

Electroorganic synthesis of the metal chelates of a novel ligand: Acetylacetone

M. Alam* and Shreya Gorai

University Department of Chemistry, Ranchi University, Ranchi-834 008, Jharkhand, India

E-mail: malamgold@yahoo.in, shreyagorai.gorai@gmail.com

Manuscript received online 12 August 2019, revised 03 November 2019, accepted 04 November 2019

Chelated coordination compounds of Cu and Zn were synthesized by electrolyzing the aqueous solution of acetone, methanol, ammonia and ligand (acetylacetone) at sacrificial Cu/Zn anode and inert platinum cathode. Gram quantities of complex can be produced in a few hours. Electrochemical synthesis of complexes formulating $M_2L_4 \cdot (H_2O)_n$ and ML_2 where (M = Cu, Zn), L = acetylacetone were synthesized. The structural features of these complexes are characterized by elemental analysis, infrared spectral data, atomic absorption spectroscopy and thermal spectral data.

Keywords: Electrochemical, acetylacetone, electrolytic oxidation, ligand, atomic absorption spectroscopy.

Introduction

Electroorganic synthesis is an organic chemical reaction which are taking place in electrolytic cells by the passage of electric current. Electrosynthesis presents many advantages over classical routes such as high efficiency, lower prices of metals and high reactivity of product. This new method allows sustainable and green production of organic complexes. Electrons are universal chemical reagent which are inherently cheaper and cleaner than corresponding chemical oxidizing or reducing agents since the absence of spent reagents circumvents many problems associated with purification, recycle and waste treatment.

Acetylacetone (2,4-pentanedione) (Fig. 1) is a diketone compound with the empirical formula C_5H_8O . It is a clear, colorless to light yellow liquid ketone with a pleasant odor. It

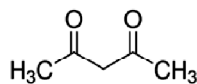
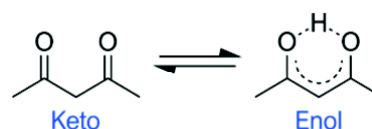


Fig. 1

is miscible in water, benzene, chloroform, ether, acetone, ethyl acetate and acetic acid¹. Acetylacetone have specific properties due to their structure (the presence of two carbonyl groups separated with one carbon atom). Their crucial feature is keto-enol tautomerism, the presence of the ketone and the enol forms in equilibrium (Scheme 1).



Scheme 1

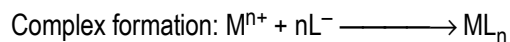
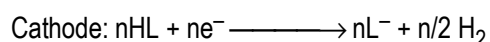
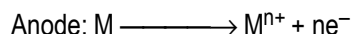
The equilibrium is strongly shifted towards the enol form due to the formation resonance structure as a six-membered ring. The capacity to form stable complexes with most metals is a direct consequence of the occurrence of such compounds in the enol form^{2,3}.

Zinc acetylacetonate complex is an effective component of a silver anti-tarnish agent⁴. It is also used in synthesis of CZTSSe (copper acetate zinc acetylacetonate tin acetate elemental sulphur and oleylamine) nanocrystals which is used in thin films of solar cells⁵. The atomic layer deposition using the $Cu(acac)_2$ ($acac$ = acetylacetonate) precursor was studied by atomistic mechanism⁶.

Electrochemical cell involves two separate electrode processes occurs simultaneously which allow electrons to move through the solution. The substrate will either undergo oxidation at the anode, where electrons are removed from the substrate to the electrode, or reduced at the cathode, where electrons are transferred from the electrode to the substrate in solution, and this is the driving force to complete the circuit and carry out electrochemical synthesis⁷.

Electrochemical cell can be schematically be represented

by:



An advantage of the electrochemical procedure for synthesis of metal complexes are considerably carried in lower temperature (0–100°C) in comparison with traditional methods (generally at 170–250°C, although sometimes at 100°C⁸).

In our present work of electrosynthesis, we have used metals (Cu/Zn) as anode to form complexes with acetylacetone. Platinum electrode is used as cathode material because of its inertness in most electrolyte environments and its high oxygen over potential in aqueous media. We have carried out these electrochemical synthesis in undivided cell. Acetone, ammonia, and methanol were used as solvent and lithium perchlorate as electrolyte with 3 V DC supply under atmospheric condition.

