

Synthesis and Characterization of Metal-Complexes Rigid Rod Formation in Water from Dicarboxylic Bolaamphiphile

Giriraj S. Mandloi¹, P. M. Selvakumar², Smita Joshi³, Sulbha Amlathe^{1*}

¹Research Scholar, BUIT, BU, Bhopal, M. P. (INDIA)

^{1*}Supervisor and HOD, Department of Applied Chemistry, University Institute of Technology (UIT), Barkatullah University, Bhopal-462 064, M. P., (INDIA)

²Department of Chemistry, Karunya University, Coimbatore 641114, Taminadu, (INDIA)

³Head of Chemistry Department, Sarojini Naidu Govt. Girls College, Bhopal-462 064, M. P., (INDIA)

Abstract: The synthesis, characterization of, 2,2'-[ethane-1,2-diylbis(oxycarbonyl)]dibenzoic acid, and rigid rod formation of diester-based bolaamphiphiles in water was analyzed by FE- SEM/EDS, UV-Visible and using simultaneous TGA, DSC and DTA measurement under non-isothermal condition in N₂ atmosphere. The bolaamphiphiles proved to be coordinated to divalent transition-metal cat ions, such as Co⁺, Ni²⁺, Cu²⁺, and Zn²⁺, giving precipitates, and colloidal dispersions upon self-assembly at room temperature. FT-IR and powder XRD measurement supported the existence of a rigid rods completing [M (L₁H₂) OH] with metal cat ions indicates the formation of self-assembled rigid rod structure mediated through O-H . . . O; C-H . . . O interaction of the end carboxylic acids.

Keywords: Self assemble bolaamphiphile, 2, 2'-[ethane-1, 2-diylbis (oxycarbonyl)] dibenzoic acid, rigid rod.

I. Introduction

Our current interest in transition chemistry began with the preparation and characterization of metal complexes rigid rod formation in water containing dicarboxylic acid. The reports on metal acetates [1-3] and the preparation of metal complexes rigid rod structures have attracted much attention in materials science field [4-6]. Carboxylic amphiphiles form a variety of self-assemblies such as micelles, vesicles, fibres, and crystals in water. The formation behaviour strongly depends upon hydration states, salt concentrations, and pH conditions in aqueous dispersions [8, 9]. In particular, molecular self-assembling system has provided well-defined one, two, and three-dimensional organic templates for the metal complexation [10-12]. The pH values and the kind of counter cations have a remarkable effect on their self-assembling properties because of hydrophilic carboxylic functionalities in water [12-13].

The thermal behaviour of solid organic compounds depends mainly on the characteristic intermolecular cohesive forces in the crystal structure [14]. Carboxylic acids can form hydrogen bonds as they exhibit the O-H proton-donating and the C=O proton accepting group. Decomposition processes for various carboxylates metal complexes under heating were studied widely during last decades; a detailed review is presented in [15], therefore, this paper describes the coordinating properties of the acids and thermal characterisation of their metal complexes.

II. Experimental

All the chemicals were procured from Aldrich & Co. and are used without any further purification. The preparation and characterization of 2, 2'-[ethane-1, 2-diylbis (oxycarbonyl)] dibenzoic acid has been reported [16-18]. The thermal gravimetric analysis (TGA, DSC and DTA) were carried out on Mettler Toledo analyzer (Model TGA/DSC1, STAR^e System SW 9.20., USA), at central instrument facility centre CSIR, AMPRI, Bhopal using nitrogen atmosphere (40-50 cm³/min), with the experimental set up consisted of a heating ramp from 25 to 1200°C at 10°C min⁻¹. The morphology (FE-SEM/EDS) was performed on a Model JOEL JSM-5600, Japan, Powder X-ray diffraction (XRD) patterns of dried samples were taken by the reflection method on a Rigaku diffractometer (RINT 2000) using graded d-space elliptical side by side multilayer optics monochromated CuK α radiation (50 kV, 40 mA) and FT-IR spectra were recorded using KBr pellets on a Perkin-Elmer Spectrum GX FT-IR spectrometer.

