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Synthesis, Characterization and Physico-Chemical Studies of Schiff-base Complexes of Praseodymium and Neodymium

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ABSTRACT

Complexes of praseodymium (III) and neodymium (III) ions with schiff-base camphor and 4-aminobenzoic acid (BA) and their mixed ligand complexes have been prepared and characterized by molar conductance, molar mass determination and spectral studies. The complexes are found of the type $\text{Ln}(\text{ClO}_4)_3(\text{BA})_3$, $\text{Ln}(\text{ClO}_4)_3(\text{BA})_2\text{DMSO}$, where Ln = Pr and Nd. Molar conductance studies showed the non-electrolytic behaviour of the complexes. Molar masses of the complexes are in agreement with the structures of the complexes. Infrared spectral studies revealed that BA acts as a neutral monodentate ligand and the perchlorate ions are coordinated to the metal ions in a unidentate fashion. A coordination number of six is suggested for perchlorate complexes.

Key words: Synthesis, Aminobenzoic acid, Perchlorate, Schiff-base.

INTRODUCTION

Aminobenzoic acid is included as a member of the vitamin B group. Deficiency of aminobenzoic acid in living beings could not be demonstrated. Aminobenzoic acid and its extracts find use by tropical application in alcoholic lotions or creams as sunscreen agents¹. Smith *et al.*² have studied the molecular co-crystals of carboxylic acid and amino-substituted benzoic acids assuming the structure of aminobenzoic acid. The derivatives of p-aminobenzoic acid with a potential anti-arrhythmic activity is reported by Chabler *et al.*³ and its medical value is discussed and spectroscopic and structural

studies of 4-aminobenzoic acid complexes of divalent alkaline earth metals are reported by Murugavel *et al.*⁴. Schiff bases of 4-aminobenzoic acid and camphor are well known for their antistaphylococcal activity on coordination with lanthanides⁵⁻¹⁰.

The number of binding sites and the effect of chelation must be responsible for the increased activity of the complexes. Lanthanide complexes have received considerable importance due to their antibacterial, antifungal and antitumour activities and pharmacological properties^{11,12}. In the present study, schiff-base ligand derived from camphor and

4-aminobenzoic acid and its Pr(III) and Nd(III) complexes were prepared and characterized.

EXPERIMENTAL

Methanolic solution of $\text{Ln}(\text{ClO}_4)_3$ where Ln=Nd, Pr and the ligand BA are mixed together in a molar ratio 1:3 and refluxed on a water bath for 7h. The solution was concentrated by evaporation on a water bath. After cooling, the complex was washed with diethyl ether and recrystallised from methanol. Cream colored complex was collected and dried in vacuo over phosphorous oxide. Purity of the sample was checked by thin layer chromatography^{13,14}. $\text{Ln}(\text{ClO}_4)_3$ in methanol, BA in methanol and dimethylsulfoxide (DMSO) in methanol are mixed together in a molar ratio 1:3:1 and refluxed on a water bath for 8h. The resulting solution was concentrated, washed with diethyl ether and recrystallized from methanol. Dirty yellow colored complex was collected, dried and the melting points were taken in open capillary tubes. The complexes are soluble in methanol and ethanol and insoluble in chloroform, dimethylsulfoxide, CCl_4 , pet ether. The metal content of the complexes were determined by gravimetric method. The Rast method using biphenyl as solvent is used for the determination of molar mass of the complexes.

Molar conductance were measured in methanol at room temperature using an ELICO conductivity bridge with a dip type conductivity cell having platinum electrodes. The molar conductance studies showed the non-electrolytic behavior of the complexes. The IR spectra were recorded using a Perkin-Elmer FT-IR spectrometer using KBr pellets.

