New Tripodal Ligands Containing Aza-Thioethers as Selective Extractants for Silver(I)

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Abstract

A new series of tripodal receptors bearing imine and thioether units, have been synthesized in high yields by simple condensation method. The binding properties of these ligands towards alkali, alkaline earth and transition metal ions have been established by extraction and transport experiments. These podands have highest extraction and transport rate for Ag(I). The complexation of Ag(I) with the receptors has been established using ^{1}H-and ^{13}C-NMR spectroscopy.

Introduction

Strong Ag(I) recognition is important for [111]Ag-based radio immunotherapy [1–3] and useful for photographic technology and recovery of Ag^+ from waste water. The presence of sulfur, a soft Lewis base, is highly desirable in the ligands meant for Ag(I) recognition. One big advantage of thioether ligands is their ability to behave as selective metal extraction agents for soft metal ions [4]. Several sulfur containing cyclic [5–6], macrocyclic [1–2] and calixspherands [3] as Ag^+ binders have been reported followed by thiolariat ethers [7–9]. As far as metal binding is concerned thiolariat ethers have an edge upon crown ethers because introduction of sulfur atom into a crown ring gives rise to an unfavorable entropy change upon complexation [1, 10] with the metal ion. In contrast to thioether macrocycles, the chemistry of azathioether macrocycles is studied to a much lesser extent [11] due to comparatively difficult synthetic procedures involved. In view of these facts, syntheses of tripodal ligands having aza-thioethers in a non-cyclic framework, will take care of the above mentioned unfavorable entropy factor. At the same time it will be supplemented by facile synthesis and inherent flexibility of the podands. In continuation of our ongoing studies on podands [12–14] we present here syntheses and characterization of new flexible tripodal ligands, bearing aza-thioethers as donor groups. Their metal ion recognition properties have been determined from solvent extraction and transportation across a liquid membrane. The solvent extraction of heavy metals with chelating and macrocyclic ligands, requires rapid selective complexation, high stability against hydrolysis, minimal affinity for alkali or alkaline earth ions, high metal-

extractant binding strength and easy recovery of metal [15–17]. The latter requires a decomplexation process, to regenerate the ligand and isolate the metal ion. We have made an attempt to achieve it and metal has been successfully removed from the extracts.

Results and discussion

Characterization of ligands

All the ligands (**2a–e**) were prepared in good yields by condensation of **1** with various aldehydes as given in Scheme 1. These ligands have been fully characterized by elemental analyses, Mass, ^{1}H- and ^{13}C-NMR spectroscopic studies. The X-ray crystal structure of one of them i.e. **2b** has already been reported [14]. The presence of imine linkages was characterized by a band around 1635–1645 cm^{-1} in IR spectra which corresponds to CH=N. The same were established by having signals between δ 8.33 and 9.01 in the ^{1}H-NMR spectra and in between δ 152.8–165.8 in ^{13}C-NMR spectra. The appearance of only one peak for the imine protons in all the ligands accompanied by one peak for the – OH groups in **2b**, **2e**, one doublet for protons at C-2, C-3, C-4 of Pyridine, only two triplets for methylene protons in **2a–2c** and only two triplets and a multiplet for methylene protons in **2d–2e** show that the ligands have a threefold symmetry in the solution phase. The FAB mass and CHN data are also in accordance with the molecular formulae.

Extraction studies

The extraction efficiencies of ligands **2a–e** toward alkali, alkaline earth and some transition metal ions were determined by the picrate extraction method developed

