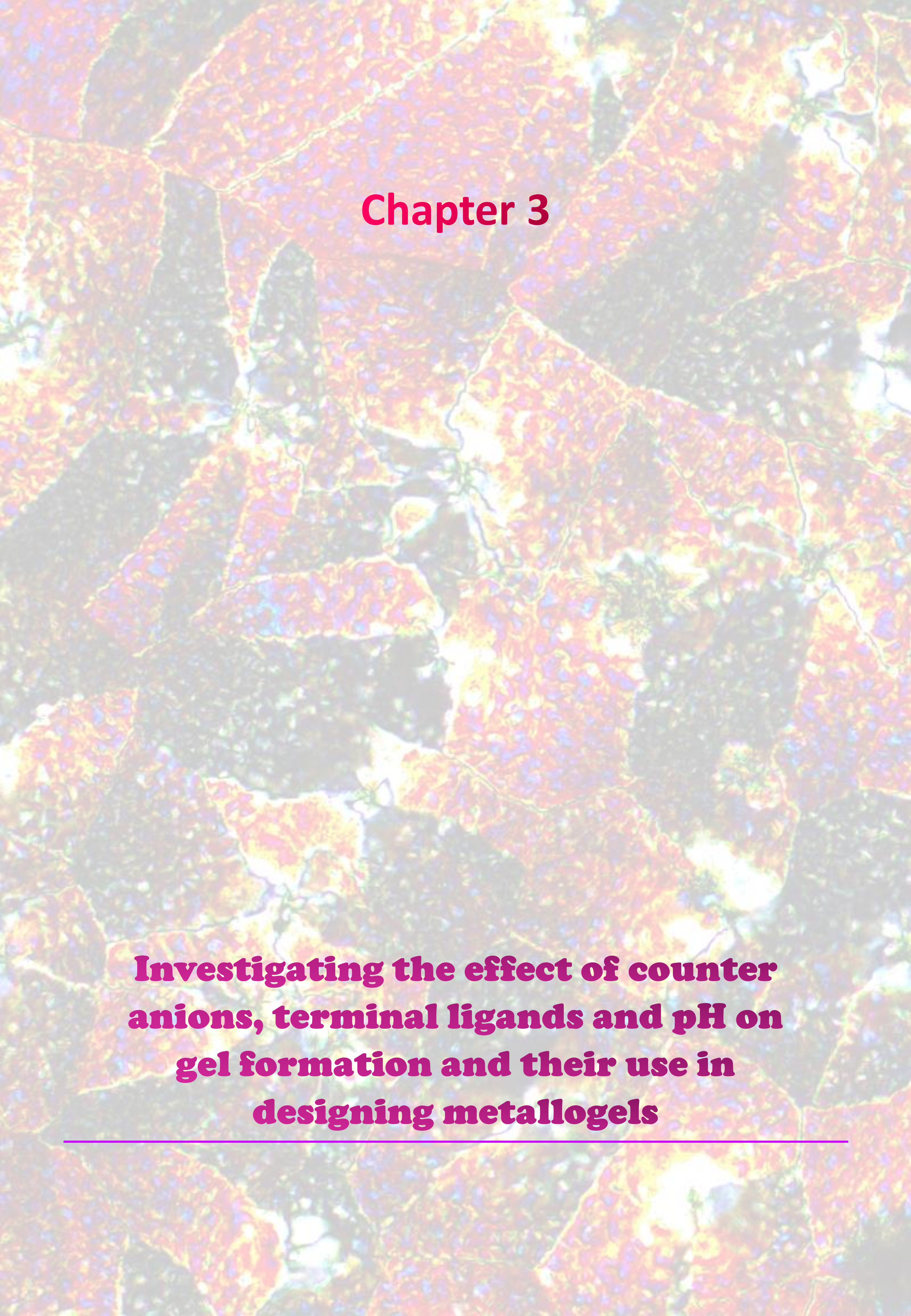

Chapter 3

Investigating the effect of counter anions, terminal ligands and pH on gel formation and their use in designing metallogels

Chapter 3 Investigating the effect of counter anions, terminal ligands and pH on gel formation and their use in designing metallogels

3.1 Introduction

Supramolecular Gels are a result of the entrapment of a liquid /gas in a complex supramolecular network resulting from the non-covalent interactions like H-bonding and π-π stacking within smaller chemical entities. There is a fine line separating the gelation from solution or crystalline solid phases. If the non-covalent interactions existing in the supramolecular system are very strong the system might end up as a precipitate or as a crystal; on the other hand, if the interactions are very weak it may end up in a solution phase. The gel formation takes place only when the extent of the non-covalent interactions is optimum enough not to end up in a solution or a solid as mentioned before. Even though the gel formation to date is considered as an instance of chemical serendipity, there have been several attempts made to synthesize and design gelator molecules that end up forming a gel[1–6]. Apart from the non-covalent interactions as mentioned before, the gel formation also depends on many other factors like temperature, pH and the use of solvents. As far as metallogels are concerned, the presence of metal ion/atom brings in one more factor of variance. Here the gel formation not just depends on the nature of the metal ion/atom present in the supramolecular system, but also on the oxidation state and the % of the metal ion/atom present. Metallogels have metal atoms/ions as an integral part of the supramolecular systems ending up in the metallogel formation. Metals can lead to the formation of metallogels in 2 ways (i) metal-ligand interaction leading to the formation of metallogels by the addition of metal ions. The metal or metal ion can also be present in the form of a nanoparticles adhered in the structure of the gel. Here, metal ions do not form a discrete well-defined complex with the ligands. (ii) Formation of a metal-ligand coordination complex which itself acts as a gelator and leads to the formation of a metallogel.[7]

Apart from the above-mentioned factors that influence the gel formation, counter anions also have a significant role in deciding the gel formation and the properties of gels.

Steed *et. al.* in 2009 reported a bis(pyridylurea) ligand which in itself is not a LMWG, however, in presence of copper(II) chloride it lead to the formation of a metallogel. The gel formation, however, does not take place in presence of nitrate as anion. The authors reported the gel formation in presence of 0.5 equivalents of copper(II) chloride added to the bis(pyridylurea) ligand with methanol as a solvent. Only partial gelation was reported in presence of 0.1 equivalents of copper(II) chloride. Addition of 0.2-0.5

equivalents of copper(II) chloride resulted in the entire solvent immobilization, leading to the gel formation. Beyond 0.5 equivalents of copper(II) chloride the entire system precipitated and no gel formation was reported.

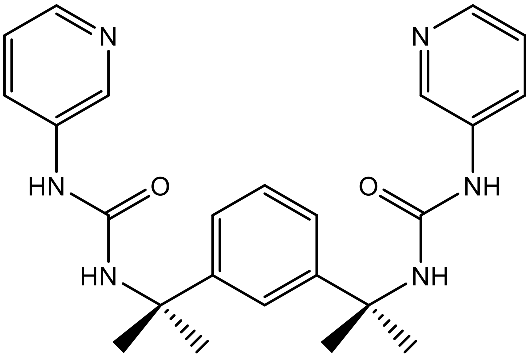

Figure 3.1.1 Structure of bis(pyridylurea) ligand which forms metallogel in presence of 0.5 equivalents of copper(II).

It was also observed that the T_{gel} was found to be highly dependent on the amount of copper(II); for 0.2 equivalents of metal salt, T_{gel} was found to be 34 ± 2 °C, rising to 63° ± 2 °C for 0.3 equivalents of copper(II) chloride. At further higher concentrations the T_{gel} reached the boiling point of the solvent.[8]

Nandi *et. al.* reported the formation of a metastable hydrogel formed by a Ag(I)-melamine coordination polymer in the molar ratio of 1:1 and 1:2. The authors reported the formation of 1:2 hydrogel to be highly dependent on the presence of the counter anion. The system precipitates when CH_3COO^- and BF_4^- are used as counter anions for silver(I). The presence of ClO_4^- lead to the crystallization of the system and did not end up as hydrogel. Gel formation was achieved when NO_3^- was used as counter anion, the authors reported that the probable reason for the hydrogel formation in presence of nitrate as counter ion was due to its small size. The gel formation was also observed to be highly specific for the metal ion and took place in presence of silver(I) only. Gel formation did not take place when metal ions like Cu^{1+}, Cu^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Mg^{2+}, Cd^{2+}, Hg^{2+}, Au^{3+}, Fe^{2+}, Fe^{3+} and Pb^{2+} were used instead of silver(I).[9]

Supramolecular gels of **pyridyl-N-oxide amides** with zinc(II) chloride and cadmium(II) chloride with water as a medium were reported by Damodaran *et. al.*[10] The formation and stability of the gels was highly anion dependent.

