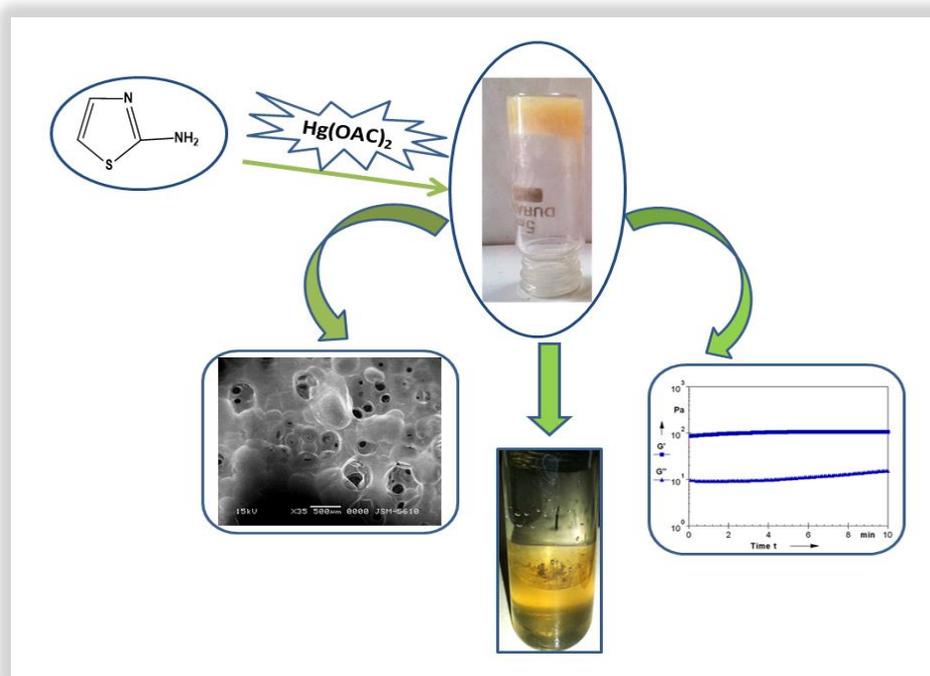


Chapter-5

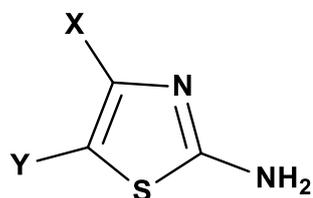


Room temperature metallogelation for a simple series of aminothiazole ligands with potential applications in identifying and scavenging mercury ions

5.1 Introduction

A metal-ligand mediated supramolecular assembly capable of immobilizing a solvent (aqueous, organic or both), commonly known as Metallogel¹⁻⁴ is relatively a new member to a vast family of supramolecular or non-covalent gels.⁵⁻⁷ Metal-organic frameworks (MOFs) such as metallogels are attractive not only for its designer aspect but also for many potential applications, namely, gas storage, molecular sieves, ion exchange, sensing, magnetism, catalysis, etc.³⁻⁴ Design and synthesis of new metallogels have to deal with many fundamental questions such as how the nature of metal centre, metal coordination geometry, ligands structural diversity, nature of counter ions, hydrogen bond, if any, effect the supramolecular assembly leading to entrapment of solvent. Moreover, real life application of supramolecular gelators requires room temperature gelation without the aid of external stimuli such as heat, light, etc. , which is observed quite rarely.⁸

In our search for simple low molecular mass gelators (LMOGs) we discovered melamine salt, 2-aminothiazole salt and aliphatic thiazole amide based hydrogelator/organogelator. Furthermore, 2-amino-4-methylthiazole is well documented as gravimetric agent for mercury (II) ion.⁹ However; thiazole moiety based metallogels are not well documented in literature. This prompted us to investigate and establish the thiazole moiety as a versatile structural backbone for supramolecular gelation with or without substitution. In the present study, various 2-aminothiazole and its derivatives, namely, 2-aminothiazole (**1a**), 2-amino-4-methylthiazole (**1b**) and 2-amino-5-methylthiazole (**1c**) (**Scheme 5.1**) were explored as ligands in metallogel formation. To the best of our knowledge ligands used in present study represent one of the simplest classes of ligands used for supramolecular metallogelation.



X=H, Y=H	1a
X=CH ₃ , Y=H	1b
X=H, Y=CH ₃	1c

Scheme 5.1 List of ligands used as Mercury (II) metallogel.

5.2 Experimental

5.2.1 Materials

2-Aminothiazole (97%), 2-Amino-4-methylthiazole (98%), 2-Amino-5-methylthiazole (98%), Mercuric acetate (98%) (All from Aldrich) were used as received. The other chemicals were of the highest commercial grade available and were used without further purification. The liquids used for the preparation of gels were reagent grade. All solvents used in the synthesis were purified, dried and distilled as required.

5.2.2 Instrumentation

5.2.2.1 FT-IR Spectroscopy

FT-IR Spectra were recorded on a perkin elmer –RX FTIR instrument. Solid samples were recorded as an intimate mixture with powdered KBr.

5.2.2.2 ¹HNMR Spectroscopy

The ¹HNMR spectra were measured by using a Bruker AVANCE, 400MHz, using TMS as internal standard and DMSO as solvent.

5.2.2.3 Scanning Electron Microscopic Study

Morphologies of all reported gel materials were investigated using scanning electron microscopy (SEM). For SEM study, solution of a gelator is placed on a SEM sample holder and allowed to form gel, which was then dried under vacuum to give xerogel, followed by recording micrographs in a SEM apparatus (JEOL JSM5610 LV microscope).

5.2.2.4 UV-visible Spectroscopy

The spectrum was recorded using Perkin Elmer UV-Visible Spectrometer.