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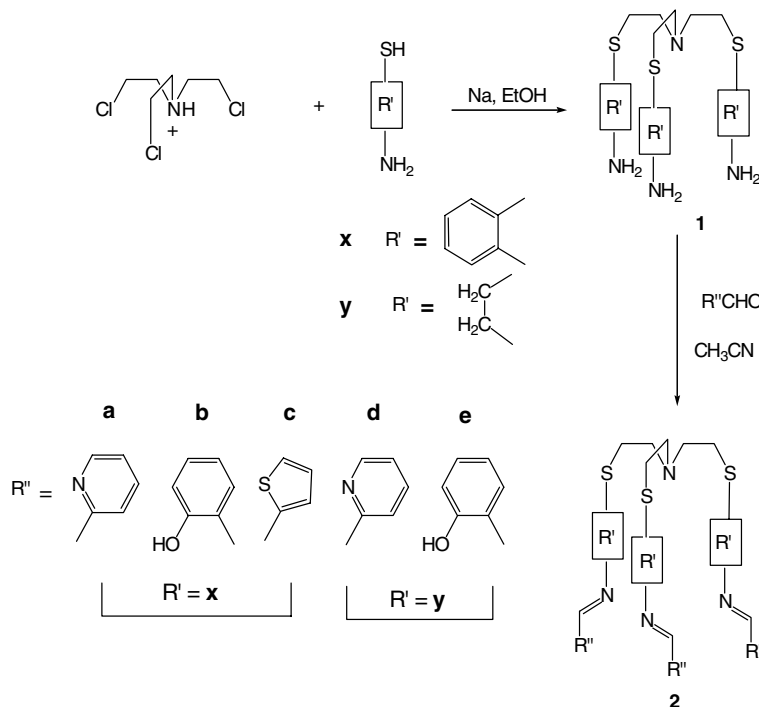
Scheme 1.

by Pederson. Solvent extraction of aqueous metal cation into water saturated organic hosts' solutions, were performed at 25 °C. An aqueous solution containing metal picrate (1.0 mM) was extracted with the host solution (CHCl$_3$, 1.0 mM), and the data are expressed as percentages of the cation extracted (%E) by the ligand, as given in the Table 1 and represented in Figure 1. Since these ligands have UV bands around $\lambda_{max} = 375$ nm, so the amount of metal picrate extracted by organic phase is difficult to determine and hence concentration of metal picrates left in aqueous phase after extraction was taken as a measure to determine the percentage of cation extracted by the ligand. It is clear from the Table 1 that the complexation ability of **2a–e** toward Ag$^+$ is much higher. The

Table 1. Showing extraction (%) of metal ions by various ligands

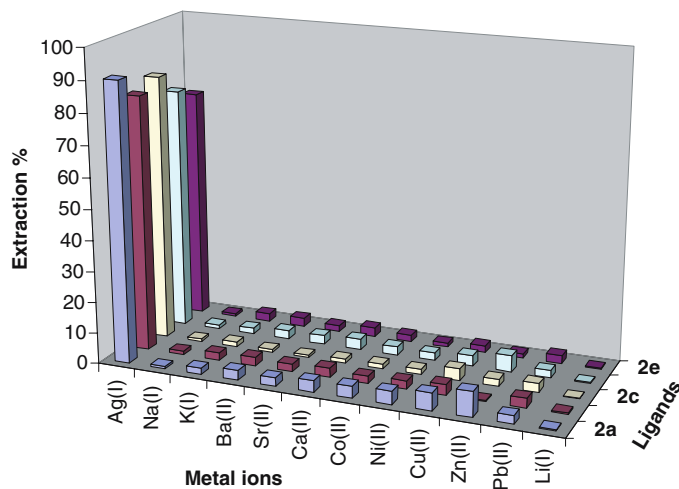|	2a	2b	2c	2d	2e
Li$^+$	0.4	0.5	0.2	0.4	0.3
Na$^+$	0.76	1.20	0.8	1.2	0.8
K$^+$	2.1	2.4	1.5	1.9	2.6
Ba^{2+}	3.2	2.9	0.9	2.8	2.7
Sr^{2+}	2.7	2.5	0.8	2.9	1.9
Ca^{2+}	3.7	3.1	1.4	3.5	2.9
Co^{2+}	3.9	2.3	1.5	2.7	2.1
Ni^{2+}	4.3	2.7	1.8	2.5	1.3
Cu^{2+}	5.7	3.5	3.8	3.5	2.2
Zn^{2+}	8.1	0.4	2.3	5.3	1.3
Pb^{2+}	2.7	3.1	2.9	2.3	2.6
Ag$^+$	90.1	82.5	85.7	78.3	74.7

