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Electrochemical synthesis of complex of Cu with benzoyl acetone

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ABSTRACT:

In this paper, the electro-chemical synthesis of complex of Cu with benzoyl acetone (BA) – another β diketone, is discussed. We have used acetone + DMF as solvent, sacrificial anode of the metal and Pt cathode.

KEY WORDS: BA, FTIR, TGA, DTA

INTRODUCTION:

Organic electrochemistry, though known for almost two hundred years, remained largely unutilized as a preparatory method of compounds of vital importance on a commercial basis. This is all the more surprising and to some extent unfortunate too as this route has several significant advantages over conventional chemical methods as discuss below-

It employs the universal chemical reagent – electron(s) [1] inherently cheaper and cleaner than corresponding chemical oxidizing or reducing agents since the absence of spent reagent circumvents many problems associated with purification, recycle and waste treatment. The same advantages may be offered by heterogeneous catalysis, but since the activation is by voltage and not by temperature, electrochemical processing leads to minimal thermal degradation of sensitive functionalities, which may result in higher selectivity for desire products [2-5]. Advantages of electrochemical processing are that monitoring and control of electrochemical factor is straight forward since the rate of an electrochemical reaction is proportional to the applied current. Moreover, it is in consonance with the need of the hour -less damage to environment. In addition to this electro-organic synthesis technology is associated with high product selectivity, mild reaction conditions easy monitoring making the technique suitable for developing green technologies for specific chemicals [6-8].

Although the art of organic electrochemistry is old, the science of this area has been major advances only in the last two decades. This has been largely due to the non-availability of instrumentation capable of providing conclusive mechanistic information by means of better measurements and more through and sophisticated data treatments which allow models to be more accurate. Better mechanistic understanding results in novel cell designs tailored to particular reaction type to give higher selectivity and space-time yields. The lac of familiarity with recent advances in organic electrochemistry among most chemists and engineers may account in large part for the view that electrolysis is not a viable process alternative. This attitude appears to be slowly changing as more basic understanding of electro chemical mechanisms and engineering improves.

Basic ideas-

Electro organic synthesis employs electrochemical cell in which two electrodes (anode and cathode) are submerged in an organic/aqueous solvent with supporting electrolyte dissolved to facilitate passage of current through the cell (to separate process taking place simultaneously enabling the electron(s) to move through the solution). The substrate either looses electron(s) to the anode (oxidation) or gains electron(s) from the cathode (reduction) completing the circuit culminating in the electro chemical synthesis [9-10].

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

Anode Reaction:

$nL^- + M \Longrightarrow [ML_n] + ne^-$

Cathode Reaction:

$nHL + ne^- \Longrightarrow nL^- + n/2H_2$

Overall Reaction:

$nHL + M \Longrightarrow [ML_n] + n/2H_2$

In the present work complex of Cu with benzoyl acetoneis 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. 1g of Benzoyl Acetone was added with help of glass rode. Sodium acetate solution was prepared by dissolving Sodium acetate to acetone and water (1:1). The pH of the solution was found to be 8. The solution was subjected to electrolysis using Pt-electrode as cathode and Cu-electrode as sacrificial anode under 4V DC supply. The continuation of electrolytic process was confirmed through bubbles emerging out Pt- electrode. After 10 hours the bright turquoise powder was 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 Cu-BA.

Sample name- Cu-BA

Color- Bright turquoise

% COMPOSITION –

C	61.05
H	5.26
O	16.38
Cu	16.32

Empherical Formula - $C_{20}H_{20}O_4Cu$

IR INTERPRETATION:

Table

Peaks	Nature of peaks	Group assignments
3377	Broad	O-H stretching (H-bonded)
2935	Medium	C-H; CH_3 stretching
1648	Sharp	C=O stretching
1555	Sharp	C=O stretching+Aromatic C=C stretching
1487	Sharp	C=O stretching+Aromatic C=C stretching
1259	Sharp	C-O stretching
1104	Sharp	C-C-H in Aromatic bending
662	Sharp	Cu-O stretching
551	Sharp	Cu-O bending

