Optical Absorption Spectra of Pr^{3+} Chelates with 2-Amino-1-Phenylethanol

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ABSTRACT. Trivalent Pr^{3+} chelates of the type Pr(PhCHOHCH$_2$NH$_2$)$_4$ have been synthesised by the direct reaction of 2-amino-1-phenylethanol with Pr(NO$_3$)$_3$.5H$_2$O. Spectral studies reveal the presence of a 1:4 (metal-ligand) stoichiometry. Various spectroscopic parameters have been evaluated from the UV. Vis. and near i.r. spectra.

Introduction

As a part of our program on the spectral studies of the Pr^{3+} ion in solution,[1-3] we report the synthesis of praseodymium (III) nitrate and chloride chelates with 2-amino-1-phenylethanol. These complexes are characterized by electronic and vibrational spectral studies. The energy levels of the 4f^2-configuration of the Pr^{3+} ions have been analysed in arc spectra[4], o-hydroxyacetophenone oxime[5], POCl$_3$:SnCl$_4$[6], and crystal PrCl$_3$[7]. Surna *et al.*[8] have studied the absorption spectrum of Pr^{3+} in haloacetate solutions. Lakshman and Buddhudu[9] reported the Slater-Condon, configuration, spin-orbit, nephelauxetic, bonding, and Judd-Ofelt parameters of Pr^{3+} in the acetates of praseodymium complexes in the presence of magnesium, calcium, and cadmium complexes. Buddhudu and Badu[10] reported the Racah and Judd-Ofelt parameters for Pr^{3+} ion in methyl, butyl, isopropyl and amyl alcohols. In general, Semiempirical calculations based in the Judd-Ofelt theory were not satisfactory for the Pr^{3+} ion[11]. Recently, Misra and Sommerer[12] have studied the UV-Vis. bands of Pr^{3+} complexes in solution. Their values of the T$_2$ parameter are mainly negative.

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Experimental

Materials and Chemicals

The chemicals used were praseodymium nitrate pentahydrate of 99.9% purity (Fluka), praseodymium chloride hexahydrate 99.9% purity (Aldrich), dimethylsulphoxide (DMSO), acetic acid (BDH) and 2-amino-1-phenylethanol which was prepared.

Preparation of 2-amino-1-phenylethanol

Mandelonitrile (6 g) (*ca* 0.045 mole) in dry THF (73 ml) was added dropwise to a sullry of LiAlH$_4$ (5.8 g), (*ca* 0.150 mole) in dry THF (290 ml). The mixture was stirred and cooled at 0°C during the addition, for 6 hr. After completion of the addition, the reaction mixture was left at room temperature overnight. The reaction mixture was then refluxed for 4 hr, then decomposed with water (8 ml), followed by aqueous sodium hydroxide (20%, 15 ml), and finally water (8 ml). The product obtained was refluxed for 30 min., then filtered hot and washed with hot THF. The filtrate was dried over anhydrous K$_2$CO$_3$. Evaporation under reduced pressure afforded an oily product (3.96g, 57.3%) m.p. 41°C which was identified as 2-amino-1-phenylethanol. The ^{1}H-nmr in (CDCl$_3$) spectrum showed the following signals: 2.8 (2H,d, J = 6Hz, methylene protons), 3-3.1 (3H, broad, OH, NH$_2$ exchanged with D$_2$O), 4.6 (1H, J = 6Hz, methine protons), and 7.3-7.5 (5H, m, Arh) ppm.

Synthesis of Praseodymium (III)-2-amino-1-phenylethanol chelates

A series of solutions were prepared and analysed according to Job's[13,14] method. A solution of Pr(NO$_3$)$_3$. 5H$_2$O 0.1 M (100 ml) in (DMSO) was prepared. A solution of PhCHOHCH$_2$NH$_2$ (ligand) 0.1M in (DMSO, 100 ml) also was prepared. In each of nine flasks a mixture of metal salt and the ligand was stirred (the sum of the total concentration of the metals salt and the ligand is kept constant, while the mole fractions of the reactants are varied).