The solids formed were isolated in the pure form and characterized on the basis of spectral analysis.

Experimental

Copper metal chelated with acetylacetone:

Electrochemical cell consisted of a 100 ml tall form beaker in which two electrode: platinum as cathode and copper as anode are suspended in a liquid phase containing ligand: Acetylacetone (4 ml); solvent: acetone (30 ml), liquid ammonia; and supporting electrolyte: LiClO₄ (0.05 g) dissolved in 5 ml of methanol. Firstly a solution was prepared by dissolving 0.5 g LiClO₄ in a mixture consisting of 5 ml of methanol and 30 ml acetone in a 100 ml of beaker. Then 3 ml of acetylacetone and 2 ml of liquid ammonia was added to it. Immediately a bright yellow precipitate was formed. On allowing the mixture to stand for 2 min precipitate disappear leaving behind clear solution of light yellow colour. It was electrolyzed using platinum as cathode and copper as sacrificial anode. The electrolysis was conducted at current strength of 20 mA and voltage 3.5 V for 8 h at room temperature. As the electrolysis proceeded, gas evolved at the cathode and a light green colour product is formed at the anode. This material gradually get deposited at the bottom of the cell. At the end of the experiment it was collected by filtration, washed with acetone (5 ml) and dried in a vacuo. Light green colour amorphous product was obtained and named

as SH-SA. The complex obtained in pure state was subjected to elemental (Table 1), spectral and thermogravimetric analysis.

Table 1. Elemental analysis: copper complex

Sample	Colour	Analysis (%): Obsd. (Expt.)				Empirical formula
		C	H	O	M	
AcCu	Blue	37.79 (35.47)	6.92 (5.31)	35.27 (36.72)	20 (22.50)	Cu ₂ C ₂₀ H ₄₄ O ₁₄
Molecular formula: Cu ₂ (OCCH ₃ CH ₂ CH ₃ CO) ₄ (H ₂ O) ₆						

The electrochemical cell can be represented as:



Zinc metal chelated with acetylacetone:

A solution was prepared by dissolving 0.5 g LiClO₄ in a mixture consisting of 5 ml of methanol and 30 ml acetone in a 100 ml of beaker. Then 3 ml of acetylacetone and 2 ml of liquid ammonia was added to it. Immediately a bright yellow precipitate was formed, on allowing the mixture to stand for 2 min precipitate disappear leaving behind clear solution of light yellow colour. Then it was electrolyzed using platinum as cathode and zinc as sacrificial anode. The electrolysis was conducted at current strength of 20 mA and voltage 3.5 V for 8 h at room temperature. As the electrolysis proceeded, hydrogen gas evolved at the cathode and a white colour product is formed at the anode. This material gradually deposited at the bottom of the cell. At the end of the experiment it was collected by filtration, washed with acetone (5 ml) and dried in a vacuo. White colour crystalline product was obtained and named as ZnAC. The complex obtained in pure state was subjected to elemental (Table 2), spectral and thermogravimetric analysis.

Table 2. Elemental analysis: zinc complex

Sample	Colour	Analysis (%): Obsd. (Expt.)				Empirical formula
		C	H	O	M	
ZnAC	White	45.57 (44.47)	5.31 (5.31)	24.30 (23.2)	24.80 (22.50)	ZnC ₁₀ H ₁₄ O ₄
Molecular formula: Zn(CH ₂ =COCH ₂ COCH ₃) ₂						

The electrochemical cell can be represented as:



Results and discussion

Copper complexes:

FTIR spectral analysis:

The FTIR spectrum exhibit the following characteristic absorption have been collected in Table 3. The complex spectrum shows two prominent bands at 1577(sh) and 3155 cm^{-1} are assigned as $\nu\text{C}=\text{O}$ and $\nu\text{C}=\text{C}$ vibrations respectively. These bands were observed at downfield shift, going from free ligand to metal complex $\nu\text{C}=\text{O}$, suggests neutral ketonic coordination of carbonyl groups to the metal. It is expected that coordination of oxygen atom to the metal would reduce the electron density on oxygen atom and thus lower the $\text{-C}=\text{O}$ absorption. Furthermore, the presence of peak in the region 400–650 cm^{-1} for the complex is indicative of Cu-O stretching vibrations. The IR stretching frequency observed at 1419 cm^{-1} in the complex has been attributed to the pres-

ence of C-O group. The downward shift of the broad band at 1613 cm^{-1} corresponding to enolic form of acetyl group to 1536–1400 cm^{-1} indicated the coordination of oxygen atom to the metal ion. This supports the replacement of chelated proton of the ligand by a metal in these bands are reported in the literature for $[\text{Cu}(\text{acac})_3]$ complexes grafted on silica⁹. The presence of coordinated water is revealed by the appearance of broad band at 3155 cm^{-1} due to stretching absorption of $\nu(\text{O-H})$ of water. The presence of coordinated water is further confirmed by the appearance of bands in the region of 998–1023 cm^{-1} assignable to the rocking mode of coordinated water. This IR spectrum results are supported by similar FTIR literature studies^{10–13}. Hence, the proposed structure for the complex is as given in Fig. 2.

Table 3. IR absorption bands. In AcCu

Bands (cm^{-1})	Nature of bands	Group assignment
3155.54	Medium	=C-H + O-H stretching
3070.68	Medium	=C-H
2997.38	Medium	C-H, CH_3
2920.23	Medium	C-H, CH_3
2627.05	Weak	Overtone
2372.44	Weak	Overtone
2291.43	Weak	Overtone
2121.70	Weak	Overtone
1959.68	Weak	Overtone
1577.77	Sharp	C=O stretching
1535.34	Sharp	C=O stretching
1419.61	Sharp	C-O stretching
1357.89	Sharp	C=C stretching
1273.02	Sharp	C-C, C- CH_3 , C-O stretching
1188.15	Medium	C-H, in-plane bending
1018.41	Sharp	CH_3 rocking
937.40	Sharp	C- CH_3 + C-O + O-H rocking (coordinated H_2O)
783.10	Sharp	C-H, out-of-plane bending
682.80	Medium	Ring deformation
613.36	Sharp	C- CH_3 bending + M-O stretching
455.20	Sharp	Ring deformation + M-O skeletal vibration

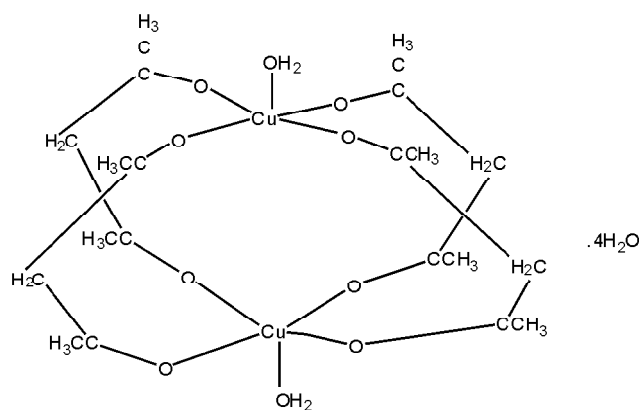


Fig. 2

Thermogravimetric analysis:

Thermoanalytical measurements of complex AcCu at reduced pressure (10⁻² torr) and in nitrogen atmosphere shows single stage decomposition which indicate complete volatilization below 220°C. The weight loss in the temperature range between 50–225°C give endothermic DTA bands which occurred at same temperature region in TGA curve. It was verified that the presence of endothermic peak at 222.92°C corresponding to fusion and thermal decomposition respectively. The complete volatilization upon heating is supported by similar TGA study^{14–17}. The Fig. 2 shows the IR spectra of complex that shows similar bands to the bands observed for the infrared spectra of the volatilized product. The proposed formulation in Fig. 2 is supported by FTIR bands and thermogravimetric loss pattern.