2.1 Self-assemble of the metal-complexed diester dicarboxylic bolaamphiphiles

The diester dicarboxylic bolaamphiphile metal-complexes have been synthesized by deprotonation of the terminal carboxylic group by the addition of 1 mmol of sodium hydroxide can allow the bolaamphiphiles to be soluble in water. Aqueous solutions of the sodium salts of the bolaamphiphile 2, 2'-[ethane-1, 2-diylbis(oxycarbonyl)]dibenzoic acid (2 mmol, 5 mL) were added to aqueous solutions of metal salts Co(OAc)₂, Ni(OAc)₂, Cu(OAc)₂, Zn(OAc)₂ (2 mmol, 5 mL) with stirring at room temperature. The reaction mixtures were

allowed to stand for 1 day at same temperature and they were subjected to the structural and morphological analyses.

III. Results and discussion

3.1 Self-assembly of the diester dicarboxylic bolaamphiphile with metal cations

The self-assembling behaviours of the bolaamphiphile with Co^{2+} , Ni^{2+} , Cu^{2+} , and Zn^{2+} at room temperature were summarized. The complexes of **1–4** appeared as precipitates, colloidal dispersions and hydrogel, in aqueous solutions. Fig. 1 shows the appearance of the all metal complexes upon self-assembly at room temperature. A proposed structure of the copper (II) acetates complex and a schematic illustration of the molecular arrangement within the metalcomplexed rigid rod are shown in Fig. 2. We can also observe colored solutions with trace amount of colloidal dispersions and hydrogel with all metals at 50, 60 and 70⁰C temperature. The colloidal dispersions of **1**/ Co^{2+} , and **2**/ Ni^{2+} can be considered as a loose hydrogel because they occasionally converted into hydrogels at above 50⁰C. We found recrystallization of the **3**/ Cu^{2+} complex upon self-assembly at room temperature in 1:1 ethanol: water mixture showing the production of rigid road structure of the complex. Metal cations have a remarkable effect on the formation of the precipitation and colloidal dispersions. **4**/ Zn^{2+} and **3**/ Cu^{2+} are easy to form the colloidal dispersions at 50⁰C in comparison with Co^{2+} and Ni^{2+} respectively. The formation of participation was more favoured with increasing the self-assembling temperature and the connecting mediated through O–H . . . O; C–H . . . O interaction of the end carboxylic acids [16-18]. For the **4**/ Zn^{2+} complexe, we observed remarkable temperature effect on the appearance. When the bolaamphiphile was complexes with **3**/ Cu^{2+} at 50, 60, and 70⁰C, the obtained complexes gave precipitates at temperatures below 50⁰C, whereas a colloidal dispersion above 60⁰C.

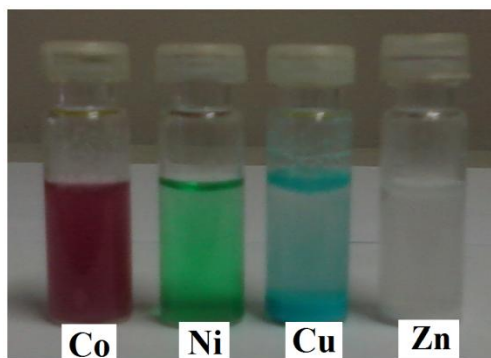


Fig. 1. The appearance of the metal complexes upon self-assembly at room temperature.