Absorption Spectra

All UV, Visible, and near IR spectra of the samples and of the solvents were recorded with a Cary D- 17 spectrophotometer or a UV-260 spectrophotometer. Optical cells with pathlengths of 5 mm or 10 mm were used in the absorption measurements. All absorption spectra were recorded at room temperature (22-24°C). L = PhCHOHCH$_2$NH$_2$, M = Pr^{3+} : Pr(NO$_3$)$_3$. 5H$_2$O

Results and Discussion

To study the complexation of Pr^{3+} with PhCHOHCH$_2$NH$_2$ (L) in (DMSO) a series of solutions were prepared in which the total concentration of Pr^{3+} and 2-amino-1-phenylethanol is constant, but their proportion is varied, *i.e.*, [Pr^{3+}] + {L} = constant. The data obtained for Pr^{3+} PhCHOHCH$_2$NH$_2$ complexes in DMSO appropriate to Job's method are listed in Table (1). A plot of absorbance versus mole fraction of the ligand (X$_L$) is shown in Fig. (1). The maximum absorbance is always at mole fraction of X$_L$ = 0.8. This indicates that the formula of the complex is [PrL$_4$]$^{3+}$. A tentative structure is suggested in Fig. (2).

Data of Pr^{3+} – $PhCH(OH)CH_2NH_2$ complexes in dimethylsulphoxide for Job's method.

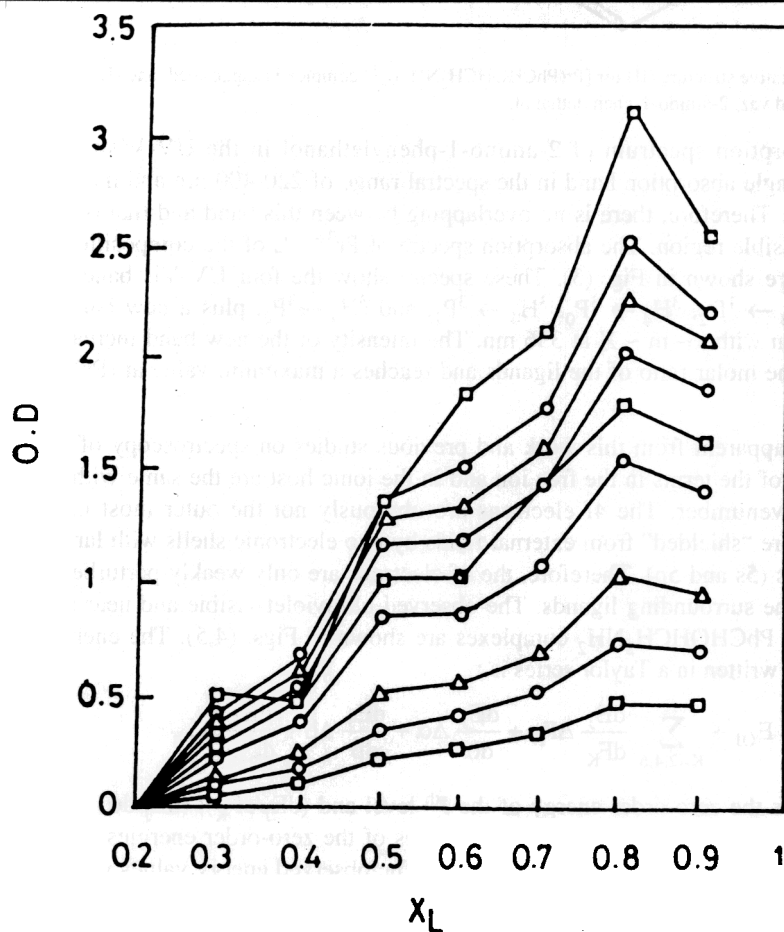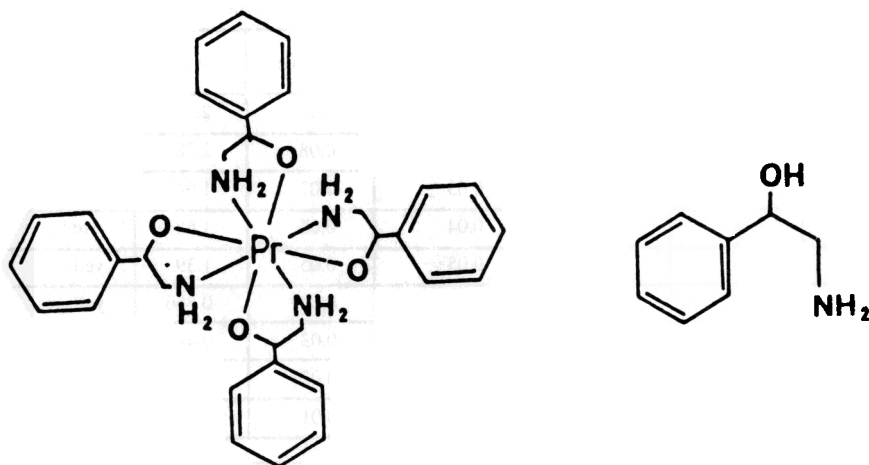| No.	Milliliters of (M)	Milliliters (L)	(M) Molar	(L) Molar	A_{max}	Colour
1	1	9	0.01	0.09	2.30	red
2	2	8	0.02	0.08	2.78	red
3	3	7	0.03	0.07	1.94	red
4	4	6	0.04	0.06	1.68	red
5	5	5	0.05	0.05	1.39	yellow
6	6	4	0.06	0.04	0.556	yellow
7	7	3	0.07	0.03	0.476	yellow
8	8	2	0.08	0.02	0.020	green
9	9	1	0.09	0.01	0.010	green

