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COORDINATION POLYMERS OF SOME LANTHANIDE(III) NITRATE WITH SCHIFF BASES

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The Schiff bases derived from 2-hydroxy-1-naphthaldehyde and salicylaldehyde with *o*-dianisidine, *p*-phenylene diamine and benzidine and their lanthanide(III) complexes have been synthesized and characterized by elemental, I.R. thermal, magnetic and D.R.S. studies.

INTRODUCTION

Coordination polymers of 3*d* transition metals have been extensively studied[1-5], but corresponding coordination polymers of rare earths have been less studied. We report here the synthesis and characterization of rare earths complexes with Schiff bases derived from 2- hydroxy-1-naphthaldehyde and salicylaldehyde with o^{-}-dianisidine, p^{-}-phenylene diamine and benzidine.

EXPERIMENTAL

The Schiff bases of *o*-dianisidine (H_2L^{I}, H_2L^{II}), *p*-phenylenediamine (H_2L^{III}, H_2L^{IV}), and benzidine (H_2L^{V}, H_2L^{VI}) with salicylaldehyde and 2-hydroxy-1-naphthaldehyde respectively have been prepared; salicylaldehyde or 2-hydroxy-1-naphthaldehyde (0.02M) in ethanol was refluxed with 0.01M ethanolic solution of *o*-dianisidine or *p*-phenylenediamine or benzidine respectively on water bath for 10–30 minutes and allowed to cool at room temperature with continuous stirring. Coloured precipitates were obtained. Precipitates were recrystallized and finally dried over $CaCl_2$. The purity of the compounds was checked on TLC.

The DMF solutions of Schiff bases (0.01M) were mixed with ethanol : DMF (4 : 1) solution of lanthanide (III) nitrate (0.01M) and the mixture was stirred magnetically. After 15 minutes ammonia solution (1 : 5) was added in excess. The solution was refluxed for 3–6 hrs as necessary in different cases. The coloured precipitates were filtered, washed with DMF and dried in vacuo over P_2O_5.

RESLULTS AND DISCUSSION

Microanalytical results suggest the general formula of the complexes as $(ML.NO_3.H_2O)_n$ where M = La(III), Pr(III), Nd(III), Sm(III), Gd(III) and Tb(III), H_2L = Schiff bases = H_2L^{I}, H_2L^{II}, H_2L^{III}, H_2L^{IV}, H_2L^{V}, and H_2L^{VI}. The magnetic moments measured at room temperature show that La is diamagnetic and other complexes are paramagnetic. The DRS study[6] shows a very broad band in the visible region bear 385 nm which is assigned to L → M charge transfer transition. This band is so strong that *f-f* bands of lanthanide ions are obscured. The ir spectral bands of the ligands are observed in the region 3300–3400 cm^{-1}, 1315 cm^{-1}, attributed to OH stretching and deformation modes respectively.

The absorption near 1555–1530 cm^{-1} and 1290–1265 may be assigned to C–O stretching and C–O deformation respectively due to phenolic group. The formation of Schiff bases is indicated by the appearance of C=N stretching bands in the region 1655–1625 cm^{-1}. The disappearance of OH stretching and OH deformation bands in the complexes suggest the involvement of phenolic OH in complexation. This is further confirmed by positive shift of C–O stretching and C–O deformation frequency by 5–15 cm^{-1}. The involvement of azomethine nitrogen in complexation is indicated by the negative shift of C=N stretching by 10–60 cm^{-1} in the complexes. Association of water molecule[7] in complexes is confirmed by the appearance of new bands in the region 3600–3200 cm^{-1}, 1680–1600 cm^{-1} and 970–900 cm^{-1} assigned to OH stretching, OH deformation and rocking mode of coordinated water respectively. The percentage weight loss observed between 200–300° by T.G. analysis correspond to the elimination of one H_2O supporting the above assumption.

The two medium bands at 1460 and 1340 cm^{-1} which are present only in the IR spectra of the complexes are assigned to ν_4 and ν_1 vibrations respectively of the coordinated nitrate ion. The magnitude of $\nu_4 - \nu_1 \approx 120$ cm^{-1} in these complexes which indicates that the nitrate group is coordinated to the lanthanide ion in a monodentate fashion. The other bands appear in the region 400–600 cm^{-1} and 355–430 cm^{-1} assigned to $\nu_{M\text{-}N}$ and $\nu_{M\text{-}O}$ respectively. Thus ligand behaves as dibasic tetradentate.

On the basis of above discussion, a six coordinated octahedral structure is tentatively suggested for these polymer complexes. The nature of the ligand, thermal stability and insolubility of the complexes in common organic solvents suggest their polymeric nature.

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