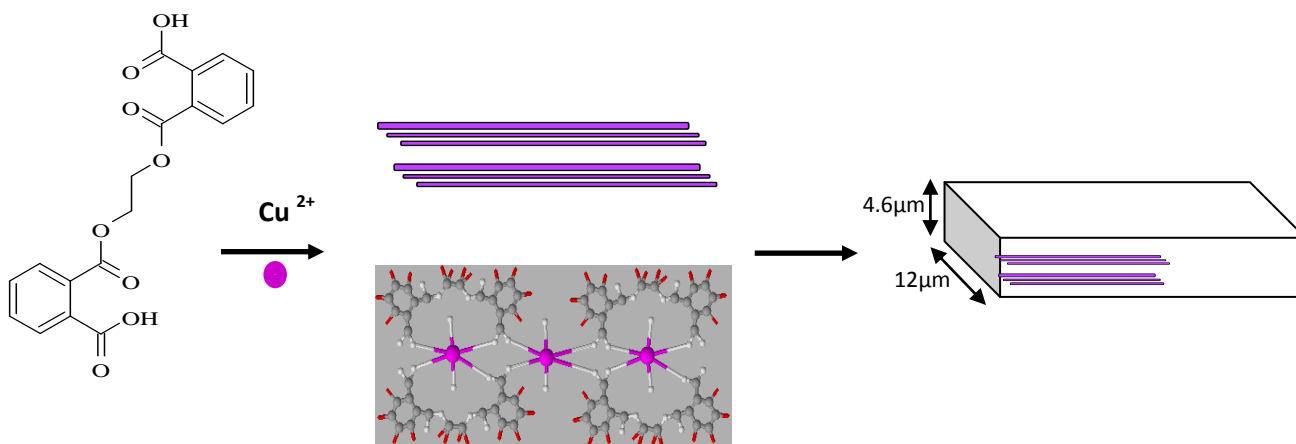


Fig.2. A proposed structure of the copper (II) acetates complex and a schematic illustration of the molecular packing within the rigid rod.

3.2 Electron microscopic observation

Field-emission scanning electron microscopy (FE-SEM) of the diester dicarboxylic bolaamphiphile metal complexes was recorded to understand the formation of rigid rod. To clarify the rigid rod structures responsible for the precipitation and the colloidal dispersions, we carried out FE-SEM. Fig. 3 displays microscopic images of the **3**/ Cu^{2+} complexes upon self-assembly at room temperature. EF-SEM images revealed

the existence of rigid rod with widths of 12–15 μm and lengths of several hundred micrometers. The widths of the $3/\text{Cu}^{2+}$ complexed rod are almost similar to those of the organic nanofibers as previously reported [19-20]. The colloidal dispersions of the metal cation complexes are also composed of the rigid rod. We also carried out energy dispersive EDX for the metal complexes. EDX of each rigid rod shows the peaks ascribable to cobalt, nickel, copper, and zinc, respectively Fig. 4.

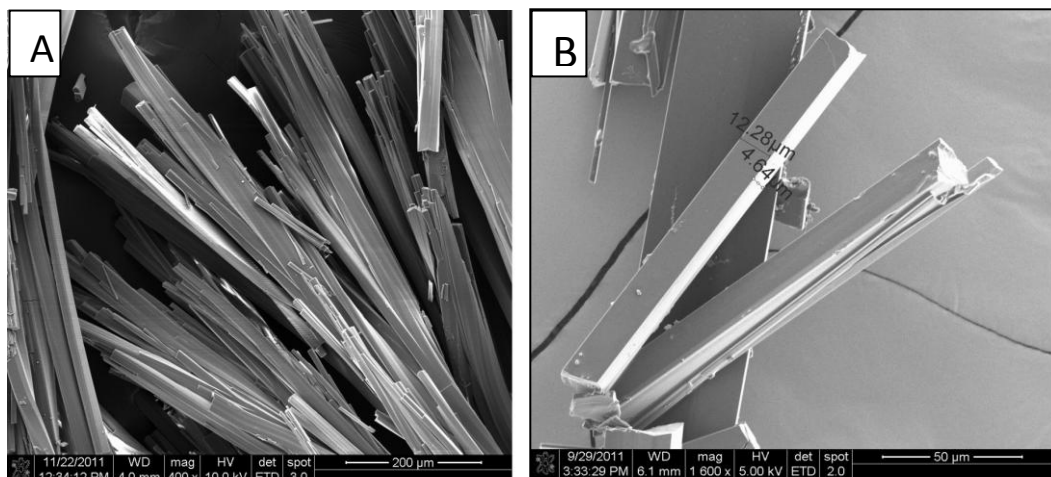


Fig. 3. FE-SEM images of (A) and (B) the Cu^{2+} complex, self-assembled at room temperature

