

COMPLEXES OF SOME LANTHANIDES WITH *p*-DIMETHYLAMINOANIL OF FLOURENE GLYOXAL

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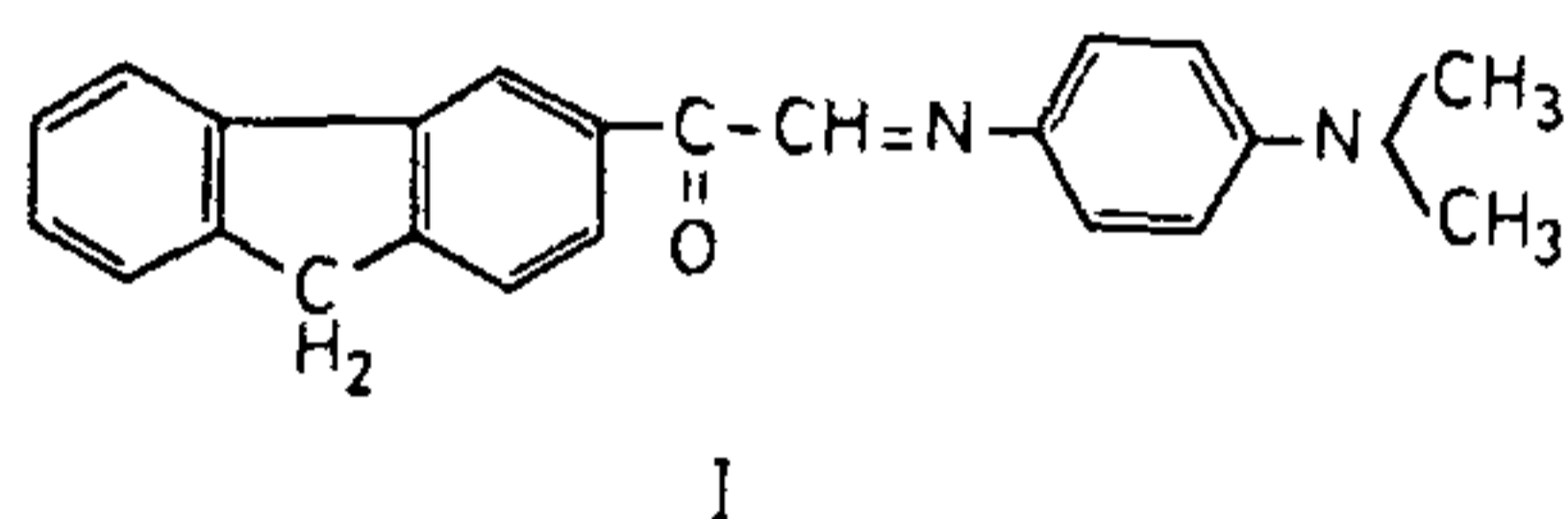
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ABSTRACT

Coordination compounds with *p*-dimethylaminoanil of flourene glyoxal have been prepared and characterised. The complexes of Ce(III), Pr(III), Sm(III) and Dy(III) are paramagnetic and La(III)—complex is diamagnetic. The electronic spectral studies indicate that the covalency decreases as the atomic number of lanthanide ion increases. The i, r. data confirm the involvement of azomethine ($-\text{CH}=\text{N}-$) and carbonyl ($\text{>C}=\text{O}$) group in coordination.

INTRODUCTION

SCHIFF bases as nitrogen donor ligands have played an important role in the synthesis of a wide variety of metal complexes. These possess tuberculostatic¹, fungicidal² and bacteriostatic³ activities and can act as potential chelating reagents⁴. We have synthesised the Schiff base under study *i.e.* *p*-dimethylaminoanil of flourene glyoxal I (abbreviated as DMAFG): and



investigated its chelating behaviour by complex formation with lanthanides. A careful literature survey revealed that no such complexes have so far been investigated. In view of the marked pharmacological importance bis-complexes of the type $[\text{Ln}(\text{DMAFG})_2]\text{Cl}$ where bis-complexes of the type $[\text{Ln}(\text{DMAFG})_2\text{Cl}_2]\text{Cl}$ where $\text{Ln} = \text{La(III), Pr(III), Nd(III), Sm(III), Gd(III) and Dy(III)}$ and their characterisation through elemental analysis, magnetic susceptibility measurements at room temperature, molar conductance values, infrared and electronic spectral studies.

EXPERIMENTAL

The specpure lanthanide chlorides (Johnson and Matheu) and all other chemicals of reagent grade were used. The ligand was prepared by the condensation of flourene glyoxal and *p*-dimethylaminoaniline in alcoholic medium in equimolar quantities. It was purified by recrystallization from petroleum ether. (b.p. 40–60°C) and the purity was checked by analysis. The m.p. of the ligand was found to be 180°C.

Preparation of Schiff base complexes of lanthanides: Methanolic solution of the ligand (20 mmol) was

added to the methanolic solution of lanthanides (10 mmol) in a 50 ml round bottom flask. The reaction mixture was refluxed on a water bath for 2 hr and concentrated in a vacuum dessicator yielding the coloured crystalline materials. The crystals were washed with ether and dried.

