Absorption and emission spectroscopic parameters of Nd^{3+} and Eu^{3+} ions in their hexamethylphosphoramide complexes

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Abstract

Syntheses of the following complexes are reported: $LnX_3 \cdot 6L$, $LnX'_3 \cdot 4L$, $LnX''_3 \cdot 3L$ and $Eu(NCS)_3 \cdot 3L$, where $Ln = Nd^{3+}$, Eu^{3+}; L = hexamethylphosphoramide (hmpa); $X = ClO_4^-$, PF_6^-; $X' = NCS^-$, NO_3^-, Br^-, ClO_4^-; $X'' = Cl^-$. Spectra of the complexes of Nd^{3+} (absorption) and Eu^{3+} (emission) in dichloromethane solutions were measured. The oscillator strengths of the Nd^{3+} f–f absorption bands within the 11 000–30 000 cm^{-1} region were determined and the τ_λ intensity parameters were obtained according to the Judd–Ofelt formalism. Covalency parameters were also determined for the Nd^{3+} complexes. The intensities relationship η_{21} of the $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_1$ transitions of the Eu^{3+} was calculated. A good correlation between τ_2 and the oscillator strength of the hypersensitive band of Nd^{3+} was found, as well as a correlation between τ_2 and η_{21}. There are only qualitative relations between τ_2 and the covalency parameter.

Introduction

Electronic spectra of lanthanide ions in the visible region are dominated by transitions which are electrically dipolar in character. Oscillator strength values are about 10^{-6}, 10^{-8} and 10^{-11} for electric dipole, magnetic dipole and electric quadrupole transitions, respectively. However, electric dipole transitions are forbidden and must be induced by a mechanism that involves an odd potential acting in the f-functions. Calculations of induced electric dipole transition intensities were developed by Judd [1] and Ofelt [2] and conducted to the following expression for the oscillator strength (P_{ED})

$$P_{ED} = \sigma \sum_{\lambda} \tau_\lambda [\langle f^N \psi_J \| U^{(\lambda)} \| f^N \psi'_{J'} \rangle]^2 (2J+1)^{-1}$$

$\lambda = 2,4,6$

Where σ is the energy of a $f^N\psi_J \rightarrow f^N\psi'_{J'}$ transition expressed in cm^{-1}; τ_λ are parameters dependent on the mechanism by which the transition acquires intensity and $\langle f^N\psi_J \| U^{(\lambda)} \| f^N\psi'_{J'} \rangle$ are the reduced matrix elements of the unity tensor operator $U^{(\lambda)}$. The $4f^N$ configuration states are taken as linear combinations of Russell–Saunders coupling states (intermediate coupling) by considering the strong spin–orbit coupling.

Such an expression can only be applied to spectra taken at temperatures where it is assumed that the states are equally populated. The matrix elements were computed by Carnall *et al.* [3–5], and included second order electrostatic interactions.

Of special interest are the transitions characterized by high values of matrix elements $U^{(2)}$. These transitions show high sensitivity to the ion environment and are called hypersensitives. In the intermediate coupling, they follow selection rules for radiative quadrupolar processes but they are as intense as electric dipole transitions. This fact suggests that radiation–molecule interaction processes are electrically dipolar in character. Therefore, hypersensitive transitions are also referred to as pseudo-quadrupolar.

Several mechanisms have been proposed to explain the hypersensitivity phenomenon [6–11] and they have been successfully applied, although with some restrictions, the major hindrance being the experimental difficulty in isolating the effects of all the factors that seem to contribute to the phenomenon. Several of those important factors are related to a covalent contribution in the essentially electrostatic Ln–ligand interactions, although the relations between ligand characteristics and hypersensitivity are not completely understood. The observed nephe-

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lauxetic effect and some UV broad band transitions in the lanthanide ion electronic spectra are evidence of the covalent contribution.