5.2.2.5 Atomic absorption Spectroscopy (AAS)

Atomic absorption Spectroscopy (AAS) measurements were taken on a Perkin-Elmer Analyst 200. The detection limit for mercury was approximately 0.1 ppm. Mercury was analyzed with a wavelength of 253.652 nm. Two measurements were taken for each sample and averaged.

5.2.2.6 Rheological measurement

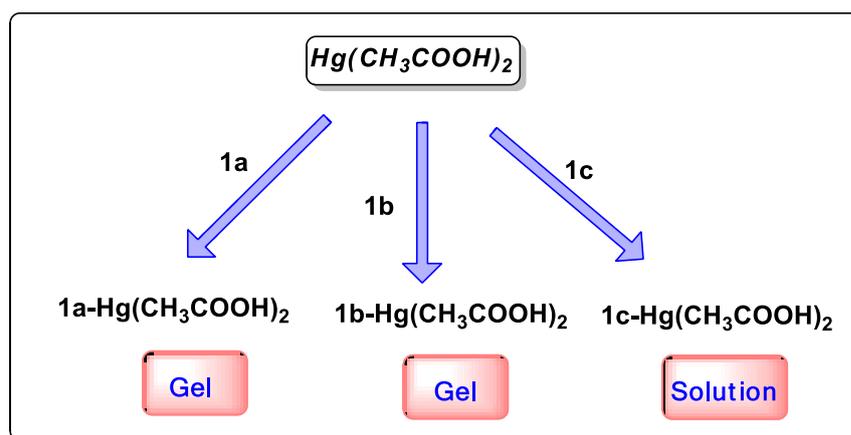
The shear viscosity was measured on an Anton Paar, Physica MCR 301 rheometer USA, using parallel plate PP50/P-PTD200 geometry (50 mm diameter; 0.1 mm gap). Temperature was maintained at 25 °C ± 1° C by Viscotherm VT2 circulating water bath. Linear viscoelastic properties (controlled deformation mode with 0.1%

strain) of gels were done in dynamic mode. All the dynamic rheological data were checked as a function of strain amplitude to ensure that the measurements were performed in the linear viscoelastic region. For frequency sweep measurements 0.06 – 600 s⁻¹ angular frequencies was applied to the samples at 0.1% strain. The G' and G'' were also monitored over a time sweep of 10 minutes at room temperature at 1 Hz frequency and 10% strain. All the measurements were made in triplicates.

5.2.3 Procedure

5.2.3.1 In situ Gel Formation

In a vial containing aqueous Hg(OAc)₂ (0.8 ml, 0.125M), methanolic solution of 1a, 1b and 1c (0.2 ml, 0.5M) was added (**Scheme 5.2**). Gel formation starts spontaneously if any. The sample vial was turned upside down to observe if the solution inside could still flow, to confirm the gel formation (**Table 5.1**).



Scheme 5.2 List of coordination polymers synthesized.

Table 5.1

	Hg(OAc) ₂	HgCl ₂	Ag(NO ₃) ₂	Co(OAc) ₂	Ni(OAc) ₂	Cd(OAc) ₂	Zn(OAc) ₂	Cu(OAc) ₂	Pb(OAc) ₂
1a	G(3.952)	P	P	S	S	S	S	S	P
1b	G(2.183)	P	P	S	S	S	S	S	P
1c	S	P	P	S	S	S	S	S	P

G=gel, S=Solution, P=precipitate () =minimum gel concentration in Wt %(W/V)

5.2.3.2 Gelation selectivity experiment

Methanolic solution of 1a-1c (0.2 ml, 0.5 M) was added in aqueous solution of $\text{Co}(\text{OAc})_2$, $\text{Ni}(\text{OAc})_2$, $\text{Cd}(\text{OAc})_2$, $\text{Cu}(\text{OAc})_2$, $\text{Zn}(\text{OAc})_2$, $\text{Pb}(\text{OAc})_2$, $\text{Ag}(\text{OAc})_2$ and HgCl_2 (0.8 ml, 0.125M). No gel was observed (**Table 5.1**).

5.2.3.3 Sample preparation for AAS analysis

25 ml 1000 ppm solution of $\text{Hg}(\text{OAc})_2$ was taken in a sample vial and ligands 1a/1b dissolved in 1 mL water (12/25 mg) added in the sample water directly. The complexation starts within few seconds. Whole system was kept as such overnight and then it was filtered. 10 ml filtered solution is taken for the analysis using AAS.

5.2.3.4 Sample preparation for job's plot

The samples were prepared by extraction of the 0.1 ml solution from an in situ complex in different M/L ($\text{Hg}(\text{OAc})_2/1a$) ratio, by micropipet and diluted with water. The spectrum was recorded using UV-Visible Spectrometer.

5.3 Results and discussion

Various metal salts such as $\text{Co}(\text{OAc})_2$, $\text{Ni}(\text{OAc})_2$, $\text{Cd}(\text{OAc})_2$, $\text{Cu}(\text{OAc})_2$, $\text{Zn}(\text{OAc})_2$, $\text{Pb}(\text{OAc})_2$, $\text{Ag}(\text{NO}_3)_2$, were used for making coordination complex/ polymer of thiazole derivatives **1a-1c** (**Table-5.1**). To our delight co-ordination polymer formed between 4-methyl-2-amino thiazole (**1b**) and $\text{Hg}(\text{OAc})_2$ turned out to be excellent metallogel at room temperature (25°C) without the aid of any external stimuli, whereas other metal acetate salts turned out to be solution or precipitate. The non-thermoreversible nature and very little solubility of synthesized compounds in all the common organic solvents and water suggested the formation of coordination polymers. Furthermore, coordination polymers, synthesized in the present study were characterized by Job's method, IR spectroscopy and NMR spectroscopy and the metallogels formed from 1a- $\text{Hg}(\text{OAc})_2$ and 1b- $\text{Hg}(\text{OAc})_2$ were characterized using the inverse tube method, SEM, T_{gel} , and rheological experiments.

