

THE INTERNATIONAL JOURNAL OF SCIENCE & TECHNOLEDGE

Spectral, Fluorescence and Thermal Studies of B-Diketone Ligand and their Metal Complexes

R. Biju Bennie

PG Department of Chemistry, St. John's College, Palayamkottai, Tirunelveli, India

S. Theodore David

PG Department of Chemistry, St. John's College, Palayamkottai, Tirunelveli, India

C. Joel

PG Department of Chemistry, St. John's College, Palayamkottai, Tirunelveli, India

M. Theetharappan

PG Department of Chemistry, St. John's College, Palayamkottai, Tirunelveli, India

S. Daniel Abraham

PG Department of Chemistry, St. John's College, Palayamkottai, Tirunelveli, India

M. Seethalakshmi

PG Department of Chemistry, St. John's College, Palayamkottai, Tirunelveli, India

Abstract:

Transition metal complexes of various acetylacetonate-based ligands of the type ML (where $M = Cu(II)$ and $Zn(II)$, $L = 3$ -(aryl)-pentane-2,4-dione) have been synthesized. The structural features have been established from their molar conductance, IR, UV-Vis and ^{13}C NMR spectral studies. Conductivity measurements reveal that all the complexes are non electrolytic in nature. Spectroscopic and other analytical data of the complexes suggest octahedral geometry for $Cu(II)$ and $Zn(II)$ complexes. All synthesized compounds may serve as potential photoactive materials as indicated from their characteristic fluorescence properties. The $Cu(II)$ and $Zn(II)$ complexes have been found to be thermally stable.

Keywords: β -diketone, Transition metals, Conductance, Spectral studies, Photoactive

1. Introduction

The Knoevenagel condensation between aldehydes and active methylenes is an important reaction in organic synthesis in forming carbon-carbon double bond, and the products have E-isomer dominantly. Knoevenagel condensation has been receiving considerable attention, due to its broad spectrum of uses including cosmetic, perfume, pharmaceutical, agrochemicals, and pharmaceuticals applications. Recent years have seen an upsurge of interest on the synthesis and spectroscopic characterization of β -diketones as potential ligands. Complex formation in this class of compounds is conceived by replacement of the enolic proton by chelation with metal ions in a bidentate fashion^[1,2]. Metal chelates of β -diones have interesting properties in industrial applications^[3-5]. These compounds have diverse physiological activities e.g. acting as central nervous systems depressants and calcium sensitizing agents and possess hypnotic, diuretic, and antihistaminic, anti-inflammatory, antimicrobial and hypoglycemic activities^[6].

2. Experimental

2.1. Chemicals and Methods

Acetyl acetone, Benzaldehyde and Piperidine were purchased from Himedia. $Cu(II)$ and $Zn(II)$ metal salts were of analytical grade from Merck. All other reagents and solvents were purchased from commercial sources and were of analytical grade. The infrared spectra of the solid samples were recorded in JASCO/FT-IR 410 spectrometer in the range of $4000-400\text{ cm}^{-1}$. Potassium bromide disc method was employed for sample preparation. Electronic spectra were recorded using SYSTRONICS DOUBLE UV-VIS spectrometer: 2202 using DMSO as solvent in the range of $200-1100\text{ nm}$. The molar conductivity measurements of the metal complexes were carried out in $\sim 10^{-3}\text{ M}$ DMF solutions using a Coration digital conductivity meter. The ^1H NMR was recorded on a JEOL GSX-400 spectrometer employing CDCl_3 as solvent at ambient temperature. The mass spectral study was carried out using JEOL D-300 (EI) mass spectrometer. The emission spectra were recorded on Perkin-Elmer LS-45 Fluorescence spectrometer. TG-DTA analysis of the complexes was performed on SIINT 6300 instrument.

2.2. Synthesis of β -Diketone Ligand (L)

Equimolar quantities of Acetylacetone (3 g) and benzaldehyde (3.1 g) were mixed in a beaker. To this piperidine (0.05 cm³) in ethanol (50 mL) was added and the reaction mixture was stirred thoroughly for a period of 6 h with occasional cooling. Gradually a yellow precipitate was separated in small amounts. The reaction mixture was set aside to evaporate to dryness, and the residual solid was washed with an excess of petroleum ether to remove any unreacted reagents. Washing was repeated two to three times, and the compound was recrystallized from ethanol to give a yellow solid Knoevenagel condensate.