Usually, the nephelauxetic coefficient (β) has been used as a covalency measurement, although the energy separation between J levels is a function of the interelectronic repulsion as well as of the spin–orbit coupling constant. The other two parameters $b^{1/2}$ and δ have also been used [12, 13], $b^{1/2}$ is defined as a measurement of the mixture of 4f-ligand functions, then representing the maximum covalency degree [12]. They are given by

$$b^{1/2}=[1/2(1-\beta)]^{1/2} \quad \text{and} \quad \delta=[(1-\beta)/\beta]\times 100$$

In the present paper we report the study of some Nd^{3+} and Eu^{3+} coordination compounds containing hexamethylphosphoramide (hmpa) with the purpose of verifying the effect of ligands and anions in the hypersensitivity. Correlations between intensity parameters of the Judd–Ofelt formalism with covalency parameters are attempted.

Experimental

Synthetic procedures

Ln(III) salts were prepared by dissolving rare earth oxides 99.99% purity (Aldrich) in the corresponding diluted acids; hmpa (Aldrich) was purified by vacuum distillation, 2,2-dimethoxypropane and triethylorthoformate were used as dehydrating agents.

The compounds $Ln(ClO_4)_3\cdot 6hmpa$, $Ln(ClO_4)_3\cdot 4hmpa$ and $LnCl_3\cdot 3hmpa$ were obtained following procedures described in the literature [14, 15]. The synthesis of $LnBr_3\cdot 4hmpa$ [16] was improved by an alternative procedure: the ligand was added to an ethanolic solution of the lanthanide bromide in a molar ratio of 4:1 (hmpa:Ln) and the complexes precipitated by addition of cold diethyl ether under nitrogen. Synthesis of the nitrate complexes were performed by addition of the ligand to a methanolic solution of the lanthanide nitrate in a molar ratio of 4:1. The compounds precipitated after some hours standing in the refrigerator. To prepare the thiocyanate complexes, ethanolic solutions of the lanthanide thiocyanate were obtained by reaction of the basic lanthanide carbonate with thiocyanic acid freshly prepared from an ion exchange resin column. In each case, the ligand was added to the salt solution in a molar ratio of 4:1 and the complex was precipitated after some hours standing in the refrigerator. Successive recrystallizations of $Eu(NCS)_3\cdot 4hmpa$ in ethanol yielded $Eu(NCS)_3\cdot 3hmpa$. Several attempts to prepare the analogous neodymium compound were unsuccessful. In the synthesis of the $Ln(PF_6)_3\cdot 6hmpa$, an ethanolic solution of the lanthanide perchlorate was first added to a solution of potassium hexafluorphosphate in acetonitrile. Potassium perchlorate was filtered off and the addition of the ligand to the clear solution was immediately followed by the formation of a solid complex. All the solid compounds were recrystallized and dried in vacuum over P_4O_{10}.

Quantitative chemical analyses of the metal ion by EDTA titration, determination of phosphorus by colorimetry, elemental analysis of carbon, hydrogen and nitrogen, conductance measurements in nitromethane solutions, melting points and vibrational (infrared) spectra were carried out for the characterization of the complexes.

Spectroscopic studies

Absorption spectra were obtained at room temperature ($\simeq 22$ °C) in 10 mm glass cuvettes from dichloromethane solutions of Nd^{3+} compounds. A Carl Zeiss Jena Specord M40 was used in the 11 000–30 000 cm^{-1} spectral range. Concentrations of the solutions were about 10^{-2} M since it was observed that there is a variation in the oscillator strength value with concentrations lower than 5×10^{-3} M. Nitromethane solution was used for the $Nd(PF_6)_3\cdot 6hmpa$ compound because it is insoluble in dichloromethane.

Transition intensities were analysed by considering the Judd–Ofelt formalism [1, 2]. Oscillator strengths were experimentally obtained by the equation

$$P_{exp}=4.32\times 10^{-9}[9\eta/(\eta^2+2)^2]\int \epsilon(\sigma)d\sigma$$

where η stands for refractive index of the solution, ϵ is the molar extinction coefficient at the wavenumber σ, and the integration is to be done within each band. The integration was performed by direct planimetry and the resulting area was normalized to concentration and optical pathway.

By using P_{exp} values, tabulated matrix elements [3–5] and an appropriate least-squares computing program, the τ_λ parameters of the P_{ED} expression were calculated. Nine bands were considered. Transition energies were taken as the gravity center ($\bar{\sigma}$) of the bands in cm^{-1}. Due to the proximity of Nd^{3+} energy levels and the possible equilibria of complexes in solution, it was difficult to establish strict transition assignments. Therefore, the reduced matrix elements of the levels involved in each band were added together.

