

Room temperature metellogelation in a simple series of aminothiazole ligands with potential application in identification and scavenging mercury ion

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Supporting information

Materials:

All reagent grade materials were purchased from Sigma-Aldrich and used as received. The solvents used for the preparation of gels were purified, dried and distilled as required.

Instrumentation:

FTIR spectroscopy: FTIR Spectra were recorded on a Perkin Elmer –RX FTIR instrument. Solid samples were recorded as an intimate mixture with powdered KBr.

NMR Experiments: The ¹H- NMR spectra were measured by using a Bruker AVANCE, 400MHZ for ¹H-NMR with TMS as internal standard and DMSO as solvent.

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

UV-visible Spectroscopy: The samples were prepared by extraction of the 0.1 ml solution from an in situ complex in different M/L (Hg(OAc)₂/1a) ration ,by micropipet and diluted with H₂O (to 5 mL) , and the spectrum was recorded using Perkin Elmer UV-Visible Spectrometer.

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. A calibration curve was generated by preparing 4 standard solutions (**SI-Fig-5**). Two measurements were taken for each sample and averaged (**SI-Table-4**).

Rheological Measurment: 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 frequency 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.

Experimental

In situ Gel Formation – in a vial containing Hg(OAc)₂ (0.1mmol, dissolved in 0.8 ml water), Methanolic solution of 1a and 1b (0.2 ml,0.5M) was added. Gel formation starts spontaneously. Within few seconds entire system got converted to gel. The sample vial was turned upside down to observe if the solution inside could still flow, to confirm the gel formation (Table-1).

Complex Formation- Methanolic solution of 1a-1c (0.2 ml,0.5 M) was added in aqueous solution of Co(OAc)₂, Ni(OAc)₂, Cd(OAc)₂, Cu(OAc)₂,Zn(OAc)₂,Pb(OAc)₂,Ag(OAc)₂and HgCl₂ (0.1 mmol dissolved in 0.8ml water).No one of them could form gel. (Table-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

Sample preparation for AAS analysis-25 ml 1000 ppm solution of Hg(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

Table-S1

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

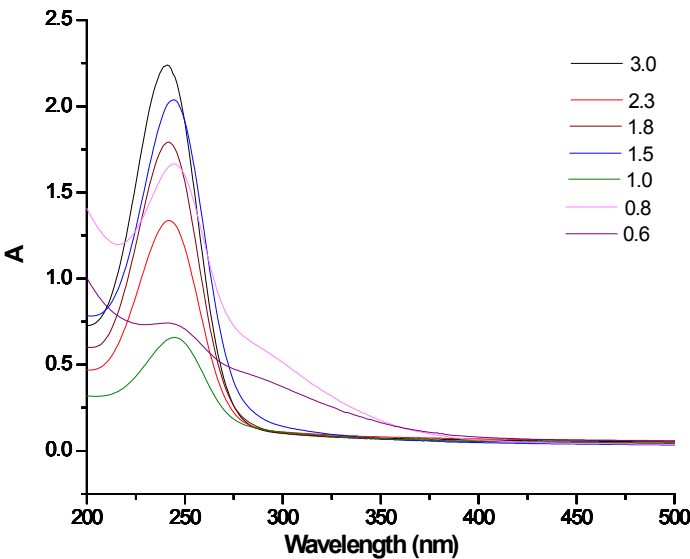


Fig.S1: UV-visible spectra of 1a/Hg(OAc)₂ system in different mole ratio(3.0-0.5)

