Variation in Symmetry Around Doped Pr(III) Ion in Saturated Solution of Medicinal Compounds with Reference to Judd-Ofelt Electronic Spectral Parameter

MS. ARYAMITRA PANDEY, K.P. SONI and G.K. JOSHI*
Rare Earth Research Laboratory
Department of Chemistry
Dungar College, Bikaner-334 003, India

The interaction of medicinal compounds with Pr(III) ion in the form of doped model have been discussed in terms of covalency (β) and Judd-Ofelt symmetry (T_4/T_6) parameters as derived from f $\leftrightarrow$ f transitions. The doped model involves small concentration of Pr(III) ion salt in saturated solution of medicinal compounds in alcohol. The medicinal compounds include anthelminthic drugs, *viz.*, thiabendazole, piperazine, mebendazole, pyrantel pamoate, albendazole, levamisole, diethylcarbamazine, antimicrobial drugs, *viz.*, sulfaacetamide, sulfadiazine, sulfaguanidine, sulfamethoxazole, pefloxacin, ciprofloxacin, tinidazole, metronidazole, atovaquone, pentamidine and antianginal drugs, *viz.*, amlodipine, atenolol and nifedipine. It also describes electronic spectral characterization in terms of various parameters. The linear relationship between oscillator strength (P) and vT_4/vT_6 has been discussed with reference to hypersensitive transition, *i.e.*, $^3P_2$ band of Pr(III) ion.

INTRODUCTION

While going through the literature it has been found that the biolgical actions of rare earth ion have been explored by some of the scientists. This includes the work of Weiss, Mines, Lettvin and others[1-3]. The biological action is almost entirely based upon the use of rare earth ion as a substitute or antagonist for Ca^{2+} in a variety of cellular and subcellular reactions. The use of La^{3+} as a relatively specific Ca^{2+} substitute or antigonist at well defined cellular location appeared justified both electrophysiologically and anatomically. The fact is well known that the general chemical characteristics of rare earth series of elements resemble those of the alkaline earth elements in many respects. Recently electronic spectral studies of lanthanide ion complexes with reference to Judd-Ofelt parameters have been found to have due significance[4]. This is because of strong validity of the theory given by Judd-Ofelt for intensity of f $\leftrightarrow$ f transitions. The various parameters given by Judd-Ofelt have been used to explain mostly covalence and symmetry around lanthanide ion. The complexing ability with respect to thermodynamic stability is poor in case of lanthanide complexes; so recently doped lanthanide ion in saturated solution of ligand has been undertaken

as a system for electronic spectral study. In the present paper some medicinal compounds have been characterized while involving them in the systems as described above on the basis of Judd-Ofelt symmetry parameter whereas Pr(III) ion acts as a doped ion. The interactions of medicinal compounds with Pr(III) ions in terms of covalency and symmetry may therefore be given on the basis of the present doped model.

EXPERIMENTAL

Twenty systems have been prepared in alcohol by doping 0.1 g of $PrCl_3 \cdot 6H_2O$ salt into 10 mL of saturated solution of each medicinal compound, at room temperature. The solution spectra of each system have been recorded by using standard spectrophotometer (Spectronic-20). Four bands, *viz.*, $^3P_2$, $^3P_1$, $^3P_0$ and $^1D_2$ have been observed in the region 350 nm to 600 nm. Intensities of all the bands have been computed in terms of oscillator strength (P) by assuming the band curve to be in Gaussian shape. The medicinal compounds (ligands) include anthelminthic drugs, *viz.*, thiabendazole (L_1), piperazine (L_2), mebendazole (L_3), pyrantel pamoate (L_4), albendazole (L_5), levamisole (L_6), diethylcarbamazine (L_7), antimicrobial drugs, *viz.*, sulfaacetamide (L_8), sulfadiazine (L_9), sulfa-guanidine (L_{10}), sulfamethoxazole (L_{11}), pefloxacin (L_{12}), ciprofloxacin (L_{13}), tinidazole (L_{14}), metronidazole (L_{15}), atovaquone (L_{16}), pentamidine (L_{17}), and antianginal drugs *viz.*, amlodipine (L_{18}), atenolol (L_{19}) and nifedipine (L_{20}).

