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Investigation into the Hypersensitive Transitions of Ln(III)—(1-phenyl-3-methyl-4-benzoyl pyrazolone-5) anthranilic acid and (1-phenyl-3-methyl-4-benzoyl-pyrazolone-5) aminoantipyrine Complexes-II

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(1-phenyl-3-methyl-4-benzoyl pyrazolone-5) anthranilic acid (PMBAA) and (1-phenyl-3-methyl-4-benzoyl-pyrazolone-5) aminoantipyrine (PMBAAP) form complexes with lanthanides of the type $[Ln(PMBAA)_2NO_3]$ and $[Ln(PMBAAP)_3]$ where Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy and Y. These compounds have been characterized from physico-chemical studies. The electronic spectra of the Nd(III) complexes have been studied in detail to investigate the phenomenon of hypersensitivity with respect to the coordination environment and solvent medium. In these compounds solvents do play a significant role to cause variation in hypersensitivity. The oscillator strengths of the hypersensitive transitions in these compounds show the following trend.

$$[Nd(PMBAA)_2NO_3] > [Nd(PMBAA)_3phen] > [Nd(PMBAA)_3bipy] > [Nd(PMBAA)_32py]$$

$$[Nd(PMBAAP)_3] > [Nd(PMBAAP)_3phen] > [Nd(PMBAAP)_3bipy] > [Nd(PMBAAP)_32py].$$

In general Nd(III) PMBAA complexes showed greater hypersensitivity than the Nd(III) PMBAAP complexes. IR and NMR have also been interpreted.

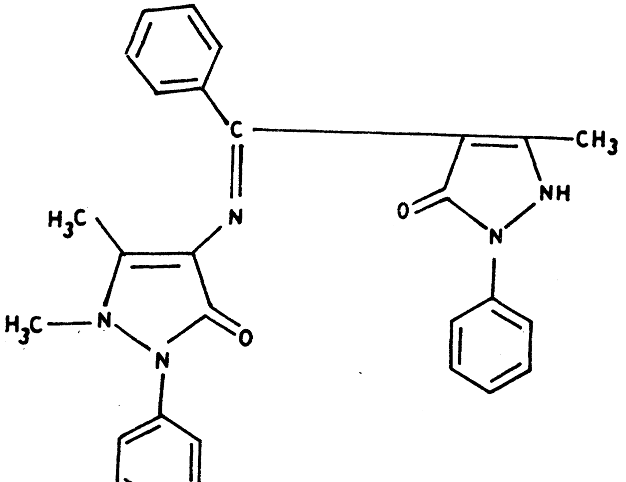
INTRODUCTION

Since the introduction of (1-phenyl-3-methyl-4-benzoyl-pyrazolone-5 (PMBP) as chelate forming extractant by Jensen's[1], extensive studies have been made on the use of this reagent for solvent extraction and separation of various metal ions[2, 3]. Extraction of various metal ions with PMBP have already been reported[4–8]. Our interest in the PMBAA and PMBAAP lanthanide complexes stems from a desire to investigate the phenomenon of hypersensitivity which is of considerable value for determining the effective extraction capability of the two ligands prepared using the same base PMBP.

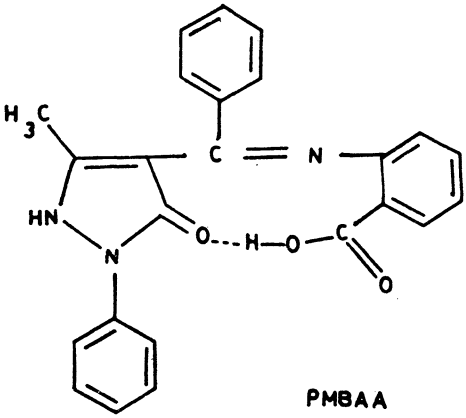
EXPERIMENTAL

Lanthanum nitrates were prepared from their respective oxides (99.9% pure) as reported earlier[6]. PMBP used for the preparation of PMBAA and PMBAAP was prepared[5, 7] by the Jensens method[1].

PMBAA, m.p. = 163°C; PMBAAP, m.p. = 211°C



PMBAAP



PMBAA

Preparation of the chelates

The method adopted for the preparation of a particular lanthanide chelate was the same for all metal ions. Here preparations were described with respect to neodymium.

Nd(PMBAA/PMBAAP)$_3$·2py: To an ethanolic solution of neodymium nitrate (1 mmol) and 1 mmol PMBAA/PMBAAP, 4 mmol of pyridine was added and refluxed on a water bath for 4 h. After filtration the filtrate was concentrated, washed to remove excess ligand and recrystallised in ethanol.

