

## Bonding and Energy Parameters for Pr and Nd Complexes of Benzimidazoles

S. MITTAL, P. C. VYAS\* AND C. K. OZA

Department of Chemistry  
University of Rajasthan, Jaipur-302 004 India

Complexes of praseodymium (III) and neodymium (III) with benzimidazoles have been synthesized and characterized by their conductance and infrared spectral studies. The values of interelectronic repulsion, i.e. Slater-Condon ( $F_2, F_4, F_6$ ), Racah ( $E^1, E^2, E^3$ ) parameters and spin-orbit interaction referred as Lande' ( $\zeta^4f$ ) parameters have been calculated from their electronic spectral data. A comparison of these parameters for the complexes with  $\text{Pr}^{3+}$  and  $\text{Nd}^{3+}$  free ion parameters is discussed. Using  $F_2$  values, the nephelauxetic ratio ( $\beta$ ) and bonding parameter ( $b^{1/2}$ ) have been calculated. The relative variation of covalent bonding in the complexes has been reported.

### INTRODUCTION

The Slater-Condon ( $F_k, F_2, F_4, F_6$ ) parameters provide useful information regarding inter-electronic repulsion, spin-orbit interaction, nephelauxetic effect and metal-ligand covalency in complexes. Although a large number of studies on the coordination behaviour of benzimidazoles with  $d$ -type transition metal ions<sup>1,2</sup> have been reported, investigations relating to the lanthanides are limited. In this communication we report the calculations of the electronic parameters and the variation of covalent bonding for Pr and Nd complexes with benzimidazoles and its 2-alkyl derivatives using partial multiple regression method<sup>3</sup>.

### EXPERIMENTAL

Complexes were prepared by refluxing the hydrated metal nitrates with benzimidazole (BzImH), 2-methylbenzimidazole (meBzIm), 2-ethylbenzimidazole (EtBzIm) and 2-propylbenzimidazole (PrBzIm) in ethylacetate in 1:4.5 molar ratio. The complex separated as sticky solids which were washed several times with ethyl acetate. Crystalline derivatives were finally obtained by treating with ether and scratching with glass rod. The complex derivatives have been characterized on the basis of their elemental analysis, infrared spectral data and conductance<sup>4</sup> ( $110-121 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ) in dimethylformamide. These data suggest general molecular formula  $\text{ML}_x(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$  [where  $\text{M} = \text{Pr}$  and  $\text{Nd}$ ;  $\text{L} = \text{BzImH}$  or  $\text{MeBzIm}$ ,  $x = 3$  and  $n = 3, 4$  or  $5$ ; for  $\text{L} = \text{EtBzIm}$  or  $\text{PrBzIm}$ ,  $x = 2$  and  $n = 4$  or  $5$ ] for the complexes. The electronic absorption spectra were recorded in ethanolic solution (0.012 M).

## RESULTS AND DISCUSSION

The absorption bands in infrared spectra of these complexes at 3500–3200, 3140–3000, 1614, 1420–1400 and 420–412  $\text{cm}^{-1}$  were assigned to  $\nu_{\text{asym}} \text{—OH}$ ,  $\nu_{\text{asym}} \text{N—H}$ ,  $\nu_{\text{asym}} \text{C=N}$ ,  $\delta \text{N—H}$  and  $\nu_{\text{asym}} \text{M—N}$  stretching modes<sup>5</sup> respectively. The imino protons of the imidazoles are not replaced by the metal ions during complex formation on coordination and bonding takes place through the tertiary nitrogen atom only. The nitrate bands in their spectra at *ca* 1390, 840–815  $\text{cm}^{-1}$  and 1530–1450, *ca* 1310, 1030–1000, 815–780  $\text{cm}^{-1}$  suggested the presence of ionic [ $\nu_3(E)$ ,  $\nu_2(A_2'')$ ]  $D_{3h}$  as well as bidentately coordinated [ $\nu_4(B_1)$ ,  $\nu_1(A_1)$ ,  $\nu_2(A_1)$ ,  $\nu_5(B_2)$ ]  $C_{2v}$  nitrate ions in these complex derivatives.

The absorption spectra of the praseodymium complexes consists of four bands, whereas ten bands were observed in the cases of derivative of neodymium. A red shift in the position of the absorption bands compared to those of the free ions<sup>6</sup> is indicative of nephelauxetic effect on the 4f orbitals of Pr and Nd ions coordinated with benzimidazoles.

