

## Electrochemical synthesis of complex of Zn with diethyl malonate

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### Abstract:

Electro-chemical synthesis (through potentiostatic approach) is exploited to prepare complex compounds using  $\beta$ -diketones (as potential ligands) and Cu, Zn or Ni (as metal ions precursors).

Acetone and DMF serve as solvents. Sacrificial anodes of relevant metal are used along with Pt cathode.

Electrolysis is carried out for about 8 to 10 hours.

**KEY WORDS: DM, FTIR, TGA, DTA**

### INTRODUCTION:

Electro-chemical route for preparing a variety of complexes has NOT been given the due credit it deserved. And as such despite having a huge advantage over other methods it is not exploited that much which is both surprising and unfortunate.

This is a process that allows chemical changes via electron transfer across the electrode/solution interface.

The driving force is the voltage applied between the electrodes in an electrolytic cell,

Electrochemical method is clearly superior to the chemical method:

- a) When compared to traditional chemical oxidants and reductants, the use of universal chemical reagents—electron(s) [1] allows for clean synthesis at a far lower cost. Due to the absence of spent reagent there is hardly any problem of purification and waste management.
- b) Activation, here, is due to voltage and not by temperature (as in case of heterogeneous catalysis) so there will be minimum thermal degradation of sensitive functionalities, which allows greater selectivity[2-5] as far as desired product is concerned.
- c) One can monitor and control the process quite easily.
- d) It allows a sort of green synthesis[6-8].

Electro-organic synthesis exploits electrochemical cell with the substrate losing/gaining electron(s) to/from the electrodes completing the circuit through the solution culminating in the synthesis[9-10].

The metal M, as the anode of a simple cell, undergoes oxidation in the presence of the parent compound of the ligand (HL) in an organic/aqueous solvent mixture resulting in the formation of a complex[11].

### **Anode Reaction:**



### **Cathode Reaction:**



### **Overall Reaction:**



In the present work complex of Zn with diethyl malonate is attempted to be synthesized using sacrificial anode[12]. Vanishing anode is believed to furnish metal ions, which engage potential complexing agent present in the electrolytic medium. Pt has been used as cathode due to its inertness in majority of the medium.

**Solvent** – dimethylformamide (DMF) and acetone are intended to be used as solvent.

**Supporting Electrolyte**– we intend to use  $LiClO_4, NaClO_4$ , etc.as supporting electrolyte.

**Electrochemical Cell** – Undivided cells will be used as they have less resistance that divided ones.

### **Electrolytic parameters** –

Experiments will be carried out in the range -20 to 50 mA depending on the electrolyte composition and cell parameters as in the usual trend [13]

This method has been used extensively to make electro-synthesis a powerful tool to prepare a variety of compounds [14-24]

## **EXPERIMENTAL:**

0.5g  $NaClO_4$  was added in 30 ml of mixed solvent of DMF and Acetone in 100 ml beaker. 3 ml of Diethyl Malonate (DM) was added in the solution. Sodium acetate solution was prepared by dissolving Sodium acetate in acetone and water (1:1) ratio. The pH of the solution was found nearly to 6. The solution was

subjected to electrolysis using Pt-electrode as cathode and Zn-electrode as sacrificial anode under 4V DC supply. The progress of electrolytic process was confirmed through bubbles emerging out Pt- electrode. After 10 hours white powder was found deposited at the bottom of the cell. It was filtered and washed with acetone. It was dried and collected in pure form. It was bottled as sample Zn-DM.

Sample name- Zn-DM

Color- White

**%Composition –**

C	26.76
H	1.48
O	47.58
Zn	24.16

Empirical Formula –  $C_6H_4O_8Zn$

**IR Interpretation**

**Table**

Peaks	Nature of peaks	Group assignments
3326.50 & 3188.78	Broad	O-H stretching (H-bonded)
2940.22	Medium	C-H; CH <sub>3</sub> stretching
1549.21	Sharp	C=O stretching, anti-symmetric in COO <sup>-</sup>
1376.62	Sharp	C=O stretching, symmetric in COO <sup>-</sup>
1280.05	Sharp	C-O stretching
924.87 & 834.14	Sharp	Rocking & wagging due to coordinated water
717.07	Sharp	C-H, out of plane bending

