

Electronic Spectral Characterisation of Pr(III) Systems Involving Some Analytically Important Reagents at pH-3 in Ethanol Medium-Part-I

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An electronic spectral investigation of some analytically important compounds with Pr(III) ion in the form of doped model have been discussed in terms of covalency (β), Judd-Ofelt symmetry parameter (T_4/T_6), bonding parameter ($b^{1/2}$), Slater-Condon parameter (F_2, F_4, F_6), Racah parameter (E^1, E^2, E^3), Landé parameter (ζ_{4F}), percentage reduction in F_2 parameter ($\% rF_2$) and percentage reduction in ζ_{4F} parameter ($\% r\zeta_{4F}$). The linear relationship between oscillator strength (P) and $\nu T_4/\nu T_6$ has been discussed with reference to hypersensitive transition, *i.e.*, 3P_2 bands of Pr(III) ion.

INTRODUCTION

In spite of extremely rapid development of coordination chemistry, the complex formation studies of ligands having nitrogen and oxygen as donor atoms with the metal ions, specially the rare earth ions in solution form have not yet reached maturity¹. The electronic spectral characterisation of various Pr(III) systems involving ligands of analytical importance in ethanol have been studied. A modified doped system^{2,3} has been undertaken to record solution spectra in ethanol medium using standard spectrophotometer (Systronics 106). The calculations involve the Judd-Ofelt equation and the other relations described in the literature⁴. The present work infers covalency in metal ligand bonding in the system undertaken. The validity of the Peacock⁵ relations $P \propto \nu T_4$ and $P \propto \nu T_6$ has been examined and found in good agreement with these systems.

EXPERIMENTAL

Fourteen systems have been prepared in ethanol by mixing 10 cm^3 of 0.012 M of $\text{PrCl}_3 \cdot 6\text{H}_2\text{O}$ in 10 cm^3 of 0.024 M ligand solution in ethanolic medium. In this way the concentration of ligand has been taken in excess which serves the purpose of modified doped model. Solution spectra for the Pr(III) ligand system have been taken in the range of 400–625 nm by using standard spectrophotometer (Systronics 106) at pH = 3. The pH was maintained by adding requisite amount of acetic acid and checked with digital pH meter model 111 E.

RESULTS AND DISCUSSION

The different parameters reported in Table-1 have been calculated by the theories given by Slater-Condon-Landé and Judd-Ofelt^{6,7}. The computerised programme for the said calculations has already been reported by the earlier

workers⁸. The system has been categorised in Set "A", wherein $\{T_4/T_6 < 0.13$ (N-N-diphenyl thiourea, benzidine, thiosemicarbazide, cacotheline, dimethyl glyoxime, hydroquinone, ninhydrin and gallic acid) and Set "B", wherein $T_4/T_6 > 0.13$ (α -benzoin oxime, 1-10-phenanthroline, diphenylamine, diphenyl carbazone, rubeanic acid and diphenyl glyoxime).

