

## LANTHANIDE IONS AS ABSORPTION SPECTRAL PROBES IN BIOCHEMICAL REACTIONS

SUDHINDRA N MISRA

*University Department of Chemistry, Bhavnagar University, Bhavnagar-364 002,  
Gujarat, India*

*(Received 7 March 1988; Accepted 14 October 1988)*

The interactions of adenine, adenosine, adenosine 5'-monophosphate, 5'-diphosphate and 5'-triphosphate with Pr(III) and Nd(III) in different stoichiometries and at varying pH levels have been investigated by electronic spectral studies. The intra  $4f-4f$  transitions yield sharp bands which were analysed individually by Gaussian curve analysis. The energy interaction ( $F^k$ ,  $E^k$ ) spin orbit interaction ( $\zeta$   $4f$ ), bonding ( $b$ ), nephelauxetic ( $\beta$ ,  $\delta$ ) and intensity parameters ( $T_\lambda$ ,  $P$ ) have been computed on HP-1000/45 computer using regression analyses refined by least square fit. The nature of bonding, coordination environment, outer and inner sphere coordination have been interpreted in terms of the magnitude of these parameters as compared to the lanthanide free ion.

In order to suplicate the solution studies the crystalline compounds of AMP, ADP and ATP with Pr(III) and Nd(III) have been isolated and characterized by IR,  $^1\text{H}$  and  $^{31}\text{P}$  NMR studies. The infrared spectral data indicated weak interaction with the imidazole nitrogen of adenine moiety and bidentate attachment of oxygen.

**Key Words :** Biochemical Reactions; Lanthanide Ions; Absorption Spectral Probes

### INTRODUCTION

TREMENDOUS upsurge in the lanthanoid spectral and magnetic characteristics has resulted because of the fact that these ions have useful physical properties<sup>1</sup> and closely resemble calcium in their chemical behaviour. Birnbaum *et al.*<sup>2</sup> have successfully developed the field of absorption difference spectroscopy to investigate the interaction of lanthanide with organic metabolites. In continuation of our work on analysis of  $f-f$  transitions in different lanthanide complexes,<sup>3</sup> in this work our investigations on the interactions of Pr(III) and Nd(III) with adenine, adenosine, adenosine mono-, di- and triphosphates which are building units for biomacromolecular architecture of DNA and RNA in aqueous medium.

### MATERIALS AND METHODS

The interaction of Pr(III) and Nd(III) with adenine and adenosine have been explored in aqueous medium at pH  $\sim 2$  and  $\sim 6$ . The spectra were recorded for metal-ligand ratio 1:2, 1:4, 1:6. The metal-phosphates were studied at the

pH  $\sim$  1.5 in the ratio 1 : 1, 1 : 2 and 1 : 3. Crystals corresponding to the stoichiometry Nd(AMP)<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub>, Nd(ADP)<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub> and Nd(ATP)<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub> were isolated. IR spectra of these crystals have been recorded on a Shimadzu 220 while <sup>1</sup>H NMR and <sup>31</sup>P NMR have been recorded on a Perkin Elmer 90MHz FT NMR. The electronic spectra was recorded on a Shimadzu UV 160 spectrophotometer.

### Significance and Evaluation of Spectral Parameters

The coulombic and magnetic interactions between 4f<sup>n</sup> electrons leads to energy levels of 4f<sup>n</sup> configurations and these interactions can be expressed in terms of the electronic repulsion parameters Slater-Condon ( $F_2, F_4, F_6$ ), Racah  $E^1, E^2, E^3$  and spin-orbit interaction parameter Land ( $\zeta_{4f}$ )<sup>4</sup>. As a first approximation, the energy  $E_j$  of the  $j^{\text{th}}$  level is given by the following equation:—

$$E_j(F_k, \zeta_{4f}) = E_{0j}(F_k^0, \zeta_{4f}^0) + \sum_{k=2,4,6} \left( \frac{\delta E_j}{\delta F_k} \right) \Delta F_k + \left( \frac{\delta E_j}{\delta \zeta_{4f}} \right) \Delta \zeta_{4f}, \quad \dots(1)$$

where  $E_{0j}$  is the zero order energy of the level  $j$ . The value of  $E_{0j}$  and partial derivatives  $\frac{\delta E_j}{\delta F_k}$  and  $\frac{\delta E_j}{\delta \zeta_{4f}}$  for different levels are known.<sup>5</sup>