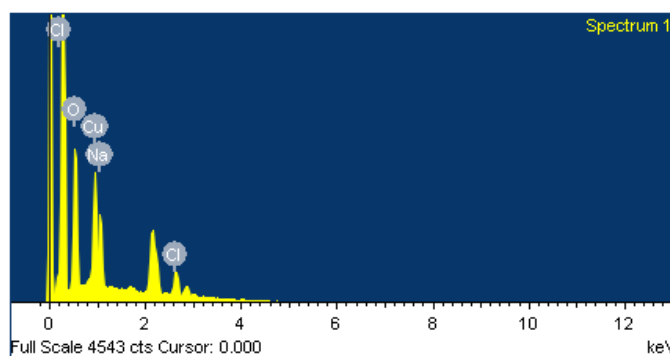


Fig. 4. EDS Spectrum of the Cu^{2+} complex, self-assembled at room temperature

This finding supported that the rigid rods are actually composed of the metal complexes of bolaamphiphiles. Uniform widths of the metal-complexed rigid rod indicate that both the length of the end terminal carboxylic acids and the kinds of metal cations have little effect on the morphologies of the rigid rod.

3.3 FT-IR and XRD analysis

All bolaamphiphilic metal compounds **1-4** possessing carboxyl unit as well as ester functional group in common Fig. 5. The peak at 1700-1730 cm^{-1} region for all compounds described to the C=O stretching mode of end COOH group characteristic of the formation of carboxylic dimers [21]. The peak appeared around 3400 cm^{-1} indicates the presence of carboxylic OH group. The additional signal in the IR region at 1700-1740 cm^{-1} region indicates the spacer COO group. Thus, the two set of IR peak appeared at this region

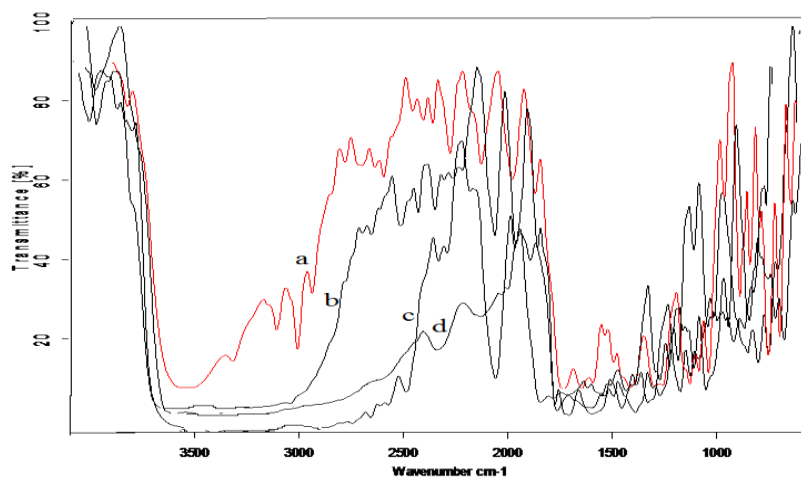


Fig. 5. FT-IR spectra (a) Co^{2+} , (b) Ni^{2+} , (c) Cu^{2+} , and (d) Zn^{2+} complexes upon self-assembly at room temperature

indicates the presence of terminal and spacer COO group in all these compounds. XRD patterns of the isolated and dried Co^{2+} , Ni^{2+} , Cu^{2+} , and Zn^{2+} complexes upon self-assembly at room temperature are shown in Fig. 6. Although the intensities are relatively sharp because of crystalline nature of the $3/\text{Cu}^{2+}$ complexed rigid rod, relatively strong reflection peaks appear in a similar way as the organic rigid rod.

