

Synthesis and Pharmacological Studies of Some Complexes of Eu(III) Ion with Schiff Bases of Sulphanilamide

G. RAJENDRAN* and S. FAISAL†

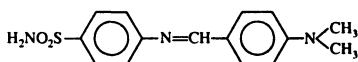
Chemistry Department, University College, Trivandrum-695 034, India

Synthesis and characterization of some complexes of Eu(III) ion with Schiff bases of sulphanilamide having the molecular formula $[\text{Eu}(\text{L})_3(\text{NO}_3)_3]$, $[\text{Eu}(\text{L})_3(\text{NCS})_3]$, $[\text{Eu}(\text{L})_3(\text{ClO}_4)_2]\text{ClO}_4$ where $\text{L} = 4[\text{N}-(4\text{-dimethylaminobenzalidene})\text{amino}]$ benzene sulphonamide (DBAB), $4[\text{N}-(4'\text{-methoxybenzalidene})\text{amino}]$ benzene sulphonamide (MBAB), $4[\text{N}-(4'\text{-hydroxy-3'-methoxybenzalidene})\text{amino}]$ benzene sulphonamide (HMBAB) and $4[\text{N}-(\text{furfuralidene})\text{amino}]$ benzene sulphonamide (FAB), have been reported. The antimicrobial activity and thermal stabilities of these complexes were also studied. All the complexes exhibited moderate antibacterial activity. The extent of activity depends on the nature of secondary coordinated ligands such as the oxoanions.

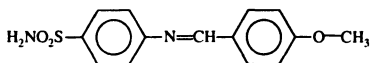
Key Words: Synthesis, Pharmacological studies, Eu(III) complex, Schiff Bases.

INTRODUCTION

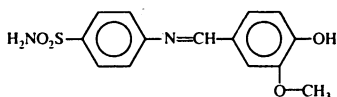
Schiff bases and their coordination compounds have gained importance for the past several years because of their application as models in biological biochemical, analytical and antimicrobial system¹. In the present paper, a number of Schiff base complexes of Eu^{3+} ions having eight- and nine-coordination number, have been synthesized, characterized and compared their thermal stabilities along with antimicrobial properties.



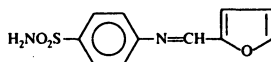
4[N-(4-dimethylaminobenzalidene)amino] benzenesulphonamide (DBAB)



4[N-(4'-methoxybenzalidene)amino] benzenesulphonamide (MBAB)



4[N-(4'-hydroxy-3'-methoxybenzalidene)amino] benzene sulphonamide (HMBAB)



4[N-(furfuralidene)amino] benzene sulphonamide (FAB)

†Lecturer, Chemistry Department, Iqbal College, Peringamala, India.

EXPERIMENTAL

The reagents and solvents were of analytical grade. The ligands were prepared by literature method². Equimolar solutions of sulphanilamide and *N,N'*-dimethylaminobenzaldehyde, *p*-anisaldehyde, vanillin or furfuraldehyde in methanol were prepared and mixed together and refluxed for 2 h. The resulting solutions were concentrated and cooled to get the solid crystals. The complexes were prepared by refluxing the acetonitrile solutions of the metal salts and the ligands in the mole ratio 1 : 3. The resulting mixture in each case was concentrated and cooled to get the solid complexes. The thiocyanato complexes were prepared from the nitrate complexes by substitution method³. They were washed repeatedly with benzene and petroleum ether to remove the excess of ligand. The coloured complexes were dried *in vacuo* over phosphorus(V) oxide.

The metal content of the complexes was estimated by oxalate-oxide method⁴. The nitrate content of the complexes was determined gravimetrically by using nitron reagent⁵ and perchlorate content by Kurz method⁶. The thiocyanate content was determined gravimetrically as AgSCN⁵. The molar conductivities of complexes in acetonitrile, methanol and nitrobenzene were determined at room temperature. The infrared and electronic spectra of all the complexes and ligands were recorded. Rast method was employed to determine the molar mass of complexes using biphenyl as solvent⁷. The magnetic moments were recorded at room temperature. The diamagnetic corrections for the rest of the molecule and the completed shells of Eu(III) ion were computed from Pascal's constant⁸. The antimicrobial studies of the complexes and ligands at varying concentrations were done using two different bacteria, viz., *Staphylococcus aureus* and *Pseudomonas aeruginosa*. The activities were determined by measuring the diameter of inhibition zones in mm. TG and DTG curves were recorded on a thermal analyzer. Pyrolysis experiment in air was done for each complex and the mass loss obtained was compared with that obtained from TG.