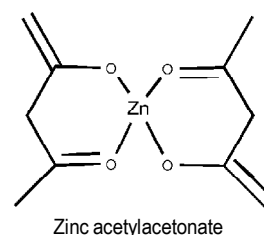
¹H NMR:

The ¹H NMR spectra of the complex was recorded in CDCl₃ solution using tetramethylsilane (TMS) as internal standard. ¹H NMR spectra shows peaks shifted to lower value ($\delta = 0.82$) than that of free ligand -C=O ($\delta = 2.2\text{--}2.4$) which probably indicate the formation of covalent bond between oxygen atom of carbonyl group and metal ion¹⁷. It confirms formation of complex with metal. The (CH₂) protons present in the ligands were observed at 1.38 ppm as a singlet. The (OH₂) proton present in the complex was observed at 2.16 ppm as a singlet. The conclusions drawn from ¹H NMR studies further support to the modes of bonding discussed in their thermal and IR spectra.

Zinc complexes:**FTIR spectral analysis:**

The FTIR spectrum exhibit the following characteristic absorption have been collected in Table 4. The complex spectrum shows two prominent bands at 1500(sh) and 3052 cm⁻¹ are assigned as γ C=O and γ C=C vibrations respectively. These bands were observed at downfield shift, going from free ligand to metal complex γ C=O, suggests neutral ketonic coordination of carbonyl groups to the metal. It is expected that coordination of oxygen atom to the metal would reduce the electron density on oxygen atom and thus lower the -C=O absorption. Furthermore, the presence of peak in the region 400–650 cm⁻¹ for the complex is indicative of Zn-O stretching vibrations. The IR stretching frequency observed at 1419 cm⁻¹ in the complex has been attributed to the pres-

ence of C-O group. The downward shift of the broad band from 1613 cm⁻¹ corresponding to enolic form of acetyl group to 1536–1400 cm⁻¹ indicated the coordination of oxygen atom to the metal ion. Band at 1793 cm⁻¹ confirms six membered cyclic ring like structure¹³. This supports the replacement of chelated proton of the ligand by a metal ion. Its future supported in the literature for the synthesis of one dimensional nanostructure [Zn(acac)₃]¹⁸. Hence, the proposed structure for the complex is as given in Fig. 3.

**Fig. 3****Thermogravimetric analysis:**

The TGA studies of the complexes were carried out in the nitrogen atmosphere at a rate of 15° per minute up to 500°C. TGA curve shows single stage decomposition which indicate complete volatilization. Decomposition step is observed in the temperature range 27–200°C and is accompanied with 16.68% loss against theoretical loss 17.03%. This is attributed to loss of propene group of ligated molecule. In DTA curve, shows that there is a large mass loss followed by mass plateau and is formed when evaporation of volatile product during desorption and drying process. The percentage loss at decomposition temperature was in good agreement with the experimental values. The proposed formulation (Fig. 3) is supported by FTIR bands and thermogravimetric loss pattern.

¹H NMR:

The ¹H NMR spectra of the complex was recorded in CDCl₃ solution using tetramethylsilane (TMS) as internal standard. The ¹H NMR spectra shows signal at 7 ppm which is attributed to the vinyl groups (CH₂=C-) of the acetylacetonate ligand¹⁷. The chemical shift due to the OH proton in ligand appears between 2–2.3 ppm. On deprotonation, which leads to complex formation shifted this signal downfield in the complexes which appeared at 1.5 ppm^{19–21}. The ¹H NMR analyses yielded results which were found to be in good agreement with the proposed molecular formula for the complex.

Table 4. IR absorption bands. In ZnAC

Bands (cm ⁻¹)	Nature of bands	Group assignment
3052.28	Broad	=C-H
2499.75	Medium	C-H, CH ₃
2056.12	Weak	Overtone
1793.80	Weak	C=O six membered cyclic ring
1500.62	Sharp	C=O stretching
1114.86	Medium	C-H, in-plane bending
1041.56	Sharp	CH ₃ rocking
979.84	Sharp	C-CH ₃ + C-O
840.10	Sharp	C-H + =CH ₂ (out-of-plane bending)
686.66	Medium	Ring deformation
474.49	Sharp	Ring deformation + M-O skeletal vibration

Conclusion

Electroorganic synthesis is a versatile tool in green synthesis. The design and innovative concepts of electrolysis cells will allow the applicability of this technique to be expanded. Electroorganic synthesis will transform from a niche technology to a common synthetic method. The present work thus reveals that the electroorganic synthesis of copper and zinc acetylacetonate coordination complexes is a single step green process and offers a versatile approach for the commercial preparation of these compounds. Electroorganic synthesis is a renewable-electricity-powered processes for the production of high-value organic chemicals which can contribute to the reduction of the chemical industry's carbon footprint.