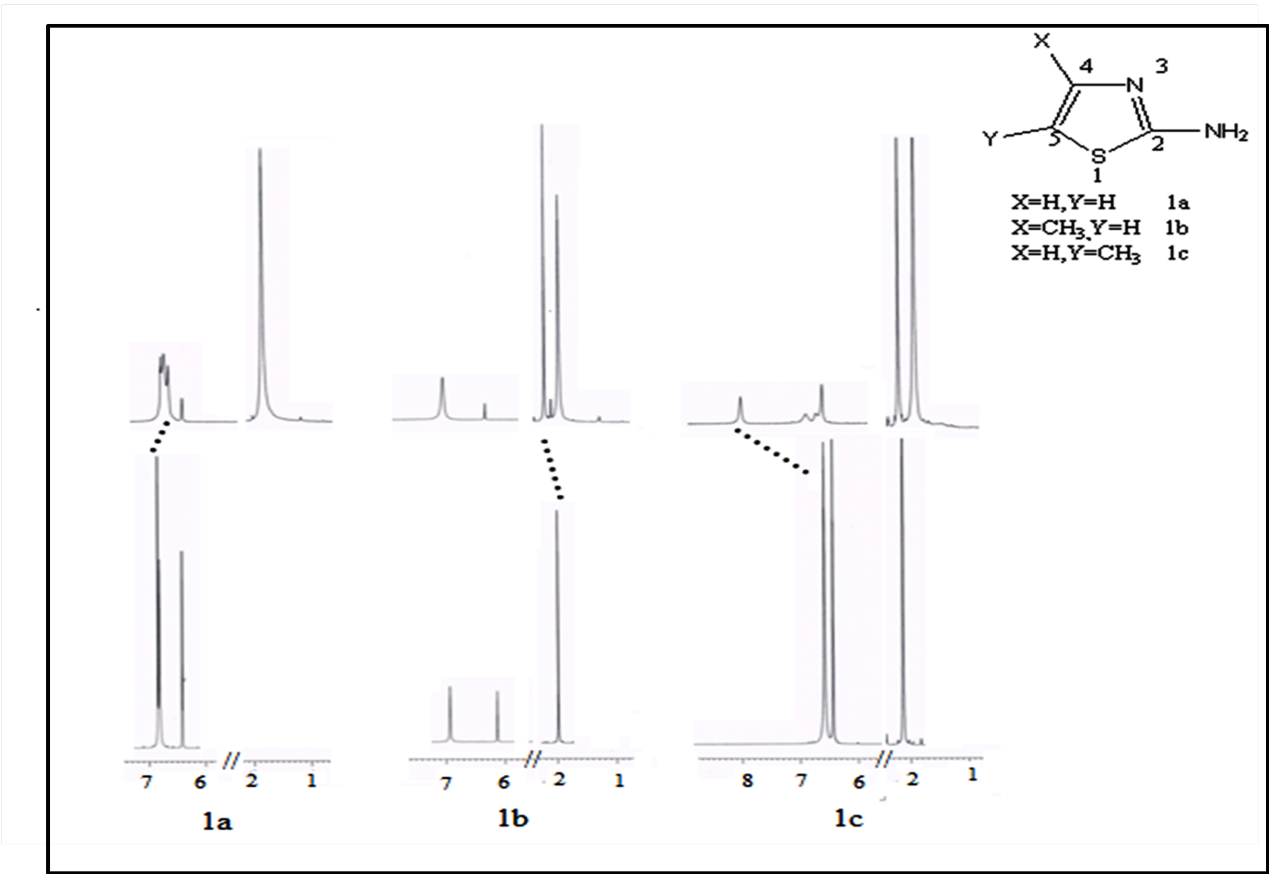


Fig. S2: ¹H NMR of 1a-1c (lower) and Hg(OAc)₂/1a-1c (upper) in DMSO

Table S2: ¹H NMR shift assignments of ligands(1a-1c) and its Hg(II)complexes

	1a	Hg-1a complex	1b	Hg-1b complex	1c	Hg-1c complex
C(4)-H	6.894	6.782	-	-	6.567	6.563
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