Figure 1. Showing extraction of metal ions with various ligands.

preference of this metal to bind to the softer thioether may be due to the larger size of the sulfur atom, which allows a closer approach to the metal ion with the least contraction of podand [18]. Among the ligands, those bearing aromatic thioethers **2a–c** have a greater ability to extract heavy metal ions than their analogous aliphatic thioethers **2d–e**. If only one lone pair of S is involved in the bonding to metal ion then the other has a pronounced steric effect (Gillespie–Nyholm approach) [19]. In principle this second lone pair may take part in bonding *via* π donation. But for Ag^+ with fully filled d orbitals, this π acceptance is not possible, so second lone pair is a source of steric repulsion. But if the donor S atom is attached to an aromatic ring or is a part of it, as in **2a–c**, then the π delocalization on the ring will enhance the stability of corresponding complexes [20]. The lower percentages found for the alkali and alkaline earth metal cations may be due to the fact that hard cations possessing high hydration energies would not interact strongly with nitrogen and sulfur moieties in the receptor while less hydrated Ag^+ ion prefers coordination to soft donor atoms.

Transport studies

Experiments testing ion transport across a liquid membrane were carried out using apparatus similar to Lamb *et al.* [21] and are given in Table 2 and represented in Figure 2. Before determining the transport rates, blank experiments were performed in the absence of receptor (i.e. in neat chloroform) to check the leakage of metal picrates. A significant leakage was observed in the case of Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+} so the transport rates with these metal ions were not determined. All the ligands show high transport rates for Ag^+. The transport rates are determined either by the rate of diffusion or by the rate of complexation and decomplexation at the interfaces. Comparing the lowest extractant **2e** to the highest extractant **2a**, it is seen that the former has the highest transport rate. As **2e** shows a weak affinity for

Table 2. Showing transport rates (10^8 mol/24 h) of metal ions by various ligands

	2a	2b	2c	2d	2e
Li^+	12	20	12	14	14
Na^+	24	34	26	25	29
K^+	34	42	43	38	46
Ba^{2+}	44	46	45	49	51
Sr^{2+}	52	54	54	59	53
Ca^{2+}	56	63	58	53	82
Ag^+	1720	1890	1830	2150	2290

Ag^+, it is expected that it releases the cation easily at the interface. For all ligands transport rates show that they bear an inverse relation with the extraction ability of ligand. Thus all ligands behave as good carriers for Ag(I) rather than being receptors.

NMR studies

To decide the binding sites in the ligands, we performed ^1H- and ^{13}C-NMR studies of 1:1 Ag^+ : ligand in the solution phase. The synergistic coordination of the imine nitrogen and sulfur atoms of the thioether group is strongly supported by ^1H- and ^{13}C-NMR spectroscopy results. Both **2b** and **2e** show small but significant shifts in the ^1H-NMR which are more pronounced in ^{13}C-NMR spectroscopy (Tables 3 and 4).

In **2b** the signals for methylene carbons are affected the most. The signal for $-CH_2S$ show a large downfield shift ($\Delta\delta$ 3.62) accompanied by an upfield shift $\Delta\delta$ 1.50 in the carbon of $-NCH_2$ group and $\Delta\delta$ 1.81 and 0.88 in the quaternary aromatic carbon bearing imine group and the imine carbon, respectively. This indicates that Ag(I) is being coordinated to thioether and the imine groups. There is not any significant shift in the chemical shift values of the quaternary C bearing $-OH$ group ($\Delta\delta$ -0.74) but the hydroxyl hydrogens show significant upfield shifts in ^1H-NMR ($\Delta\delta$ -0.60). In the X-ray crystal structure of the free ligand [14] there is strong