Nd(PMBAA/PMBAAP)$_3$ 1,10-phen/bipy: To an ethanolic solution of neodymium nitrate (1 mmol) and 3 mmol of PMBAA/PMBAAP, 2 mmol of bipy/phen, 3 mmol of sodium hydroxide was added dropwise while stirring continuously for 30 min. The mixture is concentrated to 5 mL, cooled and filtered. The product was washed free of excess ligand and recrystallised in ethanol.

All compounds were obtained in high yield of 70–80%.

Physical measurements

Metal and anion contents were determined by standard methods. IR spectra were recorded in the range 4000–400 cm^{-1} using a Perkin-Elmer 783 IR spectrometer. NMR spectra were measured with a Varian EM 360 L 60 MHz NMR spectrometer using $DHCl_3$ and TMS as internal standard. The electronic absorption spectra were obtained with two different spectrometers, a Beckmann-8 Dμ spectrometer (190–340 nm) and a UV-240 spectrometer (190–340 nm). $.1 \times 10^{-2}$ M solution was used to record the spectra.

RESULTS AND DISCUSSION

Electronic spectra

Table-1 lists the oscillator strength (ρ) for several non-hypersensitive transitions in the Nd(III) complexes in several solvents. It may be noted from a comparison of values with those of Nd perchlorate[9] that the coordination environment or the solvent medium has little effect on the variation of band intensities. This is in accordance with the model proposed by Judd[10] and Osfelt[11] for the intensities of the f→f transitions.

TABLE-1
OSCILLATOR STRENGTH (ρ) OF NON-HYPERSENSITIVE TRANSITIONS IN Nd(III) PMBAA COMPLEXES

Compound	Solvent	${}^4I_{9/2} \rightarrow {}^4F_{5/2}, {}^2H^*_{9/2}$	${}^4I_{9/2} \rightarrow {}^4F_{7/2}, {}^4S^*_{3/2}$
$Nd(ClO_4)_3$	$DClO_4$-$HClO_4$	8.54†	8.78†
$Nd(PMBAA)_2 \cdot NO_3$	Acetone	11.72	11.44
	Benzene	11.02	11.26
	Chloroform	11.62	11.46
	Methanol	11.89	11.02
$Nd(PMBAA)_3 \cdot 2py$	Acetone	11.68	11.46
	Benzene	—	—
	Chloroform	11.48	11.12
	Methanol	11.34	—
$Nd(PMBAA)_3 \cdot bipy$	Acetone	11.28	11.30
	Benzene	10.40	10.54
	Chloroform	11.42	11.02
	Methanol	11.12	11.68
$Nd(PMBAA)_3 \cdot phen$	Acetone	9.72	11.88
	Benzene	—	10.44
	Chloroform	10.82	—
	Methanol	—	9.82

*$\rho \times 10^6$
†Reference 9

Table-2 is a record of the oscillator strengths for the hypersensitive transitions in the Nd(III) PMBAA and PMBAAP complexes. It may be noted that there is a marginal variation in hypersensitivity with respect to the solvent medium.

Interestingly it was noted that the oscillator strengths in acetone were significantly higher than in chloroform and benzene. This may be rationalised by invoking a difference in symmetry of the dissociated (in acetone) and undissociated (chloroform or benzene) form of the complexes. According to Henrie *et al.*[12] symmetry does have implication on the overall intensity but hypersensitivity *per se* cannot be classified as being due to a symmetry phenomenon. Table-2 reveals the gradation of hypersensitivity in the compounds. A comparison of the oscillator strength of PMBAA and PMBAAP complexes (Table-2) reveals that in spite of being weakly basic, the oscillator strengths of PMBAA complexes are rather high. Moreover lanthanide-PMBAA complexes have relatively high formation constants (log β_3)[13, 14] which indicates that probably the complexes are stabilized to a great extent through covalent interaction. Henrie *et al.*[12] proposed a mechanism to explain that the phenomenon of hypersensitivity transitions arises from metal-ligand covalency *via* charge transfer levels. The greater the covalent interaction greater will be the hypersensitivity.

