Table 2 Characteristic FTIR absorption bands (in cm^{-1}) of ligands

S.	Ligand	Selected FTIR absorption bands (in cm^{-1})
1.	S_1	2934, 2810 (C-H), 1631 (C=N), 1242 (Ar-O-CH_2), 1116 (CH_2-O-CH_2)
2.	S_2	2918, 2867 (C-H), 1635 (C=N), 1243 (Ar-O-CH_2), 1102 (CH_2-O-CH_2)

3 ^{1}H and ^{13}C NMR spectral analysis of ligands - The characteristic ^{1}H and ^{13}C NMR spectral data of ligands are shown in table 3 and 4 respectively. Fig. 3 and 4 and 5 and 6 are ^{1}H and ^{13}C NMR spectra of ligands.

In ^{1}H NMR Spectrum of ligand S_1 the absorption peaks at 1.17 ppm (s, 2H) (2^f amine,-NH-), 2.22-2.84 ppm (m, 8H) ($-CH_2-$), 3.80 ppm (m, 4H) ($-CH_2-N=$), 4.13-4.14 ppm (m, 8H) (Ar/CH_2-O-CH_2-), 6.68-7.21 ppm (m, 8H) (Ar-H) and 8.23 ppm (s, 2H) (-CH=N-) confirm the formation of ligand S_1 and in ^{13}C NMR spectrum of ligand S_1 peaks at 59 and 67 {($-CH_2-O-CH_2-$) and (Ar-O-CH_2-)}, 117-137 ppm (Ar-C), 161 ppm (-C=N-) account for ether, aromatic and imine carbon respectively.

In ^{1}H NMR Spectrum of ligand S_2 the peaks at 2.49-2.90 ppm (m, 8H) (CH_2-), 3.84 ppm (m, 4H) (CH_2-N=), 4.14-4.16 ppm (m, 12H) (Ar/CH_2-O-CH_2-), 6.70-7.48 ppm (m, 8H) (Ar-H), 9.81 ppm (s, 2H) (-CH=N-) confirm the formation of ligand S_2 and in ^{13}C NMR spectrum of ligand S_2 peaks at 68-69 and 71 ppm {(CH_2-O-CH_2) and ((Ar-O-CH_2-)}, 116-

137 ppm (Ar-C), 161 ppm (-C=N-) accounts for ether, aromatic and imine carbon respectively.