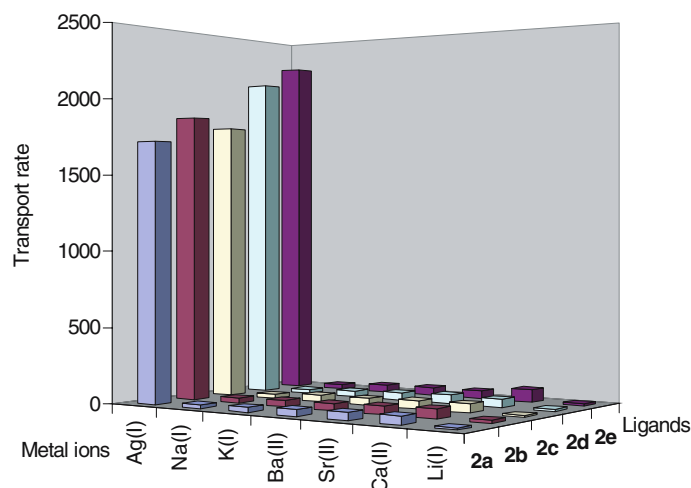*Figure 2.* Showing transport rate of metal ions with various ligands.

Table 3. Showing Shifts ($\Delta\delta$) in ^{1}H- and ^{13}C-NMR upon complexation of Ag$^+$ ion with **2b**

Compound	$-CH_2S$	$-CH_2N$	$CH=N$	$Ar-OH$	$Ar-NC$
2b	2.80	2.95	8.60	13.25	–
2b + Ag$^+$	2.73	3.06	8.56	12.63	–
$\Delta\delta$	−0.07	0.11	− 0.04	−0.60	–
2b	30.27	53.00	161.88	161.14*	146.56*
2b + Ag$^+$	33.89	51.50	162.76	160.40*	148.37*
$\Delta\delta$	3.62	−1.50	0.88	−0.74	1.81

* peak absent in DEPT-135.

Table 4. Showing the Shifts in ^{1}H- and ^{13}C-NMR upon complexation of Ag$^+$ with the ligand **2e**

Compound	$-CH_2S$	$-CH_2S$	$-CH_2N$	$-CH_2N$	$CH=N$	$Ar-OH$
2e	2.55−2.65	–	2.83	3.75	8.33	13.27
2e + Ag$^+$	2.67−2.72	–	3.01	3.87	8.42	13.21
$\Delta\delta$	0.12, 0.07	–	0.18	0.12	0.11	−0.06
2e	30.36	33.19	53.99	59.21	165.79	160.96*
2e + Ag$^+$	32.63	34.79	52.04	58.96	167.21	160.89*
$\Delta\delta$	2.27	1.60	−1.95	−0.25	1.42	0.07

* peak absent in DEPT-135.

intramolecular H-bonding between the hydroxyl groups and the imine nitrogens which causes the -OH to appear at a significantly low value of the magnetic field (δ 13.25) in the ^{1}H-NMR. The above mentioned upfield shift in the position of -OH protons on complexation, may be due to the weakening of these intramolecular H-bonds, when the imine nitrogens are engaged in coordination to the metal ion.

In **2e** the shifts (Table 4) in the methylene carbons of $\Delta\delta$ 2.27, 1.60 and −1.95 along with a $\Delta\delta$ 1.42 in the imine carbons, indicate their participation in coordination towards the metal ion. However, the shifts are comparatively less in **2e** pointing towards a weaker complexation in this case, a result which is in accordance with the results of the extraction studies. This shows that the complexation of Ag$^+$ takes place through thioethers and imine linkages help in coordination. Since none of the signal splits after complexation but only shows a change in the chemical shift value hence it may be inferred that all the three arms of the tripodal ligand remain equivalent after coordination also. This would give a coordination number six around the metal ion in a 1:1 complex. Further since there is not any significant shift in the aromatic region of the phenol bearing ring so the phenol groups in **2b** and **2e** do not seem to have any participation in complexation. The stoichiometry of the complex is 1:1 was proved by ^{1}H-NMR titration using mole ratio method. A plot of change in the chemical shift values in NCH$_2$ and SCH$_2$ protons in **2b** *versus* change in number of moles of the metal ion (Figure 3) gives a maximum corresponding to 1:1 ligand : metal ratio.