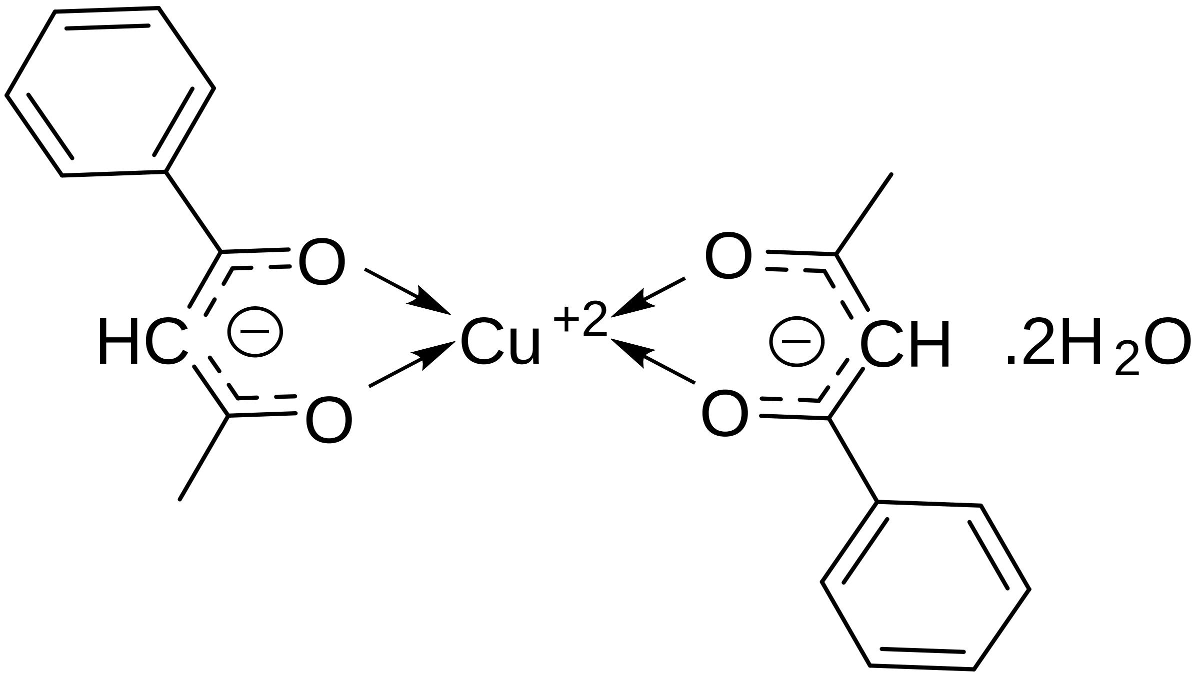
THERMOGRAVIMETRIC RESULTS:

Temperature	Formulation sequence	Experimental loss	Theoretical loss
35^0 C-600^0 C	$[Cu(C_{10}H_{10}O_2)_2].4H_2O$ ⬇ $-4H_2O$ $[Cu(C_{10}H_{10}O_2)_2]$ ⬇ $-(C_{10}H_{10}O_2)_2$	85%	83%
Residue	CuO	15%	17%

-

Based on above Molecular formula of the compound is $Cu^{2+}[(CH_3COCH^-COC_6H_5)_2].2H_2O$