RESULTS AND DISCUSSION

The results of analytical data of the complexes are presented in Table-1. All these complexes were insoluble in ether and partially soluble in nitrobenzene and moderately soluble in acetone and methanol. The nitrate and thiocyanato complexes were found to be non-conducting in nitrobenzene as shown by the values of molar conductance⁹ which lie in the range 2–10 ohm⁻¹ cm² mol⁻¹. Electrical conductance values of perchlorato complexes in nitrobenzene correspond to those of 1 : 1 electrolyte suggesting that only two of the perchlorate ions were coordinated to the metal ion. Based on these data, the present complexes can be formulated as [Eu(L)₃(NO₃)₃], [Eu(L)₃(NCS)₃], [Eu(L)₃(ClO₄)₂]ClO₄ where L = DBAB, MBAB, HMBAB or FAB.

Infrared spectra of all the four ligands exhibit a strong band around 1660–1630 cm⁻¹. These are assigned to stretching vibration of (C=N). This band undergoes a downward shift by 20–25 cm⁻¹ in the spectra of complexes. This clearly indicates the coordination of azomethine nitrogen to the metal ion. The sharp band around 3290–3250 cm⁻¹ observed in all the ligands correspond to the

stretching vibration of NH_2 group. This band undergoes a down shift by 20–25 cm^{-1} in the spectra of the complexes. This proves the coordination of amino nitrogen atom to the metal ion. The spectra of all the ligands exhibit two strong bands at 1360 and 1130 cm^{-1} which are attributed respectively to asymmetric stretching and symmetric stretching vibrations of SO_2 group. These two bands are retained in the spectra of all the complexes without any change of position, suggesting that SO_2 group does not participate in coordination. The band at 1240 cm^{-1} in the spectra of the ligands, MBAB and HMBAB is for $\nu(\text{OCH}_3)$ which is retained in the spectra of complexes without any change of position. This shows that OCH_3 group is not involved in bonding. A broad band observed in the region 3300–3100 cm^{-1} for the ligand HMBAB and its complexes is assigned to $\nu(\text{OH})$ vibration.

A strong band observed around 1510 cm^{-1} in the ligand FAB is the characteristic of furan ring. A medium intensity band observed at 830 cm^{-1} was assigned to monosubstituted furan ring. The bands at 750 and 610 cm^{-1} correspond to $\nu(\text{CH})$ out-of-plane bending of furan ring. These bands were retained in all the complexes in the same position. This supports the non-participation of furan ring in coordination. The inability of coordination of oxygen atom of furan ring may be attributed to the utilization of the lone pair electron of oxygen atom for the aromatic sextet. Thus all the ligands are acting as neutral bidentate coordinating through azomethine and amino nitrogen atoms.

The nitrate complexes observed three bands at 1464, 1384 and 1302 cm^{-1} due to ν_4 , ν_1 and ν_2 modes of coordinated nitrate ion which are absent in the spectra of the ligands and other anionic complexes. The difference between ν_4 and ν_1 is 80 cm^{-1} which supports the unidentate coordination of nitrate ion¹⁰.

The thiocyanato complexes exhibit two bands at 2056 and 834 cm^{-1} which are assigned to $\nu(\text{CN})$ and $\nu(\text{CS})$ modes of coordinated thiocyanate ion which are not present in the spectra of the ligands and other anionic complexes. Since $\nu(\text{CN})$ mode is lower than 2100 cm^{-1} and $\nu(\text{CS})$ vibration is greater than 774 cm^{-1} , the thiocyanate ions are coordinated to metal ion through nitrogen atom in unidentate fashion¹¹.

The structure and bonding of metal complexes of weakly coordinating perchlorate ions have been reviewed by Rosenthal¹². The perchlorato complexes show a strong band around 1177 cm^{-1} which is not present in the spectra of ligand and in other anionic complexes. This band is due to ν_4 vibration of monodentate perchlorate ion. The bands at 1023, 624 and 525 cm^{-1} can be assigned to ν_1 , ν_2 and ν_3 vibrations of monodentately coordinated perchlorate ions. The ν_2 band is observed at 938 cm^{-1} as a medium intensity band. All these observations confirm the unidentate coordination of perchlorate ions.

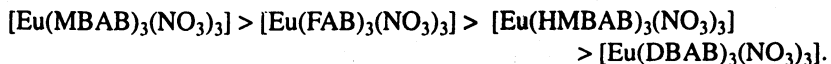
The magnetic moment values of complexes at room temperature are in good agreement with the theoretical values calculated from Van Vleck formula¹³. The thermal decomposition studies were conducted for nitrate complexes of Eu(III) with all the four Schiff bases and their thermal stabilities were compared. All the complexes undergo two stage decomposition around 250–320°C and 580–600°C. The thermogravimetric results indicate that all the nitrate complexes are quite stable up to 200°C which shows the absence of water and other coordinated

solvent molecules. The first stage decomposition is due to the dissociation of organic moiety and the second stage is the formation of metal oxide, Eu_2O_3 which is in conformity with the percentage loss of mass obtained from TG curve and independent pyrolysis experiment.

