

## Bonding and Energy Parameters for Some Praseodymium(III) Mixed Ligand Complexes

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The electronic spectra of the mixed ligand complexes of praseodymium(III) with vanillinmonoxime, benzoin- $\alpha$ -oxime as the primary ligand and diacetylmonoxime, N-phenylanthranillic acid, 8-hydroxyquinoline, bipyridyl, N-phenylthiourea and thiourea as the secondary ligands have been studied. The values of interelectronic repulsion parameters *i.e.*, Slater-Condon ( $F_k$ ), Racah ( $E^k$ ) and spin-orbit interaction referred as Lande parameter ( $\zeta_{4f}$ ) and intensity parameters have been calculated from their electronic spectral data. Using  $F_2$  values the nephelauxetic ratio ( $\beta$ ), bonding parameter ( $b^{1/2}$ ), Sinha's parameter ( $\delta$  %) and covalency angular overlap parameter ( $\eta$ ) have been calculated which give useful information regarding bonding in these complexes. The effect of screening terms is also calculated.

**Key Words:** Praseodymium(III), Electronic parameters, Mixed ligand complexes.

### INTRODUCTION

Information on the composition and structure of lanthanide mixed ligand complexes is scanty. The present investigation was undertaken with a view to making a comparative study of various spectral parameters computed from electronic spectra and coordination number. The coordination number of lanthanide ion is only rarely six and higher coordination number than six appears to be a common rule<sup>1</sup>. The situation is a reasonable consequence of the comparatively large size of lanthanide ions. Hence, it is of particular interest to know the kinds of molecular geometry that results. At least two significant conclusions can be drawn based upon examination of the available data-1) variability of coordination number either for a given lanthanide ion or for a series of lanthanide ions of the same charge is determined more by spatial accommodation of ligands than by bonding characteristics of ligands and 2) coordination number in solution may and commonly does, differ from coordination number in a crystal given by the same lanthanide ions and the same ligand. Definitive data for coordination number and molecular geometry are available only for crystals. Data for solutions are usually suggestive rather than definitive.

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The line-like electronic absorption spectra of the Ln<sup>3+</sup> ions result from inner 4*f* transitions of a predominantly electric dipole character<sup>2</sup> that for a free ion are laporte forbidden but are allowed by interactions produced by external ligand fields that mix in states of opposite parity. When these spectra for systems containing complexing ligands are compared with those of aquated cations, three general changes, all of which are related to alterations in the strength and symmetry of the ligand fields are observed<sup>3</sup>.

These changes are small shifts towards longer (occasionally shorter) wavelengths, splitting of certain bands into several small maxima and alteration of specific absorptivity of individual bands. These bands are particularly susceptible to splitting and intensity changes are termed as hypersensitive bands. Although these effects are useful in determining the symmetries of complex species in solution and thus suggesting coordination number and molecular structure, they are far less definitive for lanthanide ions than for *d*-type ions since the order of perturbation for the former is crystal field < spin-orbit coupling < interelectronic repulsion. However, hypersensitive transitions are consistent with the selection rules for quadruple radiation within the 4*f* shell and the intensities of these transitions are probably related to asymmetric distribution of electromagnetically induced dipoles surrounding the lanthanide ions.

Broadening and overlapping of bands in solution lead to lesser accuracy of the measured data. Obviously the interpretation of the solution spectra of lanthanide complexes may not lead to quantitative results as in the case of transition metal complexes. Nevertheless, the spectra parameters can be used in somewhat qualitative way to understand the structural characteristics of the species in solution. The values of the spectral parameters like Slater-Condon ( $F_K$ ), Racah ( $E^K$ ) and Lande parameter ( $\zeta_{4f}$ ) and bonding parameters like nephelauxetic ratio ( $\beta$ ), bonding ( $b^{1/2}$ ), percentage covalency ( $\delta$  %) and angular overlap parameter ( $\eta$ ) which give useful information regarding interelectronic repulsion, spin-orbit interaction and bonding in these complexes have been computed using partial multiple regression method. It has also been observed that the effect of screening terms is nearly the same for all the interaction parameters in these complexes.

## EXPERIMENTAL

**Preparation of the complexes:** The complexes were synthesized by adopting the procedure described in earlier publications<sup>4,5</sup>.

**Evaluation of spectral parameters and their significance:** The values of various energy parameters like Slater-Condon ( $F_K$ ), Racah ( $E^K$ ) and Lande parameter ( $\zeta_{4f}$ ) and bonding parameters like nephelauxetic ratio ( $\beta$ ), bonding ( $b^{1/2}$ ), percentage covalency ( $\delta$  %) have been calculated using the procedure described earlier<sup>6</sup>.