Proposed structural formulation of complex: -



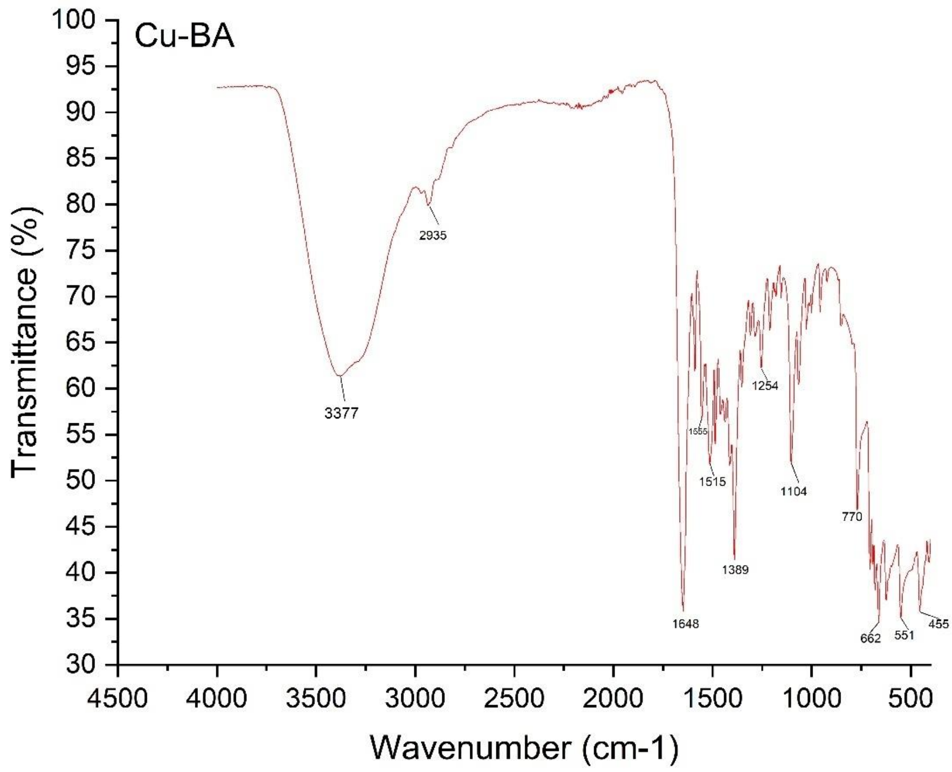
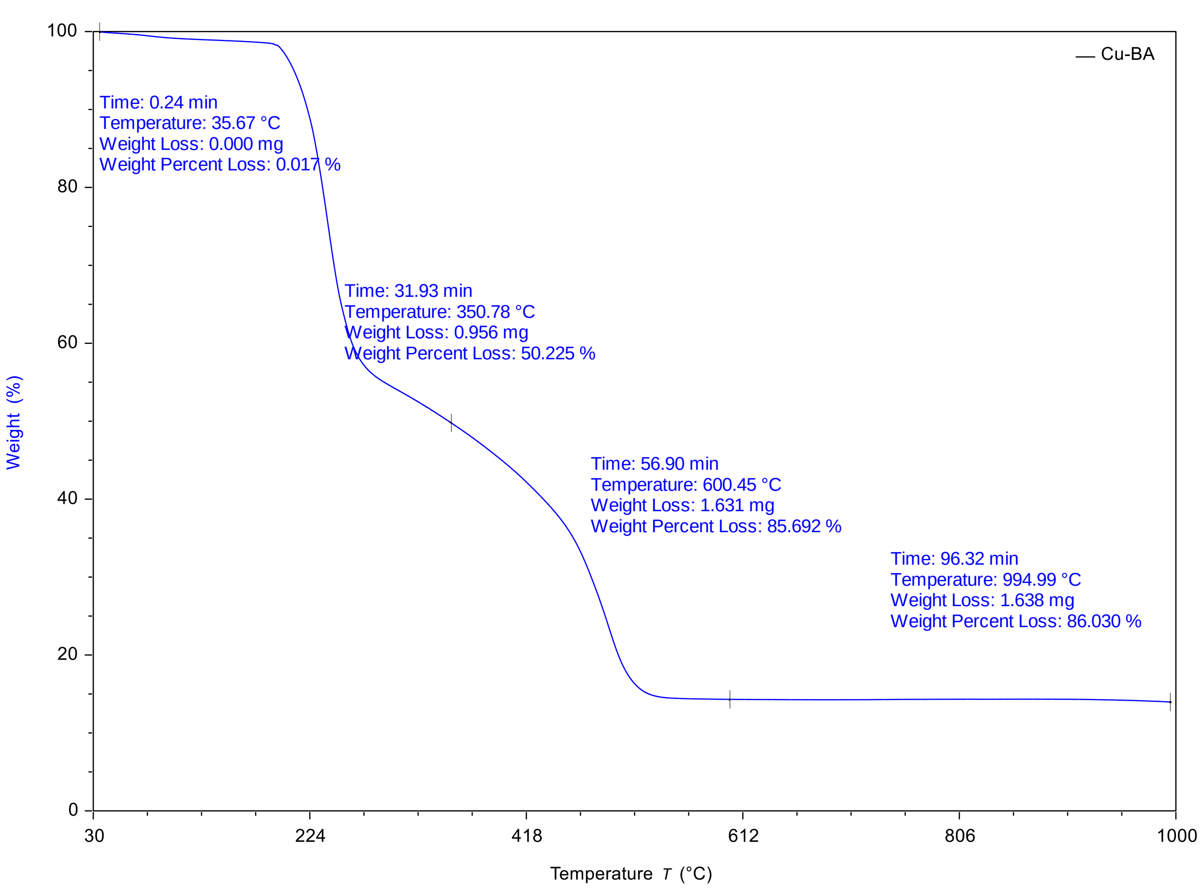