FIG. Plots of absorbance (O.D) versus mole fraction of ligand (X_l at different time for Pr^{3+}–$PhCH(OH)CH_2NH_2$ complex.

2. The tentative structure (II) for $[Pr(PhCHOHCH_2NH_2)_4]^{3+}$ complex is suggesteed, and (I) the structure of ligand vaz; 2-amino-1-phenylethanol.

The absorption spectrum of 2-amino-1-phenylethanol in the UV-Visible region showed a single absorption band in the spectral range of 220-400 mn and maximum at $\lambda = 263$ nm. Therefore, there is no overlapping between this band and that of the Pr^{3+} ion in the visible region. The absorption spectra of Pr^{3+} - L of the compositions (5:5) and (6:4) are shown in Fig. (3). These spectra show the four UV-Vis bands of Pr^{3+} namely: $^3H_4 \rightarrow {}^1D_2$, $^3H_4 \rightarrow {}^3P_0$, $^3H_4 \rightarrow {}^3P_1$, and $^3H_4 \rightarrow {}^3P_2$, plus a new band due to complexation with i ~ m ~ X at 356 mn. The intensity of the new band increases with increasing the molar ratio of the ligands and reaches a maximum value at $(Pr^{3+} : L)$ of (0.2 : 0.8).

The fact apparent from this work and previous studies on spectroscopy of Pr^{3+} are the position of the terms in the free ion and in the ionic host are the same within a few hundred wavenumber. The 4f electrons are obviously not the outer most ones, and hence they are "shielded" from external fields by two electronic shells with larger radial extensions (5s and 5p). Therefore, the 4f-electrons are only weakly perturbed by the charges of the surrounding ligands. The observed ultraviolet-visible and near i.r. spectra of Pr^{3+} - $PhCHOHCH_2NH_2$ complexes are shown in Figs. (4,5). The energy E_J of the Jth level, written in a Taylor series is :

$$E_J = E_{OJ} + \sum_{K=2,4,6} \frac{dE_J}{dF_K} \Delta F_K + \frac{dE_J}{d\alpha} \Delta\alpha + \frac{dE_J}{d\beta} \Delta\beta + \frac{dE_J}{d\zeta_{4f}} \Delta\zeta_{4f}$$

