

thus leading to depolarization. The observed polarization for the second excited state should, therefore, be less. From the Table I average value of the polarization for $\lambda_{ex} = 534 \text{ nm}$ is $\approx 29\%$ but for $\lambda_{ex} = 350 \text{ nm}$ it is far less $\approx -12\%$.

It may also be noted that the polarization for emission wavelengths from 540 nm to 580 nm is almost constant for both the excitation wavelengths. This is in conformity with Kwaski's observations⁸. In a classical sense this corresponds to one type of emission oscillator which could mean that for this concentration, the dye molecules in solution exist only in one molecular form.

The present investigation, therefore, suggests that:

1. There are two excited states for Rhodamine 6G in glycerol solution (con. $\sim 2.3 \times 10^{-6}$ Moles liter⁻¹—one corresponding to 534 nm and the other corresponding to 350 nm.
2. The absorption and emission oscillators are parallel in the first excited state while perpendicular in the second excited state.
3. Polarization for the first excited state is higher and positive while for the second state, it is negative.
4. The low value is due to depolarization caused by the reorientation of the dipole during the non-radiative transition $S_2 \rightarrow S_1$.

One of us (MLP) gratefully acknowledges the financial assistance of University Grants Commission.

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SPECTRAL STUDIES ON RARE EARTH COMPLEXES OF SCHIFF BASES

SCHIFF base, N-4-acetoacetonaphthylidene-anthranilic acid (HAANAA) and N-4-acylacetonaphthylidene-o-aminophenol (HAANAP) have been used to prepare the complexes of rare earth ions, Pr(III), Nd(III) and Sm(III). These compounds have been characterised on the basis of their analytical, conductometric, magnetic, visible and i.r. spectral data¹⁻³.

Results and Discussion

Analytical results (Table I) show 1:2 (metal:ligand) stoichiometry. All the complexes behave as univalent electrolytes as revealed by their molar conductance data (98–130 ohm⁻¹ mole⁻¹ cm²) in nitrobenzene^{4,5}. The presence of hydrogen, chloride and nitrate ions outside the co-ordination sphere of the complexes is indicated by neutralising with 1 gm-equivalent of caustic soda, adding alcoholic silver nitrate and by copper turnings test respectively.

Visible spectra.—Electronic spectral data of Pr(III), Nd(III) and Sm(III) complexes are given in Table II. For comparison, data for aqueous salt solutions are also given.

The visible spectra of the complexes have been analysed to get information about the application of the nephelauxetic effect to the lanthanide series⁶. The nephelauxetic parameter (β) was determined by the method of Jorgensen and coworkers⁷ using the relation

$$(1 - \beta) = \frac{\bar{\nu}_{\text{aquo}} - \bar{\nu}_{\text{complex}}}{\bar{\nu}_{\text{aquo}}}$$

where $\bar{\nu}$ stands for the wave number of the band. It is evident from Table II that the shift in band positions in the spectra of Pr(III), Nd(III) and Sm(III) complexes is towards lower wave numbers relative to the aquo complex. Assuming that each J level of $4f^n$ configuration linearly depends on the radial integrals, the $\Delta\bar{\nu}/\bar{\nu}_{\text{aquo}}$ of all bands of the same rare earth complex should be identical. However earlier observations⁷ as well as the present data show that the $\Delta\bar{\nu}/\bar{\nu}_{\text{aquo}}$ values for different J levels vary considerably.

We have observed hypersensitivity in DMSO solutions of neodymium complexes. Small differences in band positions occur except for the hypersensitive⁸ transition $4I_{9/2} \rightarrow 4G_{5/2}$. Since the interaction between DMSO molecules and the rather sterically hindered metal ion is likely to be small, hypersensitivity cannot be explained on the basis of phenomenon involving solvent participation⁹. The influence of the asymmetric terms of the ligand field on the electric dipole transition is likely to be the dominant factor.

The values of $(1 - \beta)$ for the present complexes show that the covalent contribution increases in the order: (HAANAP) complexes < (HAANAA) complexes,

TABLE I
Analytical, colour and conductance data of complexes

Compound	% Elemental N found (calcd.)	Analysis Metal found (calcd.)	Colour	Decomposition temp. °C	λ M ohm ⁻¹ mole ⁻¹ cm ²
H [Pr (C ₂₁ H ₁₆ NO ₂) (NO ₃) ₂]	6.20 (6.27)	15.52 (15.67)	Light-orange	315	120
H [Nd (C ₂₁ H ₁₆ NO ₂) (NO ₃) ₂]	6.18 (6.24)	15.99 (16.08)	Orange	300	110
H [Sm (C ₂₁ H ₁₆ NO ₂) Cl ₂]	3.19 (3.29)	17.48 (17.68)	Grey	290	105
[Pr (C ₂₆ H ₁₄ NO ₂) ₂] NO ₃	5.10 (5.23)	17.24 (17.45)	Brown	302	125
[Nd (C ₂₀ H ₁₄ NO ₂) ₂] NO ₃	5.16 (5.21)	17.58 (17.90)	Black	310	115
[Sm (C ₂₀ H ₁₄ NO ₂) ₂] Cl	3.44 (3.56)	19.00 (19.14)	Light-brown	320	110

Satisfactory C, H Analyses were also obtained.

