

Synthesis And Characterisation Of Cadmium(II) Chelates Azo Ligand Derived From Coumarin

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Abstract : The synthesis and characterization of cadmium chelates derived from (E)-7-hydroxy-6-((4-methoxyphenyl)diazenyl)-4-methyl-2H-chromen-2-one. The ligand was prepared in the general route of azo dyes by coupling the diazonium salt of 4-methoxyaniline with 4-methyl-7-hydroxycoumarin in sodium hydroxide 10% (w/v) solution. The azo ligand was identified on the basis of elemental analyses, MS, H-NMR and FT-IR spectra. The products of complexes with the new azo dye were isolated by the direct reactions of cadmium chloride with the alkaline solution of free ligand. The TG-DSC study confirmed the thermal stability of complexes at a wide range of average heating in inert gas of analysis and the results observed from loss weight percent investigated

IndexTerms - azo ligands; metal complexes of coumarin, Cadmium chelate, FTIR, TGA, DSC

I. Introduction

The azo dyes of 4-hydroxycoumarin and their derivatives play an important role in the co-ordination chemistry. The inorganic complexes of chromen-2-one rings have a lot of application in catalysis, manufacturing of dyes and pharmaceutical preparations. These complexes have a wide range of applications in the fabrication of diodes and solar cells. The fluorescence properties of the compounds derived from azo dyes of chromen-2-one have wide applications.

The wide applications that the coumarin azo dyes have attracted many chemical engineering researchers. An attempt is made to prepare and characterize new azo dye complexes of Cd(II) derived from (E)-7-hydroxy-6-((4-methoxyphenyl)diazenyl)-4-methyl-2H-chromen-2-one.

II. Experimental

All the chemicals used under this study including 4-methoxyaniline, 4-methyl-7-hydroxycoumarin and 4-methoxyaniline and CdCl₂·2H₂O were procured from SD chemicals. The melting points temperature of the coumarin derivatives and metal complex were determined on the Stuart melting point apparatus. The electronic spectra of ligand and its complex was determined with Shimadzu spectrophotometer. FTIR spectra was recorded on Shimadzu FTIR spectrometer in the range (3800-200) cm⁻¹. The pH of the solutions was measured using a digital pH meter.

III. Synthesis of azo ligand

The azo dye was synthesized according to the procedure available in literature, by dissolving 4-methoxyaniline in hot double distilled water. HCl was added to this solution. An aqueous solution of sodium nitrite (5 mmol) was added by maintaining the temperature of the reaction at the temperature of ice. The formed diazonium salt was gradually added to an alkaline solution of 4-methyl-7-hydroxycoumarin while stirring. The 10% NaOH was added drop wise for neutralization of the solution. The dark orange crude was then filtered, washed several times with water and ethanol, then dried. Re-crystallization was carried using ethanol yielding thick orange crystals.

IV. Synthesis of Cadmium complexes

2.236 gms of CdCl₂·2H₂O was dissolved in 30 mL of double distilled water at 90°C. An ethanolic solution of azo dye was added to this solution. The mixture was kept on magnetic stirrer for 45 min with low speed stirring. The cadmium complex was separated and filtered.

V. Results and Discussion

The physical properties of ligand and its cadmium complex were given in Table.1. The micro-analyses (C.H.N.) confirm the suggested chemical formula. The calculated and observed mole ratios were in good agreement. The molar conductivity measurements reveal that the cadmium complex does not show electrolytic nature. The loss of methoxy and methyl groups was confirmed through MS spectra. The peaks at around *m/e* = 116 and 89 were assigned to cleavage of chromen ring and points of -CH₃ and -OH respectively, as reported in literature.

Table.1. Properties of Azo dye and Cadmium complex

| | |
|---------------------|---|
| Molecular Weight | C ₃₄ H ₂₈ CdN ₄ O ₁₀ 820.53 |
| Colour | Orange |
| Melting point in °C | 327 |
| % C | 52.32 |
| %H | 4.79 |
| %N | 9.12 |
| %M | 16.04 |

The ¹H-NMR spectrum of the ligand, shows a singlet signal at δ (7.9–8.9) ppm corresponding to the -C=C-H of chromen ring. The doublet of doublet peaks at around δ (12.45) ppm reflects mainly the spin coupling of aromatic protons adjacent to each other in aromatic substituted. Aliphatic protons of -CH₃ groups attached at C-4 were resonated at around 4.43.

The ^{13}C -NMR spectrum showed peaks at 75 ppm, 96 ppm, 125-138 ppm and 143-167 ppm. These may be due to $-\text{CH}_3$ aliphatic carbon, $-\text{C}=\text{OH}$, $-\text{C}=\text{N}-$ and $-\text{C}=\text{C}-$ of coumarin respectively. The data of NMR confirmed the coordination of $\text{Cd}(\text{II})$ ion with the HL azo dye through $-\text{C}=\text{N}-$ and OH with deprotonation in the chelation reaction. As well as the deshielded protons of $-\text{HC}=\text{CH}-$ of chromene ring and hydrated water molecules was downfield shifted. This may be due to the electron donation of the active site toward the empty orbitals of $\text{Cd}(\text{II})$ ion¹⁶.