Spontaneous room temperature gelation is not frequently observed phenomenon in supramolecular gelation. Understandably, breaking and formation of new non-covalent bonds leading to three-dimensional network capable of immobilizing a solvent requires some energy (heat, light, sound, electric) or favourable environmental condition such as pH, dielectric constant. Here we report a first example of room temperature mercury based metallogellation of water. The only other example of Hg^{2+}

based metellogelation was reported by Anne J. McNeil and co-worker,¹⁰ which required heating to induce gelation. Room temperature gelation of water has been triggered by adding methanolic solution of **1a** and **1b** (1 equiv.) in aqueous solution of mercury acetate, $\text{Hg}(\text{OAc})_2$ (1 equiv.), whereas methanolic solution of **1c** when reacted with $\text{Hg}(\text{OAc})_2$ leads to the formation of solution(**Figure 5.1**). When **1a** and **1b** was dissolved in various solvents such as ethanol, chloroform or water and added to aqueous solution of $\text{Hg}(\text{OAc})_2$ selective gelation of aqueous layer was observed. Metellogelation of **1a** and **1b** was selective not only towards Hg^{2+} ion but also towards the counter anion of Hg^{2+} . The counter ion acetate (OAc^-) found to be important for realization of gelation of solvent as Chloride ion (Cl^-) under the similar condition led to precipitates (**Figure 5.2**). The preference of OAc^- ion over Cl^- ion in metellogelation may be attributed to capability of acetate ion to form coordination polymer/complex through two oxygen atoms¹¹ as well as stronger binding strength of Cl^- than OAc^- towards cationic mercury⁹.

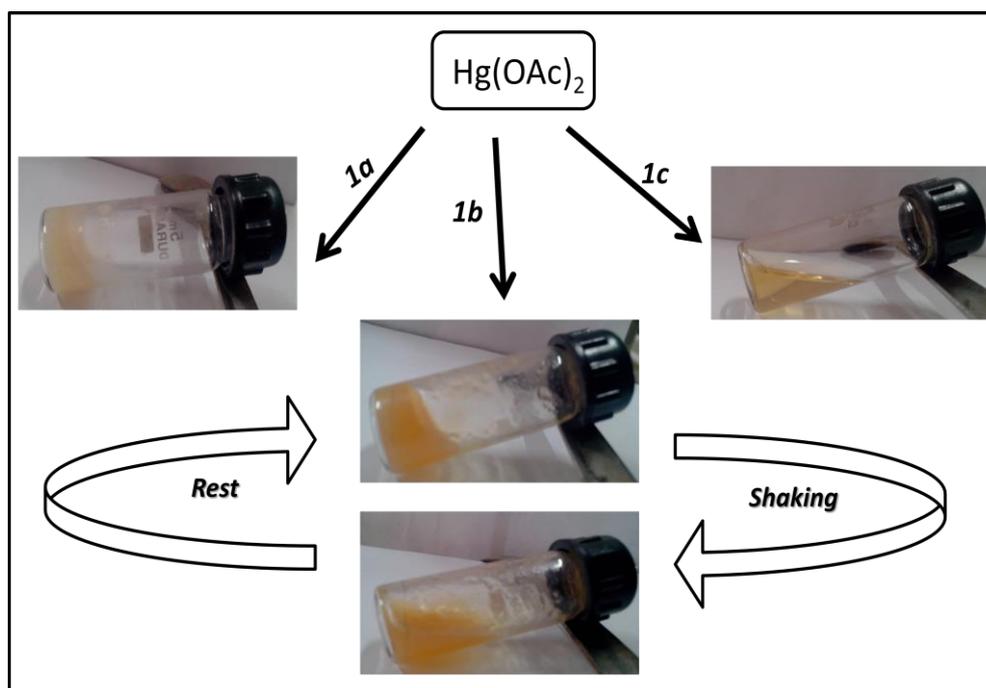


Figure 5.1 Photographic images of selective gelation and thixotropic behaviour of the gels.

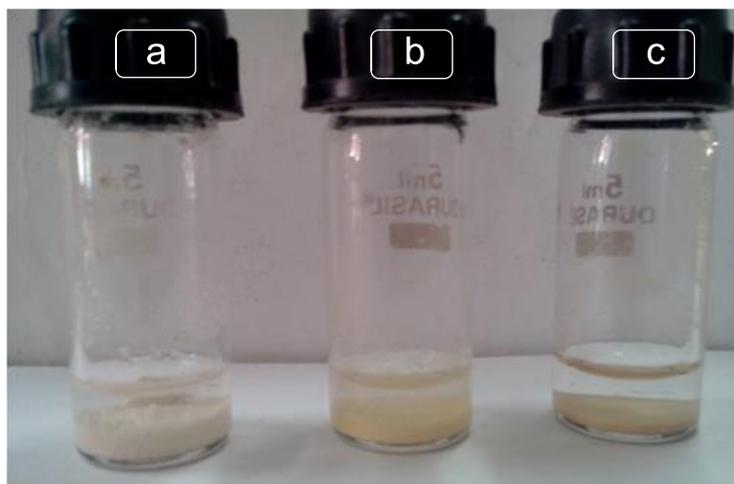


Figure 5.2 Selectivity tests showing the results of adding aq. solutions of HgCl_2 to methanolic solution of (a) **1a** (b)**1b** and (c)**1c**

Interestingly, $1b\text{-Hg(OAc)}_2$ showed “thixotropic” behaviour. When the test tube containing the gel was shaken, gel network broke down and the sample started flowing. However, when the sample was allowed to rest for a few minutes, the sample regained its shape and properties (**Figure 5.1**). Thixotropic behaviour is indeed quite unusual for gels derived from LMOGs, even though it is desirable for many industrial applications.¹²

The minimum gelator concentrations (mgc) of $1a\text{-Hg(OAc)}_2$ and $1b\text{-Hg(OAc)}_2$ were found to be 3.95 and 2.18wt% (w/v), respectively. The gel-sol transition temperature (T_{gel}) measurements were carried out using the drop-ball method. The T_{gel} measurements of $1a\text{-Hg(OAc)}_2$ and $1b\text{-Hg(OAc)}_2$ were unsuccessful due to water bubbling out at 100°C without complete breakdowns of the gelator networks, proving the non-thermoreversible nature of the coordination polymer based metallogels.