TABLE II
Electronic spectral data of complexes

Ion	Aqueous solution of salt band in cm ⁻¹	HAANAA - HAANAP complexes in DMSO		Band assignments	$(1 - \beta) \times 10^2$	
		band in cm ⁻¹	band in cm ⁻¹		HAANAA complexes	HAANAP complexes
Pr(III)	22470	22300	22400	³ H ₄ → ³ P ₂	0.75	0.31
	21320	21100	21150	→ ³ P ₁	1.03	0.79
	20750	20600	20650	→ ³ P ₀	1.72	0.48
	17000	16800	16900	→ ¹ D ₂	1.17	0.58
Nd(III)	19500	19460	19450	⁴ I _{9/2} → ⁴ G _{5/2} , ² H _{9/2}	0.51	0.25
	19000	18800	18900	→ ⁴ F _{7/2} , ⁴ S _{3/2}	1.05	0.52
	17300	17200	17250	→ ⁴ F _{9/2}	0.57	0.28
	14650	14550	14550	→ ⁴ G _{5/2} , ² G _{7/2}	0.68	0.68
	13400	13250	13300	→ ⁴ G _{7/2}	1.11	0.74
Sm(III)	12500	12400	12450	→ ⁴ G _{9/2}	0.80	0.40
	24900	24800	24800	⁶ H _{5/2} → ⁴ F _{9/2}	0.40	0.40
	23870	23750	23800	→ ⁶ P _{5/2}	0.71	0.29
	21650	21550	21500	→ ⁴ I _{13/2}	1.10	0.69

IR spectra—A comparison of i.r. spectra of HAANAA and HAANAP with those of their complexes shows the formation of complexes through nitrogen and oxygen atoms of active groups. In the i.r. spectra of ligands the bands appearing at 1600 cm^{-1} due to azomethine groups have been shifted in complexes to $1540\text{--}1575\text{ cm}^{-1}$ because of the formation of metal-nitrogen (M-N) bonds which is further confirmed by the appearance of bands at $540\text{--}565\text{ cm}^{-1}$. Formation of (M-O) bonds due to the deprotonation of carboxylic and hydroxyl groups of HAANAA and HAANAP is evidenced by the appearance of bands at $425\text{--}440\text{ cm}^{-1}$ and $440\text{--}465\text{ cm}^{-1}$ respectively. However, a band at 1700 cm^{-1} due to ketonic group in HAANAP is shifted to $1685\text{--}1725\text{ cm}^{-1}$ because of chelation through this group. The acidic complex of Sm(III) gives no white ppt with alcoholic silver nitrate solution but the appearance of a weak band at 360 cm^{-1} may suggest the formation of M-Cl bond.

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SCHIFF BASE COMPLEXES OF Cu(II) AND Ni(II) WITH 2, 4-DIHYDROXYACETOPHENONE ETHYLENEDIAMINE

THE complexes of Cu(II) and Ni(II) with 2,4-dihydroxyacetophenone ethylenediamine (DHAED) have been prepared and characterised by analytical, spectral, magnetic susceptibility and thermogravimetric data. The ligand functions as a dibasic and tetradentate one and the complexes are of 1:1 (metal-ligand) stoichiometry, each being associated with two molecules of water. The complexes are coloured and insoluble in common organic solvents and decompose above 300°C .

Experimental

Preparation of the ligand.—To 10 g of 2,4-dihydroxyacetophenone in 100 ml of 95% alcohol, 2.2 ml of ethylenediamine were added and refluxed (with a low flame) for about half an hour. The yellow precipitate (DHAED) obtained was filtered and washed thoroughly with water and next with alcohol. It was dried in vacuum over fused CaCl_2 (decomposition temperature 285°C).

Preparation of Cu(II) complex.—To 0.998 g of copper acetate monohydrate (analar) in 50 ml of 95% alcohol, 1.64 g of DHAED was added and refluxed for about one hour. The dark brown precipitate obtained was cooled, filtered and washed with water followed by 50 ml of alcohol. The complex was further purified by refluxing it with 50 ml of alcohol for one hour and finally vacuum dried over fused CaCl_2 .

Preparation of Ni(II) complex.—To 1.24 g of nickel acetate tetrahydrate (BDH) in 50 ml of 95% alcohol, 1.64 g of DHAED was added and refluxed for 3 hours. The red complex obtained was purified as in the case of Cu(II) complex.

The magnetic susceptibility measurements were made at room temperature by Guoy method using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as the calibrant. The infrared spectra ($4000\text{--}625\text{ cm}^{-1}$) in KBr pellet and the far infrared spectra ($700\text{--}100\text{ cm}^{-1}$) of the reagent as well as of the complexes were recorded using IR (Perkin Elmer-257) and Fourier Far IR spectrophotometers respectively. The ultraviolet and visible spectra in DMF and in nujol respectively were recorded on DMR-21 spectrophotometer. The thermograms of the complexes were recorded using a Stanton recording thermobalance. The conductance measurements were carried out in dimethylformamide using Toshniwal Type CL 01/02 A conductivity bridge.

Results and Discussion

The analytical data presented in Table I indicate that Cu(II) and Ni(II) complexes of DHAED can be represented as $\text{Cu}(\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_4)\cdot 2\text{H}_2\text{O}$ and $\text{Ni}(\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_4)\cdot 2\text{H}_2\text{O}$ respectively. The complexes are insoluble in water, dilute mineral acids and common organic solvents such as benzene, chloroform, nitrobenzene, etc. They are slightly soluble in dimethylformamide and 1,4-dioxan.

The Cu(II) complex is found to be paramagnetic with an effective magnetic moment of 1.88 B.M. and Ni(II) complex diamagnetic.

The conductivity measurements reveal that both the complexes are non-electrolytes in DMF at the concentration 10^{-3} M .

The electronic spectrum of Cu(II) complex shows a broad peak at 520 nm whereas that of Ni(II) complex at 540 nm. The peaks at 345 nm and