The ^{1}H- and ^{13}C-NMR spectra of 1:1 solution of Ag(I) complex with **2a** showed complications both in the aliphatic and aromatic regions, showing more peaks
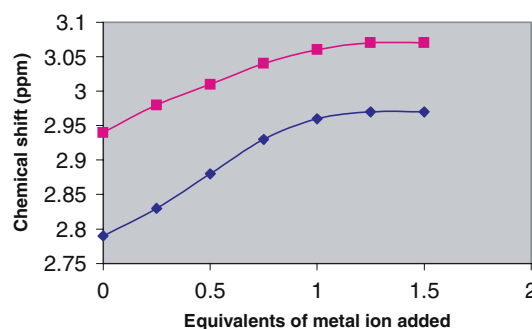

Figure 3. ^{1}H-NMR titration for complexation between **2b** and Ag$^+$. ([**2b**] 3×10^{-3} M, Lower curve corresponds to −SCH$_2$ protons and upper curve to −NCH$_2$ protons).

than required for a complex having three equivalent arms of the tripod. The methylene protons give three broad peaks at δ 2.59, 2.85 and 3.13 in the approximate ratio 1:4:1. Correspondingly the ^{13}C-NMR also shows three peaks at δ 15.93, 22.04 and 35.60. The aromatic region shows two peaks each for imine protons (δ 9.10 and 8.98) and for the protons attached at C-2 (δ 8.86, 8.56) and C-4 (δ 8.38, 8.19) positions of the pyridine group. There are complex multiplets from δ 7.00−7.12, 7.27−7.39 and 7.47−7.53 corresponding to the remaining aromatic protons. There are more peaks in the aromatic region of ^{13}C-NMR than required for three equivalent arms, with the most downfield peak having a chemical shift value of δ 160.40. This indicates that the threefold symmetry of the tripodal ligand is lost after complexation. There are again definite and significant changes in the ^{1}H- and ^{13}C-NMR chemical shift values of the methylene, imine and pyridine groups indicating their involvement in complexation. As the three arms are inequivalent and there is participation of pyridine N also in complexation hence it indicates that one arm of the tripod may not be coordinating to the metal ion and vacant sites are being taken up by the pyridine nitrogen(s).

Decomplexation of the metal ion

Experiment was done to remove metal ion from the extracts of these tripodal ligands using the reported method [22]. In case of **2b** the chloroform layer containing the complex **2b**.**Agpicrate**, was washed with a thiourea solution in D$_2$O and the ^{1}H-NMR of the chloroform layer was taken. It gave the same spectrum as found for the free ligand **2b**. The color of the solution also transferred to the upper aqueous layer on washing the lower chloroform layer with aqueous thiourea. This proves that the metal ion can be removed easily from the extract yielding the free ligand which may be reused.

Conclusions

New tripodal ligands bearing imine and thioether units have been successfully synthesized and characterized.

The ligands behave as good extractants and complexing agents for silver(I). The ligands containing aromatic thioethers have a greater ability to extract and complex silver(I) than their analogous aliphatic thioethers. The result is in accordance with the fact that an aromatic ring placed adjacent to the S atom helps in removing the steric repulsion faced by the second lone pair on S, when the first lone pair is involved in complexation with a d^{10} metal ion. An easy removal of the metal ion by a stronger complexing agent regenerates the ligands and proves that they are good carriers for silver(I).

Experimental

General

Melting points are uncorrected. Most chemicals were purchased from Aldrich and used as received without further purification. Organic solvents were purified by standard procedures. The elemental analyses and FAB mass spectra were done at RSIC at Central Drug Research Institute, Lucknow. The ^{1}H- and ^{13}C-NMR were taken on a 200 MHz Bruker and 300 MHz JEOL Instruments. TMS was used as a standard reference. IR were recorded on a PYE Unicam IR spectrometer as KBr pellets for the compounds in the solid state and as neat samples for the semisolid ones.