2.3. Synthesis of complexes (ML)

- (M=Co (II), Ni (II) and Cu (II))

The metal complexes were prepared by the addition of hot solution of the appropriate metal(II) chloride (1 mmol) in ethanol (25 mL) to the hot solution of the 3-(aryl)-pentane-2,4-dione (2 mmol) in the same solvent (25 mL). The resulting mixture was stirred under reflux for one hour. The precipitate obtained was filtered, washed thoroughly with ethanol, and dried in vacuum.

3. Results and Discussion

3.1. Structural Characterization of Ligand

The structure of the ligand has been confirmed by the analytical and spectral data summarized in Table 1. The spectral data obtained for the ligand are furnished below.

3.1.1. FT-IR Spectra

The FT-IR spectrum of the ligand shows a strong intensity band at 1655 cm⁻¹ which can be assigned to $\nu_{(C=O)}$, and the band in the 1549 cm⁻¹ region is assigned to -C=C- stretching vibration. Further, the band at 2925 cm⁻¹ region is assigned to aromatic ring -C-H stretching vibration.

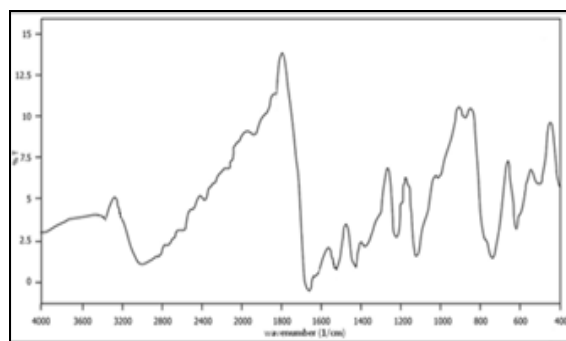


Figure 1

3.1.2. ¹H NMR Spectra

A singlet at 2.5 ppm corresponds to the methyl protons of acetyl acetone. The multiplet in the range 6.6 to 7.4 ppm is due to the aromatic protons of benzaldehyde. A singlet at 8.1 ppm is corresponds to -CH proton resulting from the -C=CH-Ar stretching of the ligand.

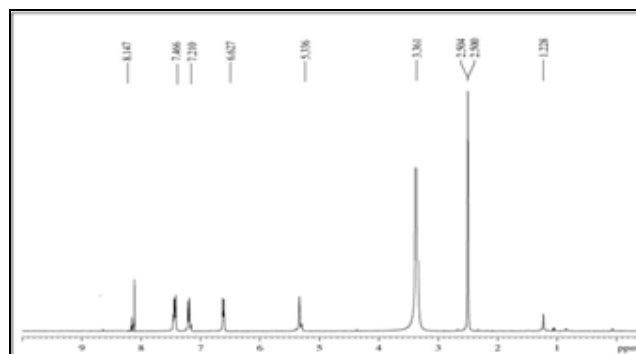


Figure 2: Proposed Structure of the Ligand

3.2 Structural Characterization of the Metal Complexes

The analytical and molar conductance data of Cu (II) and Zn (II) complexes are provided in Tables 1 & 2. The conductance data^[7] indicate that all the metal complexes synthesized are non-electrolytes. The non-electrolytic nature of the metal complexes suggests that the anions of the salts are coordinated to the metal ions in the formation of metal complexes.

3.2.1. FT-IR Spectra

In order to study the binding mode of the β-Diketone ligand to the metal in the complexes, the FT-IR spectrum of the free ligand was compared with those of the complexes. The band at 1655 cm⁻¹ assigned to the ν(C=O) stretching of the free ligand has been shifted to lower frequencies in the spectra of Cu(II) and Zn(II) complexes (1644 cm⁻¹, 1649 cm⁻¹)^[8] indicating the coordination of the carbonyl oxygen atom to metal. The FT-IR spectra of metal complexes also show some new bands in the 552 cm⁻¹ and 592 cm⁻¹ region, which is due to the formation of M-O bands.^[9]