Where E_{OJ} is the zero-order energy of the Jth level and (dE_J/dF_K); $(dE_J/d\alpha)$; $(dE_J/d\beta)$; $(dE_J/d\zeta_{4f})$ are the partial derivatives. The values of the zero-order energies and partial derivatives are taken from tables of Wong[15]. The observed energy values were substituted for E_J, in the Taylor-series expansion to evaluate changes in F_2, F_4, F_6, α, β and ζ_{4f}. A least-squares fit was employed to evaluate these parameters. The Slater-Condon $(F_2, F_4$ and $F_6)$, configurational interaction $(\alpha$ and $\beta)$ and spin-orbin (ζ_{4f}) parameters for
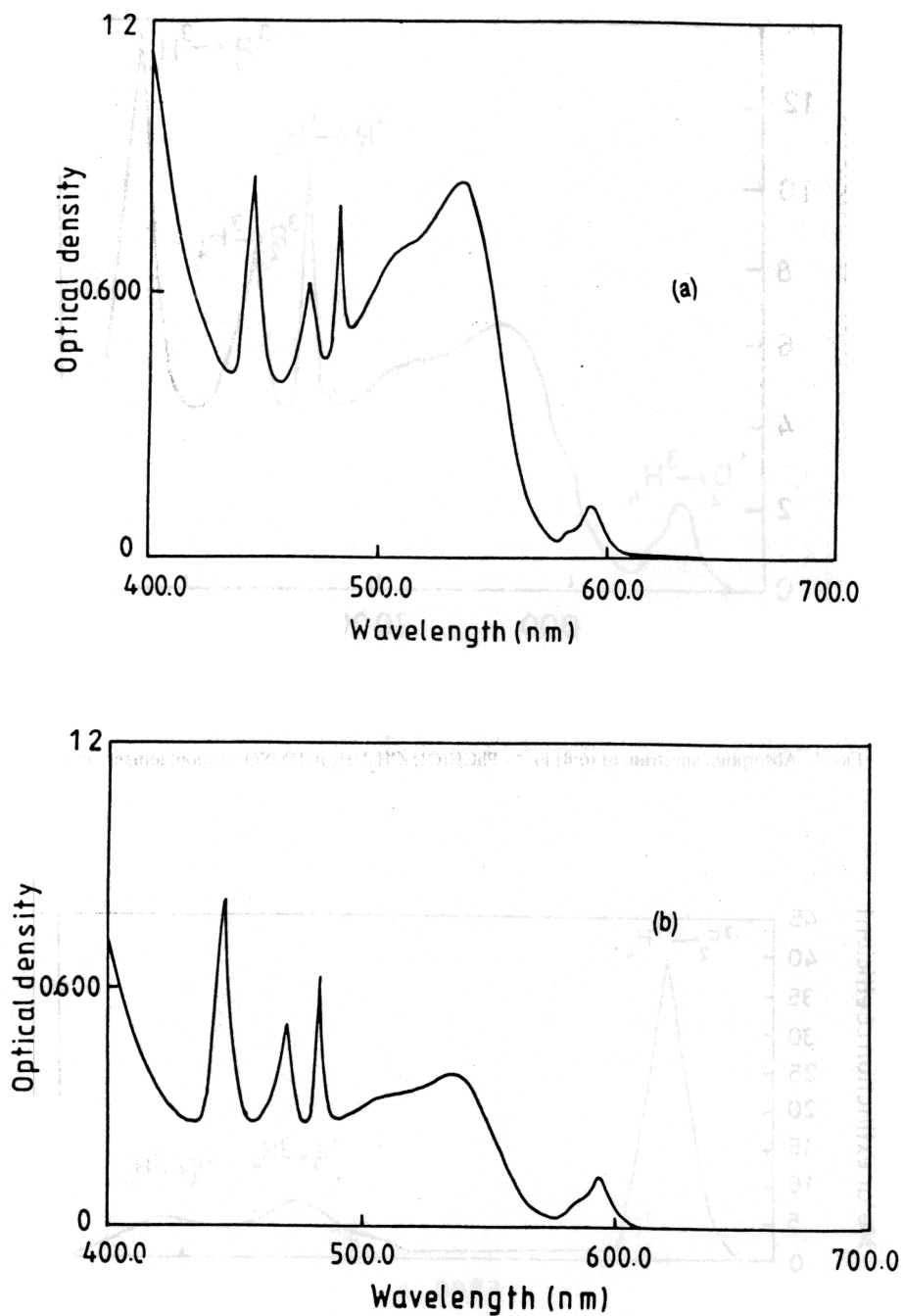
FIG. 3. Absorption spectra (a) (5:5) Pr^{3+} – PhCH(OH)CH$_2$NH$_2$; (b) (5:5) Pr^{3+} – PhCH(OH)CH$_2$NH$_2$ in DMSO.
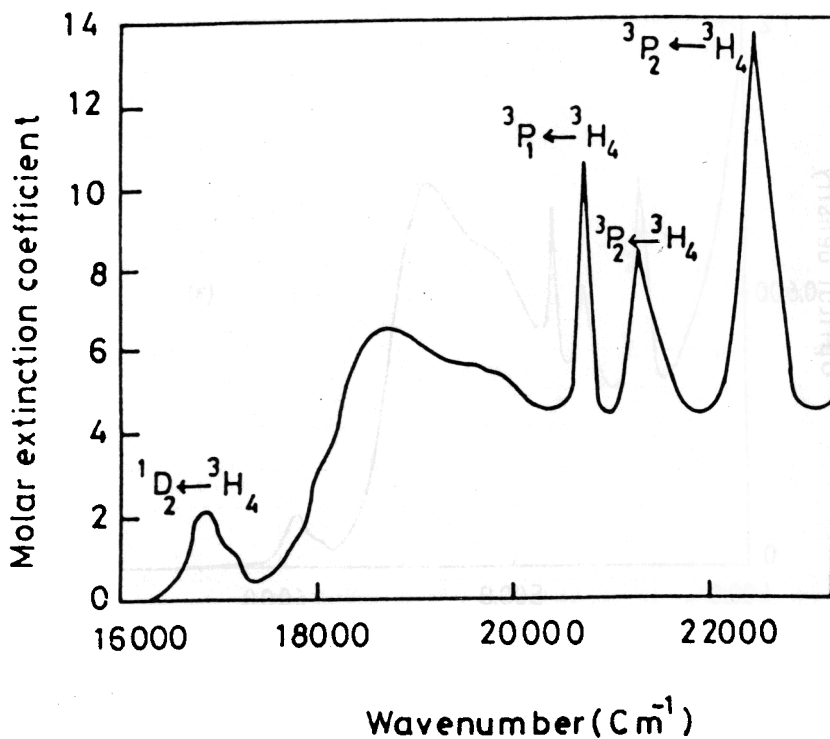
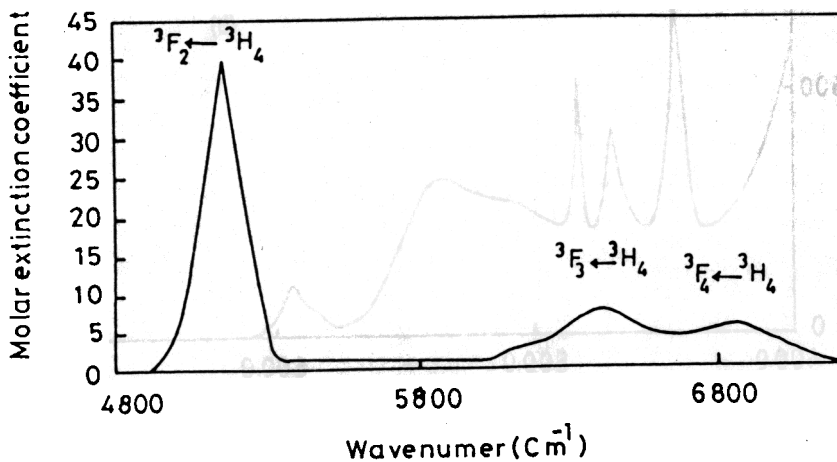FIG. 4. Absorption spectrum of (6:4) Pr^{3+} - $PhCH(OH)CH_2NH_2$ in DMSO at room temperature.

