ISSN: 0975-8585

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Bonding and energy parameters for some praseodymium (III) mixed ligand complexes

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ABSTRACT

Nine coordinate mixed ligand complexes of praseodymium (III) using benzoin- α-oxime, vanillin monoxime, N-phenylanthranilic acid as the primary ligands and phenyl derivatives of urea and thiourea as the secondary ligands, have been synthesised. The values of inter electronic repulsion parameters i.e. Slater-Condon (F_K), Racah (E^K) and Spin-orbit interaction referred as Lande parameter (ζ_{4f}) and intensity parameters have been calculated from their electronic spectral data. Using F_2 values the nephelauxetic ratio (β), bonding parameter ($b^{1/2)}$, Sinha's parameter (δ%) and covalency angular overlap parameter (η) have been calculated which give useful information regarding bonding in these complexes. The effect of screening terms is also discussed.

Keywords: interelectronic parameter, intensity parameter, nephenlauxetic effect.

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INTRODUCTION

The electronic spectra of lanthanides have earned immense interest in recent years [1-5] . The covalent contributions to bond formation have been invoked to explain certain effects of extremely complicated spectra resulting from f→f electronic transitions in the lanthanide ions [6-11]. The bonding between the ligands and the lanthanide ions is sufficiently electrostatic with appreciable interactions between the 4f orbitals and ligand orbitals.

In our previous publications [12,13] the absorption spectra of Pr(III) complexes was interpreted in terms of the parameters like Slater-Condon (F_K), Racah (E^K) and Lande parameter (ζ_{4f}), oscillator strength (P), Judd -Ofelt parameter (T_λ) nephelauxetic ratio (β), bonding ($b^{1/2}$), percentage covalency (δ%) and angular overlap parameter (η). All these parameters along with T_4/T_6 ratio were correlated to the coordination number. These observations are in conformity with the observations of previous workers [9,14]. In view of this the study has been extended for the nine-coordinate Pr(III) mixed ligand complexes. In all the eleven complexes selected for the study, the bonding parameters like β, $b^{1/2}$, δ% ,η and T_4/T_6 ratio which are characteristic of particular complexes are found to be nearly the same within the mean deviation range supporting the previous results. It has also been observed that the effect of screening terms is nearly the same for all the interaction parameters in these complexes.

MATERIALS AND METHODS

Preparation of the complexes.

The complexes were synthesised by adopting the procedure described in our earlier communications [12-15].

Evaluation of spectral parameters and their significance.

The values of various energy parameters like Slater-Condon (F_K) , Racah (E^K) and Lande parameter (ζ_{4f}) , intensity parameters like Oscillator strength (P) and Judd-Ofelt (T_λ), nephelauxetic ratio (β), bonding ($b^{1/2}$), percentage covalency (δ%) and angular overlap parameter (η) have been used to interpret the bonding and structures of the complexes. The nature of metal ligand bond and coordination environment around lanthanide ion can be understood by the shift in the bands as well as by the change in the intensity of the bands. The former reflects the nephelauxetic effect, which is due to the mixing of wave functions of the metal 4f orbitals with the ligand orbitals. It has been found that both these parameters are complimentary. Ryan [19] has suggested that the nephelauxetic effect depends on the coordination number in the lanthanide complexes and the increased nephelauxetic effect may be due to the shortening of metal ligand distance accompanying the lowering of coordination number.

To a first approximation, the energy levels of $4f^n$ configuration may be considered to arise from the electrostatic and magnetic interaction between 4f electrons [20]. The change in the value of interelectronic repulsion parameter (F_K) with respect to free ion as a result of complexation is represented by the nephelauxetic ratio (β), which is defined as,

$$\beta = \frac{F_2(\text{complex})}{F_2(\text{free ion})} .$$

The values of ΔF_2 and $\Delta\zeta_{4f}$ have been computed from the four equations obtained [6] neglecting the terms ΔF_4 and ΔF_6 in the energy relation by using partial and multiple regression method.

$$E(\text{obs.}) = E(oj) + \frac{\partial Ej}{\partial F_2}\Delta F_2 + \frac{\partial Ej}{\partial \zeta_{4f}}\Delta \zeta_{4f.}$$

The values of E(oj) and partial derivatives have been used as given by Misra [14]. The values of F_4 and F_6 were evaluated from the relation [21],

$F_4/F_2 = 0.13805$ and $F_6/F_2 = 0.01511$.

Racah parameters (E^K) are linear combinations of F_K given by the expressions [22],

$E^1 = 14.6818 F_2$; $E^2 = 0.0768 F_2$; $E^3 = 1.4844 F_2$.