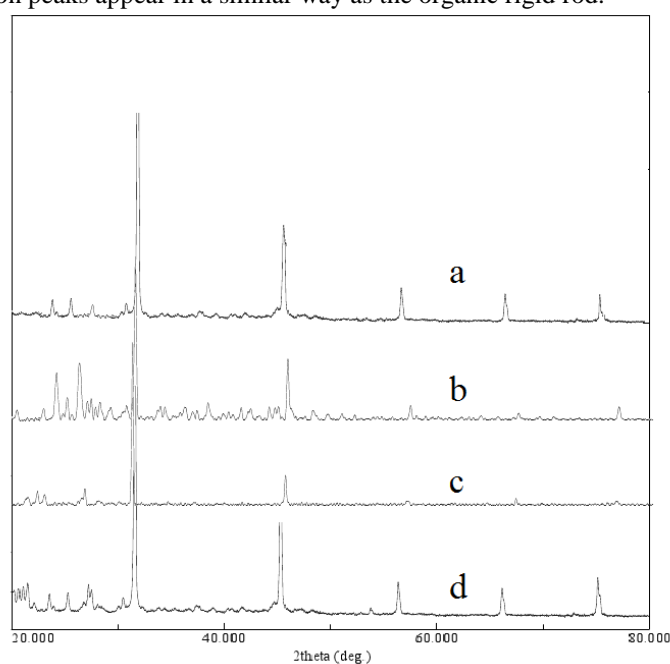


Fig. 6. XRD patterns of the isolated and dried (a) Co^{2+} , (b) Ni^{2+} , (c) Cu^{2+} , and (d) Zn^{2+} complexes upon self-assembly at room temperature

The terminal and spacer COO group in the bolaamphiphile will favourably form β -sheet type hydrogen bond networks [23]. The absence of strong and periodic reflection peaks in the small-angle region suggests that the rod are based on no long-range lamellar organization. All the results from electron microscopic observation, FT-IR spectrum, and XRD analysis supported that the metal coordination to terminal carboxylate anions takes place on the organic rigid rod.

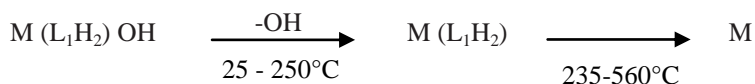
3.4 Thermal analysis

The thermo gravimetric analysis for metal complexes **1-4** are shown in Fig. 7. Because all the compounds shown similar thermal behaviour, we give below, as an example, a more detailed discussion of the complexes 1-4 series. The TGA curve are shown as % mass loss versus Temperature, the DSC curve as enthalpy changes and the DTA curve as the rate of mass loss of the temperature. The results are proved the first stage of decomposition of compound **1-4** under investigation in Nitrogen was dehydration.

Co (L₁H₂) OH Complex

The TGA, DTG and DTA profiles of Co²⁺- L₁H₂ complex are given in Fig. 7a. The first mass loss about 10.622 % occurs in temperature ranges 25 - 110°C due to dehydration of water molecules. The next exothermic decomposition of the complex occurs in 235-264 °C with 29.42 % residual mass which change to about 23.10 % in 328 - 348 °C. The heat evolved in decomposition of complex in temperature range 379 – 386°C was found to be 9.518 J mol⁻¹.

The DTA curve showed that two simultaneous decomposition peaks occurred during this stage at 264.99°C and 348.21°C respectively. The thermal decomposition process can be shown below:



Cu (L₁H₂) OH Complex

The TGA, DTG and DTA profiles of Cu²⁺- L₁H₂ complex are given in Fig. 7b. The single decomposition of the complex occurs in first in temperature range 190-249°C with mass loss of 45.21%.