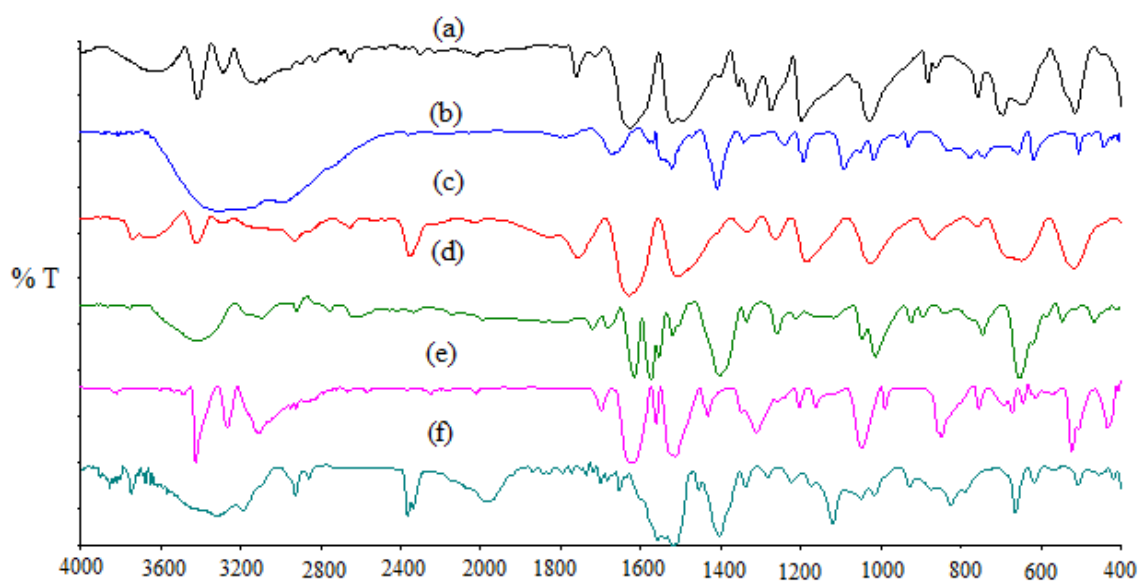


Fig. S3: FT-IR spectra of ligands 1a(a),1b(c),1c(e) and that of their complexes with Hg(II), *Hg-1a complex (b), Hg-1b complex (d), Hg-1c complex (f)*

TableS3: 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

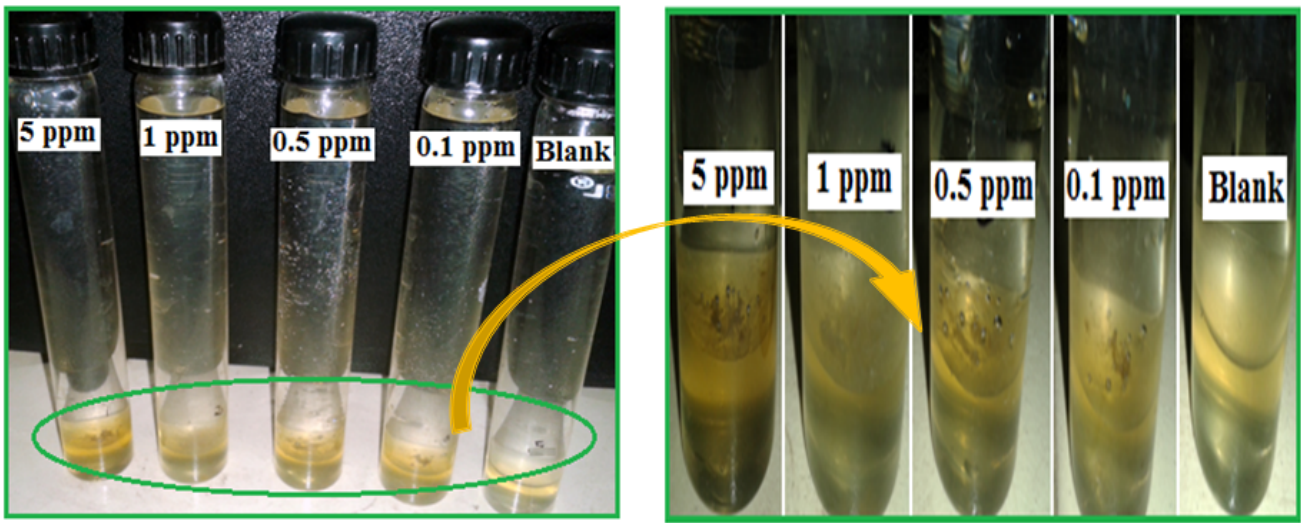


Fig. S4: Photographic image to show detection of Hg^{2+} in biphasic water/ CHCl_3 system

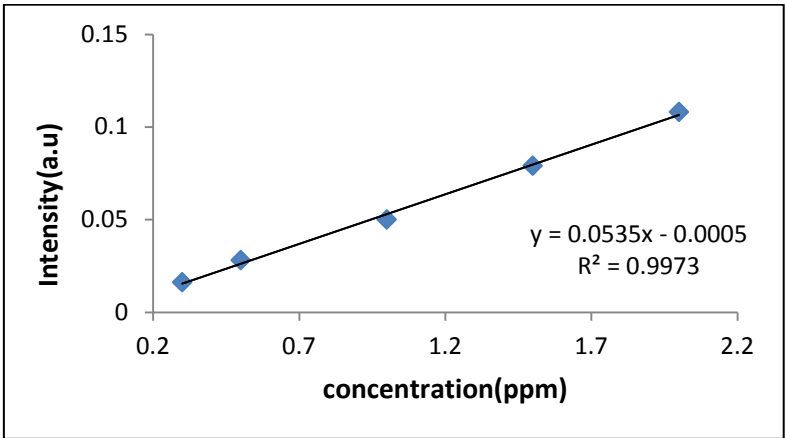


Fig.S5: Calibration curve for AAS detection of Hg^{2+}

TableS4: 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 $\text{Hg}(\text{OAc})_2$ in water sample, [Hg]_a= remaining concentration of $\text{Hg}(\text{OAc})_2$ in water sample after gelation