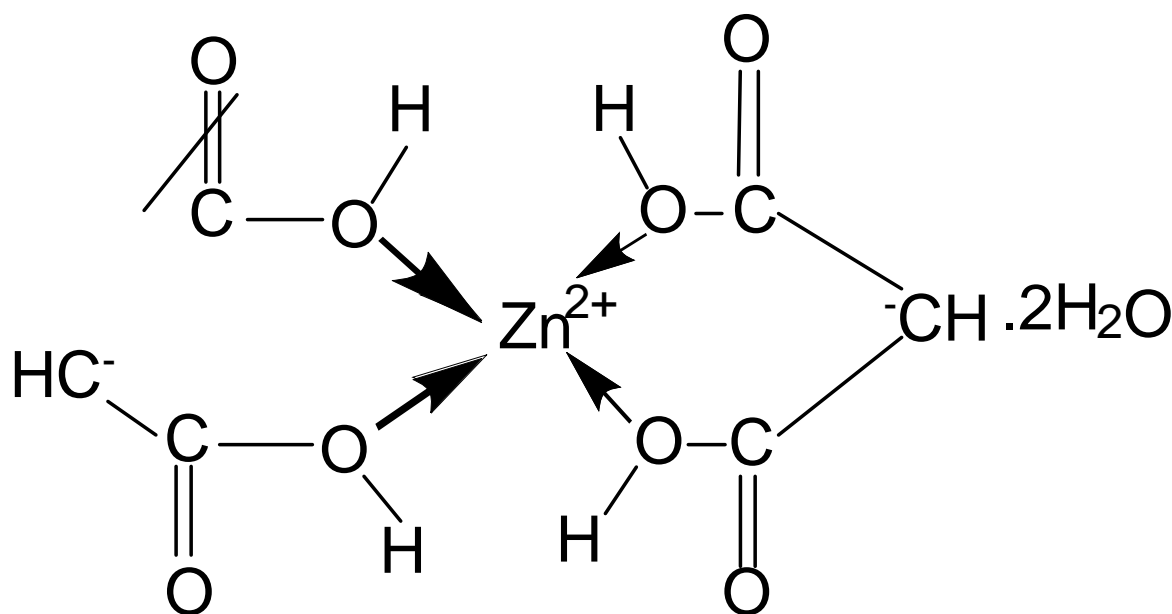
626.67	Sharp	Zn-O stretching
562.97	Sharp	Zn-O bending

**Thermogravimetric results**

Temperature	Formulation sequence	Experimental loss	Theoretical loss
31 <sup>0</sup> C-216 <sup>0</sup> C	[Zn(C <sub>3</sub> H <sub>4</sub> O <sub>4</sub> ) <sub>2</sub> ].2H <sub>2</sub> O ↓ -2H <sub>2</sub> O	13.86%	11.65%
218 <sup>0</sup> C-500 <sup>0</sup> C	[Zn(C <sub>3</sub> H <sub>4</sub> O <sub>4</sub> ) <sub>2</sub> ] ↓ -2CO <sub>2</sub>	27.36%	28.47%
502 <sup>0</sup> C-995 <sup>0</sup> C	[Zn(C <sub>2</sub> H <sub>4</sub> O <sub>2</sub> ) <sub>2</sub> ] ↓ -2H <sub>2</sub> O [Zn(C <sub>4</sub> H <sub>6</sub> O <sub>2</sub> )]	10.64%	11.65%

Based on above Molecular formula of the compound is Zn<sup>2+</sup>[(HOOCCH<sup>-</sup>COOH)<sub>2</sub>].2H<sub>2</sub>O