Percentage covalency parameter ($\delta\%$) has been calculated using the relationship,

$$\delta\% = \frac{(1-\beta)}{\beta} \text{ X } 100.$$

The amount of mixing of '4f ' orbitals and ligand orbitals represented by $b^{1/2}$ is related to the nephelauxetic ratio β by the expression [23],

$$b^{1/2} = \left[\frac{1-\beta}{2}\right]^{1/2}$$

Angular overlap parameter (η) which is also related to the nephelauxetic ratio (β) is calculated by using the relation,

$$\eta = \frac{1 - \beta^{1/2}}{\beta^{1/2}}$$

RESULTS AND DISCUSSION

In the present investigation four bands $^3H_4 \rightarrow {}^3P_2$, $^3H_4 \rightarrow {}^3P_1$, $^3H_4 \rightarrow {}^3P_0$, $^3H_4 \rightarrow {}^1D_2$ have been observed for the complexes.

Table 1Computed values (in cm^{-1}) of Slater-Condon, Lande and Racah parameters

Pr(III)Complexes	F_2	F_4	F_6	ζ_{4f}	E^1	E^2	E^3
Pr^{3+}(free ion) *	322.09	44.46	4.87	741.00	4728.86	24.73	478.11
$[Pr(Cup)_2(NPU)_3.2H_2O]Cl$	311.05	42.94	4.70	684.75	4566.77	23.88	461.72
$[Pr(Cup)_2(DPU)_3.2H_2O]Cl$	312.73	43.17	4.73	652.99	4591.42	24.02	464.21
$[Pr(Cup)_2(NPTU)_3.2H_2O]Cl.H_2O$	312.50	43.14	4.72	605.90	4588.04	23.99	463.87
$[Pr(Cup)_2(DPTU)_3.2H_2O]Cl.\ H_2O$	310.63	42.88	4.69	692.63	4560.62	23.85	461.10
$[Pr(VMO)_2(NPTU)_3.2H_2O]Cl.$	310.90	42.92	4.70	654.56	4564.55	23.88	461.50
$[Pr(NA)_3(NPU)_3]H_2O$	309.23	42.68	4.67	719.13	4540.08	23.75	459.02
$[Pr(NA)_3(DPU)_3]$	309.20	42.68	4.67	720.92	4539.61	23.74	458.97
$[Pr(NA)_3(NPTU)_3]$	312.27	43.11	4.72	679.98	4584.69	23.98	463.53
$[Pr(NA)_3(DPTU)_3]$	309.25	42.69	4.67	718.82	4540.38	23.75	459.05
$[[Pr(NPTU)_3(U)_5Cl]Cl_2.2H_2O$ **	309.54	42.73	4.68	636.07	4544.60	23.77	459.48
$[[Pr(DPTU)_3(U)_5Cl]Cl_2.2H_2O$ **	307.44	42.44	4.64	662.64	4513.77	23.61	456.36

***Reference 24. **Reference 12.**

[Cup=Benzoin-α-oxime, VMO=Vanillin monoxime, NA= N-phenylanthranilic acid, U= Urea, NPU=N-phenylurea, DPU=N,N'-diphenylurea, NPTU= N-phenylthiourea, DPTU= N,N'-diphenylthiourea]

The various energy parameters, F_K , ζ_{4f} and E^K are given in Table 1. These parameters suggest that there is a decrease in the values of F_K , ζ_{4f} and E^K when compared with the corresponding values reported for free ion, which indicates the expansion of central metal ion orbital on complexation and is in accordance with the theory of origin of intensity of infra 4f → 4f transition. The values of ζ_{4f} for the complexes are comparable to the ζ_{4f} value (730 cm^{-1}) obtained using the relation [14],

$$\zeta_{4f} = 142\ Z\ -\ 7648$$

Suggested for lanthanide ions (where Z is the atomic number of the lanthanide).

Table 2 Computed values of bonding parameters for Pr(III)complexes

Pr(III)Complexes	β	$b^{1/2}$	$\delta\%$	η	T_4/T_6
$[Pr(Cup)_2(NPU)_3.2H_2O]Cl$	0.9657	0.1309	3.65	0.018	0.4207
$[Pr(Cup)_2(DPU)_3.2H_2O]Cl$	0.9709	0.1205	2.99	0.015	0.3742
$[Pr(Cup)_2(NPTU)_3.2H_2O]Cl.H_2O$	0.9702	0.1220	3.07	0.010	0.6896
$[Pr(Cup)_2(DPTU)_3.2H_2O]Cl.\ H_2O$	0.9644	0.1333	3.69	0.013	0.5397
$[Pr(VMO)_2(NPTU)_3.2H_2O]Cl.$	0.9652	0.1318	3.60	0.018	0.3744
$[Pr(NA)_3(NPU)_3]H_2O$	0.9600	0.1412	4.16	0.021	0.2144
$[Pr(NA)_3(DPU)_3]$	0.9599	0.1411	4.17	0.021	0.2766
$[Pr(NA)_3(NPTU)_3]$	0.9695	0.1234	3.14	0.016	0.2828
$[Pr(NA)_3(DPTU)_3]$	0.9601	0.1411	4.15	0.021	0.3461
$[[Pr(NPTU)_3(U)_5Cl]Cl_2.2H_2O$	0.9610	0.1396	4.06	0.020	0.3870
$[[Pr(DPTU)_3(U)_5Cl]Cl_2.2H_2O$	0.9545	0.1508	4.77	0.023	0.3318
Mean	0.9638	0.1342	3.77	0.019	0.3852
Mean deviation	$4.24x10^{-3}$	$7.82x10^{-3}$	0.4489	$2.25x10^{-3}$	0.0902