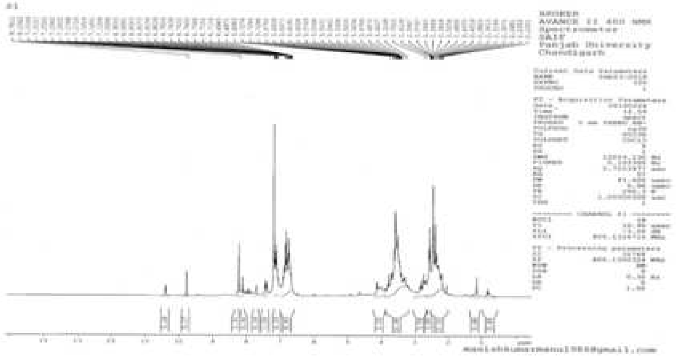


Fig. 3 ^{1}H NMR spectrum of ligand S_1

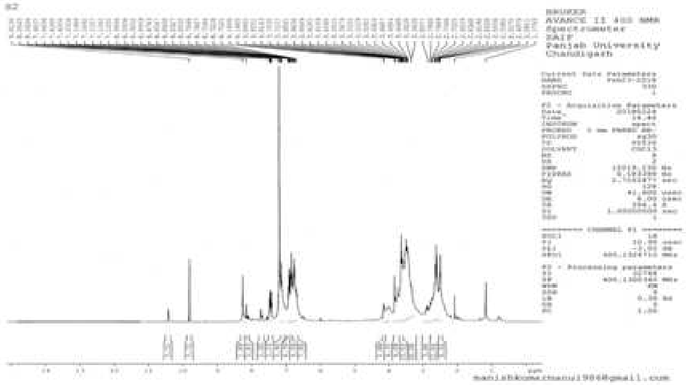


Fig. 4 ^{1}H NMR spectrum of ligand S_2

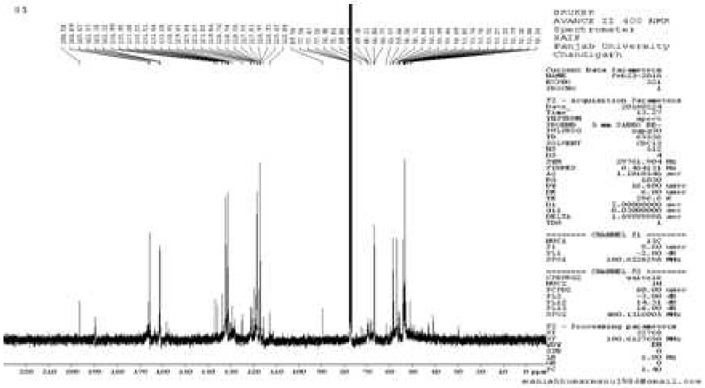


Fig. 5 ^{13}C NMR spectrum of ligand S_1

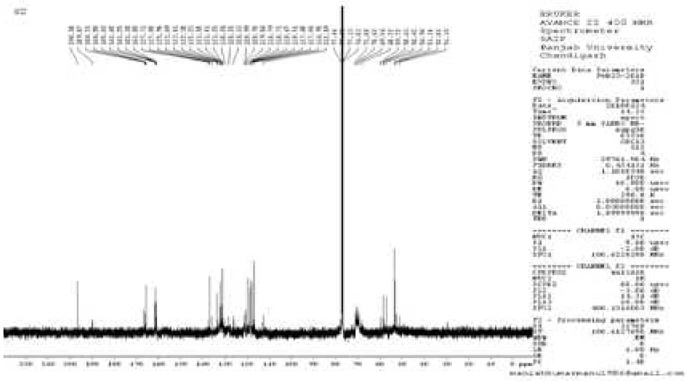


Fig. 6 ^{13}C NMR spectrum of ligand S_2

Table 3 Characteristic ^{1}H NMR peak (in ppm) of ligands

S.	Ligand	Selected ^{1}H NMR peak (in ppm)
2.	S_1	1.17 (2^f Amine, -NH-), 2.22-2.84 ($-CH_2-$), 3.80 ($-CH_2-N=$), 4.13-4.14 (Ar/CH_2-O-CH_2-), 6.69 -7.21 (Ar-H), 8.23 (-HC=N-)
3.	S_2	1.17 (2^f Amine, -NH-), 2.49-2.90 ($-CH_2-$), 3.84 ($-CH_2-N=$), 4.14-4.16 (Ar/CH_2-O-CH_2-), 6.70-7.4 (Ar-H), 9.81 (-HC=N-)

Table 4 Characteristic ^{13}C NMR peak (in ppm) of ligands

S.	Ligand	Selected ^{13}C NMR peak (in ppm)
2.	S_1	51-56 ($-CH_2-$), 58 ($-CH_2-N=$), 59 ($-CH_2-O-CH_2-$), 67 ($Ar-O-CH_2-$) 117-137 (Ar-C), 161 (-C=N-), 165 (Ar-O-)
3.	S_2	53-34 ($-CH_2-$), 56 ($-CH_2-N=$), 68-69 ($-CH_2-O-CH_2-$) 71 ($Ar-O-CH_2-$), 116-137 (Ar-C), 161 (-C=N-), 166 (Ar-O-)

4 ESI mass spectral analysis of ligands - The mass spectra are used to confirm the molecular structure along with molecular mass of the compounds. The base peak is the most abundant peak which indicates the most stable fragment of the compound while the molecular ion peak shows the molecular mass of the compound. The peaks obtained from the cleavage indicate the position of the side chain and cyclic ring structure of the compound. Fig. 7 and 8 are the mass spectra of ligands.

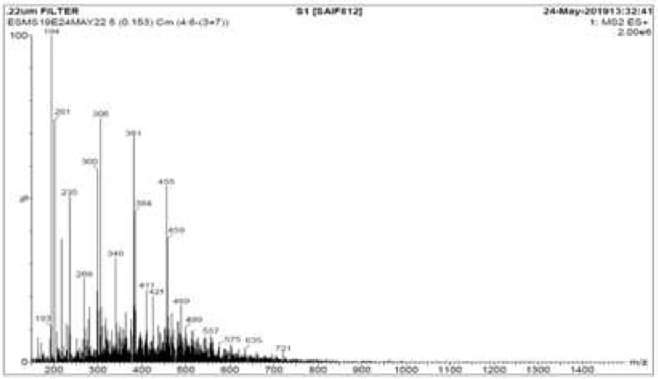
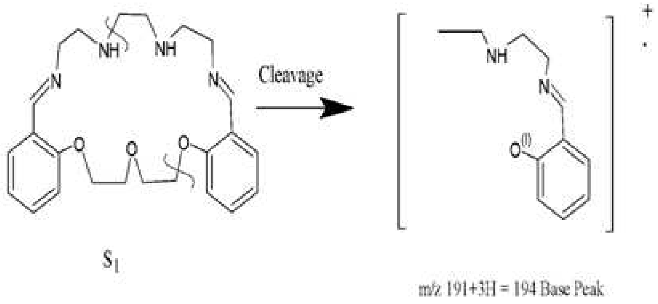