Proposed structural formulation of complex: -



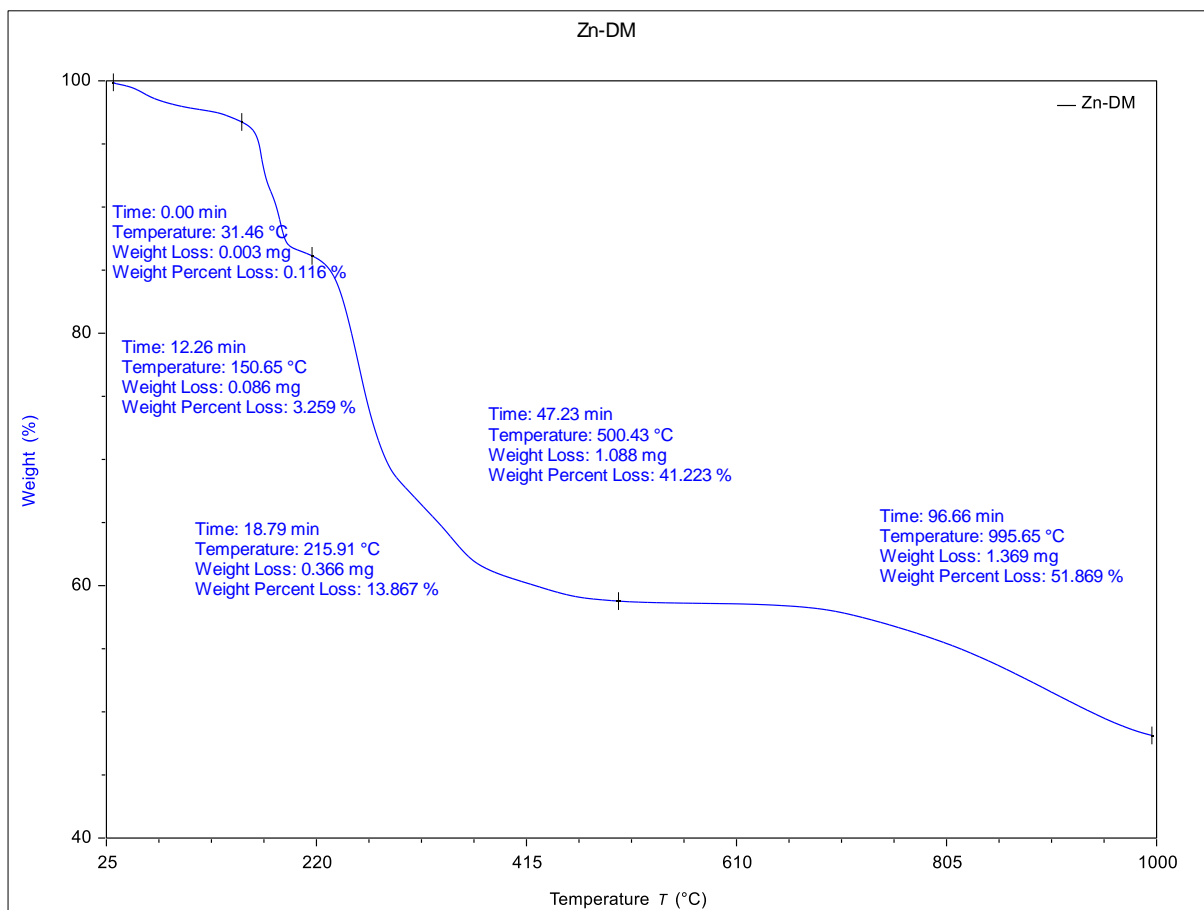
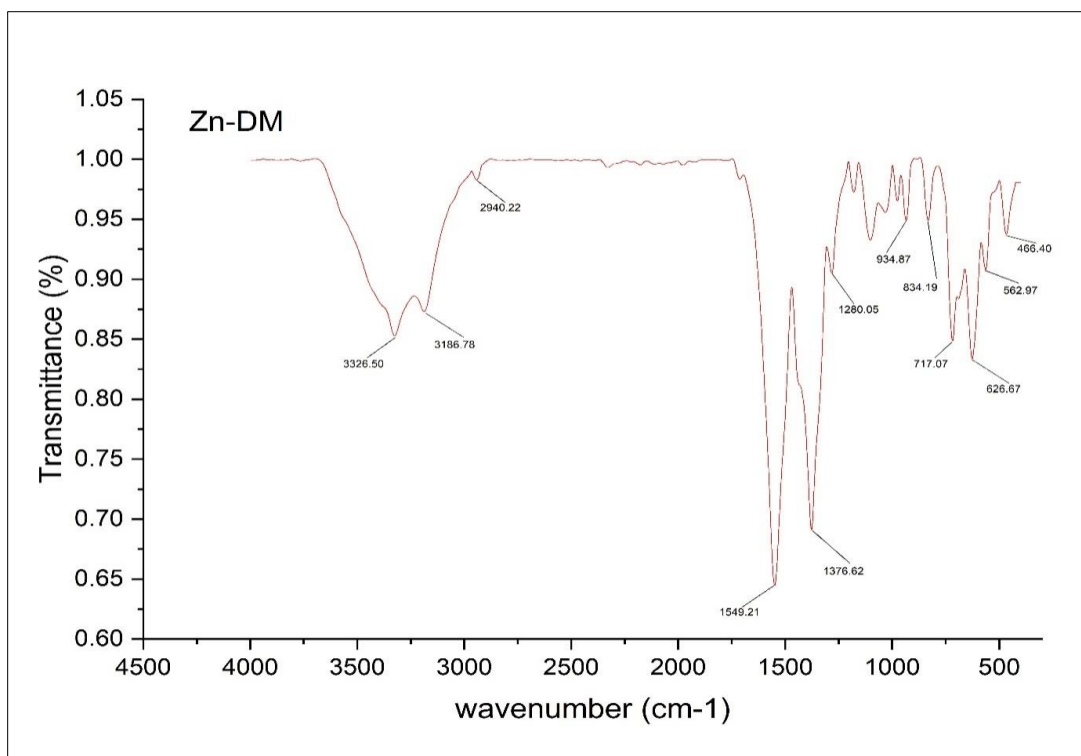