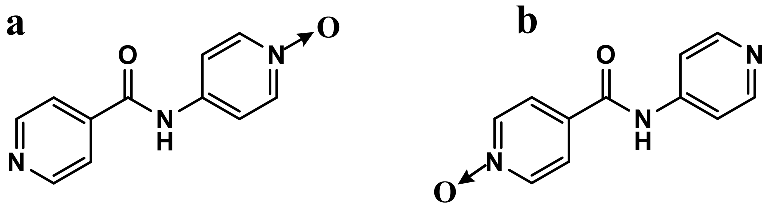

Figure 3.1.2 Structures of the ligands (a) and (b) forming metallogels with Zinc(II)chloride or Cadmium(II)chloride.

It was reported that the metallogels formed in presence of zinc(II) chloride collapsed in presence of cyanide, fluoride and iodide anions. The cadmium(II) chloride gels were stable in presence of halides but were reported to collapse in presence of cyanide anion. The reason for the collapse was suggested as the fact that cyanide being a stronger ligand, it can scavenge Cd^{2+}, making the gelator molecules free from the polymeric structure thus resulting in instability of the gels.[10]

Addition of anions always does not necessarily end up in deformation or collapsing of a metallogel. Among such reports, Yin and Lin reported two similar gelators containing acylhydrazone moiety. Yin reported that the ligand as shown in the **Figure 3.1.3 (a)** binds to Hg^{2+} to form metallogel. Among various anions (Br^-, AcO^-, I^-, F^-, Cl^-, $H_2PO_4^-$, HSO_4^-, N_3^-, SCN^-, S^{2-}, ClO_4^- and CN^-), the addition of CN^- resulted in demetallation reaction and it resulted in gel-to-gel transition.[11]

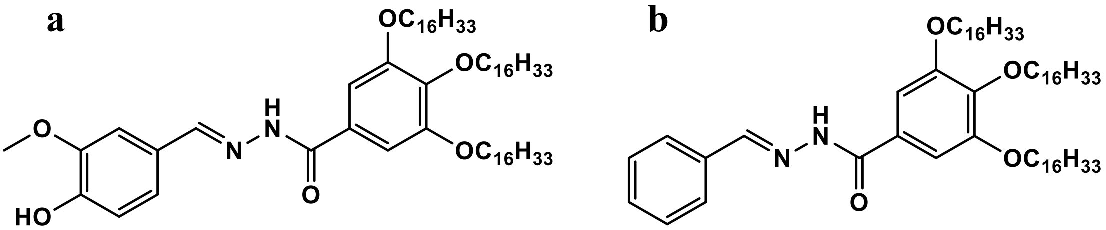

Figure 3.1.3 Structure of the ligand acylhyrazone (a) and (b) forming metallogels.

Lin reported another acylhydrazone ligand as shown in **Figure 3.1.3 (b)** that binds to Cu^{2+}, Fe^{3+}, Hg^{2+} and Cr^{3+} to form metallogel in DMF. The metallogel of Cu^{2+} and Fe^{3+} showed selective response to CN^-, SCN^-, S^{2-}, I^- and exhibited gel to gel transition.[12] There have also been reports where gelation was induced by the addition of the anions. Pandey *et al.* designed a complex Zn-TRPA-2 [4'-(4-(prop-2-yn-1-yloxy)phenyl)-2,2':6',2"-terpyridine], which underwent selectively Cl^- triggered gelation to afford metallogel ZTP2G.

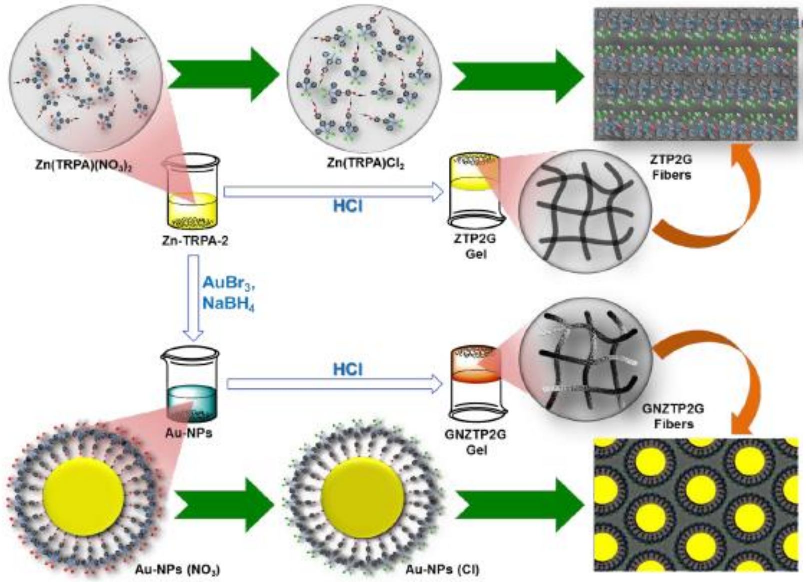

Figure 3.1.4 A plausible mechanistic view for the external and internal construction of ZTP2G and GNZTP2G fibres. (Image adapted with permission from ref.[13] reported by Pandey *et. al*. Copyright The Royal Society of Chemistry).

As shown in the **Figure 3.1.4** metallogel GNZTP2G was produced by the addition of Au-NPs into ZTP2G, which displayed superior viscoelastic properties over ZTP2G.

Lee et. al reported the formation of a metallogel in methanol using silver(I) coordinated to oxyethylene-substituted bispyridine derivatives. The structure of the ligand was like dendrites and it resulted in the formation of coordination polymers or oligomers with Ag(I). It has been reported that the morphology of the structures depended on the presence of various anions like NO_3^-, BF_4^-, and $CF_3SO_3^-$. The addition of F^- or $C_2F_5CO_2^-$ to the system resulted in the conversion of gels to solution, thus destabilizing the gel network. These kind of sol to gel transitions were reported to be reversible. [14,15]

Wu *et. al.* reported the amide-bridged hybrid of an alkyl-substituted aryl moiety and a pyridyl unit which affords Ag^+-bridged dimer complex; the triflate salt of the Ag^+ complex as shown in the **Figure 3.1.5** gelates toluene/ethanol (10:1, v/v).

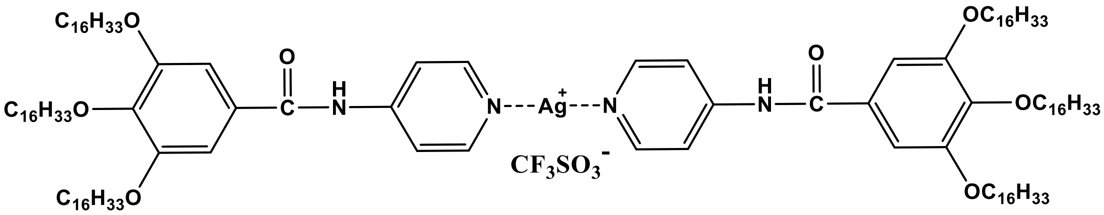

Figure 3.1.5 The structure of the coordination complex with Ag(I) leading to the formation of metallogel as reported by Wu *et. al.*[16]

They reported the precipitation in the form of AgI when KI was added to the above gelator system. The gel was reformed in the presence of excess Ag^+ salts. A similar behaviour of the gelator system was reported when Br^- or Cl^- was added in place of I^-.[16] Some of the anion-responsive supramolecular gels showed special properties and were reported to be selectively anion-sensitive. This property could be used as visual sensing of anions as gel-sol transition was observed upon addition of anions. Traditionally, most of the detection of anionic analytes are performed by using sophisticated instruments which are expensive and require highly trained personnel to operate them.[17–19] Thus, a gel-based visual detection can provide simple, cost-effective and mostly instrument-free technology. The detection of the anion can be done just by observing the gel-sol transition or by observing colour change during gel-to-gel transition. Among the anions, F^- and CN^- ions have been the most extensively studied. Detection of a particular anion by making use of the gels is still a fairly new phenomenon and the future holds a lot of promise.[20] However, there are very limited reports of the gelator molecules that are anion-responsive.[15] Despite a lot of efforts, the fact remains that it is still difficult to design and synthesize gelator molecules that are sensitive to particular anions and most of the anion-responsive gels were obtained by serendipity.