Nephelauxetic effect measures the change in  $F_k$  with respect to free ion and is expressed by nephelauxetic ratio ( $\beta$ ) which is defined as<sup>6-8</sup>

$$\beta = \frac{F_k^c}{F_k^f},$$

where  $c$  and  $f$  refer to complex and free ion.

The amount of mixing of 4f orbitals and ligand orbitals can be measured by the bonding parameter ( $b^{1/2}$ ) which is given by<sup>6-8</sup>

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

Sinha<sup>9</sup> introduced another parameter, percentage covalency parameter ( $\delta$ ) as

$$\delta = \left[ \frac{1 - \beta}{\beta} \right] \times 100$$

The experimental values of oscillator strength ( $P_{\text{exp}}$ ) of absorption bands were calculated by performing Gaussian curve analysis using the following relationship:-

$$F_{\text{exp}} = 4.60 \times 10^{-9} \text{Em}(\bar{\nu}) \text{d}\bar{\nu},$$

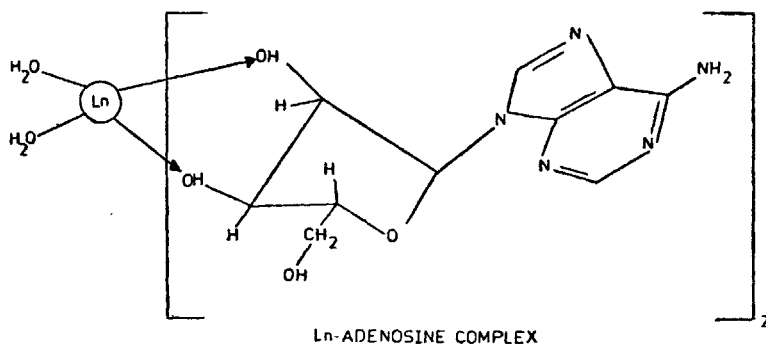
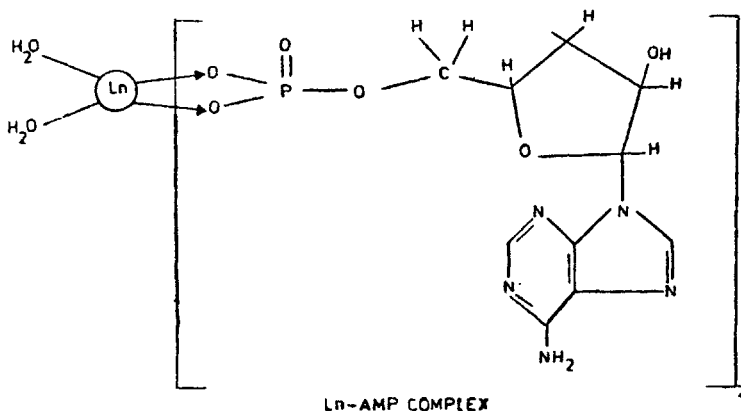
where  $\text{Em}(\bar{\nu})$  is the molar extinction coefficient corresponding to the energy ( $\bar{\nu}$ ). The equation derived by Judd<sup>9</sup> and Ofelt<sup>10</sup> for oscillator strength ( $P$ ) of a transition between the ground state  $\langle f^n \Psi^1 J |$  and the excited state  $| f^n \Psi^1 J' \rangle$  of the lanthanide ion is given as