FIG. 5. Near IR absorption spectrum of (6:4) Pr^{3+} - $PhCH(OH)CH_2NH_2$ in DMSO at room temperature.

Pr^{3+} complexes are presented in Table (2). It is interesting to note that the hydrogenic F_4/F_2 and F_6/F_2 ratio are equal to ~ 0.16 and 0.016, for Pr^{3+} - L at various ratios and are nearly the same for this ion in different environments, which suggests that the radial properties of tripositive Praseodymium ion remains unchanged in different systems. Experimental and calculated energy levels of Pr^{3+} - $PhCHOHCH_2NH_2$ complexes are listed in Table (3). A good agreement between experimental and calculated energies is apparent.

TABLE 2. Slater-Condon (F_2, F_4, and F_6) Racah (E^1, E^2 and E^3), spin-orbit (ζ_{4f}) and configuration interaction (α, β) parameters and (F_2/F_4 and F_2/F_6) ratios of the Pr^{3+}-$PhCHOHCH_2NH_2$ complex in dimethyl-sulphoxide at room temperature.

Parameter	Mole ratio of P^{3+} - $PhCHOHCH_2NH_2$					
	(0.9 : 0.1)	(0.8 : 0.2)	(0.7 : 0.3)	(0.6 : 0.4)	(0.5 : 0.5)	Pr^{3+} in solvent
F_2	313.60	313.10	315.00	314.48	314.27	314.54
F_4	51.60	51.49	51.32	51.32	51.44	52.89
F_6	5.02	5.02	5.02	5.02	5.02	5.10
E^1	4880	4874	4884	4880	4882	4938
E^2	21.55	21.53	21.80	21.74	21.68	21.29
E^3	473	472.42	475.30	474.47	474.36	475.31
ζ_{4f}	773.71	774.89	771.39	774.8	775.03	726.43
α	19.98	20.38	19.30	19.374	19.38	12.68
β	− 886.38	−.886.37	− 791.59	− 886.31	− 896.36	− 801.23
F_4/F_2	0.165	0.164	0.163	0.163	0.164	0.168
F_6/F_2	0.016	0.016	0.016	0.016	0.016	0.016

TABLE 3. Experimental and calculated energy levels of Pr^{3+} complex with $PhCHOHCH_2NH_2$ in dimethyl sulphoxide.