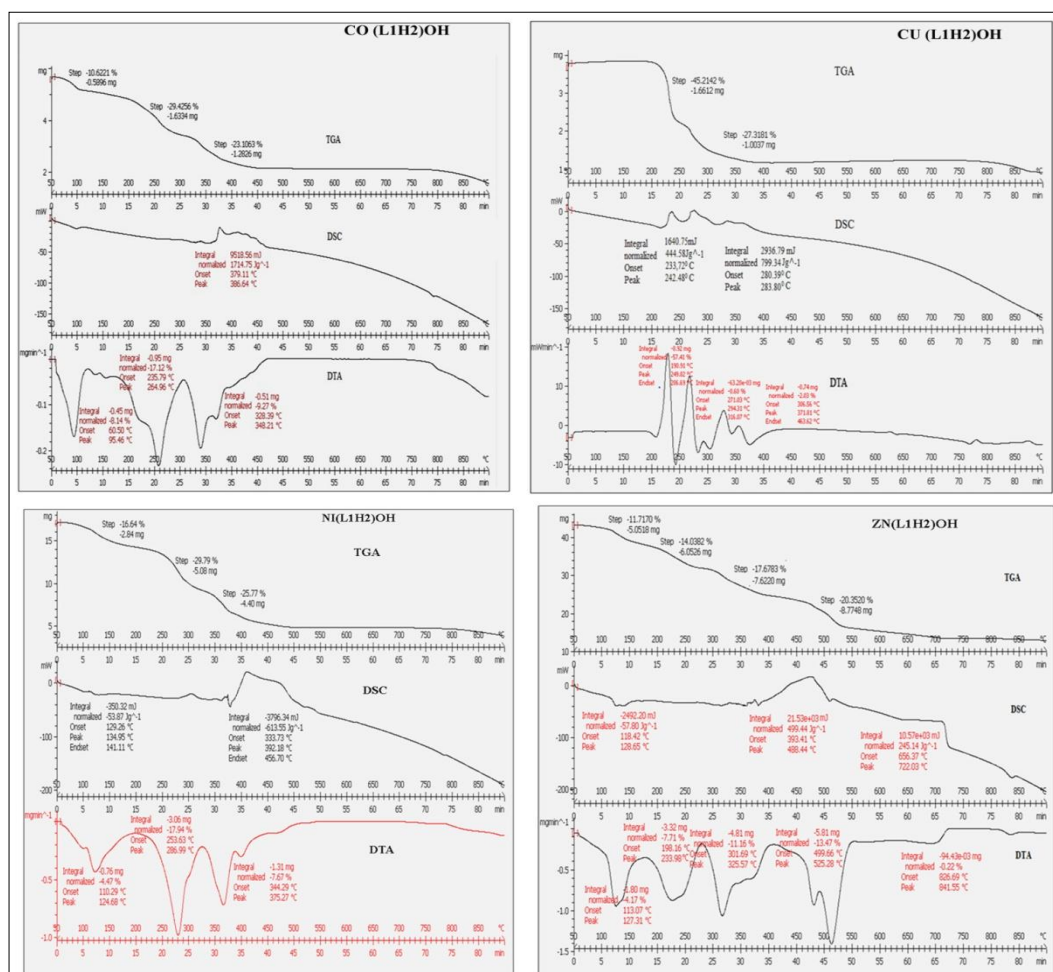


Fig. 7. The simultaneous TGA,DSC and DTA Curves of (a)Co²⁺, (b)Ni²⁺, (c)Cu²⁺, and (d)Zn²⁺ metal complexes.

The heat librated during this step was 4.445J mol⁻¹ which corresponds to the exothermic peak with maximum at 242.8°C. The nature of DSC and DTA curves corresponding to this step indicates that a number of reactions are taking place simultaneously giving a stable intermediate species. The residue mass in the temperature range 371-463°C was found to be 27.23% and corresponding to the end product L₁H₂.

Ni (L₁H₂) OH Complex

The TGA, curve (Fig. 7c) of Ni²⁺- L₁H₂ complex reveals mass loss of 10.6% its water molecules in the temperature range from 60- 100°C. The total mass loss calculated from TGA curve about 72.2 % up to 450°C. DSC curve for the complex shows one broad exothermic peak in the temperature range 379-386°C.

Zn (L₁H₂) OH Complex

The TGA, DTG and DTA profiles of Zn²⁺- L₁H₂ complex are given in Fig. 7d. The first mass loss in temperature range 50-233°C is of the order 25.7% which corresponds to the removal of the two water molecules. The complex decomposes in two stages in the temperature ranges (301-325°C and 499-525°C) as indicated by DTA curve. The DSC profile shown residue mass of the order of 17.63% and 20% were due to formation of L₁H₂ which peaks with maxima at 488 °C and 722 °C respectively.

IV. Conclusion

The dicarboxylic bolaamphiphiles make complexes in water with transition-metal cations, such as Co²⁺, Ni²⁺, Cu²⁺, and Zn²⁺, producing the precipitation, colloidal dispersions and hydrogels through molecular self-assembly. FE-SEM observation revealed the metal-complexed rigid rod of 12–15 μm wide. In a similar fashion as the rigid rods formed from the dicarboxylic acid homologue, the bolaamphiphiles were found to form the rigid rods by β-sheet hydrogen-bond networks between the terminal and spacer COO group residues. It is concluded that in these complexes, the mass loss as a function of temperature occurs as expected from the molecular formula as deduced from elemental analysis.

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