Angular overlap parameter ( $\eta$ ) which is also related to the nephelauxetic ratio ( $\beta$ ) is calculated by using the relation,

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

## RESULTS AND DISCUSSION

The energies of the bands observed have been recalculated by applying Stalter-Condon-Lande equation. The average and the root mean square deviations between the observed and the recalculated values of the bands vary from 39-55  $\text{cm}^{-1}$  and 99-134  $\text{cm}^{-1}$ , respectively. This indicates good applicability of the theory even though the radial eigenfunction was assumed to be hydrogenic.

The various energy parameters  $F_K$ ,  $\zeta_{4f}$  and  $E^K$  are given in Table-1. These parameters suggest that there is a decrease in the values of  $F_K$ ,  $\zeta_{4f}$  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  $4f \rightarrow 4f$  transition. The values of  $\zeta_{4f}$  for the complexes are smaller than those calculated by using analytical non-relativistic H-F function (for  $\text{Pr}^{3+}$  980  $\text{cm}^{-1}$ ). However, these values do not differ much from those of the aquoion and satisfy the relation,  $\zeta_{4f} = 142Z - 7648$  suggested for lanthanide ion (where  $Z$  is the atomic number of the lanthanide).

TABLE-1  
COMPUTED VALUES OF VARIOUS ENERGY PARAMETERS (IN  $\text{CM}^{-1}$ )

| Complex   | $F_2$  | $F_4$ | $F_6$ | $\zeta_{4f}$ | $E^1$   | $E^2$ | $E^3$  |
|---|--------|-------|-------|--------------|---------|-------|--------|
| [Pr(VMO) <sub>2</sub> (DAMO)·2H <sub>2</sub> O]Cl                             | 309.32 | 42.71 | 4.67  | 681.34       | 4541.40 | 23.76 | 459.16 |
| [Pr(VMO) <sub>2</sub> (NPAA)·2H <sub>2</sub> O]                               | 310.90 | 42.92 | 4.70  | 654.56       | 4564.46 | 23.88 | 461.50 |
| [Pr(VMO) <sub>2</sub> (Oxine)·2H <sub>2</sub> O]                              | 306.31 | 42.29 | 4.63  | 727.85       | 4497.26 | 23.52 | 454.69 |
| [Pr(VMO) <sub>2</sub> (NPU) <sub>3</sub> H <sub>2</sub> O]Cl·H <sub>2</sub> O | 307.22 | 42.41 | 4.064 | 709.77       | 4510.49 | 23.59 | 456.03 |
| [Pr(VMO) <sub>2</sub> (Bipy) <sub>2</sub> ·2H <sub>2</sub> O]Cl               | 311.18 | 42.96 | 4.70  | 653.48       | 4568.64 | 23.90 | 461.90 |
| [Pr(VMO) <sub>2</sub> (TU) <sub>3</sub> H <sub>2</sub> O]Cl                   | 314.93 | 43.48 | 4.76  | 597.09       | 4623.77 | 24.19 | 467.49 |
| [Pr(Cupron) <sub>2</sub> (TU) <sub>3</sub> H <sub>2</sub> O]Cl                | 310.83 | 42.91 | 4.70  | 681.52       | 4563.53 | 23.87 | 461.39 |

The bonding parameters  $\beta$ ,  $b^{1/2}$ ,  $\delta$  % are given in Table-2. The magnitude of mixing of 4f orbitals of metal with ligand orbital is represented by  $b^{1/2}$ . The positive values of  $b^{1/2}$  show covalent nature of metal ligand bond. The  $\delta$  % values have been found to be positive in the complexes indicating electron delocalization over 4f orbital. The  $b^{1/2}$  and  $\delta$  %, which indicate covalency, is also found to be nearly same for the complexes with same coordination number as expected due to some degree of covalent bonding. As a result, angular overlap parameter  $\eta$  should be same for the same coordination number<sup>7</sup>.

