

SYNTHESIS AND SPECTRAL CHARACTERIZATION OF LANTHANIDE METAL COMPLEXES OF SCHIFF BASE DERIVED FROM SUBSTITUTED COUMARIN

RISHIPAL SINGH

Department of Chemistry, Swami Vivekanad Subharti University, Meerut

SANGEETA CHAUDHARY

Department of Chemistry, Meerut College, Meerut

AND

GAJENDERA SINGH

Department of Chemistry, Ramjas College Delhi University Delhi

RECEIVED : 31 March, 2016

A schiff base synthesized from the condensation of coumarin derivative and α -amino acids. The prepared Schiff base react with La(III), Ce(III) and Pr(III) nitrate to give the complexes with stoichiometric ratio (1:1). The complexes have been synthesized by elemental analysis, molar conductance, electronic, IR and NMR spectral techniques, which indicates ligand show tridentate nature on co-ordination with metal ions.

INTRODUCTION

Coumarin derivatives are known for their physiological, anti-coagulant, bacteriostatic and anti-tumor activity. A large number of coumarin derivatives have been reported to show as anti-HIV agent *in-vitro* and *in-vivo* systems. [1]

The coumarin nucleus is well known for its diverse biological properties as exhibited through its innumerable derivatives. In fact, the compounds containing benzopyran moiety are endowed with various pharmacological activities like antibiotic, anti-inflammatory, and fungicidal properties [2-3]. The potent antibiotics like novobiocin, coumaromycin and chartcusin are coumarin derivatives [4-5]. It was envisaged that incorporation of *imine moiety* in the coumarin nucleus through formation of Schiff bases with α -amino acids /8-aminoquinoline/4-aminoantipyrin may impart enhanced biological activity to the resulting compound. This idea prompted us to undertake the present study [6-7].

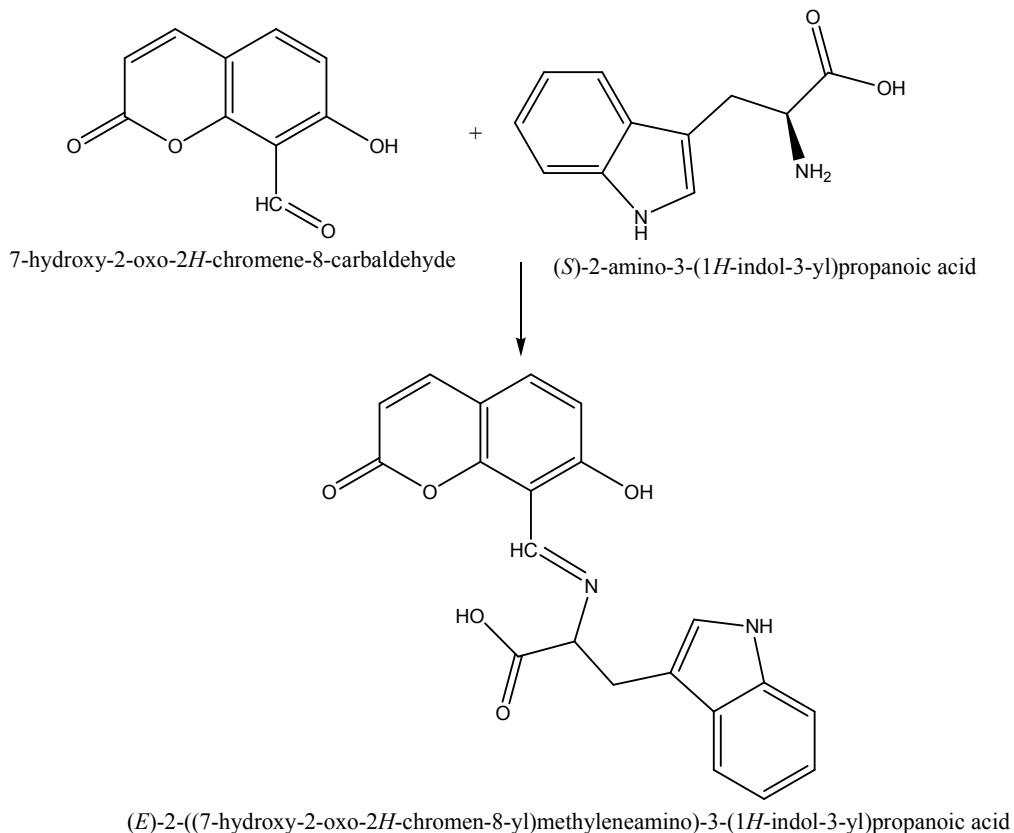
Herein we report the synthesis of macrocyclic Schiff base ligands derived from the condensation of 8-formyl-7-hydroxy-4-methyl coumarin with α -amino acids /8-aminoquinoline/4-aminoantipyrine and its lanthanide (III) metal complexes. The structure of ligand and metal complexes were determined by using spectral techniques like IR, ^1H and ^{13}C -NMR techniques.