The metallogels formed from $1a\text{-Hg(OAc)}_2$ and $1b\text{-Hg(OAc)}_2$ were further characterized by rheological experiments. The magnitude of the storage modulus (G') was found to be an order of magnitude higher than the loss modulus (G'') for both the gel samples representing the true behaviour of the viscoelastic gelmaterials (**Figure 5.3**).

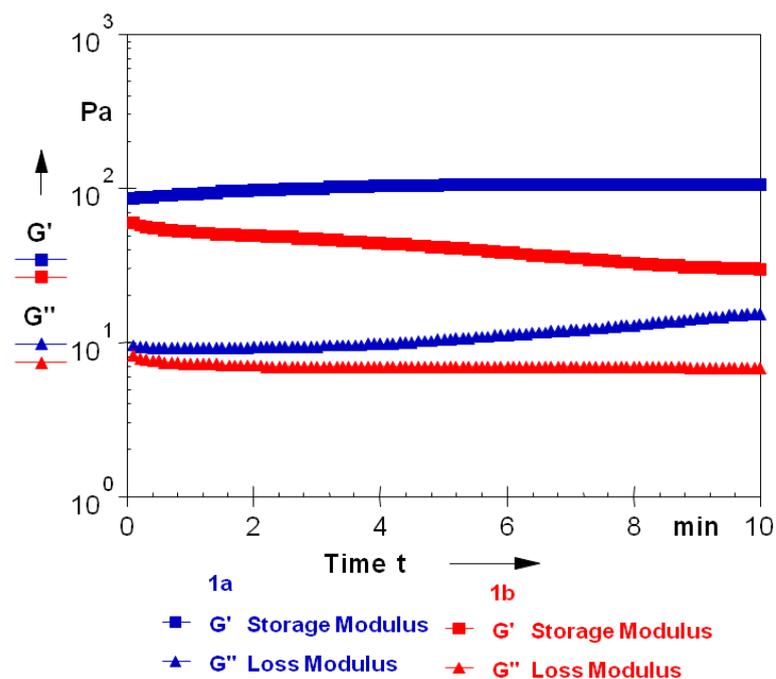


Figure 5.3 Rheological studies of the metallogels formed from 1a–Hg(OAc)₂ and 1b–Hg(OAc)₂.

The thixotropic behavior of the hydrogel (1b–Hg(OAc)₂) was also confirmed using rheology by conducting a series of shear stress loop tests (**Figure 5.4**).¹³⁻¹⁴

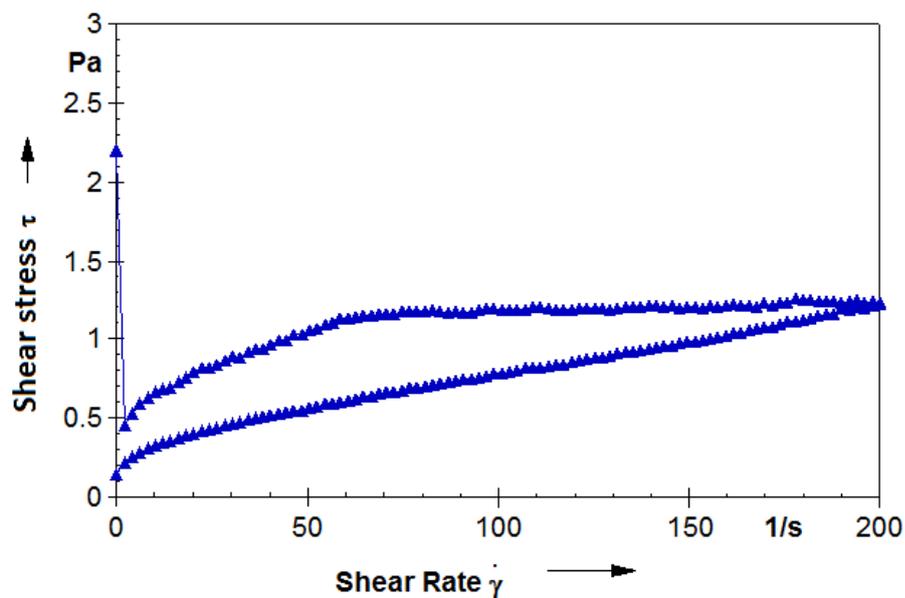


Figure 5.4 Shear stress vs shear rate graph for thixotropic hydrogel composed of 1b–Hg(OAc)₂.

Hysteresis was recognized using the hysteresis loop technique, where the shear rate is increased linearly from zero to a maximum value, followed by decreasing it to zero at the same rate. This technique quickly demonstrates that thixotropic behavior is present in 1b-Hg(OAc)₂.