Fig :- IR Spectra of Cu-BA



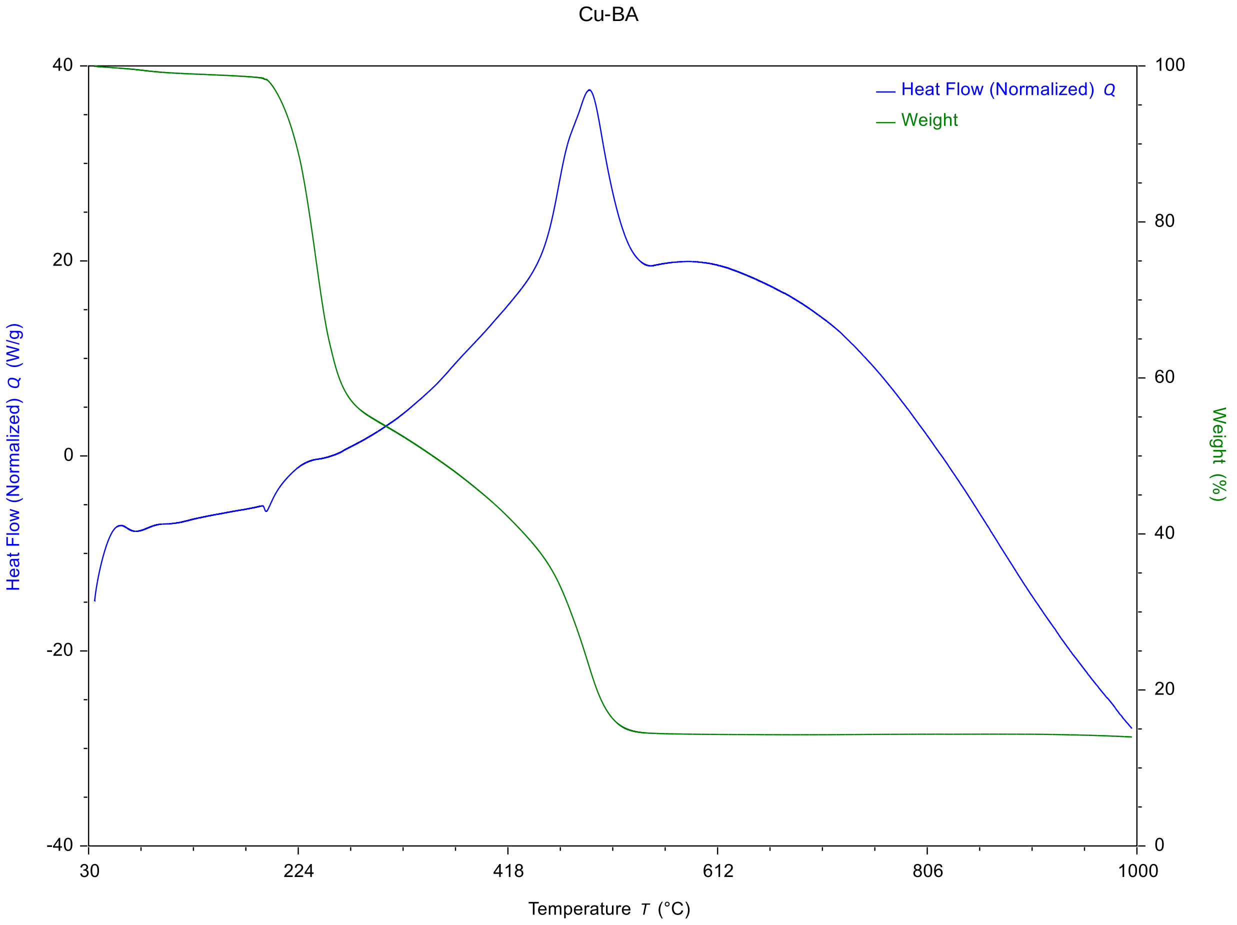


Fig: - TGA & DTA Graph of Cu-BA

RESULTS AND DISCUSSION:

The FTIR spectra (table-1) of sample Cu-BA contains almost all the peaks which are expected for the formulation. A very broad band appeared at 3377 cm^{-1} is due to stretching of O-H bond of water and due to H-bonding. The band at 2935 cm^{-1}is assigned to C-H, CH_3 stretching. The sharp band at 1648 cm^{-1} is due to C=O stretching. The bands at 1555 cm-1 and 1487 cm^{-1}are assigned to C=O stretching and aromatic C=C stretching. The sharp band appearing at 1259 cm^{-1} is due to C-O vibrational mode. The bands at 662 cm^{-1} and 551 cm^{-1} are due to Cu-O stretching and Cu-O bending respectively. Thus, FTIR curves strongly support the proposed formulation of Cu-BA.

Also, in the TGA-DTA curves, the water of hydration is lost between 35^0 C-210^0 C and further de-composition occurs until 600^0 C. A small amount of mass is additionally lost up to 995^0 C with Cu oxide asan ultimate product, however the calculated and observed value are almost same.

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References:

1. J.A Davies, C.M. Hockemsmith, V Yu. Kukushkin and Y N. Kukushkin; Synthetic Co-ordination Chemistry, Principles and Practice, 198, 1996.
2. J.O.M Bockris, B.E. Conway, E. Yeager, and R.E. White, “Comprehensive Treatise on Electrochemistry Vol.2. Plenum Press, New York, (1981).
3. C.J. Thatcher, Trans. Am. Electrochem. Soc, 36, 337, 1919
4. D.E. Danly, J. Electrochem. Soc. 435C, 131, (1984).
5. L. Carlsson, H. Holmberg, B. Johnssen A. Nilsson, “Technique of Electro Organic Synthesis” Part III, John Wiley & Sons New York, (1982) P.192.
6. D. Pletcher, F.C. Walsh, “Industrial Electrochemistry” Chapman and Hall, London, (1990).
7. B.V. Tilak, N.L Weinberg Technique of Electro Organic Synthesis, Part III John Wiley & Sons, New York, (1982).
8. F. Beck, “Elektroorganishe Chemie” Verlag Chemie. Weinheim, Germany (1974)
9. J Hulliger, R Berger, G Rosanati, P Metrangolo and E Weber, Chem.Soc.Rev.,40,3496,2011.
10. W R Dolbeir, J. Flour. Chem.,126,157,2005.
11. A S Burlov, A D Garnovskii, L I Kuznetsova and I S Vasilchenko. Russia.J. Chem,96,1999.
12. A D Garnovskii, L M Blanco, B I Kharisov, D A Garnovskii and A S Burlov. Journal of Co-ordination Chemistry,223,2006.
13. Emma K. Bullough, Marc A. Little, and Charolotte E. Willians, American Chemical Society Orgonometallics,32 (2),570,2013.
14. R X Sun, H B. Xu, N F. Wan and J Wang, Chem J Chinese Univ.,28,904,2007.
15. N Kumar and Dennis G. Tuck., and J Chem.,60,2579,2000.
16. Antonio Rodriguez, Jose A. Garcia-Vazquez., J. Phys.Chem. B,2014.
17. “Organic Electrochemistry” [Eds, M.M. Baizer, H. Lund], Marcel Dekker, (1983).
18. “Technique of Electro organic chemistry [Ed. N.L. Weinberg] Part I (1974), Part II (1975), Part III (1982), John Wiley & Sons, New York.
19. T. Shono ‘Electro Organic Chemistry as a new Tool in Organic Synthesis’ Springer Verlag (Berlin Heidelberg) (1984).
20. S. Torii’ Electro organic Synthesis, Methods and applications, Part 1. Oxidations, Kodansha VCH, (1985).
21. S. Adhikari, T. Bhattacharjee, P. Nath, A. Das, J. P. Jasinski, R. J. Butcher, D. Maiti, Inorg. Chim. Acta. 2020, 512, 119877.
22. N. Kajal, V. Singh, R. Gupta, S. Gautam, Environ. Res. 2022, 204, 112320.
23. L. Andrezálová, Z. Országhová, J. Inorg. Biochem. 2021, 225, 111624.
24. M. Pervaiz, S. Sadiq, A. Sadiq, U. Younas, A. Ashraf, Z. Saeed, M. Zuber, A. Adnan, Coord. Chem. Rev. 2021, 447, 214128.