EXPERIMENTAL

All reagents and solvents used were of BDH or Merck products. All the solvents were purified by double distillation.

Synthesis of Schiff base Ligand :

8-formyl-7-hydroxy-4-methyl coumarin was prepared as reported in the literature [8-9]. The methanolic solution of 8-formyl-7-hydroxy-4-methyl coumarin (0.01 Mole) was added to the methanolic solution of Tryptophan (0.01 mole) and stirring the content for half an hour. The bright yellow solid product separate out was filtered, dried and recrystallized.



Preparation of La(III) Metal complexes :

An methanolic solution of Schiff base ligand (0.01 mol) adding with the methanolic solution of Lanthanide nitrates (0.01 mol) and refluxed up to two hours. The precipitated product was filtered washed with methanol – water (1 : 1) mixture and dried in vacuum desiccator.

RESULTS AND DISCUSSION

The synthesized metal complexes are stable at room temperature, insoluble in water partially soluble in methanol and ethanol and completely soluble in DMF and DMSO.

The elemental analysis, magnetic moments and molar conductance data given in table-1.

Table 1. Characterization data of ligand and metal complexes

Schiff base	Found (Calculated) %				Colour	Molar conductivity (ohm ⁻¹) cm ² mole ⁻¹
	C	H	N	Metal		
C ₂₁ H ₁₆ N ₃ O ₈	67.02 (67.15)	4.28 (4.18)	7.44 (7.39)		Yellow	
(C ₂₁ H ₁₅ N ₃ O ₈)La	43.77	2.62	7.29	24.10	Yellow	108
	43.80	2.59	7.25	24.11		
(C ₂₁ H ₁₅ N ₃ O ₈)Ce	42.77	2.40	6.69	25.10	Yellow	102
	42.80	2.41	7.01	25.11		
(C ₂₁ H ₁₅ N ₃ O ₈)Pr	42.77	2.52	6.29	26.10	Yellow	103
	42.78	2.59	6.25	26.11		

Electronic spectral studies :

The electronic spectral data of metal complexes are given in table 2. The free ligand exhibited an intense band at 295 and 350 nanometer which are assign to $\pi - \pi$ transition [10-11].

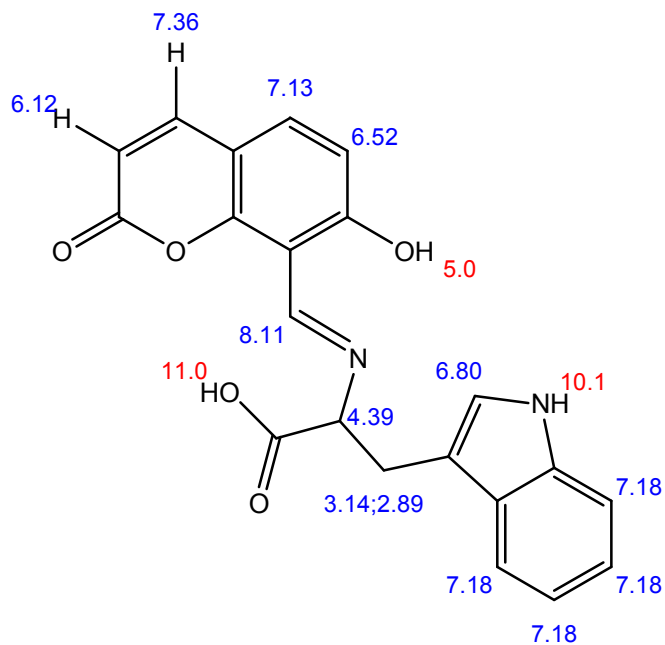
The electronic spectra of La(III) metal complex show the f-f transition at 11,924 while Ce(III) and Pr (III) metal complexes exhibited same transition at 12,390 and 13,516 nm respectively [12-13].