The red shift is used as a measure of electrostatic and magnetic interactions of the 4f electrons, characterized by Slater-Condon ( $F_k$ ), Racah ( $E^k$ ) and spin-orbit interactions, i.e. Lande' ( $\zeta_{4f}$ ) parameters. An initial set of  $F_2$ ,  $F_4$ ,  $F_6$  and  $\zeta_{4f}$  values can be evaluated by expressing the band energy as Taylor series expansion<sup>7,8</sup> and using partial multiple regression method<sup>3</sup>. The values of  $F_k$  and  $\zeta_{4f}$  for Pr and Nd complexes (Table 1) are smaller than the corresponding parameters for the free ions<sup>9</sup>. These observations confirm the general trend that central metal ions 4f orbitals expand on complexation. As a result of this, the interelectronic repulsion and spin-orbit interaction parameters decrease. A comparison of the  $F_k$  parameters shows that the decrease in  $F_2$  on complexation is much larger than those of the  $F_4$  and  $F_6$ . The average value of  $F_2$  for the Pr and Nd complexes under study are 312.51 and 329.05  $\text{cm}^{-1}$  respectively. These are smaller than those computed using analytical non-relativistic Hartree-Fock (H-F) functions<sup>10</sup>, i.e. 459.33  $\text{cm}^{-1}$  and 479.59  $\text{cm}^{-1}$ .

The decrement in  $E^1$  values is largest as compared to  $E^2$  and  $E^3$  with respect of their free ion values<sup>9,10</sup> (Table 1). Since  $F_k$  and  $E^k$  are related to each other, a parallel trend is expected in these parameters.

The values of  $\zeta_{4f}$  for the Pr(III) and Nd(III) complexes, 697.34  $\text{cm}^{-1}$  and 864.66  $\text{cm}^{-1}$ , respectively, are smaller than those calculated by using analytical non-relativistic H-F functions<sup>10</sup> (for  $\text{Pr}^{3+}$  980  $\text{cm}^{-1}$  and  $\text{Nd}^{3+}$  1130  $\text{cm}^{-1}$ ). However these values do not differ much from those of aquoion and satisfy the relation

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

suggested<sup>6</sup> for lanthanide ions (where  $Z$  is the atomic number of the lanthanide).

TABLE I  
COMPUTED VALUES OF VARIOUS PARAMETERS FOR SOME Pr<sup>3+</sup> AND Nd<sup>3+</sup> COMPLEXES

Complexes	F <sub>2</sub>	F <sub>4</sub>	F <sub>6</sub>	ζ <sub>4f</sub>	E <sup>1</sup>	E <sup>2</sup>	E <sup>3</sup>	β	b <sup>1/2</sup>
Pr <sup>3+</sup> -free ion	322.09	44.46	4.87	741.00	4729	24.78	478.13	1.000	—
Pr(BzImH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ·3H <sub>2</sub> O	312.84	42.78	4.68	701.80	4593	24.03	464.38	0.9713	0.1198
Pr(MeBzIm) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ·4H <sub>2</sub> O	312.58	42.83	4.69	695.50	4589	24.01	463.99	0.9705	0.1215
Pr(EtBzIm) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ·4H <sub>2</sub> O	312.49	42.75	4.68	700.00	4588	24.00	463.86	0.9702	0.1221
Pr(PrBzIm) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ·5H <sub>2</sub> O	312.13	42.82	4.69	692.07	4582	23.97	463.32	0.9691	0.1244
Nd <sup>3+</sup> -free ion	331.15	50.71	5.15	884.00	5024.00	23.90	497.00	1.000	—
Nd(BzImH) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ·4H <sub>2</sub> O	329.61	50.60	5.15	875.38	5007.28	23.76	494.42	0.9953	0.0483
Nd(MeBzIm) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ·3H <sub>2</sub> O	328.90	50.57	5.13	866.17	4996.79	23.67	493.75	0.9932	0.0583
Nd(EtBzIm) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ·4H <sub>2</sub> O	328.86	50.63	5.11	845.19	4994.56	23.64	494.30	0.9931	0.0588
Nd(PrBzIm) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ·4H <sub>2</sub> O	328.83	50.39	5.13	871.90	4991.38	23.72	493.31	0.9930	0.0592

The magnitude of mixing of 4f orbitals of metals with ligand orbital is represented by  $b^{1/2}$  known as bonding parameter calculated from nephelauxetic ratio ( $\beta = F_k^c/F_k^f$ ) as described in the literature.<sup>11</sup> The positive values of  $b^{1/2}$  are indicative of some covalent character by the metal ligand bond in the complex derivatives reported. The value of bonding parameters for both Pr and Nd complex (Table 1) increases with increase in alkyl chain length of 2-substituents of the ligand molecules. It shows that inductive effect of 2-alkyl group enhance the donor capacity of tertiary nitrogen of benzimidazole ring towards the praseodymium and neodymium ions.

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