RESULTS AND DISCUSSION

The important infrared spectral bands and physical and analytical data of the compounds are given in Tables 1 and 2, respectively. Infrared spectra of all metal complexes were interpreted by comparing the spectra with those of the free ligand¹⁵. The IR spectrum of the ligand exhibits a strong band at 1577 cm^{-1} which is attributed to C=N stretching of the azomethine group¹⁶. The complex shows a band at 1502 cm^{-1} which suggests that the nitrogen in the azomethine is coordinated to the metal ion. Ligand BA shows a strong band at 1705 cm^{-1} and complex shows a band at 1706 cm^{-1} which is assigned as the C=O stretching vibration of the carboxylic group indicating the non-coordination of the C=O of the carboxylic group to the metal ion.

The bands present at 3034, 1495 and 2966 cm^{-1} in the IR spectra of ligand and complexes,

Table 1: Important spectral bands (cm^{-1}) BA, DMSO and lanthanide complexes

BA	DMSO	Pr Complex	Nd Complex	Assignments
3034		3034	3034	νCH
2966	2966	2966	2966	νMe
1705		1706	1706	$\nu\text{C=O}$
1577		1502	1502	$\nu\text{C=N}$
1495		1495	1495	νPh
1606		1606	1606	νPh
1250		1250	1250	$\nu\text{C-O}$
	1100-1055	1136	1136	ν_4
		1100	1100	ν_1
		962	962	$\nu\text{S=O}$
		932	932	ν_2
		692	692	ν_3
		634	634	ν_5
		580	580	$\nu\text{Ln-N}$

Me- methyl; Ph-phenyl ring; Ln-Nd or Pr; ν -stretching.

Table 2: Physical and analytical data of the compounds

	BA	Pr(ClO ₄) ₃ (BA) ₃	Nd(ClO ₄) ₃ (BA) ₃	Pr(ClO ₄) ₃ (BA) ₂ DMSO	Nd(ClO ₄) ₃ (BA) ₂ DMSO
1. color	Silkish cream	Pale cream	Pale cream	Dirty yellow	Dirty yellow
2. solubility in					
(a) methanol	soluble	soluble	soluble	soluble	soluble
(b) ethanol	soluble	soluble	soluble	soluble	soluble
(c) chloroform	insoluble	insoluble	insoluble	insoluble	insoluble
(d) carbontetrachloride	insoluble	insoluble	insoluble	insoluble	insoluble
(e) pet. ether	insoluble	insoluble	insoluble	insoluble	insoluble
3. melting point	235°C	120°C	118°C	185°C	183°C
4. molar conductance in methanol	10	41.9	39.5	28.1	26.4
5. metal %	-	10.56	10.82	13.04	12.67
6. Molar mass of the complex	-	1284.33	1100.85	1100.85	1284.33

corresponds to aromatic CH, phenyl ring mode and methyl group stretching mode, respectively. The strong bands observed at 1136 and 1100 cm⁻¹ in the IR spectra of neodymium and praseodymium perchlorate complexes are assigned as ν_4 and ν_1 modes of unidentately coordinated perchlorate ions^{17,18}. The other modes of the unidentate perchlorate ion are observed at 932(ν_2), 692(ν_3), 634(ν_5) cm⁻¹. Presence of these bands in the IR spectrum shows that the perchlorate ions are coordinated unidentately to the metal ion. According to literature¹⁹, the preferred coordination number for metal ion is six. The S=O stretching band is expected in the range 1100-1055 cm⁻¹ for free DMSO and in the range 1157-1116 cm⁻¹ for sulfur bonded sulfoxide of DMSO²⁰. In the present case, the perchlorate complex with DMSO exhibits a band

at 962 cm⁻¹ which is assigned as S=O stretching mode and the presence of this mode suggest that the oxygen atom of the sulfoxide group of DMSO is coordinated to the metal ion.

CONCLUSION

Complexes of praseodymium (III) and neodymium (III) ions with schiff-base camphor and 4-aminobenzoic acid and their mixed ligand complexes have been prepared and characterized by molar conductance, molar mass determination and spectral studies. Perchlorate ions are coordinated to the metal ion in a unidentate fashion with a coordination number six. Presence of strong bands of perchlorate ion in the infrared spectrum support the above argument.

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