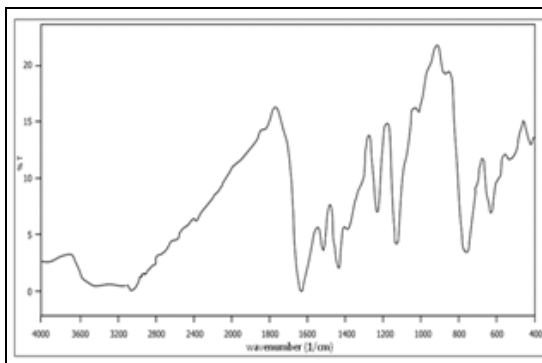


Figure 3: FT-IR spectrum of Cu (II) complex

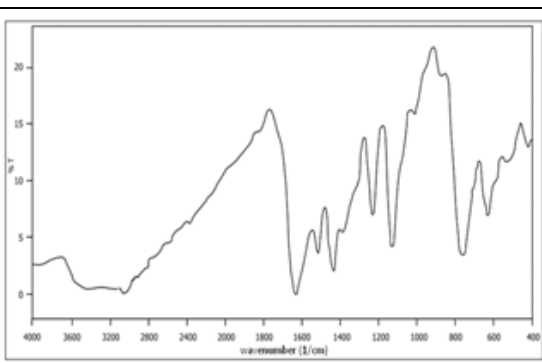


Figure 4: FT-IR spectrum of Zn (II) complex

Compound	Elemental analysis (cal) obs values %		
	C	H	N
Ligand	74.78 (74.79)	5.21 (5.24)	7.28 (7.29)
Cu(II) complex	54.13 (54.15)	4.16 (4.17)	5.25 (5.26)
Zn(II)-complex	54.16 (54.17)	4.15 (4.17)	5.25 (5.26)

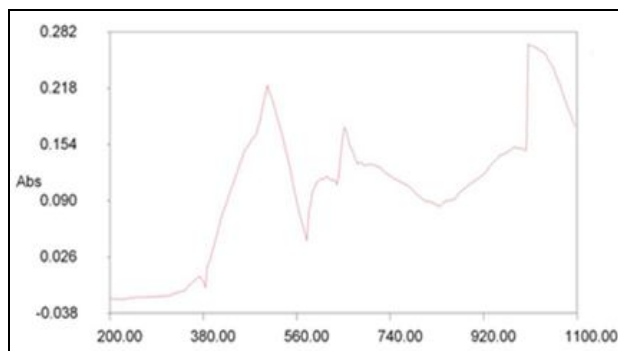
Table 1: Analytical and physical data of Ligand and its complexes

Complexes	Molar conductance (Scm ² mol ⁻¹)	Nature
Cu(II) complex	7	Non-electrolyte
Zn(II)-complex	12	Non-electrolyte

Table 2: Molar conductance data

3.2.2. Electronic Spectra

The electronic spectrum of Cu(II) complex exhibits three transitions at 540 nm, 610 nm and 720 nm respectively. The three possible d-d bands of Cu(II) complexes may be assigned to ²B_{1g} → ²E_{1g}, ²B_{1g} → ²B_{2g}, ²B_{1g} → ²A_{1g} which gives a tetragonally distorted octahedral geometry for the present Cu(II) complex.



Electronic spectra of Cu (II) complex
Figure 5: Proposed structure of metal complexes

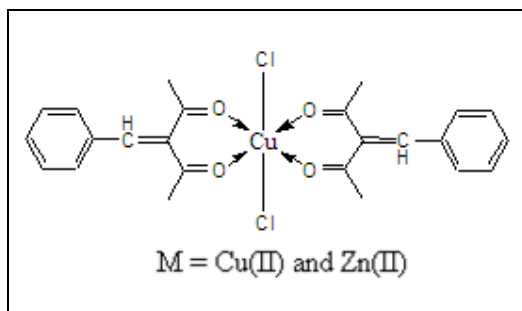


Figure 6

3.3. Thermogravimetric analysis

The thermo-gravimetric analysis (TG) was measured in the temperature 20–800 °C range. The results were in good agreement with the proposed structures. All complexes showed the same pattern of losing lattice water (76-95 °C) followed by the removal of the anion in (210-323 °C) then the organic constituents of the complexes start to decompose, finally leaving the metal oxides (509-604 °C).