RESULTS AND DISCUSSION

The values of various parameters have been reported in Table-1. This includes oscillator strength (P), energy (E), Judd-Ofelt parameters (T_2, T_4, T_6), Slater-Condon parameters (F_2, F_4, F_6), nephelauxetic ratio (β), bonding parameter ($b^{1/2}$), Racah parameters (E^1, E^2, E^3), Landé parameter (ζ_{4f}), percentage reduction in F_2-parameter ($\%rF_2$), percentage reduction in ζ_{4f}-parameter ($\%r\zeta_{4f}$) and r.m.s. deviation with respect to oscillator strength and energy (σ). The calculations of various parameters involve theories given by Slater-Condon-Landé and Judd-Ofelt as reported by earlier workers.[5-7] The computerized programmes for the said calculations have already been set up in the present laboratory by earlier workers.[5-7] The systems have been categorized in Set A (albendazole, sul-faacetamide, sulfadiazine, sulfamethoxazole, pefloxacin, amlodipine, atenolol, nifedipine) and Set B (thiabendazole, piperazine, mebendazole, pyrantel pamoate, diethylcarbamazine, levamisole, sulfaguanidine, ciprofloxacin, tinidazole, metro-nidazole, atovaquone, pentamidine). Systems included in Set A have symmetry parameter (T_4/T_6) in between 0.13 to 0.21 whereas in Set B the value of (T_4/T_6) ranges from 0.22 to 0.25. This classification is arbitrary yet it indicates variation in symmetry around doped Pr(III) ion in saturated ligand solution. Since Pr(III) ion forms complexes with coordination number six and above upto twelve, so at least two symmetries corresponding to different coordination number (maybe six and above six) are clearly indicated in the present study. Since the increase in T_4 and T_6 values causes greater perturbation in the symmetry around Pr(III) ions so the ratio T_4/T_6 value will have some basis for comparative stability.

It is more probable that the the higher values of T_4/T_6 ratio may indicate comparative higher stability. In the present study out of twenty there are twelve systems (Set B) which have T_4/T_6 value greater than 0.215 while the remaining eight (Set A) have this value less than 0.215.

TABLE-1
COMPUTED VALUES OF VARIOUS ELECTRONIC SPECTRAL PARAMETERS FOR
SET A AND SET B SYSTEMS

		Set-A $T_4/T_6 < 0.215$	Set-B $T_4/T_6 \geq 0.215$
	$T_2 \times 10^{10}$	−21.9 to −527.00	−0.279 to −259.00
	$T_4 \times 10^{10}$	3.52 to 10.60	4.50 to 11.80
	$T_6 \times 10^{10}$	21.30 to 50.70	20.20 to 54.10
$^3P_2$	$P_{exp} \times 10^6$	6.80 to 16.30	6.50 to 17.40
	$P_{cal} \times 10^6$	6.80 to 16.30	6.50 to 17.40
$^3P_1$	$P_{exp} \times 10^6$	2.10 to 6.19	2.73 to 6.75
	$P_{cal} \times 10^6$	2.10 to 6.19	2.73 to 6.75
$^3P_0$	$P_{exp} \times 10^6$	0.414 to 1.52	0.543 to 1.82
	$P_{cal} \times 10^6$	0.413 to 1.51	0.541 to 1.82
$^1D_2$	$P_{exp} \times 10^6$	0.415 to 4.54	1.46 to 5.07
	$P_{cal} \times 10^6$	0.415 to 4.54	1.46 to 5.07
r.m.s. dev $\times 10^{10}$		±6.07 to ±22.2	±7.95 to ±26.60
$^3P_2$	E_{exp}	22471	22321 to 22471
	E_{cal}	22286 to 22397	22286 to 22399
$^3P_1$	E_{exp}	21276 to 21367	21276 to 21367
	E_{cal}	21213 to 21265	21203 to 21265
$^3P_0$	E_{exp}	20682 to to 20833	20746 to 20833
	E_{cal}	20732 to 20852	20783 to 20863
$^1D_2$	E_{exp}	16835 to 16891	16849 to 16891
	E_{cal}	17071 to 17112	17061 to 17134
r.m.s. dev (σ)		⊦90.21 to ±156.76	±102.84 to ±137.81
F_2 (cm^{-1})		310.37 to 314.08	311.48 to 314.45
F_4 (cm^{-1})		42.85 to 43.36	43.00 to 43.41
F_6 (cm^{-1})		4.69 to 4.75	4.71 t0 4.75
β		0.964 to 0.975	0.967 to 0.976
$b^{1/2}$		0.111 to 0.135	0.109 to 0.127
%rF_2		2.49 to 3.64	2.37 to 3.29
E^1 (cm^{-1})		4556.80 to 4611.31	4573.12 to 4616.62
E^2 (cm^{-1})		23.83 to 24.12	23.92 to 24.14
E^3 (cm^{-1})		460.71 to 466.22	462.36 to 466.76
ζ_{4f} (cm^{-1})		614.30 to 673.41	604.10 to 667.87
%rζ_{4f}		9.12 to 17.09	9.86 to 18.47

The values of Judd-Ofelt parameters (T_4 and T_6) can also be used to indicate a linear relationship between oscillator strength (P) and vT_4 or vT_6 at least with reference to hypersensitive band ($^3P_2$). The values of proportionality constants (K_1 and K_2) with respect to vT_4 and vT_6 have been reported in Table-2 and Table-3. These values show almost negligible deviation with respect to the relation $P \propto vT_6$. The relation $P \propto vT_4$ has been followed in systems of Set B category but it has significant deviation in systems of Set A category. This may also indicate some variation in symmetry among the systems of Set A category. This includes systems involving sulfaacetamide (10.7), sulfadiazine (9.9) and atenolol (9.0). However, the remaining ones in Set A have the value for K_1 to be approximately 7.0.