IR Spectral studies

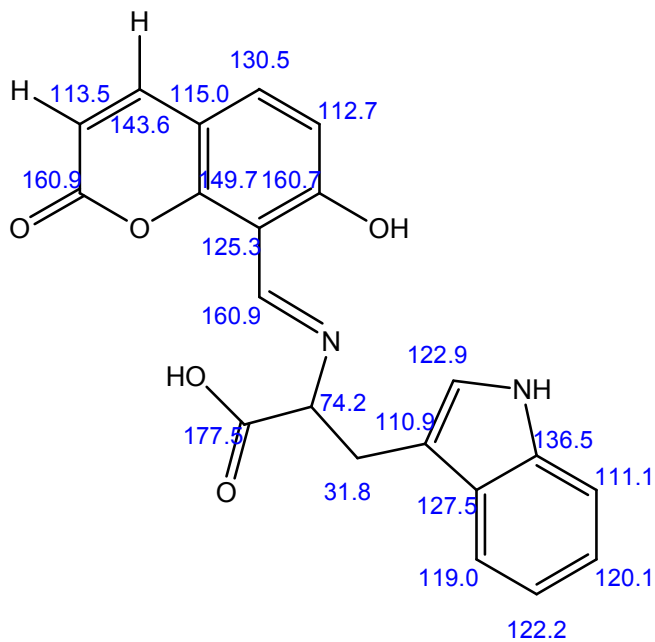
The IR spectra of ligand show a sharp band at 1610 cm⁻¹ which is shifted towards lower wavelength upto 1580 cm⁻¹ which indicate the involvement of Azomethyne group in co-ordination with metal [14].

The IR spectra of ligand show the broadband at 1167 to 1228 cm⁻¹ due to C-OH stretching vibrations which shift towards lower wavelength in the spectra of metal complexes. The involvement of carboxylic group oxygen atom in bonding is appear by the shifting of medium intensity band from 1659 cm⁻¹ upto 15 cm⁻¹ [15].

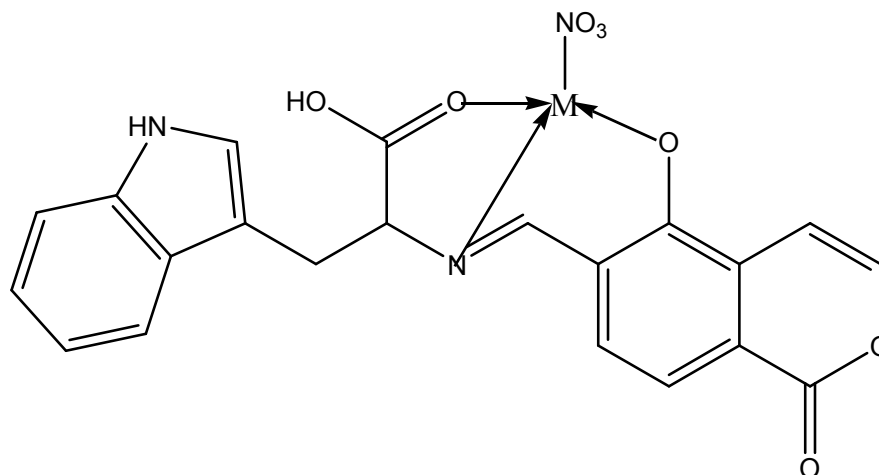
¹H NMR Spectral studies (DMSO-d₆) S, 6.12-7.36 ppm (5 H Coumarin ring), S, 5.0 ppm (OH group substituted with Coumarin ring), m, 7.18 ppm (Aromatic proton of amino acid), S, 10.1 ppm (Cyclic NH of amino acid)



¹³C NMR Spectral studies: DMSO-d₆ 110.9, 122.9, 136.5, 111.1, 120.1, 122.2, 119.0, and 127.5 ppm carbon atom of amino acid, 177.5 ppm (carbon atom of carboxylic group), 112.7-160.9 (Carbon atom of coumarin ring)



From the above spectral data the following structure of metal complexes is proposed



Where M = La(III), Ce (III) and Pr (III).

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