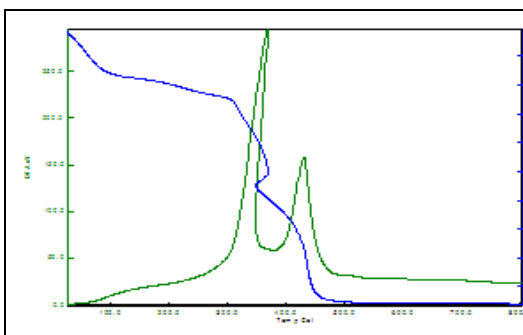


Figure 7: TG-DTA curve of Cu (II) complex

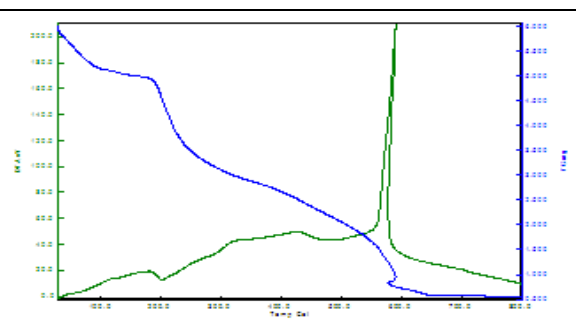


Figure 8: TG-DTA curve of Zn (II) complex

3.4. Fluorescence Studies

The emission spectra of the ligand and its complexes were studied. Significant differences in the positions of emission maximum of ligand and its complexes establish the coordination of the metal ion to the ligand. Enhancement of fluorescence through complexation is much interesting as it opens up the opportunity for photochemical applications of these complexes. The emission is readily observed for complexes with the naked eyes under UV light, whereas the ligand exhibits quite weak fluorescence. The enhanced fluorescence efficiency of the Zn(II) complex is attributed to the energy difference in zinc ion caused by the coordination environment.

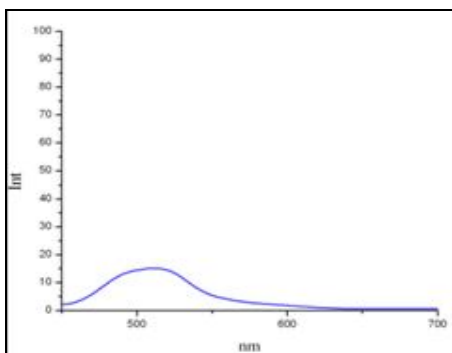


Figure 9: Fluorescence Spectra of ligand

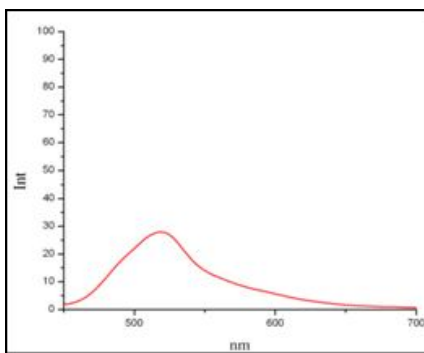


Figure 10: Fluorescence Spectra of Cu(II) complex

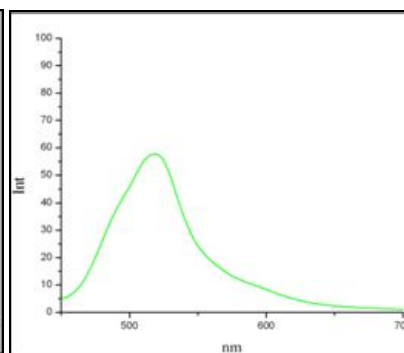


Figure 11: Fluorescence Spectra of Zn(II) complex

4. Conclusion

The β -Diketone ligand and its Cu(II) and Zn(II) complexes were characterized by FT-IR, ^1H NMR, electronic spectra and conductance measurements. The thermo-gravimetric analysis reveal that the complexes are thermally stable. The fluorescence studies reveal that Zn(II) complex exhibit higher emission than the Cu(II) complex and the ligand.

5. References

1. R. E Sievers, S. B Turnispeed, L. Huang, A. F Laglante, *Coord. Chem. Rev.*, 128 (1993) 285-291.
2. E. Knoevenagel, R. Arnot, *Chem. Ber.*, 37 (1904) 4499.
3. K. Krishnankutty, P. Venugopalan, *Indian. Chem. Soc.*, 78 (2001) 472 -473.
4. R. L. Funk, J. F. Fitzgerald, T. A. Olmstead, K. S. Para, J. S. Vos, *J. Am. Chem. Soc.*, 115 (1993) 8849.
5. K. Krishnankutty, M. B. Ummathur, *J. Indian. Chem. Soc.*, 83 (2006) 639-663.
6. W. M. Fathalla, M. Cajan, J. Marek, P. Pazdera, *Molecules*, 6 (2001) 574-587.
7. W. J. Geary, *Coord. Chem. Rev.*, 40 (1971) 437.
8. M. Yosuva Suvaikin, A. Sebastian, *Int .J. ChemTech.Res.*, 4 (2012) 805-815.
9. S. Chandra, L. K. Gupta, S. Agarwal, *Transition Met. Chem.*, 32 (2007) 240-245.
10. Long Yi, Li-Na Zhu, Bin Ding, Peng Cheng, Dai-Zheng Liao, Shi-Ping Yan, Zong-Hui Jiang, *Inorganic Chemistry Communications*, 6 (2003) 1209–1212