Thus, the detailed study on the relationship between structure and properties of gels is still necessary with the point of view of various applications. Adsorption and separation of some anions from waste, like CN^-, F^-, SCN^- that are toxic to humans, would be one such useful application.[21,22]

The exploration of anion-responsive supramolecular gels as well as their applications is still a hot topic in supramolecular chemistry and soft materials. Designing of the gelator molecules is very important in order to develop the gels that are sensitive to specific anions. However, designing such gels is very complex and difficult as it involves a lot on non-covalent interactions. In the present chapter, the anion dependence of trinuclear complex cation, $[Cu_3(H_3ins)(bipy)_3]^{3+}$, has been explored, by using various metal salts as starting materials for the gel formation and by adding different amounts of various anions to the preformed gels. Also, the effect of variation of alkali has been examined.

3.2 Experimental section

3.2.1 Materials

Cupric acetate monohydrate and 2,2'-bipyridine (bipy) were purchased from Qualigens; copper(II) bromide, myo-inositol (ins) and cesium carbonate were obtained from Sigma-Aldrich, NaOH was obtained from Merck and KOH was obtained from Qualigens.

Perchloric acid, formic acid, propionic acid, butyric acid, isobutyric acid, valeric acid, caproic acid and capric acid were obtained from Merck. Copper(II) sulphate pentahydrate, copper(II) nitrate trihydrate, copper(II) chloride dihydrate, oxalic acid, malonic acid, adipic acid, nickel(II) acetate tetrahydrate, cobalt(II) acetate tetrahydrate, zinc(II) acetate anhydrous, manganese(II) acetate tetrahydrate and lithium hydroxide were procured from SRL. Potassium carbonate was procured from LOBA and sodium carbonate was procured from SD Fine Chem Limited. Sodium bicarbonate, potassium bicarbonate, lithium carbonate and copper carbonate were procured from local manufacturers.

Sodium fluoride, sodium bromide, potassium iodide, sodium chloride, sodium sulphite, sodium peroxydisulfate, sodium nitrite, sodium nitrate, sodium sulphate, sodium bromate, potassium hydrogen phosphate, sodium isothiocyanato, potassium dichromate, potassium chromate were also obtained from local manufacturers. All the chemicals were AR or reagent grade and were used for synthesis without further purification.

Copper(II) formate dihydrate, copper(II) propionate, copper(II) butyrate, Copper(II) isobutyrate, copper(II) valerate, copper (II) caproate, copper(II) decanoate, copper(II) oxalate, copper(II) malonate and copper(II) adipate were prepared by the reaction of the corresponding carboxylic acids with cupric carbonate. These were purified by crystallization from water-ethanol.

3.2.2 Experiments to check gel formation by varying the anions in the metal salt

The basic reaction for the preparation of the gel-forming complex has been the reaction between 1 equivalent of **myo-inositol** with 3 equivalents of copper(II) acetate monohydrate and 3 equivalents of 2,2'-bipyridine (bipy). Instead of 3 equivalents of copper(II) acetate, varying amounts of different copper(II) salts were used.

Gelation using copper(II) sulphate and copper(II) acetate in varying ratios

Reaction using 0.75 equivalents of copper(II) sulphate pentahydrate + 2.25 equivalents of copper(II) acetate monohydrate*:* The reaction of 1 ml 2.5% aqueous solution (0.1388 mmol) of myo-inositol was carried out with 3 equivalents of $[Cu(bipy)]^{2+}$ complex obtained by reacting 0.078 g of copper sulphate and 0.0208 g of copper acetate with 0.0650 (0.4163 mmol) of bipy in 2.5 ml water**.** Subsequently, the pH was raised to 12 with aqueous sodium hydroxide. The solution was heated in oven at 60-70 °C for 30 minutes after which gel formation was verified.

The same procedure was repeated using different ratios of copper(II) acetate and copper(II) sulphate. The gel formation was tried using **1.5 equivalents** of copper(II) sulphate (0.0512 g) and **1.5 equivalents** of copper(II)acetate (0.04155 g), **2.25 equivalents** of copper(II) sulphate pentahydrate (0.026 g) and **0.75 equivalents** of copper(II) acetate monohydrate (0.062 g).

3 equivalents of **copper(II) sulphate** (0.1039 g) was also used for the synthesis of the gel instead of copper(II) carboxylate salts. The relative ratios of myo-inositol and 2,2'-bipyridine with respect to the copper(II) salts and the reaction conditions for the synthesis remained the same as discussed above.

Gelation using copper(II) chloride and copper(II) acetate in varying ratios

Reaction using 0.75 equivalents of copper(II) chloride dihydrate + 2.25 equivalents of copper(II) acetate monohydrate: The reaction of 1 ml 2.5% aqueous solution (0.1388 mmol) of myo-inositol was carried out with 3 equivalents of [Cu(bipy)]2+ complex obtained by reacting 0.0531 g of copper chloride and 0.0208 g of copper acetate with 0.0650 (0.4163 mmol) of bipy in 2.5 ml water. Subsequently, the pH was raised to 12 with aqueous sodium hydroxide. The solution was heated in oven at 60-70 °C for 30 minutes post which gel formation was verified. The same procedure was repeated using different ratios of copper(II) acetate and copper(II) chloride.

The gel formation was tried using **1.5 equivalents** of copper(II) chloride (0.0355 g) and **1.5 equivalents** of copper(II)acetate (0.04155 g), **2.25 equivalents** of copper(II)chloride (0.0177 g) and **0.75 equivalents** of copper(II)acetate (0.062 g).

3 equivalents of **copper(II) chloride** (0.0709 g) was also used for the synthesis of the gel instead of copper(II) carboxylate salts. The relative ratios of myo-inositol and 2,2'-bipyridine with respect to the copper(II) salts and other reaction conditions for the synthesis remained the same as discussed above.

Gelation using copper(II) nitrate and copper(II) acetate in varying ratios

Reaction using 0.75 equivalents of copper(II) nitrate trihydrate + 2.25 equivalents of copper(II) acetate monohydrate: The reaction of 1 ml 2.5% aqueous solution (0.1388 mmol) of myo-inositol was carried out with 3 equivalents of $[Cu(bipy)]^{2+}$ complex obtained by reacting 0.0754 g of copper nitrate and 0.0208 g of copper acetate with 0.0650 (0.4163 mmol) of bipy in 2.5 ml water**.** Subsequently, the pH was raised to 12 with aqueous sodium hydroxide. The solution was heated in oven at 60-70 °C for 30 minutes post which gel formation was verified. The same procedure was repeated using different ratios of copper(II) acetate and copper(II) nitrate.

The gel formation was tried using **1.5 equivalents** of copper(II) nitrate (0.5025 g) and **1.5 equivalents** of copper(II) acetate monohydrate (0.04155 g), **2.25 equivalents** of copper(II) nitrate (0.05125 g) and **0.75 equivalents** of copper(II) acetate monohydrate (0.062 g).

3 equivalents of **copper(II) nitrate** (1.005 g) was also used for the synthesis of the gel instead of copper(II) carboxylate salts. The relative ratios of myo-inositol and 2,2'-bipyridine with respect to the copper(II) salts and other reaction conditions for the synthesis remained the same as discussed above.

Gelation using copper(II) perchlorate and copper(II) bromide

The gel formation was tried using the same procedure as **scheme 2.2.2.1** and copper(II) perchlorate hexhydrate (0.155 g, 0.4163 mmol) and copper(II) bromide (0.0929 g, 0.4163 mmol) as source of copper(II). The relative ratios of myo-inositol (0.250 g, 0.1388 mmol) and 2,2'-bipyridine (0.650 g, 0.4163 mmol) with respect to the copper(II) salts and the reaction conditions for the synthesis remained the same. The results have been tabulated and discussed.

Gel formation with long chain alkyl carboxylate(II) salts

The reaction of 1 equivalent of **myo-inositol** with 3 equivalents of copper(II) acetate monohydrate and 3 equivalents of 2,2'-bipyridine (bipy) in presence of NaOH (pH=12) leads to the formation of metallogel post heating at a temperature of 60–70 °C for 30 minutes **(chapter 2, scheme 2.2.2.1)**.