Fig. 7 ESI Mass spectrum of ligand S_1



Scheme 2 Mass spectrum analysis of ligand S_1

The base peak and molecular ion peak in the mass spectrum of ligand S_1 is observed at m/z 194 and 425 respectively suggested its molecular formula to be $C_{24}H_{32}N_4O_3$. Abundant peaks are found at m/z 235, 340, 381 and 411.

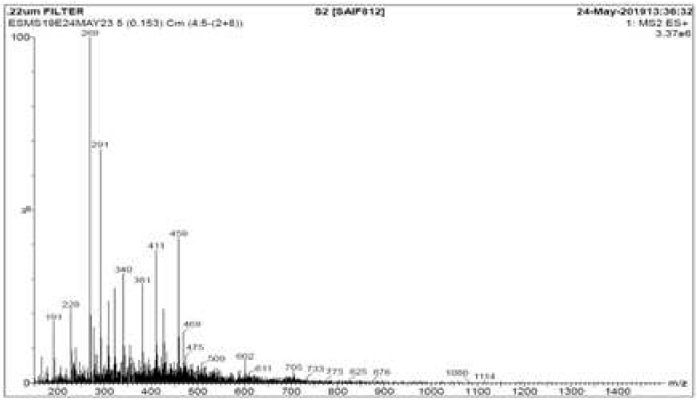
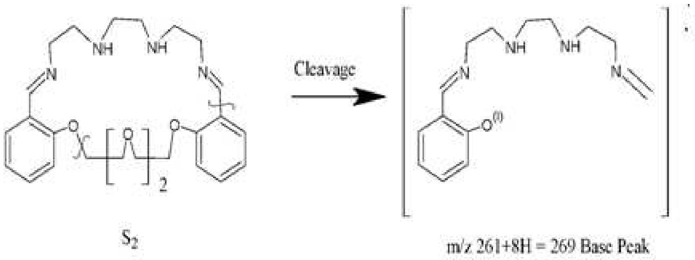


Fig. 8 ESI Mass spectrum of ligand S_2



Scheme 3 Mass spectrum analysis of ligand S_2

The base peak and molecular ion peak is observed in the mass spectrum of ligand S_2 at m/z 269 and 469 respectively suggested its molecular formula to be $C_{26}H_{36}N_4O_4$. Abundant peaks are found at m/z 228, 340, 381and 411.

Conclusion: The objective of the present research work is to prepare ligands (5E,15E)-7,8,9,10,11,12,13,14,22,23,25, 26-dodecahydr odibenzo[h,v][1,4,7]trioxa[11,14,17,20]tetraazacyclotricosine [1-chloro-2(2-chloroethoxy) ethane derived ligand (S_1)] and (5E,15E)-7,8,9,10,11,12,13, 14,22,23, 25,26,28,29-Tetradeca hydrodibenzo[k,y][1,4,7,10]tetraoxa[14,17,20,23] tetraazacyclo hexacosine [1,2-bis(2-chloroethoxy)ethane derived ligand (S_2)] have been synthesized and characterized by elemental analysis, IR, ^{1}H NMR, and Mass spectrometry method. The Ligands S_1 and S_2 were successfully synthesized and characterized. In future other derivatives of TTS can be synthesized and can be used for the liquid membrane studies of other transition metal ions.

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Conflict of Interest - There are no conflicts of interest.

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Table 1: Physical properties and elemental analysis of ligands

S.	Ligand	Molecular Formula	Molecular Weight		MP(^{0}C)	%Yield	% C		% H		% N	
			C	**F**			**C**	**F**	**C**	**F**	**C**	**F**
1.	S_1	$C_{24}H_{32}N_4O_3$	424.54	425	120	45	67.9	69.2	07.6	06.5	13.2	12.2
2.	S_2	$C_{26}H_{36}N_4O_4$	468.59	469	170	55	66.6	60.0	07.7	05.6	12.0	07.6

C = Calculated , F = Found

Table 1 shows the physical properties and elemental analysis of ligands (S.)

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