To get an insight into the gelator morphologies, SEM studies were carried out on the xerogels (dried gels) obtained by reacting 1a and 1b with Hg(OAc)₂ in 1 : 1 ratios. The SEM image of the xerogel of 1b-Hg(OAc)₂ obtained from water showed a continuous three-dimensional network with some cavities or pores. In contrast, the xerogel obtained from 1a-Hg(OAc)₂ showed a more open, macroporous structure. The better strength of the metallo-gel of 1b-Hg(OAc)₂ compared with 1a-Hg(OAc)₂ may be attributed to the robust 3-D network of the xerogel (**Figure 5.5**).

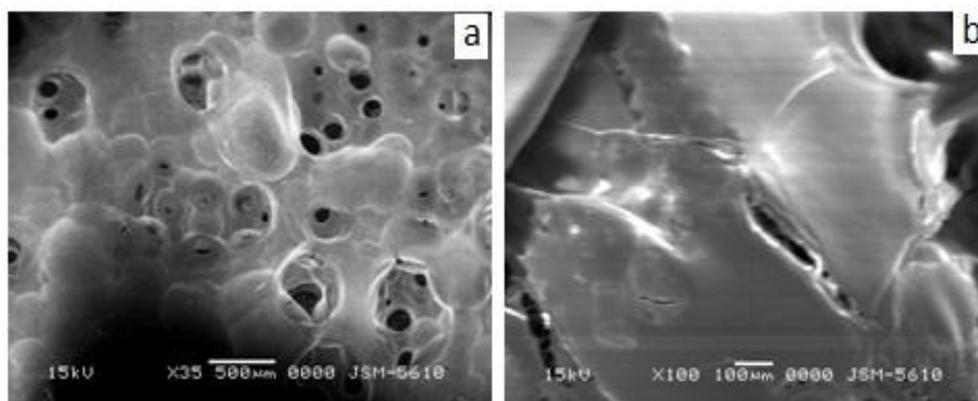


Figure 5.5 SEM images of the xerogels formed from 1:1 mixtures of (a) 1a (b) 1b with Hg(OAc)₂.

One of the major challenges is to understand the three dimensional network of gelling molecules mediated by metal-ligand complexation, especially in the absence of suitable single crystal X-ray studies.

The molar ratio of ligand to mercury acetate was found to be 1:1 as proved by Job's plot (**Figure 5.6**). The coordinative interaction as well as the probable hydrogen bonds between Hg(OAc)₂ and ligand **1a-1c** was studied by shifts in position of ¹HNMR peaks¹⁵⁻¹⁶ (**Figure 5.7**).

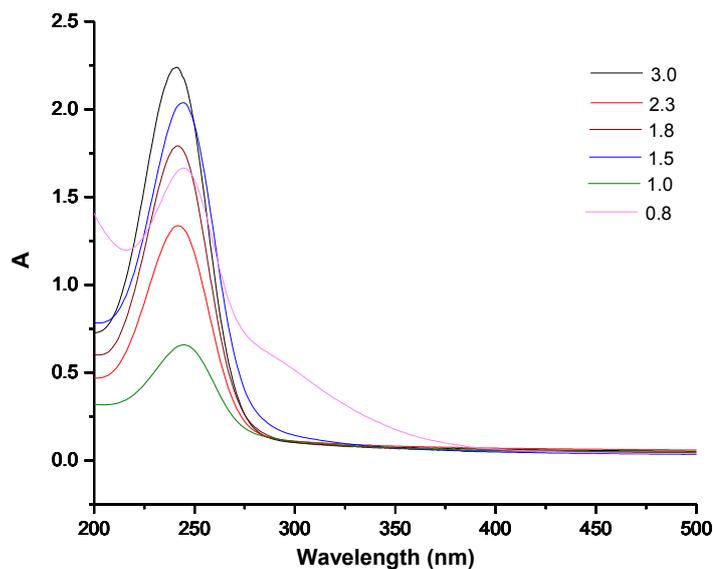


Figure 5.6 Uv-visible spectra of 1a/Hg(OAc)₂ system in different mole ratio(3.0-0.8).

The addition of Hg(OAc)₂ to 1a shifted the signals of the protons adjacent to the thiazole ring nitrogen atom and the addition of Hg(OAc)₂ to 1b caused a significant shift for the -CH₃ protons (neighbouring the ring nitrogen atom). The other peaks remained almost unaffected. This suggests the participation of the thiazole ring proton as well as methyl protons in hydrogen bonding in 1a-Hg(OAc)₂ and 1b-Hg(OAc)₂, respectively. The shift in the position of the methyl protons may be attributed to intermolecular hydrogen bonding, such as C_(methyl)-H.....S_(thiazole). Surprisingly, on the addition of Hg(OAc)₂ to 1c, the proton signal of the adjacent group to the thiazole ring N atoms as well as the methyl protons signal remained unaltered, while the signal of the -NH₂ protons shifted (**Table 5.2**), suggesting the participation of the -NH₂ protons in hydrogen bonding. The lack of participation of the methyl protons in hydrogen bonding in the supramolecular network of the coordination polymer 1c-Hg(OAc)₂ due to its position on the thiazole ring seems to govern the gelation behaviour of the metallogel.