Use of copper(II) formate dihydrate or copper(II) propionate instead of copper(II) acetate monohydrate also leads to the formation of metallogels as reported in chapter 2.

Apart from these copper(II) carboxylate salts, the above mentioned procedure was used to try gel formation by using copper(II) salts of alkyl carboxylates with longer alkyl chains. **Copper(II) butyrate** (0.0989 g, 0.4163 mmol), **copper(II) isobutyrate** (0.0989 g, 0.4163 mmol) and **copper(II) valerate** (0.111 g, 0.4163 mmol), **copper(II) salt of caproic acid** (C-6) (0.122, 0.4163 mmol) and **copper(II) salt of capric acid** (C-10) (0.169, 0.4163 mmol) were used as starting materials to try the gelation. The relative ratios of myo-inositol (0.250 g, 0.1388 mmol) and 2,2'-bipyridine (0.650 g, 0.4163 mmol) with respect to the copper(II) salts and the reaction conditions for the synthesis remained the same as discussed earlier in scheme **2.2.2.1**.

Gel formation in presence of copper(II) salts of dicarboxylic acids

The reaction of 1 equivalent of **myo-inositol** with 3 equivalents of copper(II) oxalate and 3 equivalents of **2,2'-bipyridine (bipy)** was carried out. The reaction of 1 ml 2.5% aqueous solution (0.1388 mmol) of myo-inositol was added to 3 equivalents of $[Cu(bipy)]^{2+}$ complex obtained by reacting 0.0631 g (0.4163 mmol) of copper oxalate with 0.0650 g (0.4163 mmol) of bipy in 2.5 ml water. Subsequently, the pH was raised to 12 with aqueous sodium hydroxide. The solution was heated in oven at 60-70 °C for 30 minutes post which gel formation was verified.

In place of copper(II) oxalate in the above reaction, 0.4163 mmol of **copper(II) malonate (0.0689 g)** and **copper(II) adipate (0.0864 g)** were also used as starting materials to check the formation of gels. The relative ratios of myo-inositol and 2,2'-bipyridine with respect to the dicarboxylate copper(II) salts and the reaction conditions for the synthesis remained the same as discussed above.

3.2.3 Metallogel formation in presence of various transition metal ions

The reaction of 1 equivalent of **myo-inositol** with 3 equivalents of **nickel(II) acetate tetrahydrate** and 3 equivalents of **2,2'-bipyridine (bipy)** was carried out. NaOH was chosen as an alkali in order elevate the pH of the solution to 12, at which gelation sets in. The reaction of 1 ml 2.5% aqueous solution (0.1388 mmol) of myo-inositol was carried out with 3 equivalents of $[Ni(bipy)]^{2+}$ complex obtained by reacting 0.103 g (0.4163 mmol) of nickel(II) acetate tetrahydrate with 0.0650 (0.4163 mmol) of bipy in 2.5 ml water**.** The solution was heated in oven at 60-70 °C for 30 minutes after which gel formation was verified.

The gel formation was tried using the procedure mentioned above with other transition metal ions. 0.4163 mmol of **zinc(II)acetate anhydrous (0.0764 g), manganese(II)**

acetate tetrahydrate (0.102 g) and **cobalt(II) acetate tetrahydrate (0.104 g)** were used in place of nickel(II) acetate tetrahydrate.

3.2.4 Tolerance of various anions by the gels formed by $[Cu_3(H_3ins)(bipy)_3](CH_3COO)_3$ complex metallogelator

The reaction of 10 mL of a 2.5% aqueous solution (1.388 mmol) of **myo-inositol** was carried out with 3 equivalents of $[Cu(bipy)]^{2+}$ complex obtained by reacting 0.831 g (4.163 mmol) of cupric acetate and 0.650 g (4.163 mmol) of bipy in 25 mL of water **(As mentioned in chapter 2, scheme 2.2.2.1.)**. Subsequently, the pH was raised to 12 with aqueous sodium hydroxide. The solution was held at 60–70 ˚C for 30 minutes and allowed to settle at room temperature to obtain the gel **(112)**. In order to check the effect of anions **300 μL** of this solution was taken in a glass vial before the gel formation sets in and various anions were added to it such that the **metal (copper): anion ratio** varied from **1:2 to 1:0.035.** This was done to check the tolerance of anions by the metallogels. The results have been Tabulated in the **Table 3.3.8** and discussed further.

3.2.5 Instrumentation and Techniques

Mass spectrometry: The ESI mass spectra of the hydrogels were recorded using a Waters UPLC-TCD or a Maxis Impact (Bruker) and an Applied Biosystem API 200 mass spectrometer.

3.3 Results and Discussion

Effect of variation of anions in the metal salt on gel formation

It was observed that the formation of the gels by the complex cation $[Cu_3(H_3ins)(bipy)_3]^{3+}$ is highly dependent on the presence of anions. Use of the salts of oxyanions like nitrate, sulphate and especially carboxylates resulted in the formation of gels. While the gel formation did not take place when copper chloride or copper nitrate was used as a starting material for preparing the complex. In order to explore the role of anions in the formation of gels, copper chloride, copper nitrate and copper sulphate were used with copper acetate in different ratios as starting materials. The results summarized in **Table 3.3.1** to **Table 3.3.3** clearly show that the alkyl carboxylate anions like acetate assists the gel formation while the presence of chloride is only tolerated to a certain extent when it is accommodated in the acetate gel. The gel formation did not take place when copper chloride alone was used as a starting material for preparing the complex. The tolerance of nitrate anions by the gel is even poorer, the presence of nitrate anions leads to precipitation even in smaller ratios and does not yield gel **(Table 3.3.2).** Unlike chloride and nitrate, the presence of sulphate is quite well tolerated **(Figure 3.3.1).** Furthermore, sulphate alone in the absence of acetate can also form a gel.

Table 3.3.1 Effect of different ratios of copper acetate and copper chloride as staring materials on metallogel formation

Sr No.	Copper Chloride (%)	Copper Acetate (%)	Result/Observation
1	0	100	Gel
2	25	75	Gel + solid
3	50	50	Gel + solid
4	75	25	Gel + solid
5	100	0	Precipitation

Table 3.3.2 Effect of different ratios of copper acetate and copper sulphate as staring materials on metallogel formation

Sr No.	Copper Sulphate (%)	Copper Acetate (%)	Result/Observation
1	0	100	Gel
2	25	75	Gel
3	50	50	Gel
4	75	25	Gel
5	100	0	Gel

Table 3.3.3 Effect of different ratios of copper acetate and copper nitrate as staring materials on metallogel formation

Sr No.	Copper Nitrate (%)	Copper Acetate (%)	Result/Observation
1	0	100	Gel
2	25	75	Precipitation
3	50	50	Precipitation
4	75	25	Precipitation
5	100	0	Precipitation

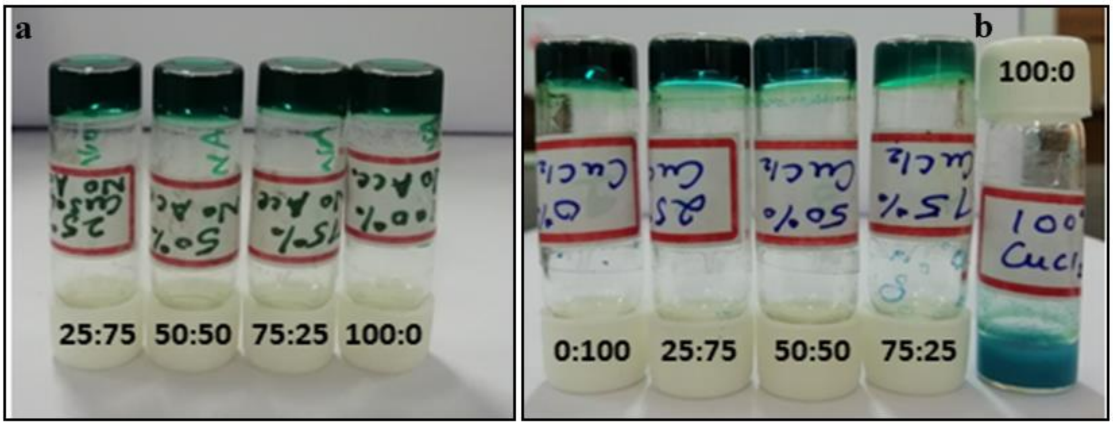

Figure 3.3.1 Effect of different ratios of copper chloride: copper acetate (a) and copper sulphate copper acetate (b) on gel formation.