TABLE-2
OSCILLATOR STRENGTH (ρ) OF SOME NON-HYPERSENSITIVE TRANSITIONS IN ND(III) PMBAAP COMPLEXES

Compound	Solvent	$^4I_{9/2} \rightarrow {^4F_{5/2}}, {^2H^*_{9/2}}$	$^4I_{9/2} \rightarrow {^4F_{7/2}}, {^4S^*_{3/2}}$
$Nd(ClO_4)_3$	$DClO_4$-$HClO_4$	8.54†	8.78†
$Nd(PMBAAP)_3$	Acetone	11.62	11.42
	Benzene	10.80	11.08
	Chloroform	11.58	10.12
	Methanol	11.66	11.76
$Nd(PMBAA)_3 \cdot 2py$	Acetone	10.62	10.38
	Benzene	—	—
	Chloroform	10.40	9.58
	Methanol	—	—
$Nd(PMBAAP)_3 \cdot bipy$	Acetone	11.12	11.22
	Benzene	9.82	10.48
	Chloroform	11.02	10.62
	Methanol	10.18	11.02
$Nd(PMBAAP)_3 \cdot phen$	Acetone	11.30	11.48
	Benzene	—	—
	Chloroform	11.29	10.98
	Methanol	10.32	11.32

*$\rho \times 10^6$
†Reference 9

The electronic spectral characteristics of Pr(III) PMBAA and Pr(III) PMBAAP complexes in chloroform have been investigated. Although $^3H_4 \rightarrow {^3P_2}$ and $^3H_4 \rightarrow {^1D_2}$ transitions have been reported[13] to exhibit their hypersensitivity they do not obey quadrupole selection rules. In the Pr(III) PMBAA and PMBAAP complexes the $^3H_4 \rightarrow {^1D_2}$ transition is completely swamped by the ligand or by the charge transfer tail. The molar extinction coefficients of $^3H_4 \rightarrow {^1D_2}$ (*ca.*

18×10^{-3} cm^{-1}) in the complexes on comparison with the corresponding value for the aquated Pr^{3+} ion reveal that there is a significant increase in intensity in these complexes. In fact, the gradation in intensity is similar to that of the Nd(III) complexes.

TABLE-3
OSCILLATOR STRENGTHS OF HYPERSENSITIVE TRANSITIONS IN Nd(III) PMBAA AND Nd(III) PMBAAP COMPLEXES

Compound	${}^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G^*_{7/2}$				
	Acetone	Benzene	Chloroform	Dioxane	Methanol
$Nd(PMBAA)_2 \cdot NO_3$	64.6	58.2	60.2	61.8	59.8
$Nd(PMBAA)_3 \cdot 2py$	—	66.6	68.8	64.2	60.8
$Nd(PMBAA)_3 \cdot bipy$	68.2	62.8	66.7	64.6	58.6
$Nd(PMBAA)_3 \cdot phen$	78.2	—	74.3	72.6	—
$Nd(PMBAAP)_3$	68.8	60.2	58.2	59.6	59.2
$Nd(PMBAAP)_3 \cdot 2py$	—	64.8	68.4	63.6	59.6
$Nd(PMBAAP)_3 \cdot bipy$	67.8	60.2	64.8	62.4	57.2
$Nd(PMBAAP)_3 \cdot phen$	78.6	—	72.6	70.8	—

$*\rho \times 10^6$

IR and NMR spectra

Infrared spectra (Table-4) indicate that PMBAA acts as a neutral tridentate ligand bonding through carboxylate and carbonyl oxygens and the azomethine nitrogen whereas PMBAAP acts as a neutral bidentate one bonding through both the carbonyl oxygens.

TABLE-4
INFRARED SPECTRAL BANDS (cm^{-1}) OF PMBAA AND PMBAAP AND THEIR Nd(III) COMPLEXES

	PMBAA	$Nd(PMBAA)_2NO_3$	PMBAAP	$Nd(PMBAAP)_3$
$\nu(OH)$	3010	—	—	—
$\nu(C{=}O)$	1640	1680	1640	1685
$\nu_{asym}(OCO)$	—	1600	—	—
$\nu_{sym}(OCO)$	—	1380	—	—
$\nu(C{=}N)$	1560	1585	—	—
$\nu_4(NO_3)$	—	1430	—	—
$\nu_1(NO_3)$	—	1310	—	—
$\nu_2(NO_3)$	—	1020	—	—
$\nu(Ln{-}N)$	—	540	—	—
$\nu(Ln{-}O)$	—	410	—	—

NMR spectrum of PMBAA shows a broad band at 10.08 δ which is absent in the complexes indicating bonding through deprotonation. Also the *ortho*(benzoyl) groups in both the PMBAA and PMBAAP complexes are deshielded to a greater extent occuring at *ca.* 8.4 δ as compared to the ligand where it is found to occur at 8 δ. This may be due to the *ortho*(benzoyl) groups being adjacent to the bonding site and hence greater deshielding.

From the present study it can be concluded that hypersensitivity indeed increases with greater covalent interaction, but a linear correlation between the ligand basicity and hypersensitive band intensity is an overemphasized one.

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