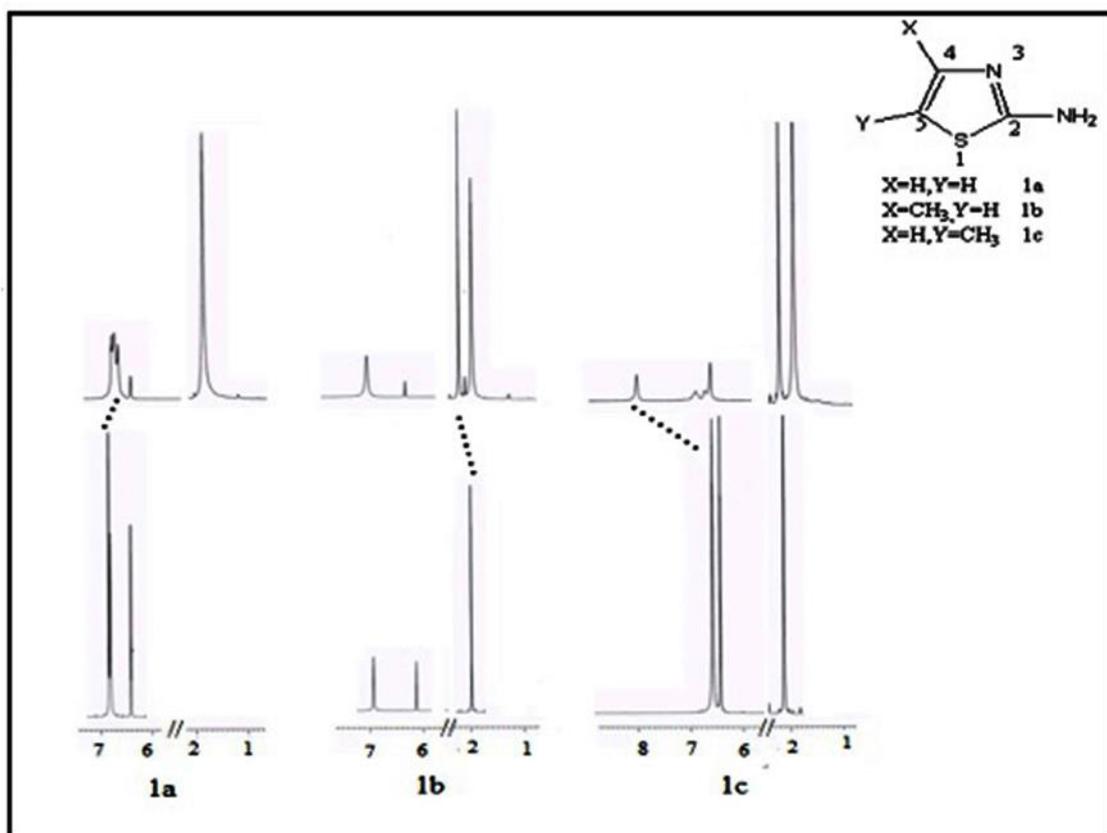


Figure 5.7 ^1H NMR of 1a-1c (lower) and $\text{Hg}(\text{OAc})_2/1\text{a-1c}$ (upper) in DMSO.

Table 5.2 ^1H NMR shift assignments of ligands(1a-1c) and its $\text{Hg}(\text{II})$ complexes

	1a	Hg-1a complex	1b	Hg-1b complex	1c	Hg-1c complex
C(4)-H	6.894	6.782	-	-	6.567	6.463
C(5)-H	6.541	6.537	6.075	6.071	-	-
C(4)-CH ₃	-	-	2.048	2.158	-	-
C(5)-CH ₃	-	-	-	-	2.173	2.150
-NH ₂	6.917	6.921	6.788	6.782	6.648	7.865

FT-IR studies of the free ligands (1a- 1c) and their complexes with $\text{Hg}(\text{OAc})_2$ were carried out (**Figure 5.8 and Table 5.3**). Very broad peaks at $3400\text{--}3200\text{ cm}^{-1}$ were observed in all the IR spectra of the coordination complexes indicating the presence of hydrogen bonds. The shift of $\nu(\text{C}=\text{N})$ at 1504 cm^{-1} in the ligand 1a to 1519 cm^{-1} can be attributed to the coordination of $\text{Hg}(\text{II})$ to the ring nitrogen atom. Additional peaks at 1560 cm^{-1} [$\nu_{\text{asym}}(\text{CO}_2)$], 1405 cm^{-1} [$\nu_{\text{sym}}(\text{CO}_2)$] and 438 cm^{-1} [$\nu(\text{M}-\text{N})$] were obtained in the spectrum of the metal complex. Similar results were observed for the coordination polymers $1\text{b}-\text{Hg}(\text{OAc})_2$ and $1\text{c}-\text{Hg}(\text{OAc})_2$. The IR spectra of all the coordination polymers suggested the formation of bridging or chelating interactions of the acetate functional group, as the difference in the stretching frequency of CO_{sym} and CO_{asym} was found to be about 150 cm^{-1} .¹¹

