SPECTRAL CHARACTERIZATION OF Sm (III)- ANTIBIOTIC COMPLEXES IN SOLUTION

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ABSTRACT

The spectral study of Sm (III)-antibiotic complexes is carried out in 50% DMSO- water solvent. The ligands included five antibiotics (Ceftizoxime, Pipercillin, Cefuroxime, Cefotaxime and Cefazolin). The effect of the ligand environment on electronic spectra of the metal ion with special reference to complexation and nature of metal-ligand bond has been investigated. Various intensity parameters [Oscillator strength (P), Judd-Ofelt parameter (T$_\lambda$)] have been evaluated for different metal ligand stoichiometries.

Key words: Sm (III), Antibiotics, Electronic spectra, Intensity parameters.

INTRODUCTION

The design of newer lanthanide complexes is becoming an important goal for researchers, due to their potential applications in various industrial fields. The fluorescent properties of lanthanide chelates complexes are well known. These materials have been used as active medium in dye lasers[1]. Some β-diketonates are vaccum sublimable and offer the possibility for the application in organic light emitting diodes based on low mass molecular thin films[2]. In the field of enantioselective catalysis, numerous highly enantioselective catalysts and reagents have been successfully prepared[3]. Binaphthol[4] and pybox[5-7] are the most consistently useful ligands for enantioselective catalysis. Many reactions like aldol condensation[8], Diels-Alder reaction[9], borane reduction of ketones[10] etc. have been performed with a high quantum yield. The biological properties of lanthanides, primarily based on their similarity to calcium, have been the basis for research into therapeutic applications[11] of lanthanides. More recent investigated drug is the redox active lanthanide texaphyrin complex, motexafin gadolinium. This is in phase III clinical trials in combination with whole body irradiation for the treatment of brain metastasizes in non small cell lung

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cancer[12]. With the increasing demand of lanthanide complexes in various fields, an attempt to synthesize some Sm (III) antibiotic complexes, which are supposed to enhance the efficacy of the parent drug.

EXPERIMENTAL

The experimental procedure used by earlier workers[13] was followed for the present work. 50 % DMSO was prepared by using deionized water. 0.01 M solutions of ligands and $SmCl_3$ were prepared. The metal ion and ligand solutions were mixed in 1 : 1, 1 : 2, 1 : 3, and 1 : 4, ratio. The pH of these systems were adjusted between 6 and 7, immediately after mixing the metal ion and ligand solution, by gradual addition of dil. NaOH or dil HCl. All these systems were kept for one hour to attain equilibration. The spectra of systems were recorded in UV- Visible region.

RESULTS AND DISCUSSION

From the observations, it has been found that metal-ligand stoichiometry is 1 : 2, as obtained in most of lanthanide complexes[14,15]. It is the most favourable condition for the formation of lanthanide-antibiotic complexes. Therefore, all the spectral parameters discussed here are at 1 : 2 M-L stoichiometry. The UV-VIS absorption bands of Sm (III), systems were observed in the region of 300-500 nm due to the f-f transition consisting multiplets. The treatment of results obtained in the spectral studies, was based on the calculation of various intensity parameters as well as the application of various theories proposed for the spectral behaviour of lanthanide complexes.

Oscillator strength (P)

The intensity of an absorption band is measured by its oscillator strength, which is directly proportional to the area under the absorption curve. Oscillator strength corresponding to the induced electronic dipole transition $\psi J \to \psi' J'$ at energy v (cm^{-1}) can be written in the form –

$$P = \Sigma T_\lambda \, \bar{v} (f^n \psi_j || U^\lambda || f^N \psi_{j'})^2 \qquad \qquad ...(1)$$

Where U^λ is a tensor operator of rank λ

$$P_{obs} = 4.6 \times 10^{-9} \times \in_{max} \times \Delta v_{1/2} \qquad \qquad ...(2)$$

Where $\in_{max}$ is the molar extinction coefficient of the peak maximum and $\Delta v_{1/2}$ is half intensity band width.

Judd-Ofelt intensity parameters (T_λ , $\lambda = 2, 4$ and 6)

These three parameters are related to the radial wave functions of the states, the refractive index of the medium and the ligand field parameters, that characterized the interaction between the central ion and the immediate environment. T_2 parameter shows high sensitivity towards coordination changes, while T_4 and T_6 exhibit more sensitivity towards symmetry changes. These are evaluated by computational method.

Using P_{obs}, the values of T_2, T_4 & T_6 parameters were evaluated by multiple regression method. The values of these parameters (Table 1) show an appreciable variation in all the three T_λ parameters (T_2, T_4 and T_6). T_2 parameters show high sensitivity towards coordination changes while T_4 and T_6 have been found to exhibit more sensitivity towards symmetry changes. The ratio of T_4/T_6 showed smaller change; thereby, suggesting that symmetry changes are less prominent. However; the absolute values of T_4 and T_6 vary significantly; thus, indicating high sensitivity of these parameters.

The energy level density has been reported to be very high in Sm (III) ion[16]. Only weak bands have been observed in the visible and U.V. region. This causes uncertainties in the values of T_4 and T_6[17]. In this case, the value of T_6 is not found greater than T_4. The oscillator strength of some transitions was found abnormally high as compared to other peaks. This phenomenon is called "hypersensitivity"[18] and exhibits a relatively strong sensitivity and variability of the oscillator strength to the environment about the ion. Hypersensitive transition of Sm (III) system is attributed to $^6H_{5/2} \rightarrow {}^6P_{3/2}$.

The value of νT_6 is found directly propotional to the intensity of hypersensitive transition which indicates the dependence of intensity on covalency. The increase in intensity is in the order–

<div align="center">Ceftizoxim > Piperacillin > Cefroxime > Cefotaxim > Cefazolin</div>
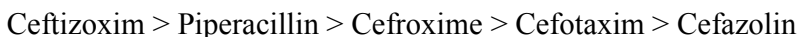
which is relevant to the steric effects of the ligands. The proportionality constant (K) has been computed for all the systems. The value of K was found nearly constant. Some ligands exhibited a little deviation from the linear relationship, which can be attributed to the higher value of magnetic dipole interaction. All the data prove validity of Peacocks relation.

CONCLUSION

The results obtained are in agreement with the theories of Judd and Ofelt. The intensity aspects of lanthanide absorption spectra can be predicted to a good approximation

on the basis of two parameters T_2 and T_4. The peacocks relation proves the inclusion of covalency in metal ligand bond.

Table 1: Computed values of intensity parameters of Sm (III) complexes

Ligand	$T_2 \times 10^9$ (cm)	$T_4 \times 10^9$ (cm)	$T_6 \times 10^9$ (cm)	T_4/T_6	OS of Hypersensitive peak $P_{obs} \times 10^6$	$\bar{\nu} T_6 \times 10^6$	$K = \dfrac{P_{obs}}{\bar{\nu} T_6}$
Ceftizoxime	24.04	1.986	0.3576	5.554	8.83	8.76	1.0071
Pipercillin	11.05	1.855	0.5582	3.334	8.25	13.85	0.5956
Cefuroxime	4.38	1.585	0.6308	2.513	7.02	15.64	0.4490
Cefotaxime	12.29	1.505	0.5830	2.581	6.72	14.45	0.4650
Cefazolin	24.90	1.355	0.4903	2.765	5.97	12.19	0.4895

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