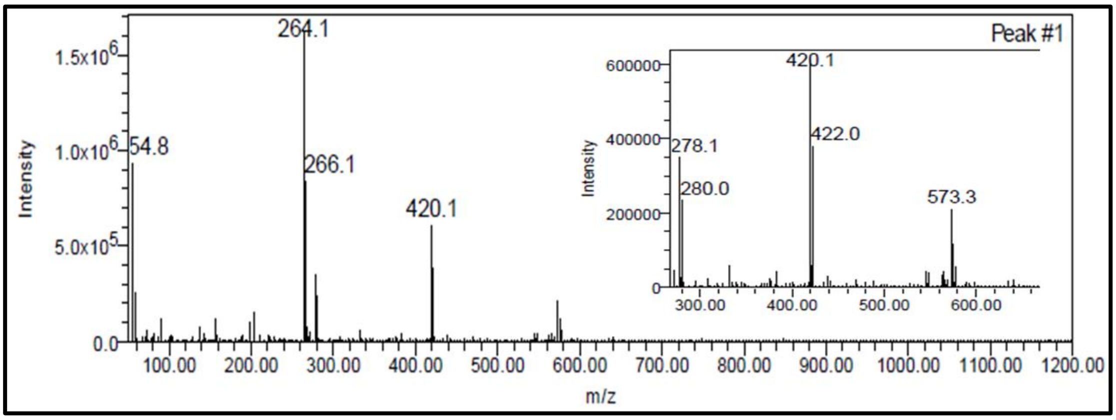

Figure 3.3.2 ESI-MS of the metallogel formed by the trinuclear copper complex synthesized using copper sulphate as starting material.

As it can be clearly seen in the **Figure 3.3.1,** the presence of sulphate anions like alkyl carboxylates assists in the formation of gels. Even when copper sulphate was used as a starting material in place of alkyl carboxylate copper salts, the metallogel formation could still be achieved. In order to prove that the trinuclear metallogelator remains the same, ESI-MS of the synthesized gels was carried out.

In the mass spectrum of this sulphate containing gel **(Figure 3.3.2)** the peaks corresponding to the trinuclear complex cation $[Cu_3(H_3ins)(bipy)_3]^{3+}$ were observed at m/z = 278 and 280 as in all carboxylate gels. This further supports the existence of the trinuclear trication $[Cu_3(H_3ins)(bipy)_3]^{3+}$ as the species involved in the supramolecular gel forming assembly. This also emphasizes the significant role played by the anions in the formation of the supramolecular gel forming assembly and the fact that these are multicomponent gels rather than being formed by a single gelator and that the kind of interactions present are of very complex nature.

From the studies mentioned earlier it can be concluded that the anions present as a part of the starting material in copper salts do play a significant role in the gel formation. Thus, apart from copper sulphate, copper nitrate and copper chloride, other copper salts were also used as starting material as mentioned in the **Table 3.3.4.**

Table 3.3.4 Use of different copper salts as starting material for gel formation

Sr No.	Copper salt	Observation
1	$CuCl_2$	Precipitation
2	$CuBr_2$	Precipitation
3	$CuSO_4$	Gel
4	$Cu(NO)_3$	Precipitation
5	$Cu(ClO_4)_2$	Precipitation

The metallogels are a supramolecular system, the formation of which only depends on the trinuclear complex and the bases used but also depends on the counter anion and the metals that are used. As discussed above in **Table 3.3.4** certain anions assist in gel formation while in presence of some anions like nitrate, perchlorate the gel formation does not take place. It was concluded from the studies in chapter 2 that in presence of alkyl carboxylate anions the gel formation takes place. It has also been reported in the previous chapter that the T_{gel} of the metallogels depends on the length of the alkyl chain. In the previous chapter different alkyl carboxylates like formate, acetate and propionate were used and it was observed that the T_{gel} value increases as the chain length of the carbon atom in the alkyl carboxylates increases.[23] Thus, it was thought to explore other carboxylate anions as the starting material. Copper(II) butyrate, copper(II) isobutyrate and copper(II) valerate were synthesized by the reaction of copper carbonate with butyric acid, isobutyric and valeric acid respectively. The salts thus synthesized were used as starting compounds in place of cupric acetate for the prepatation of gels and it was observed that the metallogel formation takes place in presence of all the 3 salts. However, when the carbon atoms in the alkyl carboxylate salts goes beyond 5 the gel formation does not take place. No gel formation was achieved when the salts of caproic (hexanoic acid) and capric acid (decanoic acid) with copper(II) were used as starting materials. Low solubility of these copper salts in aqueous media might be a reason for which they are unable to entrap water molecules and form gels. The results have been summarized in the **Table 3.3.5.** NaOH was used as an alkali in all these experiments to maintain pH and to assist the formation of assembly and gel formation.

Table 3.3.5 Use of different copper carboxylates salts as starting material for gel formation

Sr No.	Copper salt	No of carbon atoms	Observation
1	Cu-formate	1	Gel
2	Cu-acetate	2	Gel
3	Cu-propionate	3	Gel
4	Cu-butyrate	4	Gel
5	Cu-isobutyrate	4	Gel
6	Cu-valerate	5	Gel
7	Cu-caproate	6	No Gel
8	Cu-decanoate	10	No Gel

Apart from the copper salts of monocarboxylic acids, copper(II) dicarboxylates were also used as starting compounds to check gel formation in presence of dicarboxylates. Copper oxalate, copper malonate and copper adipate were synthesized by the reaction of copper carbonate with oxalic acid, malonic acid and adipic acid, respectively. The gel formation was achieved when copper oxalate and copper malonate were used as salts for the synthesis of trinuclear copper(II) complex. When copper adipate was used as a starting material, the gel formed was unstable and hazy. This is observation is similar to the long chain monocarboxylates. This is mainly because of low solubility of copper carboxylates having longer carbon chains resulting in precipitation rather than gel formation.

Table 3.3.6 Use of different copper(II) dicarboxylates salts as starting material for gel formation

Sr No.	Copper salt	No of carbon atoms	Observation
1	Cu-oxalate	2	Gel
2	Cu-malonate	3	Gel
3	Cu-adipate	6	Hazy Gel

The metallogels synthesized using the trinuclear complex have copper(II) as the metal center. Copper(II) generally prefers 4-coordinate geometry and forms a square planar complex which can result in the formation of stacks of complex molecules over each other. These stacks are held together by the CO_3^{2-} or OH^- anions present in the solution when carbonate or hydroxide bases are used. These anions must be occupying the axial positions in copper(II) through weak coordination, thus helping the supramolecular assembly. It was thought of interest to check if other transition metal ions preferring 4 coordination or having resemblance with copper(II) can also form metallogels. The experiments have been carried out with nickel(II), zinc(II), cobalt(II) and manganese(II) in place of copper. The results are summarized below in the **Table 3.3.7.**

Effect on gel formation by variation of transition metal ions

Table 3.3.7 Use of different transition metal salts as starting material for gel formation

Sr No.	Metal salts	Observation
1	Zn-acetate	No Gel
2	Ni-acetate	Gel
3	Co-acetate	No Gel
4	Mn-acetate	No Gel

As seen from the **Table 3.3.7** gel formation takes place when nickel acetate reacts with 2,2’-bipyridine and myo-inositol in the ratios of metal acetate : 2,2’-bipy : myo-inositol = 3:3:1. The pH of the reaction mixture was increased to 12 using NaOH as an alkali. The ratios of different reagents and the reaction conditions for the gelation were kept same as those used in case of copper(II) containing gels. Zinc(II), cobalt(II) and manganese(II) did not form any gel. Nickel(II) could form a gel but the gel failed to show a clear sol-gel transformation and hence these were not used for any further studies or applications.