TABLE-2  
COMPUTED VALUES OF BONDING PARAMETERS

| C.N. | Complexes   | $\beta$ | $b^{1/2}$ | $\delta$ % | $\eta$ |
|------|---|---------|-----------|------------|--------|
| 8    | [Pr(VMO) <sub>2</sub> (DAMO)·2H <sub>2</sub> O]Cl                             | 0.9630  | 0.1407    | 4.13       | 0.019  |
| 8    | [Pr(VMO) <sub>2</sub> (NPAA)·2H <sub>2</sub> O]                               | 0.9652  | 0.1318    | 3.60       | 0.018  |
| 8    | [Pr(VMO) <sub>2</sub> (Oxine)·2H <sub>2</sub> O]                              | 0.9510  | 0.0164    | 5.15       | 0.025  |
| 8    | [Pr(VMO) <sub>2</sub> (NPU) <sub>3</sub> H <sub>2</sub> O]Cl·H <sub>2</sub> O | 0.9538  | 0.1519    | 4.84       | 0.024  |
| 10   | [Pr(VMO) <sub>2</sub> (Bipy) <sub>2</sub> ·2H <sub>2</sub> O]Cl               | 0.9661  | 0.1301    | 3.51       | 0.017  |
| 10   | [Pr(VMO) <sub>2</sub> (TU) <sub>3</sub> H <sub>2</sub> O]Cl                   | 0.9777  | 0.1054    | 2.27       | 0.011  |
| 10   | [Pr(Cupron) <sub>2</sub> (TU) <sub>3</sub> H <sub>2</sub> O]Cl                | 0.9650  | 0.1322    | 3.62       | 0.018  |

The effect of screening terms of the  $F_k$  and  $\zeta_{4f}$  parameters due to high order interactions may be estimated by subtracting the parameters from their Hartree-Fock values. The estimated values of screening factors ( $F_k^s$ ,  $\zeta_{4f}^s$ ) for the complexes are given in Table-3. A study of Table-3 reveals that the values of  $F_4^s$ ,  $\zeta_6^s$  are nearly the same in all the complexes and are smaller than those of  $F_2^s$  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.

TABLE-3  
SCREENING FACTORS (IN  $\text{cm}^{-1}$ ) OF Pr(III) COMPLEXES

| Complexes   | $F_2^s$ | $F_4^s$ | $F_6^s$ | $\zeta_{4f}^s$ |
|---|---------|---------|---------|----------------|
| [Pr(VMO) <sub>2</sub> (DAMO)·2H <sub>2</sub> O]Cl                             | 150.0   | 17.74   | 1.736   | 298.7          |
| [Pr(VMO) <sub>2</sub> (NPAA)·2H <sub>2</sub> O]                               | 148.4   | 17.52   | 1.712   | 325.4          |
| [Pr(VMO) <sub>2</sub> (Oxine)·2H <sub>2</sub> O]                              | 153.0   | 18.15   | 1.782   | 252.1          |
| [Pr(VMO) <sub>2</sub> (NPU) <sub>3</sub> H <sub>2</sub> O]Cl·H <sub>2</sub> O | 152.1   | 18.03   | 1.768   | 270.2          |
| [Pr(VMO) <sub>2</sub> (Bipy) <sub>2</sub> ·2H <sub>2</sub> O]Cl               | 148.2   | 17.48   | 1.708   | 326.5          |
| [Pr(VMO) <sub>2</sub> (TU) <sub>3</sub> H <sub>2</sub> O]Cl                   | 144.4   | 16.96   | 1.651   | 382.9          |
| [Pr(Cupron) <sub>2</sub> (TU) <sub>3</sub> H <sub>2</sub> O]Cl                | 148.5   | 17.53   | 1.713   | 298.5          |

Hartree-Fock values:  $F_2 = 459.33$ ,  $F_4 = 60.44$ ,  $F_6 = 6.41$ ,  $\zeta_{4f} = 980 \text{ cm}^{-1}$ .

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.

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#### REFERENCES

1. T. Moeller, E.R. Birnbam, J.H. Forsberg and R.B. Gayhart, *Prog. Sci. Tech. Rare Earth's*, **3**, 61 (1968).
2. W.G. Wybourne, *Spectroscopic Properties of Rare Earth's* (New York Inter Science Publisher), Chp. 6 (1965).
3. T. Moeller, D.F. Martin, L.C. Thompson, R.R. Ferrus, G.R. Feistal and W.J. Randall, *Chem. Rev.*, **65**, 1 (1965).
4. M.C. Chavan, S.D. Palsokar, N.R. Lokhande and V.D. Deshpande, *Indian J. Chem.*, **33A**, 343 (1994).
5. M.C. Chavan, V.D. Deshpande and P.V. Vaidya, *Asian J. Chem.*, **4**, 246 (1992).
6. M.C. Chavan, P.V. Vaidya, N.R. Lokhande, C.V. Deshpande and V.D. Deshpande, *Indian J. Pure Appl. Phys.*, **32**, 778 (1994).
7. S.N. Misra, *J. Sci. Ind. Res.*, **44**, 366 (1985).