Fig: - IR

Spectra of Zn-DM

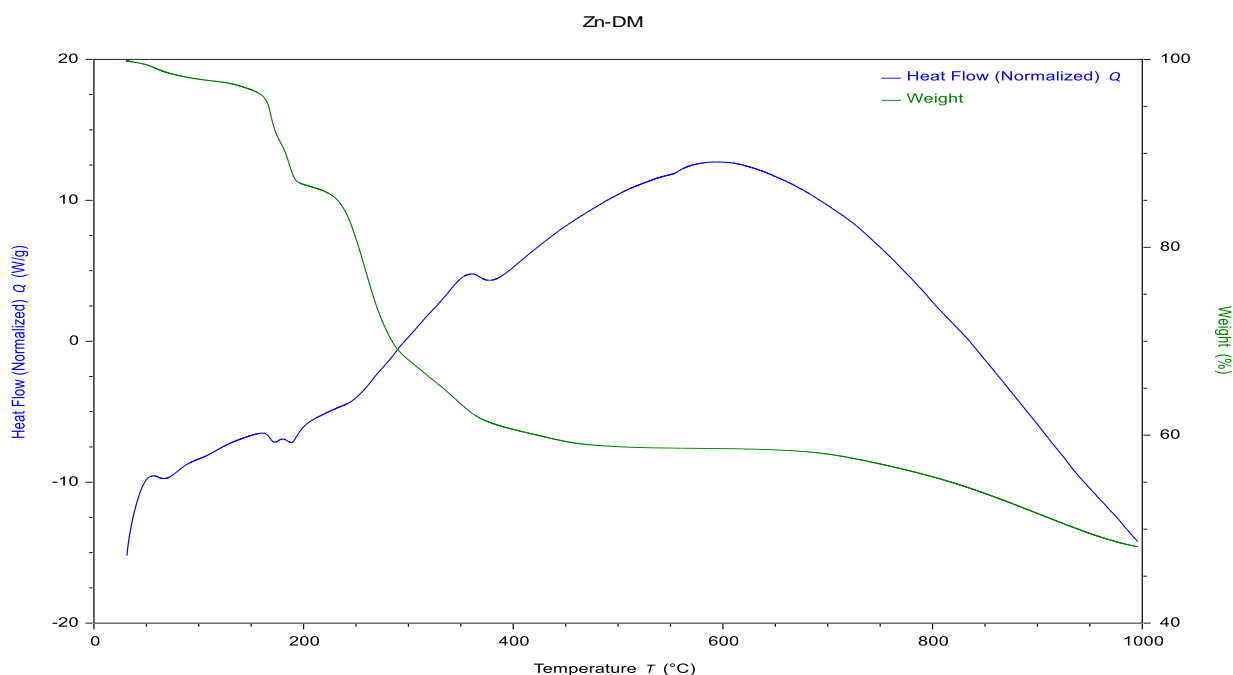


Fig: - TGA & DTA Graph of Zn-DM

## Results and Discussion:

The experimental data suggest that Diethyl malonate, in deprotonated mode, acts as a chelating agent and appears to have coordinated to zinc metal ion through O- atoms and forms two six membered stable rings.

The presence of lattice water is revealed by the appearance of broad bands at  $3326\text{ cm}^{-1}$  to  $3188\text{ cm}^{-1}$  due to absorption of O-H bond of water. The presence of water is further indicated by the appearance of bands in the region of  $924\text{ cm}^{-1}$  to  $834\text{ cm}^{-1}$  due perhaps is to rocking and wagging mode of coordinated water. The sharp band at  $1549.21\text{ cm}^{-1}$  is due to C=O stretching anti symmetric in  $\text{COO}^-$  whereas the sharp band at  $1376.62\text{ cm}^{-1}$  is due to C=O stretching symmetric in  $\text{COO}^-$ . The C-O stretching is confirmed by the appearance of sharp band at  $1280.5\text{ cm}^{-1}$ . The sharp bands found at  $626\text{ cm}^{-1}$  and  $562\text{ cm}^{-1}$  are due to Zn-O stretching and Zn-O bending respectively.

The formulation is also supported by thermogravimetric loss. The curve of the complex shows first weight loss of 13.86% between temperature range  $31^{\circ}\text{C}$ - $216^{\circ}\text{C}$ , which may be attributed to the loss two water

molecules and the second weight loss of 27.36% is observed at 500<sup>0</sup> C due to loss of two mole of carbon dioxide, which is in close agreement with theoretical loss (28.47%) and third loss of 10.64% is happened at 995<sup>0</sup> C, which may be due to loss of two molecule of H<sub>2</sub>O. The final product percentage is nearly same as the experimental value.

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