Physical measurements: The analysis of carbon, hydrogen and nitrogen were carried out at Central Drug Research Institute, Lucknow, India. The metals were estimated by complexometric titrations⁵. Molecular weights were determined ebullioscopically in chloroform using a Gallen Kamp ebulliometer. The other measurements *viz.* magnetic susceptibility (on a Gouy's balance), infrared spectra (on Perkin-Elmer infrared spectrophotometer model-521 fitted with NaCl and KBr optices), absorption spectra (using UNICAM SP-500 spectrophotometer) and molar conductance (using Phillips conductivity bridge type LBR/B) have been recorded at room temperature.

RESULTS AND DISCUSSION

All the complexes were coloured and fairly stable at room temperature. The purity of these complexes was checked by TLC. Their magnetic moment values were normal. The molecular weight determinations in boiling chloroform showed them to be monomers indicating thereby the hexacoordinated environment for the central rare earth metal atom. This was further supported by their electronic and infrared spectral studies.

The molar conductance values in DMF at the concentration 10^{-3} M showed that these are uni-univalent electrolytes in DMF.

The lanthanum(III) and Ce(III) complexes have no significant absorption in the visible region. The praseodymium complex exhibits four bands which have been assigned to $^3\text{H}_4 \rightarrow ^1\text{D}_2$, $^3\text{P}_0 \rightarrow ^3\text{P}_1$ and $^3\text{P}_2$ transition respectively. There was a little difference in the molar absorptivities of the samarium complex and the samarium salt. But the difference in the case of praseodymium and neodymium complexes was more

TABLE I

Analytical and spectral data, formulae and other properties of complexes

| Complex | Colour | Analysis* — | | | | μ_{eff} | Molecular weight | Molar conductance $\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$ | Spectral data | |
|--|--------|------------------|------------------|----------------|------------------|--------------------|--------------------|---|------------------------------|----------------------------------|
| | | % M | % C | % N | % Cl | | | | $(1-\beta) \times 10^2$ | $b^{1/2}$ |
| [LaL ₂ Cl ₂] Cl | grey | 14.87 (15.00) | 59.62 (59.65) | 6.00 (6.05) | 11.49 (11.50) | dia. | 597.30 (585.40) | 121.6 | — | — |
| [PrL ₂ Cl ₂] Cl | buff | 15.00 (15.19) | 59.24 (59.52) | 5.96 (6.02) | 11.37 (11.48) | 3.60 | 575.80 (587.40) | 119.4 | 1.10 0.82 0.72 0.44 | 7.416 6.400 6.000 4.690 |
| [NdL ₂ Cl ₂] Cl | black | 14.95 (15.49) | 59.12 (59.20) | 5.89 (6.01) | 11.40 (11.44) | 3.58 | 585.60 (590.74) | 118.8 | 0.72 0.44 0.92 0.51 | 6.000 4.690 6.782 5.049 |
| [SmL ₂ Cl ₂] Cl | buff | 15.99 (16.04) | 58.90 (58.92) | 5.91 (5.97) | 11.32 (11.36) | 1.60 | 608.60 (596.90) | 118.6 | 0.51 0.91 0.40 | 5.049 6.745 4.246 |
| [GdL ₂ Cl ₂] Cl | buff | 16.35 (16.66) | 58.37 (58.49) | 5.90 (5.93) | 11.24 (11.20) | 8.00 | 590.80 (603.75) | 119.9 | — | — |
| [DyL ₂ Cl ₂] Cl | brown | 17.20 (17.12) | 58.12 (58.10) | 5.80 (5.90) | 11.12 (11.12) | 10.30 | 586.80 (609.00) | 117.2 | — | — |

*Theoretical values are given in brackets. L = C₂₃H₂₀NO₂

substantial. The spectral data show a decrease in the frequencies of the bands in the complexes relative to their aquo ions. A hypersensitive transition $^4I_{9/2} \rightarrow ^4G_{5/2}$ in the neodymium complex is observed at 17200 cm^{-1} . The effect of hypersensitivity in other neodymium complexes has been observed by other workers^{6,7}.

The nephelauxetic effect $(1 - \beta)$ was calculated using the relation:

$$1 - \beta = (\nu_{\text{aqua}} - \nu_{\text{complex}}) / \nu_{\text{aqua}}$$

where ν corresponds to the wave numbers of corresponding bands. The nephelauxetic effect depends on the expansion of the electron cloud of an orbital by the ligand and may be regarded as a measure of covalency of the coordinate bond. The parameter of bonding ($b^{1/2}$), which measures the amount of metal-4f-ligand mixing can be obtained in terms of nephelauxetic (β) using the relation $b^{1/2} = 1/2(1-\beta)$. The values were found to be positive indicating covalent bonding.

Infrared spectral studies of DMAFG and its complexes with lanthanides indicate that frequencies corresponding to $>C=O$ and $-CH=N-$ (1710 cm^{-1} and 1640 cm^{-1}) are perturbed on complex formation. The frequencies are shifted to lower values ranging from $1635-1680 \text{ cm}^{-1}$ and $1530-1600 \text{ cm}^{-1}$ respectively, during complexation indicating that

these two groups participate in chelation. Appearance of new bands⁸⁻¹⁰ in the range 500 cm^{-1} to 520 cm^{-1} and 340 cm^{-1} to 500 cm^{-1} which are attributed to metal-nitrogen and metal-oxygen link respectively further confirms the involvement of these group in complex formation. Bands in the range 380 cm^{-1} to 415 cm^{-1} suggest metal-chloride link as a result of complexation.

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