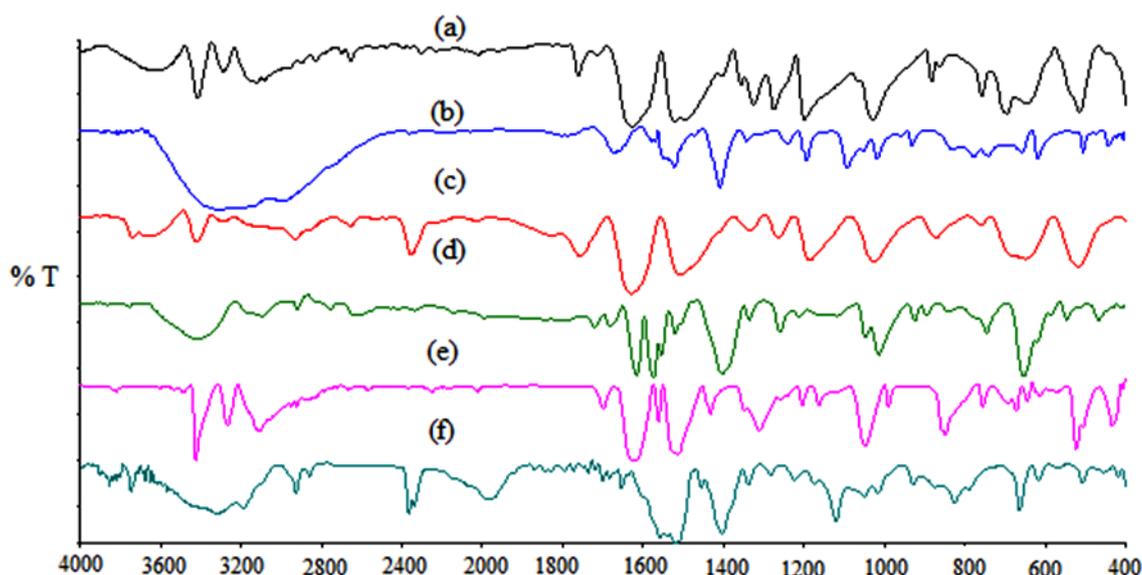
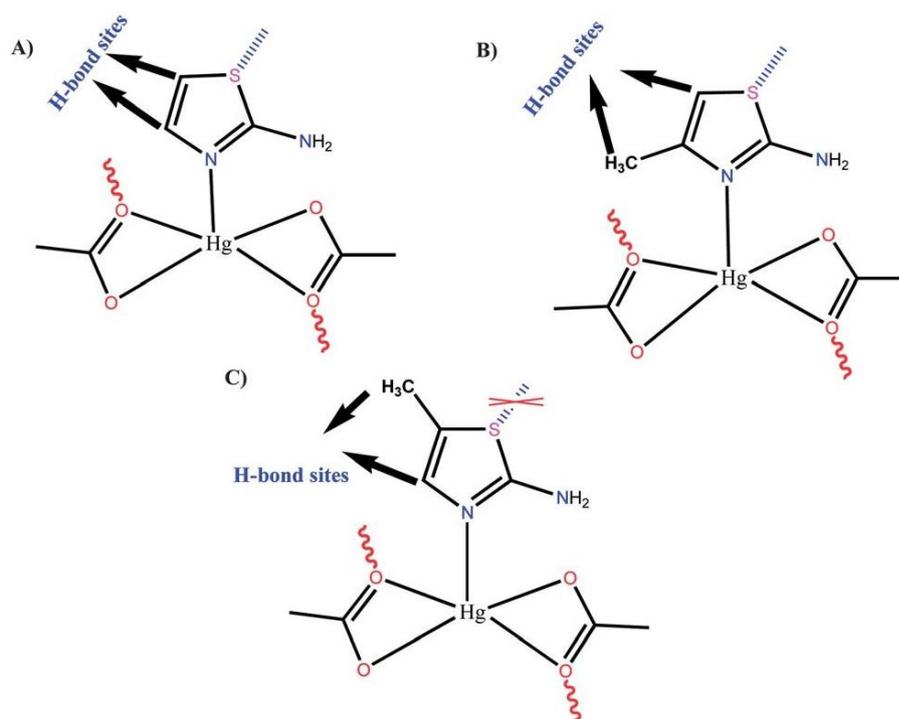


Figure 5.8 FT-IR spectra of ligands 1a (a), 1b(c), 1c (e) and that of their complexes with $\text{Hg}(\text{II})$, Hg-1a complex (b), Hg-1b complex (d), Hg-1c complex (f).

Table 5.3 IR peak shift assignments of ligands(1a-1c) and its Hg(II)complexes

	ν (C=N)	ν (C-S)	ν_{asym} (CO ₂)	ν_{sym} (CO ₂)	ν (M-N)
1a	1504	860	-	-	-
Hg-1a complex	1519	854	1560	1405	438
1b	1506	841	-	-	-
Hg-1b complex	1518	839	1551	1400	460
1c	1514	847	-	-	-
Hg-1c complex	1518	839	1557	1402	432

Evidently, suitable positioning of the methyl group on the thiazole moiety enhanced the gelation behaviour. On the other hand, the presence of the methyl group at position 5 on the thiazole ring totally destroyed the gelation property. We propose that a 1-D coordination polymer leads to fibers, which may further entangled among themselves through weak C–H...N and/or C–H...S interactions as observed in our earlier studies. Simple partial charge calculations of 1a–1c were carried out to ascertain the role and position of the methyl group in the coordination bond formation and the probable H-bond.¹⁷ No significant changes in the partial charges on the ring nitrogen and sulphur atoms were observed, suggesting similar coordination bonding interactions in all three coordination polymers. We propose that the coordination polymer 1c–Hg(OAc)₂ showed no gelation behaviour towards any solvent studied in the present study due to changes in the overall supramolecular assembly and the lack of C_(methyl)–H...S interactions due to steric hindrance of the neighbouring bulky methyl group. Probable coordination polymeric networks of 1a–Hg(OAc)₂, 1b–Hg(OAc)₂ and 1c–Hg(OAc)₂ are shown in **Scheme 5.3**.



Scheme 5.3 Probable coordination polymeric networks of (A) 1a–Hg(OAc)₂, (B) 1b–Hg(OAc)₂ and (C) 1c–Hg(OAc)₂. Hashed bonds show the probable intermolecular hydrogen bonds and the crosses on them indicate a low probability.

A high selectivity and efficiency in the complexation of ligands 1a and 1b towards mercury ions prompted us to explore the role of metallogels in eliminating the mercury contamination from drinking water. Mercury pollution in water is a severe hazard to natural ecosystems. A variety of methods are currently used to remove mercury from water, which include photoremediation, bioremediation, activated carbon adsorption, solvent extractions, etc.¹⁸ Chemical reagents such as thiol based ligands are very attractive for mercury removal from aqueous systems. However, the practical utility of chemical methods is challenged due to leaching of precipitates into the water causing ecological risks. Effective removal of mercury from water will be facilitated if mercury can form a stable metallogel, which can be easily skimmed off or filtered from polluted water. We used metallogels 1a–Hg(OAc)₂ and 1b–Hg(OAc)₂ for the effective detection and removal of Hg²⁺ ions. We found that when the water sample containing Hg(II) ions was treated with a 1 wt% (w/v) solution of 1b in chloroform, a metallogel was formed at the interface. This simple method of visual observation of gel formation (slight yellowish in colour) at the interface between

CHCl_3 and water indicated the presence of mercury ions in the water samples. The detection limit of mercury ions without any optical aid was found to be 0.1 ppm in a 50 ml water sample (**Figure 5.9**).