Tolerance of various anions by the gels formed by $[Cu_3(H_3ins)(bipy)_3](CH_3COO)_3$ complex metallogelator

The studies reported in chapter 2, indicated that the gel properties depend on the alkyl carboxylates and the nature of the alkali used. Hence, it was thought of interest to examine the effect of presence of various anions and their influence on the gel formation. In order to carry out these studies the trinuclear complex $[Cu_3(H_3ins)(bipy)_3]^{3+}$ was synthesized using copper acetate, 2,2'-bipyridine and myo-inositol. The pH of the solution was increased upto 12 using NaOH as an alkali **(Scheme 2.3.1 as discussed in chapter 2)**. The solutions of different anions were added to this trinuclear gelator solution after the pH was raised to 12 in order to study the amount/concentration of the anions that can be accommodated in the metallogels. The concentration of anions in the trinuclear gelator solution has been varied to have **metal (copper): anion ratio** from **1:2 to 1:0.035**

The effect of following anions has been examined:

Fluoride (F^-), Bromide (Br^-), Iodide (I^-), Chloride (Cl^-), Thiocyanate (SCN^-), Sulphite (SO_3^{2-}), Peroxydisulfate ($S_2O_8^{2-}$), Nitrite (NO_2^-), Nitrate (NO_3^-), Sulphate (SO_4^{2-}), Bromate (BrO_3^-), Dichromate ($Cr_2O_7^{2-}$), Chromate (CrO_4^{2-}), Thiocyanate (SCN^-), Hydrogen phosphate (HPO_4^{2-}), Carbonate (CO_3^{2-}) and Bicarbonate (HCO_3^-).

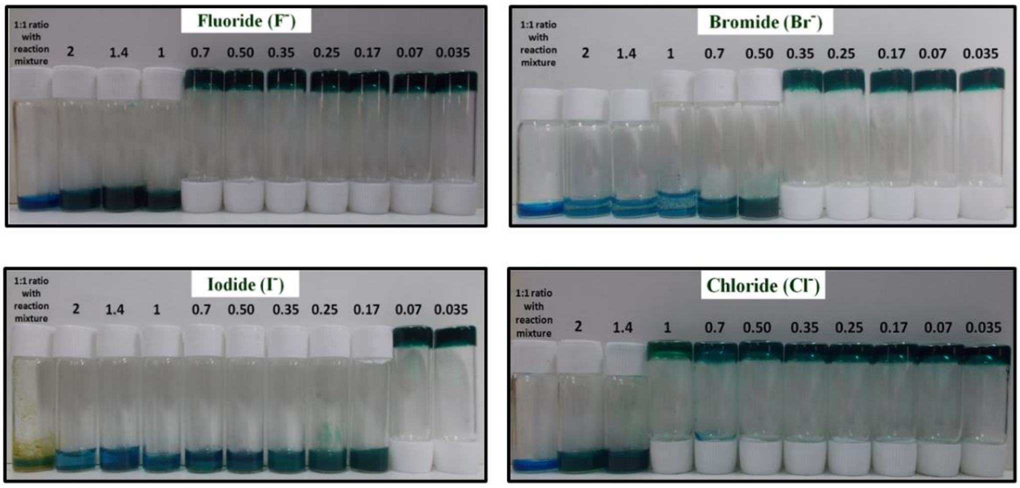

Figure 3.3.3 The gel formation in presence of different halides salts.

As can be seen in **Figure 3.3.3,** that when various salts containing halides as counter anion were added in the trinuclear gel forming mixture in various ratios, they are accommodated into the gels to certain extent. It was observed that the halides having smaller size, namely, fluoride and chloride could be accommodated in the structure of the gel to a significant extent, upto 0.7-1.0 molar ratio. However, the larger halides like bromide and iodide cannot be accommodated it larger quantities and leads to a collapse of the supramolecular assembly responsible for gel formation **(Table 3.3.5),** which results in conversion to the solution.

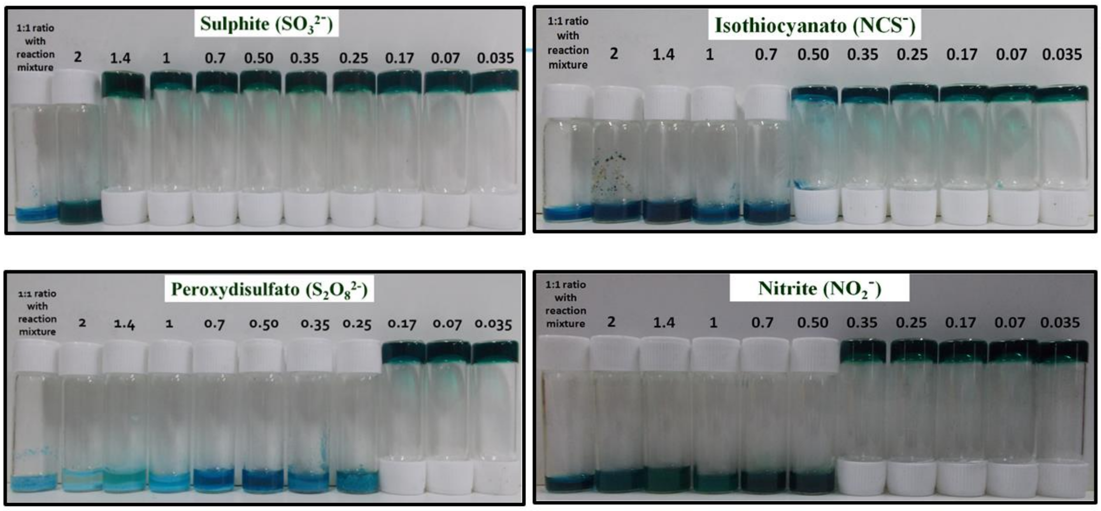

Figure 3.3.4 The influence on gel formation by various anions namely SO_3^{2-}, $S_2O_8^{2-}$, NO_2^-, NCS^-.

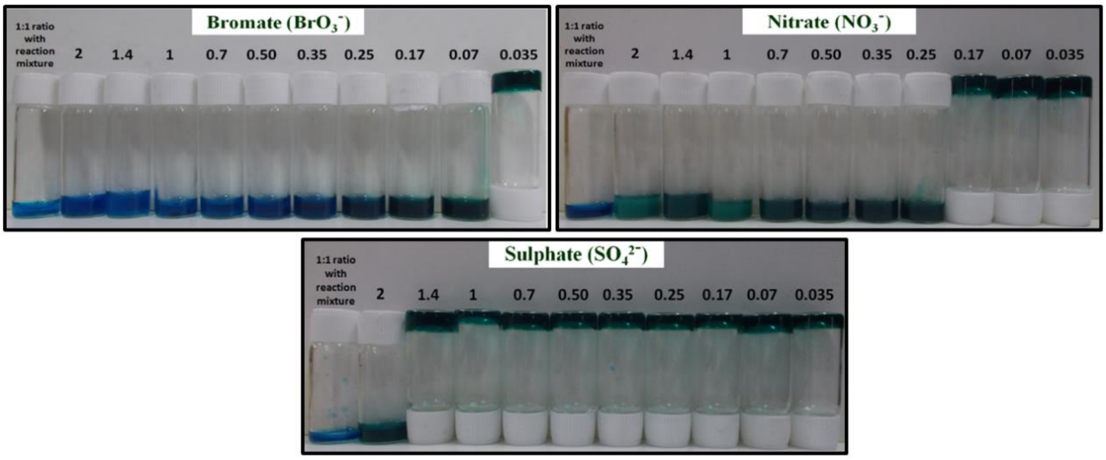

Figure 3.3.5 The influence on gel formation in presence of various anions namely SO_4^{2-}, BrO_3^-, NO_3^-.

It was also observed that thiocyanate and oxyanions containing electronegative elements e. g. nitrate, nitrite, bromate were not much accommodated and result in the destabilization of metallogels at a higher ratio. The accommodation of bromate is even worse as compared to nitrate and nitrite owing to its bigger size in addition to the presence of more electronegative bromine at the center. On the contrary oxyanions like sulphite and sulphate can be accommodated in the structure of the gel to a larger extent. $S_2O_8^{2-}$ can also be accommodated in the gel but leads to precipitation when present in larger amounts.