Synthesis

Compound 1x

Tripodal aromatic amine can be prepared by method given in literature [23] or can be synthesized in high yield as reported by us [14] Yield = 80%; M. P. = 55 °C; ^{1}H-NMR (CDCl$_3$, 200 MHz): δ 2.57 (t, 6H, $-$CH$_2$, $J=6.0$ Hz), 2.67 (t, 6H, $-$CH$_2$, $J=6.0$ Hz), 4.31 (s, 6H, $-$NH$_2$), 6.64 (m, 6H, Ar), 7.09 (m, 3H, Ar), 7.28 (m, 3H, Ar). ^{13}C-NMR (CDCl$_3$, 50 MHz): δ 32.1 ($-$CH$_2$), 53.0 ($-$CH$_2$), 114.7 (Ar), 117.2 (Ar), 118.1 (Ar), 129.5 (Ar), 135.5 (Ar), 146.2 (Ar).

Compound 1y

Tripodal aliphatic amine can be prepared by the reported method [23] or alternatively by the following method in a much better yield. Took 1.15 g of freshly cut sodium metal in dry absolute ethanol. Allowed to dissolve this metal in ethanol and then added 2-mercaptoethylamine hydrochloride (3.4 g, 30 mmol) and refluxed the reaction mixture for half an hour. Added trischloroethylamine (2.4 g, 10 mmol) and refluxed for 6 h Upon completion of the reaction, evaporated whole of ethanol and poured the contents into crushed ice and extracted the material three times with the dichloromethane. Mixed all the fractions and dried over sodium sulphate and decolorized over activated charcoal. Evaporated the solvent to provide solid tripodal amine 1y of light yellow color. Yield = 50%. ^{1}H-NMR (CDCl$_3$, 200 MHz): δ 2.33-2.63 (m, 24H, $-$CH$_2$), 2.71 (t, 6H, $-$NH$_2$, $J=6.0$ Hz). ^{13}C-NMR (CDCl$_3$, 50 MHz): δ 29.4 ($-$CH$_2$), 29.7 ($-$CH$_2$), 66.5 ($-$CH$_2$), 69.0 ($-$CH$_2$).

Compound 2a

Took tripodal amine 1x (470 mg, 1.0 mmol) in dry acetonitrile. Added to it 2-pyridinecarbaldehyde (321 mg, 3.0 mmol) and allowed to stir and reflux the reaction, TLC did not show the completion of reaction even after two days, then more of 2-pyridinecarbaldehyde (107 mg, 1.0 mmol) was added. Reaction completed within 2 h. Evaporated whole of the acetonitrile from the reaction mixture. Repeated recrystalization in methanol gave compound 2a as a yellow colored solid. Yield = 65%; M.P. = 110 °C; IR 1640 cm^{-1}; FAB-MS [M]$^+$ = 738, ^{1}H-NMR (CDCl$_3$, 200 MHz): δ 2.85 (t, 6H, $-$CH$_2$, $J=4.6$ Hz), 3.02 (t, 6H, $-$CH$_2$, $J=4.0$ Hz), 7.01$-$7.19 (m, 6H, Ar), 7.36$-$7.42 (m, 6H, Ar), 8.35 (d, 3H, Ar, $J=8.0$), 8.40 (s, 3H), 8.70 (m, 6H, Ar, $J=4.0$), 9.01 (S, 3H, $-$CH=N). ^{13}C-NMR: (CDCl$_3$, 50 MHz): δ 29.7 ($-$CH$_2$), 52.9 ($-$CH$_2$), 114.8 (Ar), 117.8 (Ar), 118.3 (Ar), 124.0 (Ar), 126.1 (Ar), 131.8 (Ar), 135.1 (Ar), 135.8 (Ar), 149.5 (Ar), 151.0 (Ar), 152.1 (Ar), 157.1 (CH=N). Anal. Calcd: C$_{42}$H$_{39}$N$_7$S$_3$, C 68.38; H 5.29; N 13.30; Found: C 68.42; H 5.33; N 13.57.

