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NOTE

Synthesis, Spectral and Thermal Studies of Praseodymium(III) and Samarium(III) Complexes with N,N′,N″-Tri(2,4-dihydroxybenzophenone)triaminotriethylamine

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A new Schiff base ligand N,N′,N″-tri(2,4-dihydroxybenzophenone)-triaminotriethylamine (H_6L) has been synthesized. Its complexation behaviour with praseodymium(III) and samarium(III) have been observed. The complexes has been characterized by elemental analysis, IR spectra molar conductivity measurements and thermal analysis. The praseodymium(III) and samarium(III) cations coordinate with the tridentate Schiff base nitrogen atoms, the bridgehead nitrogen atoms and phenolic hydroxyl oxygen atoms.

Key Words: Synthesis, Pr(III) and Sm(III) complexes, N,N′,N″-tri(2,4-dihydroxybenzophenone)triaminotriethylamine.

The growth in lanthanide chemistry in last two decade has many reasons but three areas responsible for this may be (a) interest in mixed oxide 'warm-superconductors', (b) medicinal applications including magnetic resonance imaging agents (poly amino carboxylate complexes) as a one-electron reductant (SmI_2) and (c) lanthanide triflates as lewis acid in synthetic organic chemistry[1]. Lanthanide(III) chelates have been used in various applications including fluorimetric determination of ions[2,3], in the development of luminescent labels in clinical chemistry and molecular biology[4]. But lanthanide complexes with Schiff base as the ligand are less studied[5,6]. Here, synthesis of ligand N,N′,N″-tri(2,4-dihydroxy-benzophenone)triaminotriethylamine has been completed and its complexing behaviour has been studied with praseodymium(III) and samarium(III) ions. The complexes have been characterized by its elemental analysis, electrical conductance, magnetic susceptibility measurements, IR and thermal studies.

All chemicals used for the synthesis were of AnalR grade and used without further purification. $PrCl_3$ and $SmCl_3$ (Indian Rare-Earth's Udyog Mandal, 99.99 % purity) were used.

Synthesis of N,N′,N″-tri(2,4-dihydroxybenzophenone)triaminotriethylamine ligand: Anhydrous $ZnCl_2$ (24 mmol) was mixed slowly to hot benzoic acid (54 mmol) and then added 1,3-Benzene diol (20 mmol). The reaction mixture was refluxed for *ca.* 1 h. On cooling the mixture to room temperature, the product was precipitated. It was washed with 1:3 HCl and water and dried under vacuum. It yielded 2,4-dihydroxylbenzophenone as brownish powder.

Now a mixture of 15 mmol 2,4-dihydroxylbenzophenone and triamino-triethylamine (5 mmol) in anhydrous ethanol (20 mL) was refluxed for *ca.* 5-6 h at 60 ºC. It yielded a brown precipitate. This precipitate was collected, washed with ethanol and dried under vacuum to yield N,N′,N″-tri(2,4-dihydroxybenzophenone)triaminotriethylamine (H_6L).

Synthesis of complexes: To an alcoholic solution of $PrCl_3$ or $SmCl_3$ (1.0 mmol in 10 mL ethanol) alcoholic solution of H_6L ligand (1.0 mmol in 10 mL ethanol) was slowly added drop wise. After stirring for 3 h at room temperature, the excess solvent was removed by distillation and the remaining solution was left for over night. The solid complex separated out. It was washed with ethanol and dried in vacuum.

The percentage of Pr and Sm-metal was estimated by heating to oxide, then dissolved in 50 % HCl and the remaining solution was titrated with EDTA using xylenol as indicator[7]. Elemental analysis was done on Heraeus Carlo Erba 1108 analyzer. IR spectra were recorded on a Perkin-Elmer model 125 spectrophotometer using KBr dishes. Magnetic susceptibility measurements of the complexes were carried out by Gouy method using $Hg[Co(SCN)_4]$ as a calibrant. The molar conductance was measured on systronics digital conductivity meter with a dip type cell using 10-10 molar solution of the complexes in DMF at 25 ºC.

The ligand $C_{35}H_{41}N_4O_6$ (brown in colour), m.p. 201-204 ºC, has been found to contain C-67.35 (37.37), H-6.62 (67.37), N-9.04 (9.13) %.

The complex $C_{35}H_{41}N_4O_9Pr$ (brown in colour) has C-51.41 (51.48), H-4.98 (5.05), N-6.88 (6.90), M-18.41 (18.49) %. μ_{eff} 3.50 BM and conductance 11.4 ohm^{-1} cm^2 mol^{-1}.

The complex $C_{35}H_{41}N_4O_9Sm$ (brown in colour) has C-52.34 (52.37), H-5.10 (5.11), N-6.93 (6.98), M-17.50 (17.58) %. μ_{eff} 1.58 BM and conductance 9.7 ohm^{-1} cm^2 mol^{-1}.

Both complexes are soluble in DMSO, THF, DMF and in CH_3OH, but sparingly soluble in water, ethyl acetate and ethanol. Elemental analyses show the formula of the complexes to be $LnH_3L\cdot 3H_2O$ (where Ln = Pr, Sm). This indicates that these complexs conform to 1:1 metal:ligand stoichiometry. The molar conductances of complexes show its non-electrolytic nature in DMF[8].

Infrared spectra of both metal complexes are similar suggesting a close structural relationship between the complexes the IR spectrum of free ligand shows bands at 1632 cm^{-1} assignable to ν(C=N) of the Schiff base. This band shifts *ca.* 30 cm^{-1} (1602 cm^{-1}) in complexes indicating that Schiff base N atom takes part in coordination. Also vibration ν(C–N) of free ligand at 1241 cm^{-1} is shifted to 1218 cm^{-1} in metal complexes. It indicates that the bridgehead nitrogen atom of ligand is coordinated to the lanthanide ions[9]. Further deprotonation of three hydroxyl groups among the six hydroxyl groups of the ligand is supported by the fact that the oxygen atom of phenolic hydroxyl is also coordinated to the metal ions as suggested by ν(C–O) of phenolic group in ligand (1220 cm^{-1}) 1190 cm^{-1} in complexes[10,11]. The new bands at 432, 438 and 548, 551 cm^{-1} in two complexes are assigned to ν(Ln–O) and ν(Ln–N) vibrations, respectively.

Thermal analysis: Both complexes are stable in air. The DTA curve of the Pr(III) complex shows two endothermic peak at around 97 and 196 ºC, indicating weight loss of *ca.* 4.67 % and 83-121 ºC and *ca.* 2.289 % at 182-203 ºC.

This corresponds to the loss of two water molecules and one coordinated water molecules, respectively indicating that both lattice water molecules and coordinated water molecules are in the complex. On heating to 630 ºC, the complex decomposes step by step since there are two exothermic peaks at 300 and 419 ºC. The residual weights fundamentally do not change beyond 540 ºC. This indicates that at 540 ºC, lanthanide oxides are formed.

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