TABLE-1
COMPUTED VALUES OF VARIOUS ELECTRONIC SPECTRAL PARAMETERS

		Set "A"	Set "B"
	$T_2 \times 10^9$	-14.45 to -5.25	-9.18 to -0.65
	$T_4 \times 10^9$	0.25 to 1.76	0.54 to 1.06
	$T_6 \times 10^9$	2.29 to 15.93	3.84 to 7.88
3P_2	$P_{\text{exp}} \times 10^6$	7.07 to 49.94	12.22 to 24.86
	$P_{\text{cal}} \times 10^6$	7.07 to 49.94	12.22 to 24.86
3P_1	$P_{\text{exp}} \times 10^6$	1.19 to 8.55	2.66 to 4.94
	$P_{\text{cal}} \times 10^6$	1.19 to 8.55	2.66 to 4.94
3P_0	$P_{\text{exp}} \times 10^6$	0.64 to 4.04	1.25 to 3.00
	$P_{\text{cal}} \times 10^6$	0.63 to 4.02	1.24 to 2.99
1D_2	$P_{\text{exp}} \times 10^6$	1.76 to 13.84	3.51 to 7.05
	$P_{\text{cal}} \times 10^6$	1.76 to 13.84	3.51 to 7.05
$\sigma_{\text{rms}} \times 10^9$		1.48 to 9.35	2.89 to 6.94
3P_2	E_{exp}	22321 to 22472	22321 to 22727
	E_{cal}	22252.73 to 22435.94	22382.96 to 22570.95
3P_1	E_{exp}	21008 to 21505	21186 to 21505
	E_{cal}	21140.69 to 21333.10	21290.79 to 21406.84
3P_0	E_{exp}	20619 to 20833	20661 to 20921
	E_{cal}	20665.05 to 20872.27	20760.54 to 20941.93
1D_2	E_{exp}	16835 to 16949	16835 to 15684
	E_{cal}	17013.33 to 17163	17016.06 to 17214.09
σ_{rms}		101.63 to 177.13	100.06 to 162.59
F_2 (cm^{-1})		308.626 to 313.388	310.168 to 315.294
F_4 (cm^{-1})		42.605 to 43.263	42.818 to 43.526
F_6 (cm^{-1})		4.663 to 4.735	4.686 to 4.764
β		0.958 to 0.973	0.963 to 0.979
$b^{1/2}$		0.116 to 0.144	0.102 to 0.136
$\% rF_2$		2.701 to 4.180	2.109 to 3.701
E^1		4531.186 to 4601.106	4553.831 to 4629.091
E^2		23.702 to 24.068	23.821 to 24.214
E^3		458.124 to 465.193	460.414 to 468.023
ζ_{4F}		645.728 to 705.472	618.992 to 693.931
$\% r\zeta_{4F}$		4.794 to 12.857	5.812 to 16.465

A linear relationship between oscillator strength 'P' and $\nu T_4/\nu T_6$ has been found for the hypersensitive band (3P_2). The values of proportionality constants (K_1 and K_2) with reference to νT_4 and νT_6 have been reported in Table-2. The values show almost negligible deviation with respect to relation $P \propto \nu T_4$ and $P \propto \nu T_6$, and hence prove the validity of the said relation.

TABLE-2
COMPUTED VALUES OF K_1 AND K_2 FOR THE RELATIONSHIP $P \propto \nu T_4$ AND
 $P \propto \nu T_6$ RESPECTIVELY IN CASE OF SET "A" AND SET "B" SYSTEMS

Set "A"	$T_4/T_6 < 0.13$	K_1	K_2
1	N, N. diphenyl thiourea	1.5039	0.1388
2	Benzidine	1.2632	0.1395
3	Thiosemicarbazide	1.2401	0.1396
4	Cacotheline	1.1536	0.1399
5	Dimethyl glyoxime	1.2193	0.1396
6	Hydroquinone	1.0962	0.1401
7	Ninhydrin	1.2773	0.1374
8	Gallic acid	1.1093	0.1401
Set "B"	$T_4/T_6 > 0.13$	K_1	K_2
1	α -Benzoin oxime	0.9999	0.1406
2	1, 10-Phenanthroline	0.9623	0.1408
3	Diphenyl amine	1.0388	0.1404
4	Diphenyl carbazone	1.0374	0.1404
5	Rubeanic acid	1.0455	0.1404
6	Diphenyl glyoxime	1.0565	0.1403

The values of the other parameters also show covalency in metal-ligand bonding. This is reflected from the values of the following:

- (i) The percentage reduction in F_2 parameter comes from 2.7 to 4.1 and from 2.1 to 3.7 for set "A" and set "B" respectively. This indicates decrease in spin-orbit interaction in metal-ligand bonding.
- (ii) The value of nephelauxetic ratio ' β ' has been found less than one in all the systems.
- (iii) The percentage reduction in ζ_{4F} parameter comes from 4.790 to 12.857 and from 5.812 to 16.465 for set "A" and set "B" respectively. This indicates decrease in spin-orbit interaction in metal-ligand bonding.
- (iv) Validity of the Judd-Ofelt theory has been established by the fact that r.m.s. deviation ($\sigma_{r.m.s.}$) values of oscillator strength of all the bands comes from $\pm 1.49 \times 10^{-9}$ to $\pm 9.35 \times 10^{-9}$ and from $\pm 2.89 \times 10^{-9}$ to $\pm 6.94 \times 10^{-9}$ for set "A" and set "B", respectively.
- (v) Validity of the Slater-Condon-Landé theory has been proved by the r.m.s. deviation ($\sigma_{r.m.s.}$) values of energies of all the bands comes from ± 101.63 to ± 177.13 and ± 100.06 to ± 162.59 for set "A" and set "B" system, respectively.

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