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Synthesis, Characterization and Antimicrobial Activity of Pr(III) and Nd(III) Complexes of Schiff base Ligands

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ABSTRACT

Schiff base complexes of camphor and para aminobenzoic acid (BA) with praseodymium(III) and neodymium(III) nitrate have been synthesized and characterized by electronic and infrared spectral studies, elemental analysis, molar conductance, molar mass determination and antimicrobial activity. Mixed ligand complexes are also characterized.

Key words: Neodymium, Praseodymium, Nitrate, Antimicrobial activity.

INTRODUCTION

Coordination complexes are widely used in several areas of chemistry such as analytical chemistry, medicinal chemistry, agriculture and industrial chemistry¹. Lanthanide complexes with high coordination number six to ten are reported²⁻⁵. Schiff bases find extensive applications in organic synthesis, antibacterial and antifungal fields^{6,7}. In the present study Pr(III) and Nd(III) nitrate complexes with the Schiff base ligand is prepared and characterized.

EXPERIMENTAL

Camphor in ethanol was mixed with para aminobenzoic acid in ethanol (1:1 mmol) and refluxed for 6 h. On cooling, silky solids

separated, filtered and recrystallized from ethanol. Nd or Pr (III) nitrate in methanol and ligand in methanol were treated in the ratio 1:3 with stirring. The solution was refluxed for 7 h. on a water bath. Complexes were collected after filtration, washed with diethyl ether, recrystallized from methanol⁸ and dried in vacuo over P₂O₅. Methanolic solution of metal salt, ligand and dimethyl sulfoxide were mixed in the molar ratio 1:3:1 and refluxed for 7 h. The resulting solution was concentrated and the complex was washed with diethyl ether and recrystallized from methanol and dried in vacuo over P₂O₅.

RESULTS AND DISCUSSION

The complexes have the general composition Ln(BA)₄(NO₃)₃ and the mixed ligand complexes have Ln(BA)₃(NO₃)₃DMSO where Ln=

Pr or Nd. The complexes are nonhygroscopic and soluble in methanol and ethanol. Electrical conductance in methanol shows their non electrolytic nature⁹. The electronic spectra of the ligands and their complexes were recorded on a double beam Hitachi 220A. UV visible spectrometer in the range 185-900 nm in methanol¹⁰ is used for absorption spectra measurement. Very little information is available on the electronic spectra of the complexes. The spectrum of ligands exhibits two absorption maxima assignable to $n \rightarrow \pi^*$ transition at 340 nm and $\pi \rightarrow \pi^*$ transition at 276 nm. The complex has the same two bands and an additional band at 300 nm is present in all the spectra of the complexes due to L! M charge transfer transitions. There is no absorption band due to f-f bands in the complex which indicates that f-f transitions are too weak to be observed.

Antibacterial and antifungal activities of the ligand and the complexes were evaluated by disc diffusion method¹¹⁻¹⁴ and given in table 1. The study revealed that the metal complexes are much potent

bactericide/fungicide than the ligand. Mixed ligand complexes are more reactive than the complexes. The results of elemental analysis¹⁵, molar conductance¹⁶, molar mass, melting points are given in table 2. Infrared spectra¹⁷ of the complexes are compared with the spectra of the ligand. IR spectrum of the ligand shows a very strong band at 1575 cm^{-1} which is due to C=N stretching of the azomethane group of the ligand. In the complex this band is shifted to lower region 1505 cm^{-1} which suggests that the nitrogen in the azomethane is coordinated to the metal ion. The ligand and complexes show a band at 1704 cm^{-1} which is C=O stretch and this indicates the non coordination of the carboxylic group to the metal ion. The infrared spectra of ligand and complexes show bands at 3034, 1495, 2966 cm^{-1} corresponding to aromatic CH stretch, stretching mode of phenyl ring and methyl stretching mode. The bands present at 1436, 1318, 1020 cm^{-1} in the complexes are not present in the spectra of ligand. These bands are assigned to ν_{34} , ν_1 and ν_2 modes of the coordinated nitrate ions. ν_4 and ν_1 are the split modes of the degenerate ν_3 mode of the

Table 1: Antimicrobial activity of the ligand BA and its complexes

Sample	Reference cultures used					
	<i>Aspergillus flavus</i>	<i>Aspergillus niger</i>	<i>Penicillium crysogenum</i>	<i>Pseudomonas aeruginosa</i>	<i>E. coli</i>	<i>S. aureus</i>
BA	0.9 cm	Nil	Nil	1.4 cm	1.1 cm	1.6 cm
Pr(BA) ₄ (NO ₃) ₃	1.5 cm	Nil	Nil	1.7 cm	1.3 cm	2.0 cm
Pr(BA) ₃ (NO ₃) ₃ DMSO	1.4 cm	Nil	Nil	1.8 cm	1.5 cm	2.4 cm
Nd(BA) ₄ (NO ₃) ₃	1.6 cm	Nil	Nil	1.8 cm	1.4 cm	2.1 cm
Nd(BA) ₃ (NO ₃) ₃ DMSO	1.7 cm	Nil	Nil	1.9 cm	1.5 cm	2.8 cm

Table 2: Elemental analysis of ligand BA and its complexes

Compound	Molecular mass	Found (calc.) %				Molar conductance	m.p. (°C)
		Metal	C	H	N		
BA	271.38	-	75.22 (75.17)	6.58 (6.63)	5.12 (5.16)		235
Pr(BA) ₄ (NO ₃) ₃	1412.442	9.84 (9.97)	56.05 (57.77)	4.87 (5.09)	6.72 (6.93)	41.5	183
Nd(BA) ₄ (NO ₃) ₃	1414.462	9.98 (9.99)	57.55 (57.92)	4.92 (5.21)	6.81 (6.99)	30.8	185

uncoordinated nitrate ion. There is a separation of 118 cm^{-1} between ν_4 and ν_1 modes in the spectra of nitrate complex. Curtis and Curtis¹⁸ reported that the splitting of ν_3 mode of free nitrate ion in the order of $100\text{-}150\text{ cm}^{-1}$ for a unidentate ion and 200 cm^{-1} for a bidentate nitrate ion. The combination bands of nitrate groups are observed at 1720 cm^{-1} and 1700 cm^{-1} in the spectra of the complex. The frequency separation is only 20 cm^{-1} which is in agreement with the reported value for unidentately coordinated nitrate. The nitrate complex with DMSO shows a band at 964 cm^{-1} which is assigned to S=O stretching of sulfoxide group of DMSO. Hence sulfoxide group of DMSO is coordinated to the neodymium and praseodymium through the oxygen atom and not through the sulfur atom.

CONCLUSION

On the basis of elemental analysis, conductance measurements and IR spectral studies the nitrate complexes have the coordination number seven. The general formula of the complex was found to be $\text{Ln}(\text{BA})_4(\text{NO}_3)_3$ and $\text{Ln}(\text{BA})_3(\text{NO}_3)_3\text{DMSO}$ where $\text{Ln} = \text{Pr}$ or Nd . Antimicrobial studies revealed that the metal complexes are much potent bactericide/fungicide than the corresponding ligands. Mixed ligand complex with dimethylsulfoxide was shown to be more potent bactericide or fungicide than other complexes.

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