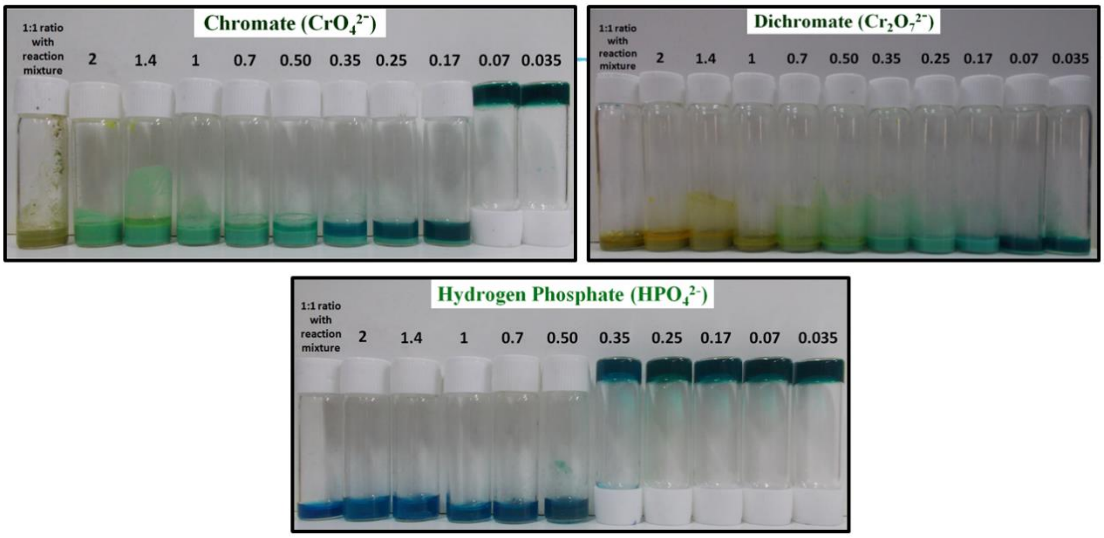

Figure 3.3.6 The influence on gel formation by various anions namely $Cr_2O_7^{2-}$, CrO_4^{2-}, HPO_4^{2-}.

The uptake of anions like chromate and dichromate by the metallogels was very poor. No gel formation was observed in presence of dichromate anions even in ratios as small as **1: 0.035 (Cu: Anion ratio)**. In comparison to dichromate the uptake of chromate by the metallogels was slightly better and the chromate anions can be tolerated in the framework of the metallogels up to a ratio of **(1: 0.07)**, the ratio represents the Cu: anion as mentioned in the **Table 3.3.8.** The uptake of hydrogen phosphate was similar to nitrite and it could be accommodated to a ratio of **1: 0.50 (Cu: Anion ratio).**

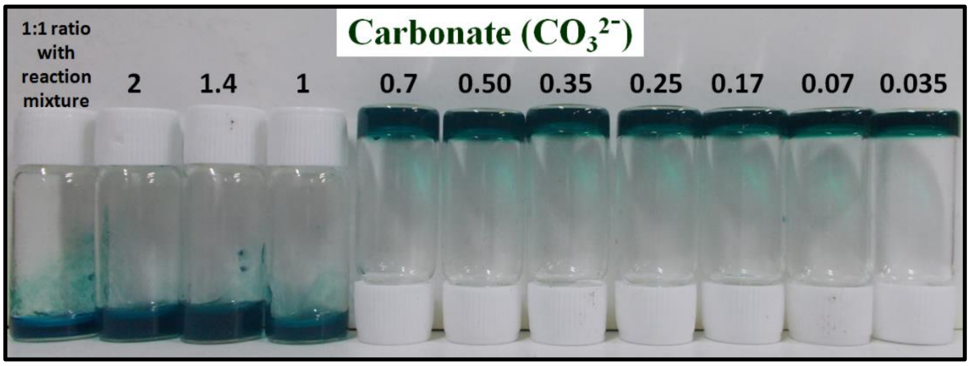

Figure 3.3.7 Image showing the influence on gel formation in presence of carbonate as anion.

When carbonate salts, sodium or potassium carbonate was used, it was observed that the uptake of these anions by the gels was significantly higher **(1:0.7)**. However, in a unique observation the gel formation takes place when sodium carbonate was added to the trinuclear gel forming solution without the presence of alkali. Thus, it was observed that carbonate salts which are also basic in nature assist in the formation of supramolecular assembly. Similar observation was made when bicarbonate anion was added in the trinuclear gel forming solution. The metallogel formation thus can take place in presence of carbonate or bicarbonate bases instead of strong alkalis to raise the pH and assist the formation of supramolecular assembly leading to the metallogels. The carbonate or bicarbonate anions was thought to assist the formation of stacks by getting arranged between the 2 trinuclear complexes leading to the formation of supramolecular assemblies. Various parameters like temperature, concentration and the volume of water for the metallogels formed in presence of carbonate salts/bases were optimized to yield gel formation, the synthesizes and characterization was which is discussed in the next chapter i.e., **chapter 4**.

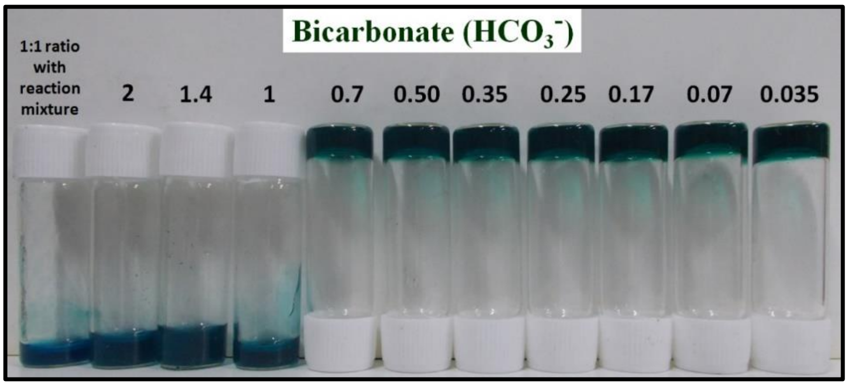

Figure 3.3.8 Image showing the influence on gel formation in presence of bicarbonate as anion.

Table 3.3.8 Anion uptake capacity of metallogels at different concentrations

(The ratio presents Cu: anion present in the metallogel)

Sr No.	Name of Anion	1 (Reaction mixture without base)	2	1.4	1	0.7	0.50	0.35	0.25	0.017	0.07	0.035
1	Fluoride					G	G	G	G	G	G	G
2	Chloride				G	G	G	G	G	G	G	G
3	Bromide							G	G	G	G	G
4	Iodide										G	G
5	Bromate											G
6	Sulphate			G	G	G	G	G	G	G	G	G
7	Nitrate									G	G	G
8	Nitrite							G	G	G	G	G
9	Chromate										G	G
10	Dichromate											
11	Sulphite			G	G	G	G	G	G	G	G	G
12	Thiocyanate (SCN^-)						G	G	G	G	G	G
13	$S_2O_8^{2-}$									G	G	G
14	HPO_4^{2-}							G	G	G	G	G
15	Carbonate	G				G	G	G	G	G	G	G
16	Bicarbonate		G			G	G	G	G	G	G	G

**G notation in the table indicates gel formation*

As it was observed that metallogel formation takes place in presence of carbonate and bicarbonate bases even in absence of caustic alkalis, the gel formation ability in presence of carbonate and bicarbonate salts at different ratios was tried. The optimum gel formation takes place at 1:1 ratio of carbonate anion: copper and in the case of bicarbonate anion the optimum gel formation was achieved at 2:1 ratio of bicarbonate: copper. The results are summarized in the **Tables 3.3.9 and Table 3.3.10.**

Table 3.3.9 Gel formation at different concentrations of potassium carbonate

Sr No	Volume of K_2CO_3 (14.94 mM)	Gel forming solution (7.47 mM)	Observation
1	50	200	Blue solution
2	60	200	Blue solution
3	70	200	Blue solution
4	80	200	Viscous solution
5	90	200	Loose gel
6	95	200	Gel
7	100	200	Gel
8	105	200	Gel
9	110	200	Gel
10	120	200	Precipitation
11	130	200	Precipitation
12	150	200	Precipitation
13	175	200	Precipitation
14	200	200	Precipitation

Table 3.3.10 Gel formation at different concentrations of potassium bicarbonate

Sr No.	Volume of $KHCO_3$ (14.94 mM)	Gel forming solution (7.47 mM)	Observation
1	50	200	Blue solution
2	60	200	Blue solution
3	70	200	Blue solution
4	80	200	Blue solution
5	90	200	Blue solution
6	95	200	Blue solution
7	100	200	Blue solution
8	105	200	Blue solution
9	110	200	Blue solution
10	120	200	Blue solution
11	130	200	Blue solution
12	150	200	Blue solution
13	175	200	Gel
14	200	200	Gel

The above tables show that carbonate and bicarbonate bases are effective in assisting the formation of metallogels. All these experiments related to the data reported in the **Table 3.3.9** and **Table 3.3.10** were all carried out at room temperature. However, it was observed that the gels formed even at optimum ratios were not very stable and ended up in precipitation after 24 hours. So, the reaction conditions were further optimized by elevating the temperature of the gel forming reaction mixture of trinuclear complex and carbonate/ bicarbonate bases to get stable gels. The details of these experiments have been included in **chapter 4**. The gels formed in presence of bicarbonate even after heating were not as stable as those formed in presence of carbonate. Hence, further studies were focused more of carbonate containing gels and the gels formed in presence of bicarbonate were not explored further.