The bonding parameters β, $b^{1/2}$, δ% and η along with T_4/T_6 ratio are given in Table 2. The positive values of $b^{1/2}$ show covalent nature of metal ligand bond. It is interesting to note that in our previous study on Pr(III) complexes having different coordination numbers regular variation of β and $b^{1/2}$ was observed [13]. The values of these parameters in the present study for Pr(III) complexes having same coordination number are nearly the same confirming our previous observations. The δ% values have been found to be positive in the complexes indicating electron delocalisation over 4f orbital, which also indicate covalency are found to be nearly same for all the complexes suggesting the same degree of covalent bonding as expected due to same coordination number. According to the angular overlap model for f→f transition in the absorption spectra of praseodymium complexes the angular overlap parameter η is given by the equation [14].

$$\eta = \frac{H^2 L}{(H_M - H_L)^2} \times (S_R)^2 N$$

Where N is the coordination number, H_M and H_L are coulomb integrals of atomic orbital, S the overlap integral and R the radius of the orbit. In the present study as all the complexes are having nearly the same values of β, $b^{1/2}$ and δ% and also same coordination number, the term on the right hand side of the above equation can be a constant. As a result, angular overlap parameter η should be theoretically same for the complexes under study .The experimental values of angular overlap parameter η calculated using nephelauxetic ratio are given in Table 2 which are having nearly the same value for all the complexes confirming the angular overlap model for f→f transition. The T_λ parameters are considered to be characteristic of particular lanthanide complex. In the present study T_4/T_6 ratio has been found to be nearly same indicating that the coordination environment around the metal ion remains unaltered.

Table 3 Screening factors (in cm^{-1}) of Pr(III) complexes.

Pr(III) complexes	F^S_2	F^S_4	F^S_6	ζ_{4f}^S
$[Pr(Cup)_2(NPU)_3.2H_2O]Cl$	148.3	17.50	1.71	259.3
$[Pr(Cup)_2(DPU)_3.2H_2O]Cl$	146.6	17.27	1.68	327.0
$[Pr(Cup)_2(NPTU)_3.2H_2O]Cl.H_2O$	146.8	17.30	1.69	314.1
$[Pr(Cup)_2(DPTU)_3.2H_2O]Cl.H_2O$	148.7	17.56	1.72	287.4
$[Pr(VMO)_2(NPTU)_3.2H_2O]Cl$	148.4	17.52	1.71	325.4
$[Pr(NA)_3(NPU)_3]\ H_2O$	150.1	17.76	1.74	260.9
$[Pr(NA)_3(DPU)_3]$	150.1	17.76	1.74	259.1
$[Pr(NA)_3(NPTU)_3]$	147.1	17.33	1.69	300.0
$[Pr(NA)_3(DPTU)_3]$	150.1	17.75	1.74	261.2
$[Pr(NPTU)_3(U)_5Cl]Cl_2.2H_2O$	149.8	17.71	1.73	317.8
$[Pr(DPTU)_3(U)_5Cl]Cl_2.2H_2O$	151.9	18.00	1.77	317.3

Hartree-Fock values: F_2=459.33, F_4=60.44, F_6=6.41, ζ_{4f} =980 cm^{-1}

The effect of screening terms on the F_K and ζ_{4f} parameters due to high order interactions may be estimated by subtracting the parameters from their Hartree-Fock values.

The estimated values of screening factors ($F^{s}_{k\,,}\ \zeta_{4f}{}^{s}$) for the complexes are given in Table 3. A study of Table 3 reveals that the values of F^{s}_{4} , F^{s}_{6} are nearly the same in all the complexes and are smaller than those of F^{s}_{2} and $_{,}\ \zeta_{4f}{}^{s}$ which suggest that the screening of F_4 and F_6 parameters is nearly to the same extent in all the complexes studied.

Thus, the study of these spectral parameters provides valuable information regarding the nature of bonding and coordination in the complexes in accordance with the proposed theories.

ACKNOWLEDGEMENT

The authors respectfully acknowledge the valuable guidance of Late Dr.V.D.Deshpande. The authors also express their gratitude to the Principal, V.R.C.E., Nagpur, for providing necessary facilities for the work and to the Principals of their respective Colleges for granting permission to carry out the research work.

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