Compound 2b

This compound was prepared by Zn^{2+} mediated templated synthesis as already reported by us [14]. Yield = 85%; M.Pt. = 102 °C; IR 1645 cm^{-1}; FAB-MS [M]$^+$ = 783, ^{1}H-NMR (CDCl$_3$, 200 MHz): δ 2.80 (t, 6H, $-$CH$_2$S, $J=4.0$ Hz), 2.95 (t, 6H, $-$CH$_2$N, $J=4.0$ Hz), 6.92 (t, 3H, Ar), 7.03 (d, 3H, Ar), 7.17$-$7.58 (m, 18H, Ar), 8.60 (S, 3H, $-$CH=N), 13.25 (S, 3H, $-$OH). ^{13}C NMR (CDCl$_3$, 75 MHz): δ 30.27 ($-$CH$_2$S), 53.0 ($-$CH$_2$N), 117.4 (Ar), 117.7 (Ar), 119.0 (Ar), 119.2 (Ar), 126.3 (Ar), 127.4 (Ar), 127.8 (Ar), 132.3 (Ar), 132.5(Ar), 133.3(Ar), 146.6 (Ar), 161.1 (ArOH), 161.9 (CH=N). Anal. Calcd: C$_{45}$H$_{42}$N$_4$S$_3$O$_3$, C 69.02; H 5.41; N 7.16; Found: C 68.98; H 5.38; N 7.23.

Compound 2c

This compound was prepared by the same method as that of 2a, except that (336 mg, 3.0 mmol) thiophenecarbaldehyde was taken instead of 2-Pyridinecarbaldehyde. Purification of the crude product was carried out by column chromatography using neutral alumina. Pure product is solid and yellow in color. Yield = 80%; M. Pt. = 107 °C; IR 1635 cm^{-1}; FAB-MS [M]$^+$ = 752, ^{1}H-NMR (CDCl$_3$, 200 MHz): δ 2.83 (t, 6H, $-$CH$_2$, $J=4.0$ Hz), 2.99 (t, 6H, $-$CH$_2$, $J=4.2$ Hz), 6.92$-$7.97 (m, 3H, Ar), 7.07$-$7.19 (m, 9H, Ar), 7.26$-$7.31 (m, 3H, Ar), 7.46$-$7.50 (m, 6H, Ar), 8.46 (s, 3H, $-$CH=N). ^{13}C-NMR (CDCl$_3$, 50 MHz): δ 29.8 ($-$CH$_2$), 53.1 ($-$CH$_2$), 118.1 (Ar), 126.21 (Ar), 127.7 (Ar), 130.8 (Ar), 131.4 (Ar), 132.3 (Ar), 142.8 (Ar), 150.0 (Ar), 152.8 (CH=N). Anal. Calcd. C$_{39}$H$_{36}$N$_4$S$_6$, C 62.23; H 4.79; N 7.45; Found: C 62.49; H 5.00; N 7.57.

*Compound **2d***

Tripodal amine **1y** (326 mg, 1.0 mmol) was taken in dry methanol and (375 mg, 3.5 mmol) 2-pyridine carbaldehyde was added to it. The reaction mixture was allowed to stir and then was refluxed for 5 h. Upon completion of reaction, whole methanol was distilled off and the material was washed with diethyl ether several times. The pure ligand is a viscous, light brown material. Yield = 63%; IR 1640 cm^{-1}; FAB-MS [M]$^{+}$ = 593, ^{1}H-NMR (CDCl$_3$, 200 MHz): δ 2.66–2.81 (m, 12H, −CH$_2$), 2.88 (t, 6H, −CH$_2$, $J = 6.8$ Hz), 3.96 (t, 6H, −CH$_2$, $J = 6.6$ Hz), 7.30–7.38 (m, 3H, Ar), 8.10 (d, 3H, Ar, $J = 3.8$), 8.33 (s, 3H, Ar), 8.66 (d, 3H, Ar, $J = 4.0$ Hz), 8.87 (s, 3H, −CH═N). ^{13}C-NMR (CDCl$_3$, 50 MHz): δ 30.3 (−CH$_2$); 32.9 (−CH$_2$); 53.9 (−CH$_2$); 61.6 (−CH$_2$); 123.5 (Ar); 131.2 (Ar); 134.4 (Ar); 150.0 (Ar); 151.3 (Ar); 159.1 (CH═N).