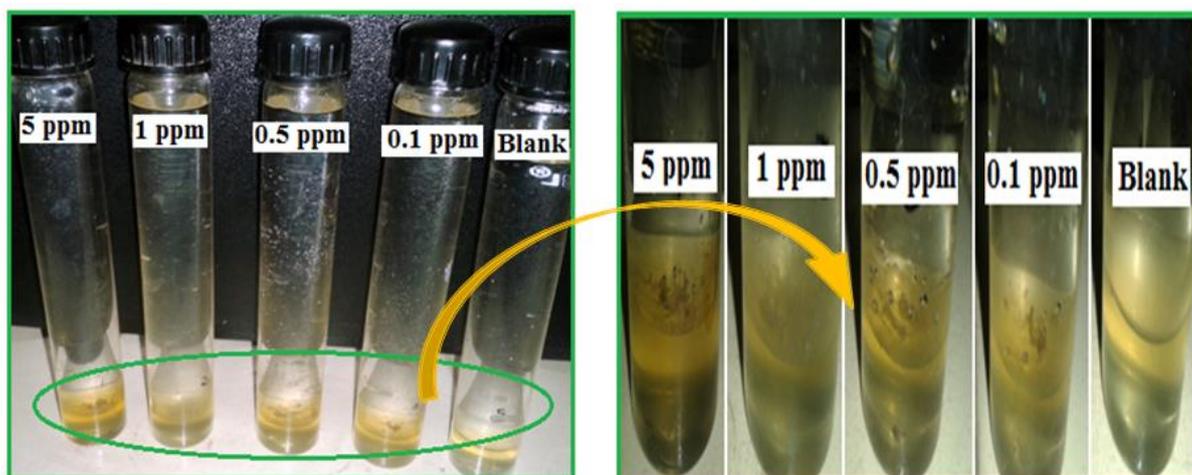


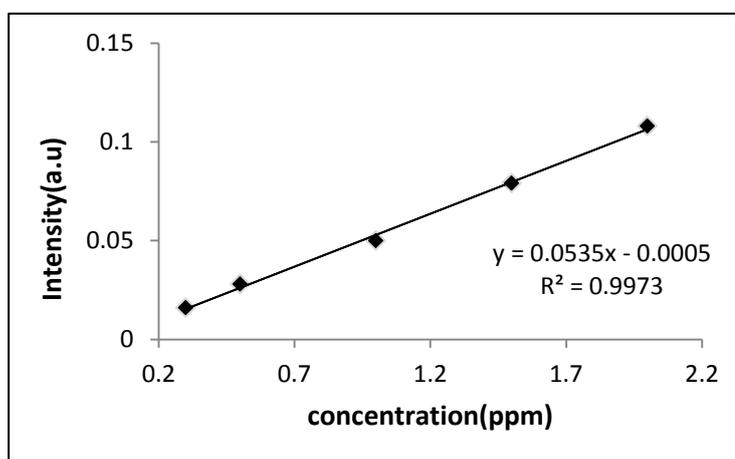
Figure 5.9 Photographic images to show detection of Hg^{2+} in biphasic water/ CHCl_3 system.

To explore the quantitative removal of Hg^{2+} ions from water samples, a controlled experiment was carried out. A stock solution of 1000 ppm $\text{Hg}(\text{OAc})_2$ was reacted with methanolic solutions of ligand 1a or 1b giving rise to spontaneous gelation. The resultant metallogel could easily be skimmed off (manually) or filtered using common filter paper. The filtrate collected was subjected to AAS analysis to reveal the amount of mercury remaining in the water sample. The water sample polluted with mercury ions (1000 ppm) and treated with 1b, showed a remarkable decrease in the mercury ion concentration in the solution after the gelation process, i.e. 1.0–0.5 ppm of mercury ions (**Table 5.4**). A calibration curve was generated by preparing four standard solutions (**Figure 5.10**). We present a simple and efficient way of detecting and removing mercury ions from polluted water.

Table 5.4 AAS data of the mercury concentration remaining after gelation

Ligand	ligand(mg)	[Hg] ₀ (ppm)	[Hg] _a (ppm)
1a	12	961.5	1.0
1a	25	961.5	0.7
1b	12	961.5	0.9
1b	25	961.5	0.5

[Hg]₀= initial concentration of Hg(OAc)₂ in water sample, [Hg]_a= remaining concentration of Hg(OAc)₂ in water sample after gelation.

**Figure 5.10** Calibration curve for AAS detection of Hg(OAc)₂.

5.4 Conclusions

Synthesis and characterization of coordination polymers based on aminothiazole ligands (1a–1c) with $\text{Hg}(\text{OAc})_2$ has been carried out. Coordination polymers, 1a– $\text{Hg}(\text{OAc})_2$ and 1b– $\text{Hg}(\text{OAc})_2$ demonstrated room temperature gelation of water along with thixotropic behaviour for 1b– $\text{Hg}(\text{OAc})_2$. The role of the methyl functional group in controlling and enhancing the gelation behaviour has been demonstrated. Coordination polymer based metallogels were found to be an ideal candidate for mercury ion detection (detection limits as low as 0.1 ppm with visual observation in a biphasic system of water/chloroform) and almost quantitative removal of Hg^{2+} ions from contaminated water.

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