As sodium carbonate and potassium carbonate bases ended up in forming metallogels, other carbonate, bicarbonate and hydroxide bases were also explored. The results have been summarized in the **Table 3.3.11.** All bases were found to help gel formation.

Table 3.3.11 Use of different bases to maintain pH for gel formation

Sr No.	Bases	Observation
1	NaOH	Gel
2	KOH	Gel
3	LiOH	Gel
4	Li_2CO_3	Gel
5	Na_2CO_3	Gel
6	K_2CO_3	Gel
7	Cs_2CO_3	Gel
8	$(NH_4)_2CO_3$	Gel
9	$NaHCO_3$	Gel
10	$KHCO_3$	Gel

3.4 Conclusions

- The ability of the gels to accommodate various anions have been examined by mixing a solution of $[Cu_3(H_3ins)(bipy)_3](CH_3COO)_3$ with solutions of sodium/potassium salts of various anions in the required ratio, followed by maintaining the conditions for gel formation using NaOH.
- The ability of the gels to accommodate the anions more or less depends on coordinating ability and / or size of the anions.
- SO_4^{2-}, Cl^- CO_3^{2-}, HCO_3^- which have fairly good coordinating ability have been accommodated by gels even at higher concentrations.
- Br^-, F^-, I^-, NO_3^- which are having very weak coordinating ability were not accommodated by gels at higher concentrations.
- The gel formation was not achieved when copper chloride, perchlorate, bromide and nitrate were used as starting materials, while alkyl carboxylates, dicarboxylates and sulphate resulted in the formation of gels.
- Among manganese(II), cobalt(II), nickel(II), copper(II) and zinc(II), only copper(II) and nickel(II) could form gels.

References

1. Kurbah, S. D. & Lal, R. A. Vanadium(V) Complex Based Supramolecular Metallogel: Self-Assembly and (Metallo)gelation Triggered by Non-covalent and N+-H…O Hydrogen Bonding Interactions. *Inorg. Chem. Commun.* **111**, 107642 (2020).
2. Karan, C. K. & Bhattacharjee, M. Self-Healing and Moldable Metallogels as the Recyclable Materials for Selective Dye Adsorption and Separation. *ACS Appl. Mater. Interfaces* **8**, 5526–5535 (2016).
3. Karan, C. K., Mallick, S., Raj, C. R. & Bhattacharjee, M. A Self-Healing Metal–Organic Hydrogel for an All-Solid Flexible Supercapacitor. *Chem. - A Eur. J.* **25**, 14775–14779 (2019).
4. Bera, S., Chakraborty, A., Karak, S., Halder, A., Chatterjee, S., Saha, S. & Banerjee, R. Multistimuli-Responsive Interconvertible Low-Molecular Weight Metallohydrogels and the in Situ Entrapment of CdS Quantum Dots Therein. *Chem. Mater.* **30**, 4755–4761 (2018).
5. Wei, C. W., Wang, X. J., Gao, S. Q., Wen, G. B. & Lin, Y. W. A Phenylalanine Derivative Containing a 4-Pyridine Group Can Construct Both Single Crystals and a Selective Cu-Ag Bimetallohydrogel. *Eur. J. Inorg. Chem.* **2019**, 1349–1353 (2019).
6. Dixit, M. K. & Dubey, M. Li+-Induced fluorescent metallogel: A case of ESIPT-CHEF and ICT phenomenon. *Phys. Chem. Chem. Phys.* **20**, 23762–23772 (2018).
7. Tam, A. Y. Y. & Yam, V. W. W. Recent advances in metallogels. *Chem. Soc. Rev.* **42**, 1540–1567 (2013).
8. Piepenbrock, M. M., Clarke, N. & Steed, J. W. Metal Ion and Anion-Based “ Tuning ” of a Supramolecular Metallogel. **25**, 8451–8456 (2009).
9. Bairi, P., Roy, B. & Nandi, A. K. pH and anion sensitive silver (I) coordinated melamine hydrogel with dye absorbing properties : metastability at low melamine concentration. *J. Mater. Chem.* **21**, 11747–11749 (2011).
10. Ghosh, D., Deepa & Damodaran, K. K. Metal complexation induced supramolecular gels for the detection of cyanide in water. *Supramol. Chem.* **32**, 276–286 (2020).
11. Yin, Z. Y., Hu, J. H., Fu, Q. Q., Gui, K. & Yao, Y. A novel long-alkyl-chained acylhydrazone-based supramolecular polymer gel for the ultrasensitive detection and separation of multianalytes. *Soft Matter* **15**, 4187–4191 (2019).
12. Lin, Q., Lu, T.-T., Zhu, X., Sun, B., Yang, Q.-P., Wei, T.-B. & Zhang, Y.-M. A novel supramolecular metallogel-based high-resolution anion sensor array. *Chem. Commun.* **51**, 1635–1638 (2015).
13. Biswas, A., Dubey, M., Mukhopadhyay, S., Kumar, A. & Pandey, D. S. Anion triggered metallogels: Demetalation and crystal growth inside the gel matrix and improvement in viscoelastic properties using Au-NPs. *Soft Matter* **12**, 2997–3003 (2016).
14. Liu, Q., Wang, Y., Li, W. & Wu, L. Structural characterization and chemical

response of a Ag-coordinated supramolecular gel. *Langmuir* **23**, 8217–8223 (2007).

15. Maeda, H. Anion-responshe supramolecular gels. *Chem. - A Eur. J.* **14**, 11274–11282 (2008).
16. Kim, H. J., Lee, J. H. & Lee, M. Stimuli-responsive gels from reversible coordination polymers. *Angew. Chemie - Int. Ed.* **44**, 5810–5814 (2005).
17. Roda, A., Mirasoli, M., Michelini, E., Di Fusco, M., Zangheri, M., Cevenini, L., Roda, B. & Simoni, P. Progress in chemical luminescence-based biosensors: A critical review. *Biosens. Bioelectron.* **76**, 164–179 (2016).
18. Khoshroo, A. & Fattahi, A. Electrochemical analysis of anionic analytes in weakly supported media using electron transfer promotion effect: a case study on nitrite. *Sci. Rep.* **10**, 1–9 (2020).
19. Martín Várguez, P. E., Brunel, F. & Raimundo, J. M. Recent Electrochemical/Electrical Microfabricated Sensor Devices for Ionic and Polyionic Analytes. *ACS Appl. Mater. Interfaces* **5**, 4733–4742 (2020).
20. Singh, W. P. & Singh, R. S. Gelation-based visual detection of analytes. *Soft Mater.* **17**, 93–118 (2019).
21. Lito, P. F., Aniceto, J. P. S. & Silva, C. M. Removal of anionic pollutants from waters and wastewaters and materials perspective for their selective sorption. *Water. Air. Soil Pollut.* **223**, 6133–6155 (2012).
22. Desai, A. V., Sharma, S. & Ghosh, S. K. *Metal-organic frameworks for recognition and sequestration of toxic anionic pollutants (Eds. Ghosh, S.K.).* (Elsevier Inc., 2019).
23. Puranik, A. A., Salunke, P. S. & Kulkarni, N. D. Supramolecular Birefringent Metallohydrogels formed by Trinuclear Copper(II) complexes containing myo-inositol and bipyridyl ligands. *New J. Chem.* **43**, 14720–17727 (2019).

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