The bands of IR spectrum was assigned with reference to the literature. The broad absorption at 3496 cm^{-1} was assigned to $-\text{OH}$ of coumarin azo ligand. The strong band at 1654 cm^{-1} was assigned to $-\text{C}=\text{O}$ of chromene ring. The band at 1612 cm^{-1} is associated with $-\text{CH}=\text{CH}-$ as reported in literature^{12,15}. The shift of $-\text{N}=\text{N}-$ to lower frequencies at $1450-1433\text{ cm}^{-1}$ confirms the coordination of ligand via nitrogen. The TGA and DTA analysis was carried out on the sample under study. The loss of water was occurred around 160 to 275°C . The weight loss was in good agreement with the theoretical data. The mass loss around temperature $294-386^\circ\text{C}$ was assigned due to the loss of 2 hydrated H_2O molecules $-\text{OCH}_3$ and the loss of phenyl 2Cl anion and decomposition of the $\text{C}_6\text{H}_7\text{N}_2\text{O}$ has occurred at 415 to 560 Degrees. The loss of $\text{C}_6\text{H}_5\text{CH}_3$ occurred at $445-546^\circ\text{C}$. The formation of final product seems to occur at $550-920^\circ\text{C}$.

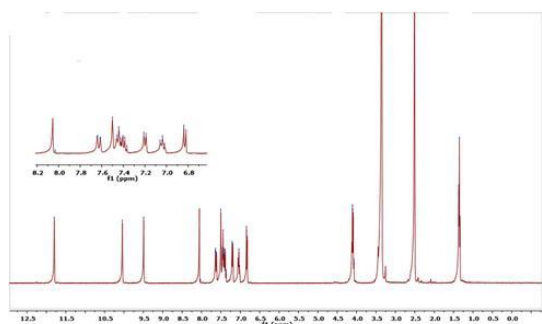


Fig 1. ^1H NMR of azo ligand

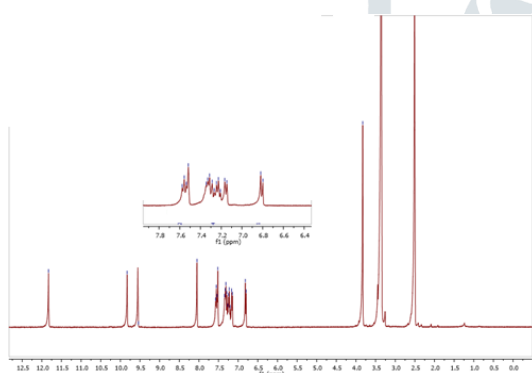


Fig 2. ^1H -NMR of Cd complex

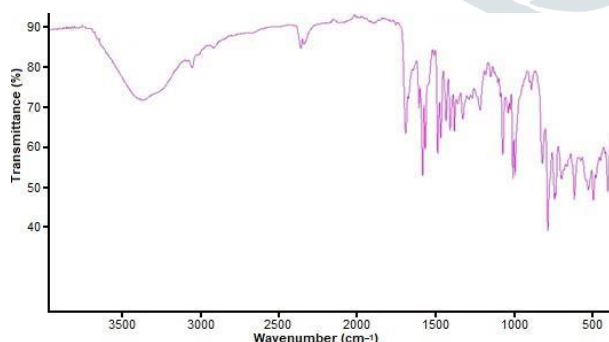


Fig 3. FT-IR spectrum of the sample under study

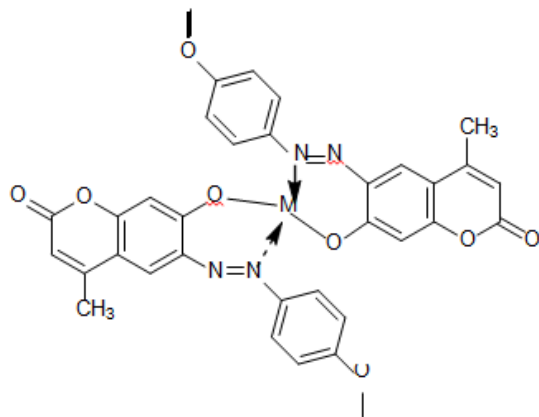


Fig.4. Structure of the Cadmium complex under study

VI. Conclusions

According to the results obtained from elemental analyses, FT-IR, NMR and EI-MS spectra and electronic spectra in ethanol and DMSO solvents, the tetrahedral geometry was identified for cadmium(II) complex. The thermal analyses and molar conductivity measurements confirmed tetrahedral environment around cadmium(II).

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