Levels	Pr^{3+}- L (0.9 : 0.1)		Pr^{3+}- L (0.8 : 0.2)		Pr^{3+}- L (0.7 : 0.3)		Pr^{3+}- L (0.6 : 0.4)		Pr^{3+}- L (0.5 : 0.5)		Pr^{3+} in solvent DMSO	
$^3H_4$	$E_{EXP.}$	$E_{CAL.}$	$E_{EXP.}$	$E_{CAL.}$	$E_{EXP.}$	$E_{CAL.}$	$E_{EXP.}$	$E_{CAL.}$	$E_{EXP.}$	$E_{CAL.}$	$E_{EXP.}$	$E_{CAL.}$
$^3P_2$	22420	22490	22420	22460	22420	22530	22470	22520	22500	22510	22420	22120
$^3P_1$	21230	21290	21190	21260	21280	21340	21280	21320	21280	21320	21280	20970
$^3P_0$	20700	20620	20660	20590	20700	20670	20660	20650	20660	20640	20700	20400
$^1D_2$	16840	16820	16840	16810	16870	16880	16860	16860	16840	16840	16840	16550
$^3F_2$	,5147	5119	5147	5120	5155	5140	5147	5112	5155	5142	5155	5110
$^3F_3$	6410	6392	6410	6393	6431	6328	6423	6394	6431	6400	6439	6077
$^3F_4$	6849	6829	6849	6828	6859	6809	6849	6819	6846	6824	6863	6612
rms	51.72		48.09		71.87		31.79		28.54		32.61	

The intensity of an absorption band is measured by its oscillator strength which is directly proportional to the area under the absorptive curve. The experimental oscillator strength ($P_{exp.}$) of the band is evaluated from the formula.

$$P_{exp.} = 4.32 \times 10^{-9} \int_{v1}^{v2} \varepsilon(v)dv$$

where ε is the molar absorptivity, v is the energy of the transition in wavenumber and $\int \varepsilon(v)dv$ is the area under absorption curve.

The intensity of a band can be affected by electric dipole, magnetic dipole, and electric quadrupole transitions. The bands of lanthanide ions essentially arise from electric dipole transitions. But some magnetic dipole character will be present in some transitions. The electric quadrupole and magnetic dipole component are very small in this case and can be neglected.

Judd-Ofelt[16,17] have independently shown that the oscillator strength of an induced electric dipole transition may be related to the energy of transition(v) and the square of the matrix elements of the unit tensor operator U^λ connecting the initial and final states ($\Psi J_i \rightarrow \Psi J_f$) via three phenomenological parameters $T_\lambda(\lambda = 2, 4, 6)$. These three parameters are complex expressions relating the radial wave functions of the state, the refractive index of the medium, and the ligand field parameters which characterize the environmental field. According to Judd-Ofelt theory the induced electric dipole oscillator strength (P_{ed}) is given by :

$$P_{ed} = \sum_{\lambda=2,4,6} v T_\lambda (f^N \Psi J_f |U^\lambda| f^N \Psi J_f)$$

where v (cm^{-1}) is the mean energy of the transition ($\Psi J_i \rightarrow \Psi J_f$), U^λ is the unit tensor operator of rank λ, and sum extends over λ(2,4 and 6). The experimental and calculated spectral intensities for seven observed bands using component U^λ for ($^3P_1 + {}^1I_6$) are given in Table (4). This indicates a good fit between observed and calculated oscillator strength. Unlike most reported results, our values of the T_2 parameter are positive. The T_2 parameter has been related to the hypersensitivity being more dependent on the covalent metal-ligand interactions, while T_4 and T_6 have been considered more dependent on the coordination cluster symmetry[18,-22]. A linear relationship between ($P_{exp.}$ values) of the hypersensitive band ($^3H_4 \rightarrow {}^3F_2$) and T_2 for Pr^{3+} - L complexes is shown in Fig. (6).