TABLE -2

COMPUTED VALUES OF K_1 AND K_2 FOR THE RELATIONS $P \propto vT_4$ AND $P \propto vT_6$ RESPECTIVELY IN CASE OF SET A SYSTEMS

A.	$T_4/T_6 < 0.215$	K_1	K_2
1.	Albendazole	7.50	1.42
2.	Sulfaacetamide	10.71	1.39
3.	Sulfadiazine	9.92	1.41
4.	Sulfamethoxazole	7.49	1.42
5.	Pefloxacin	6.74	1.43
6.	Amlodipine	7.06	1.43
7.	Atenolol	8.92	1.41
8.	Nifedipine	6.84	1.43

TABLE-3

COMPUTED VALUES OF K_1 AND K_2 FOR THE RELATIONS $P \propto vT_4$ AND $P \propto vT_6$ REPECTIVELY IN CASE OF SET B SYSTEMS

B.	$T_4/T_6 \geq 0.215$	K_1	K_2
1.	Thiabendazole	5.83	1.45
2.	Piperazine	6.42	1.43
3.	Mebendazole	6.48	1.43
4.	Pyrantel pamoate	6.52	1.44
5.	Levamisole	6.65	1.43
6.	Diethylcarbamazine	6.43	1.44
7.	Sulfaguanidine	6.15	1.43
8.	Ciprofloxacin	6.50	1.44
9.	Tinidozole	5.90	1.45
10.	Metronidazole	6.44	1.44
11.	Atovaquone	6.58	1.44
12.	Pentamidine	5.89	1.44

In addition to symmetry around Pr(III) ion for the systems undertaken with reference to T_4 and T_6 parameters the values of other parameters also show covalency in metal-ligand bonding. This is reflected from the values of the following:

1. Value of nephelauxetic ratio (β) has been found to be less than one in all the systems.

2. The percentage reduction of F_2 parameter comes to be 2.49 to 3.64 and 2.37 to 3.29 for Set A and Set B respectively. This indicates decrease in interelectronic repulsions between metal-ligand bonding.

3. The percentage reduction in ζ_{4f} parameter comes to be 9.12 to 17.09 and 9.86 to 18.47 for Set A and Set B respectively. This indicates decrease in spin-orbit interactions in metal-ligand bonding.

4. Validity of the theory given by Slater-Condon-Landé has been established with the fact that the r.m.s. deviations (σ) between experimental (E_{exp}) and calculated values of energies of all the bands comes to be ± 90.21 to ± 156.76 (cm^{-1}) and ± 102.84 to ± 137.81 (cm^{-1}) for Set A and Set B systems respectively.

5. Validity of the theory given by Judd-Ofelt has been established with the fact that r.m.s. deviation (σ) between experimental (P_{exp}) and calculated (P_{cal}) values of oscillator strength of all the bands comes to be $\pm 6.07 \times 10^{-10}$ to $\pm 22.2 \times 10^{-10}$. There are some other derived parameters such as bonding parameter ($b^{1/2}$), Slater-Condon (F_4 and F_6) and Racah (E^1, E^2 and E^3) which have also been computed so as to indicate variation in electronic spectral characterization and given in Table-1.

The variation in symmetry around doped Pr(III) ion involving various medicinal compounds (ligands) has also been shown in Fig. 1. The ligands (L_1 to L_{20}) have been described in an earlier para (Experimental).
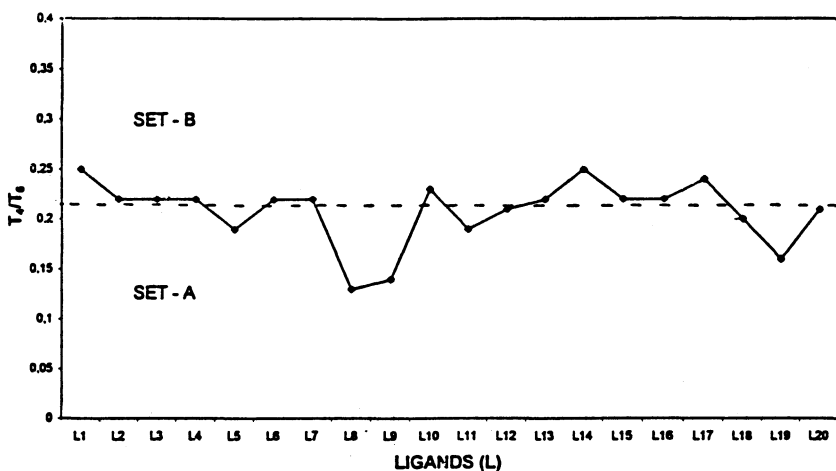

Fig. 1.   Variation of symmetry parameter (T_4/T_6) for set A and set B systems

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