Acknowledgement

We thank the Head of the University Department of Chemistry, Ranchi University, Ranchi for providing necessary facilities and encouragement. We are grateful to acknowledge IIT Mumbai, CIF, BIT Meshra, Ranchi, SAIF, NEHU, Shillong and SAIF, Tezpur University for providing the facility to carry out thermal, elemental, NMR and FTIR analysis.

References

1. J. Stary, "Solvent extraction of metal chelates", 1st ed., Pergamon, New York, 1964, **5**, 51.
2. C. R. Bhattacharjee and M. K. Chaudhuri, *Proc. Indian Natn. Sci. Acad.*, 1984, **2**, 194.
3. H. Lamprey, *Annals of the New York Academy of Sciences*, 1960, **88**, 519.
4. Q. Ashton Acton, "Sulfur compounds-advances in Research and Application", Scholar Editions, Atlanta Georgia, 2013, **1**, 66.
5. P. O'Brien and P. J. Thomas, "Nanoscience", 1st ed., Royal Society of Chemistry, UK, 2014, **2**, 23.
6. A. Hamerich, L. Lottermoser and J. Muller, *Surface and Coating Technology*, 1993, **59**, 212.
7. K. G. Watts, "Design and fabrication of an electrochemical microreactor and its use in electroorganic synthesis", Cardiff University, 2013, **1**, 6.
8. B. I. Kharisov, A. D. Garnovskii, O. V. Kharisov, U. O. Mendez and A. Y. Tsivadze, *J. Coord. Chem.*, 2007, **60**, 1435.
9. J. J. Spivey, "Catalysis", 1st ed., Royal Society of Chemistry, UK, 2007, **1**, 105.
10. H. Golchoubian and H. Fazilate, *Iranica Journal of Energy & Environment*, 2012, **3**, 264.
11. D. S. Suslov, M. V. Bykov, P. A. Abramov, M. V. Pakhomova, I. A. Ushakov, V. K. Voronav and V. S. Tkach, *Inorg. Chem. Commun.*, 2016, **66**, 1.
12. H. Lamprey, *Annals of the New York Academy of Sciences*, 1960, **88**, 519.
13. S. Browning, "On the electrochemical synthesis of metal acetylacetonates", University of Texas, Austin, 2006, **1**, 1.
14. Ringkasan, *Pertanika*, 1981, **2**, 197.
15. K. C. Patil, G. V. Chandrashekhar, M. V. George and C. N. R. Rao, *Canadian Journal of Chemistry*, 1968, **46**, 257.
16. B. M. Weckhuysen, R. Ramachandra Rao, J. Pelgrins, R. A. Schoonhydt, P. Bodart, G. Debras, O. Collart, P. V. D. Voort and E. F. Vansant, *Chemical European Journal*, 2000, **16**, 2960.
17. D. L. Pavia, G. M. Lapman, G. S. Kriz and J. R. Vyvyan, "Introduction to Spectroscopy", 5th ed., Cengage Learning, Canada, 2015.
18. N. D. Cooper, *Proceedings of the National Conference on Undergraduate Research*, 2015, **1**, 1.
19. National Center for Biotechnology Information. PubChem Database. Acetylacetonate, CID=31261, <https://pubchem.ncbi.nlm.nih.gov/compound/Acetylacetonate> (accessed on Nov. 2, 2019).
20. L. W. Reeves and W. G. Schneider, *Canadian Journal of Chemistry*, 1951, **36**, 793.
21. P. E. Hansen, *Wiadomosci Chemiczne*, 2017, **71**, 427.