The energies at which the various bands appear are low as compared to the aquo ion. This red shift has been ascribed to a nephelauxetic effect[23]. The extent of the red shift is related to covalence in the metal ligand bond. Sinhh[24] has proposed a scale to express this covalence.Sinha's parameter, $\delta(\%)$ is given by the relation

$$\delta\% = \frac{(1-\beta)}{\beta} \times 100$$

where β

$$\beta = \frac{1}{n} \sum \frac{v_{complex}}{v_{aqua}}$$

TABLE 4. Experimental and calculated oscillator strengths ($P \times 10^6$) doe Pr^{3+}-$PhCHOHCH_2NH_2$ in dimethylsulphoxide.

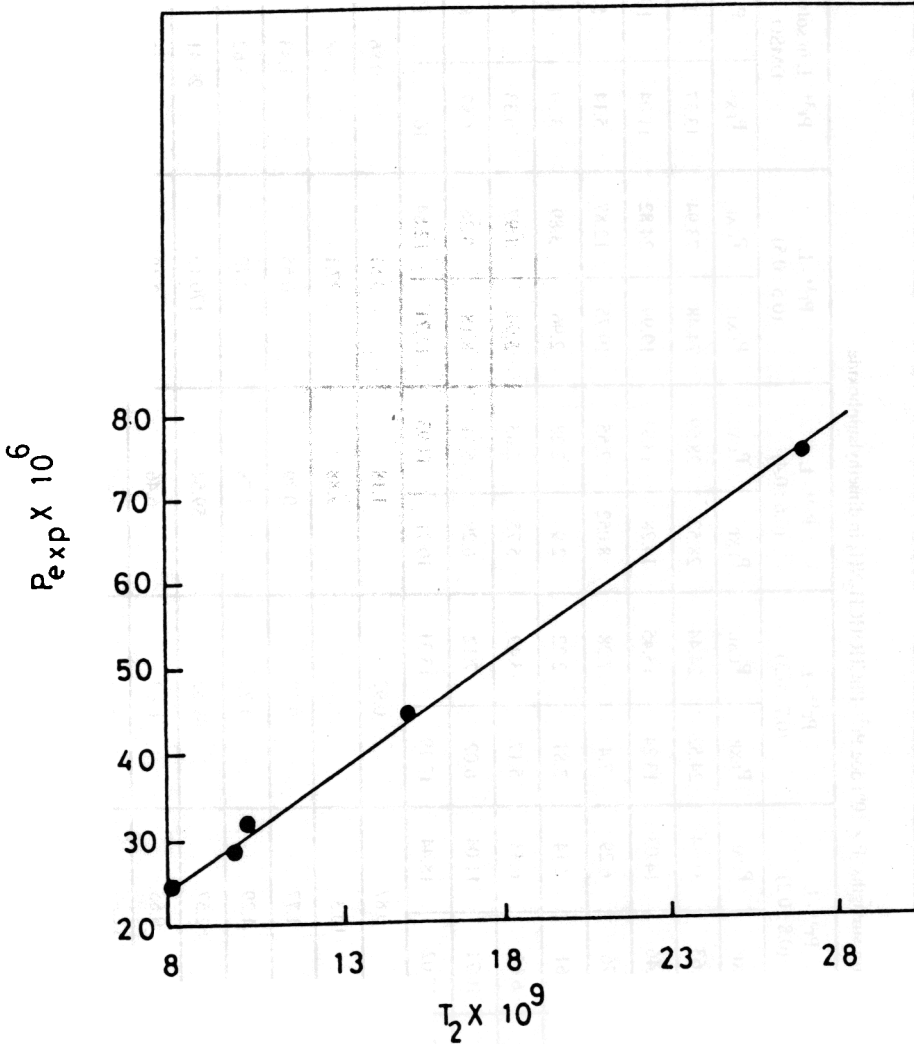| Levels $^3H_4$	Pr^{3+} - L (0.9 : 0.1)		Pr^{3+} - L (0.8 : 0.2)		Pr^{3+} - L (0.7 : 0.3)		Pr^{3+} - L (0.6 : 0.4)		Pr^{3+} - L (0.5 : 0.5)		Pr^{3+} - L in solvent DMSO	
	$P_{EXP.}$	$P_{CAL.}$	$P_{EXP.}$	$P_{CAL.}$	$P_{EXP.}$	$P_{CAL.}$	$P_{EXP.}$	$P_{CAL.}$	$P_{EXP.}$	$P_{CAL.}$	$P_{EXP.}$	$P_{CAL.}$
$^3F_2$	43.8	43.37	31.63	31.44	24.52	24.44	28.52	28.59	74.48	73.94	13.37	13.3
$^3F_3$	13.39	16.46	12.46	14.03	13.24	13.45	14.28	13.91	19.99	24.82	11.04	10.92
$^3F_4$	10.56	10.54	7.76	6.29	7.4	7.28	8.052	7.55	19.75	12.87	5.14	5.61
$^1D_2$	3.09	3.12	2.61	2.14	3.81	2.22	2.9	2.28	2.96	3.89	3.29	1.79
$^3P_0$	4.56	4.88	6.14	6.33	5.17	3.49	5.75	2.83	5.94	1.97	6.33	5.12
$^3P_1 + {}^1I_6$	9.07	8.88	10.71	11.04	6.02	7.12	6.29	6.61	8.18	9.36	6.97	8.19
$^3P_2$	17.38	15.99	19.02	18.44	13.19	13.31	10.71	11.93	12.71	12.84	16	15.9
$rms \times 10^6$	1.73		0.87		0.93		1.18		3.51		0.86	
$T_2 \times 10^9$	15.1		10.3		8.14		9.88		27.1		1.38	
$T_4 \times 10^9$	1.00		1.77		9.77		0.79		0.55		1.43	
$T_6 \times 10^9$	2.49		1.29		1.75		1.78		2.72		3.62	
$\Omega_2 \times 10^{20}$	94.68		62.57		49.52		59.54		170.19		20.41	
$\Omega_4 \times 10^{20}$	6.23		9.85		6.03		6.46		3.48		8.47	
$\Omega_6 \times 10^{20}$	15.76		15.02		14.64		13.67		19.21		14.06	