TABLE-I
ANALYTICAL DATA OF Eu(III) COMPLEXES

Complex (Colour)	m.w., Calcd. (Found)	Percentage analysis, Calcd. (Found)					Molar conductance in nitrobenzene ($\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$)
		Eu	Anion	C	H	N	
[Eu(DBAB) ₃ (NO ₃) ₃] (Black)	1247 (1245)	12.2 (12.1)	14.9 (14.0)	43.3 (42.9)	4.1 (3.9)	13.5 (13.3)	6.20
[Eu(MBAB) ₃ (NO ₃) ₃] (Reddish brown)	1209 (1208)	12.6 (12.5)	15.4 (14.9)	41.7 (40.8)	3.5 (3.1)	10.4 (10.1)	6.58
[Eu(HMBAB) ₃ (NO ₃) ₃] (Brown)	1257 (1255)	12.1 (11.9)	14.8 (14.6)	40.1 (39.9)	3.6 (3.4)	10.0 (9.9)	10.10
[Eu(FAB) ₃ (NO ₃) ₃] (Black)	1089 (1085)	13.9 (12.9)	17.1 (16.9)	36.4 (36.3)	3.0 (2.9)	11.6 (10.9)	7.50
[Eu(DBAB) ₃ (ClO ₄) ₂]ClO ₄ (Reddish brown)	1359 (1357)	11.2 (11.1)	22.0 (21.5)	39.7 (39.0)	3.8 (3.7)	9.3 (9.1)	25.40
[Eu(MBAB) ₃ (ClO ₄) ₂]ClO ₄ (Brown)	1321 (1320)	11.5 (10.9)	22.6 (21.9)	38.1 (37.7)	3.2 (3.0)	6.4 (6.1)	27.20
[Eu(HMBAB) ₃ (ClO ₄) ₂]ClO ₄ (Brown)	1369 (1368)	11.1 (10.9)	21.8 (21.4)	36.8 (35.5)	3.3 (3.1)	6.1 (6.0)	26.30
[Eu(FAB) ₃ (ClO ₄) ₂]ClO ₄ (Brown)	1201 (1199)	12.6 (11.9)	24.8 (23.9)	32.9 (31.9)	2.7 (2.1)	6.9 (5.9)	25.80

The initial decomposition temperature is frequently used to define the relative thermal stabilities of complexes. On the basis of experimental findings in the present course of study, the relative thermal stabilities of the chelates under examination can be given as



The highest stability was observed in MBAB complex and lowest stability in DBAB complex. The stabilities of the other two, *viz.*, HMBAB and FAB were in between these two complexes. All these observations suggest the proposed formulae of these complexes as:



where L = DBAB, MBAB, HMBAB and FAB. Thus a coordination number of nine is assigned to nitrate and thiocyanate complexes and eight to perchlorate complexes. The antimicrobial activity assay was carried out by using disc diffusion method¹⁴ where the zones of inhibition are measured in mm. All the

complexes were screened in various concentrations and their antibacterial activity against *Staphylococcus aureus* and *Pseudomonas aeruginosa* was determined (Table-2). Results showed that perchlorate complexes exhibited significant antibacterial profile and more action.

TABLE-2
ANTIBACTERIAL ACTIVITY DATA OF Eu(III) COMPLEXES

Complex	Zone of inhibition (mm)			
	<i>Staphylococcus aureus</i>		<i>Pseudomonas aeruginosa</i>	
	5 mg/disc	10 mg/disc	5 mg/disc	10 mg/disc
[Eu(DBAB) ₃ (NO ₃) ₃]	6	7	6	7
[Eu(MBAB) ₃ (NO ₃) ₃]	8	12	9	10
[Eu(HMBAB) ₃ (NO ₃) ₃]	—	—	6	8
[Eu(FAB) ₃ (NO ₃) ₃]	13	14	12	13
[Eu(DBAB) ₃ (ClO ₄) ₂]ClO ₄	7	9	7	9
[Eu(MBAB) ₃ (ClO ₄) ₂]ClO ₄	11	18	12	14
[Eu(HMBAB) ₃ (ClO ₄) ₂]ClO ₄	6	6	7	11
[Eu(FAB) ₃ (ClO ₄) ₂]ClO ₄	18	21	17	18

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