*Compound **2e***

Tripodal amine **1y** (326 mg, 1.0 mmol) was taken in dry methanol and (366 mg, 3.0 mmol) salicyaldehyde was added to it. Allowed to stir the reaction at room temperature, yellow color appeared immediately in the reaction mixture and some viscous material started to separate out on the walls of reaction mixture. Took this viscous material and washed several times with chilled methanol to give a semisolid product. Yield = 68%; IR 1645 cm^{-1}; FAB-MS [M]$^{+}$ = 638, ^{1}H-NMR (CDCl$_3$, 200 MHz): δ 2.55–2.65 (m, 12H, −CH$_2$S), 2.83 (t, 6H, −CH$_2$N, $J = 6.6$ Hz), 3.75 (t, 6H, −CH$_2$N, $J = 6.6$ Hz), 6.83–7.01 (m, 6H, Ar), 7.23–7.53 (m, 6H, Ar), 8.33 (s, 3H, −CH═N), 13.27 (s, 3H, −OH), ^{13}C-NMR (CDCl$_3$, 75 MHz): δ 30.4 (−CH$_2$S), 33.2 (−CH$_2$S), 54.0 (−CH$_2$N), 59.2 (−CH$_2$N), 116.8 (Ar), 118.5 (Ar), 120.5 (Ar), 131.4 (Ar), 132.2 (Ar), 160.9 (Ar−OH), 165.8 (CH═N).

Extraction experiments

The percent extraction (%E) of metallic picrates (1.0 × 10^{-3} M, 2 ml) extracted from water to chloroform layer-containing ligand (1.0 × 10^{-3} M, 2 ml) was determined at 25 °C. Similarly the blank analysis was performed by taking metal picrate (1.0 × 10^{-3} M, 2 ml) dissolved in water and 2 ml of neat chloroform. Usually aliquot of chloroform layer (1 ml) was withdrawn with the syringe and diluted with acetonitrile to 10 ml and then the UV absorption were measured against CHCl$_3$:CH$_3$CN (1:9) solution at $\lambda_{\max} = 374$ nm. But this method could not be followed under present investigation because most of the ligands themselves had an absorption band near this wavelength. So alternatively the concentration of metal picrate in aqueous layer was determined after extraction and also in blank analysis. %E = (concentration of metal picrates in aqueous phase in blank analysis − concentration of metal picrate remain in aqueous phase after extraction) × 100/ (concentration of metal picrate in aqueous phase before extraction), the average value of three independent determinations is reported.

Transport experiments

Transport experiments were carried out in a cylindrical glass consisting of outer and inner jackets. Transport conditions: Source phase (aqueous solution of metal picrate 3 ml, 1.0 × 10^{-2} M); membrane phase (chloroform, 15 ml, 1.0 × 10^{-3} M); receiving phase (water, 10 ml); internal diameter of glass vial = 20 mm. After stirring for 6 h the amount of metal picrate transported in the outer aqueous phase was determined from UV absorption at 355 nm. Average value of three independent determinations was taken and results are reproducible. Blank experiments were also carried out in the absence of any ligand. In the blank experiments the metal picrates were not transported to the receiving phase except in the case of Pb^{2+} and some transtion metal ions, which shows significant transport and hence the results for the transportation of these metal ions are not reliable.

Metal complexation studies

The metal complexation studies were carried out by taking one equivalent of ligand in CDCl$_3$ and adding to it one equivalent of AgNO$_3$. The material was kept in the dark for some time to complete its complexation and then its ^{1}H- and ^{13}C-NMR spectra were recorded.

The stochiometry of the complex of Ag(I) with **2b** was determined by ^{1}H-NMR titration in CDCl$_3$:CD$_3$CN (3:2) as solvent. A series of ^{1}H-NMR spectra were recorded by adding 0.25 equivalent of metal salt each time and monitoring the shifts on −CH$_2$ protons, till further addition of metal salt did not cause any change in the spectra.

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