FIG. 6. Oscillator strength of the $^3F_2 \leftarrow {}^3H_4$ transition (hypersensitive transition) as a function of the Judd-
Ofelt T_2 parameter of Pr^{3+}-$PhCH(OH)CH_2NH_2$ complex.

he bonding parameter, $b^{1/2}$, the magnitude of which suggests the extent of involvement
of the 4f orbital in the metal-ligand bond, is correlated to the nephelauxetic ratio (β) by
the expression :

$$b^{1/2} = [\tfrac{1}{2}(1-\beta)]^{1/2}$$

The bonding parameters β, $\delta(\%)$ and $b^{1/2}$ were calculated, and their values are presented in Table (5). The positive values of bonding parameters (Table 5), suggest the occurrence of some covalent character in the metal-ligand bond. The magnitude of the parameters reach maximum when the molar ratio of ligand: Pr^{3+} is (8:2). Thus, on the basis of the above evidence, it can concluded that the Pr^{3+} ion is surrounded by four neutral ligand molecules each bound in a bidentate N, O fashion forming a coordination number of eight. A suggested structure of the complex is shown in Fig. (2).

TABLE 5. Nepheluxetic effect for Pr^{3+}-$PhCHOHCH_2NH_2$ complexes in dimethylsulphoxide.

Parameter	Mole ratio of Pr^{3+}-$PhCHOHCH_2NH_2$				
	(0.9 : 0.1)	(0.8 : 0.2)	(0.7 : 0.3)	(0.6 : 0.4)	(0.5 : 0.5)
β	0.9951	0.9940	0.9960	0.9961	0.9959
$\delta(\%)$	0.4956	0.6013	0.3996	0.3959	0.4095
$b^{1/2}$	0.0497	0.0547	0.0446	0.0444	0.0452

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أطياف الامتصاص الضوئية لأيون Pr^{3+} مع المركب المخلبي
٢-أمينو-١-فينيل إيثانول

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** قسم العلوم ، كلية المعلمين ، أبهـــا – المملكة العربية السعودية

المستخلص .   تم تحضير متراكبات Pr^{3+} من النوع $Pr (phCHOHCH_2NH_2)$ وذلك بالتفاعل المباشر لـ (٢-أمينو-١-فينيل إيثانول) مع $Pr (NO_3)_3 . 5H_2O$. وأثبتت الدراسات الطيفية أن نسبة الفلز – متصل في المركب الناتج هي 1:4 كما تم تقدير العديد من المعاملات الطيفية من الطيف المسجل في منطقة UV-Vis ومنطقة طيف الأشعة تحت الحمراء للمركب الناتج .