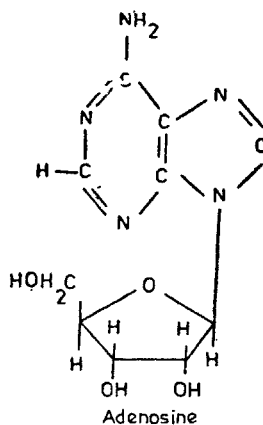
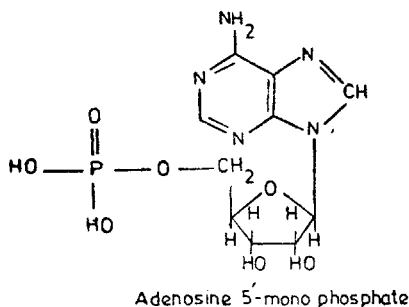
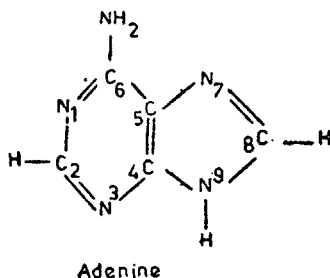
$$P_{\text{exp}} = \sum_{\lambda=2,4,6} T_{\lambda\nu} \langle f^n \Psi_J \| U^{(\lambda)} \| f^n \Psi'_{J'} \rangle^2,$$

where unit tensor operator  $U^{(\lambda)}$  connect the initial and final states through three phenomenological parameters  $T_{\lambda}(\lambda = 2, 4, 6)$ . These parameters are related to the radial part of the  $4f^n$  wave function of the perturbing configuration and ligand parameter characterizing the environment of the ion.

### RESULTS AND DISCUSSION

In all cases  $F_k$ 's and  $\zeta_{4f}$  exhibit decrease from the corresponding values of the lanthanids free ion. Red shift as a result of the decrease in the interelectronic repulsion ( $F_k, E^k$ ) indicates the expansion of the metal ion orbital by complexation and in accordance with the theory for the origin and intensity of  $f-f$  transitions. Smaller magnitude of oscillator strength is observed for 1:4 species of adenine and adenosine. This might be due to the possibility of stacking which is of common occurrence in these bases and nucleosides. This stacking will naturally bring the complex molecules closer and thus can initiate intermolecular and

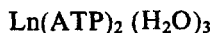
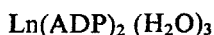
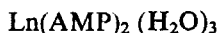




intramolecular interactions. These interactions between the ligand molecules reduce their urge to interact strongly with the metal ion and hence leads to weaker interactions as reflected in weak intra *f-f* band.

The spectral pattern shows that the absorption spectra of the Ln-AMP/ADP/ATP is not significantly more intense than that observed for aquo ion. The weak intra *f-f* absorption bands show the predominance of ionic mode of binding of nucleotide moiety.

The isolated crystalline species for Ln-AMP/ADP/ATP were studied by IR and NMR spectra. All these show that the lanthanide is bound to phosphate moiety of the nucleotides as well as some weak interactions from the purine system. The presence of coordinated water molecules is also indicated. The estimation of coordinated water molecules by Karl-Fischer method suggested the following stoichiometry for these complexes:



Thermodynamic data show that these complexes in solution behave as 1:1 electrolyte.

## REFERENCES

- 1 R J P Williams *Structure and Bonding* Springer Verlag Berlin 50 (1982) 79
- 2 E R Birnbaum, J E Gomez and D W Darnall *J Am chem Soc* 91 (1970) 5287
- 3 S S L Surana, M Singh and S N Misra *J inorg nucl Chem* 42 (1980) 61, A Kothari and S N Misra *Can J Chem* 61 (1983) 1778
- 4 H H Crosswhite and G H Dieke *Spectra and Energy Levels of Rare Earth Ions in Crystals* Wiley New York (1968)
- 5 E Y Wong *J chem phys* 36 (1961) 544; 38 (1963) 976
- 6 S N Misra, G K Joshi and M P Bhutra *J inorg nucl Chem* 43 (1981) 527
- 7 W T Carnall, P R Field and B G Wybornne *J chem phys* 46 (1965) 3797
- 8 S N Misra *J scient ind Res* 44 (1985) 367
- 9 B R Judd *Fhys Rev* 127 (1962) 750
- 10 G S Ofelt *J chem Phys* 37 (1962) 571