An average nephelauxetic coefficient was calculated from the equation

$$\bar{\beta}=\frac{1}{n}\sum_{1}^{n}\bar{\sigma}(\text{complex})/\bar{\sigma}(\text{aquo})$$

where $\bar{\sigma}$(aquo) corresponds to the gravity center of each band of the neodymium perchlorate spectrum in aqueous solution at pH 5.0. The covalency parameter δ was obtained by using $\bar{\beta}$.

Emission spectra of Eu^{3+} compounds in 10^{-2} M dichloromethane solutions were obtained with a Perkin-Elmer MPF-44B spectrofluorimeter, the sample being excited by the 394 nm line from a 150 W Xenon lamp. The η_{21} parameter defined by the ratio between the intensities of $^5D_0 \rightarrow {}^7F_2$ to $^5D_0 \rightarrow {}^7F_1$ luminescent transitions was calculated. The intensities were measured by direct planimetry of the emission bands.

Results and discussion

Conductance measurements in nitromethane solutions indicated that the complex $NdCl_3 \cdot 3hmpa$ is neutral while the complexes $NdX_3 \cdot 4hmpa$ are 1:1 electrolytes and the complex $Eu(PF_6)_3 \cdot 6hmpa$ contains only hmpa coordinated to the metal ion. A previous study [17] on the dissociation of the complexes $Nd(ClO_4)_3 \cdot 6hmpa$ and $Nd(ClO_4)_3 \cdot 4hmpa$ in nitromethane and dichloromethane solutions showed that species with low charges are predominant in dichloromethane solutions. Thus, in nitromethane solution the complex $Nd(ClO_4)_3 \cdot 6hmpa$ is a 1:2 electrolyte containing $[Nd(ClO_4)(hmpa)_5]^{2+}$ and in dichloromethane solution the predominant species is $[Nd(ClO_4)_2(hmpa)_4]^+$ as for the complex $Nd(ClO_4)_3 \cdot 4hmpa$. The intensity parameters η_{21} and τ_λ and the covalency parameter δ are shown in Table 1.

Oscillator strength

Although these values are not presented here, some comments can be pointed. The first point is that there is a good agreement between $P_{calc}(P_{ED})$ and P_{exp} showing that the Judd–Ofelt formalism can be applied for these systems. The second point is that a distinguished variation of intensities among the spectral bands exists, the Nd^{3+} hypersensitive transition ($^2G_{7/2}$, $^4G_{5/2} \leftarrow {}^4I_{9/2}$) being the most intense in each spectrum. For example, the highest P values of the nearest transition of the infrared region ($^4F_{3/2} \leftarrow {}^4I_{9/2}$) were observed for the compounds $Nd(ClO_4)_3 \cdot 6hmpa$ and $Nd(ClO_4)_3 \cdot 4hmpa$. For the hypersensitive transition, the compound $Nd(NO_3)_3 \cdot 4hmpa$ showed the highest P value, and for the nearest transition of the UV region ($^4D_{1/2}$, $^4D_{5/2}$, $^2I_{11/2}$, $^4D_{3/2} \leftarrow {}^4I_{9/2}$) the highest P value was found for the complex $Nd(NCS)_3 \cdot 4hmpa$.

TABLE 1. Intensity parameters η_{21} and τ_λ and covalency parameter δ

	Nd^{3+}				Eu^{3+}
	τ_2	τ_4	τ_6	δ	η_{21}
$Ln(NO_3)_3 \cdot 4hmpa$	11.78	2.72	8.32	0.477	6.74
$LnBr_3 \cdot 4hmpa$	2.74	0.535	0.476	0.726	2.19
$Ln(NCS)_3 \cdot 4hmpa$	9.72	3.57	5.22	0.764	4.39
$Ln(ClO_4)_3 \cdot 4hmpa$	7.78	3.02	6.05	0.592	4.16
$Ln(ClO_4)_3 \cdot 6hmpa$	8.46	2.45	6.31	0.632	2.98
$Ln(PF_6)_3 \cdot 6hmpa$	6.88	3.21	3.31	0.592	5.19
$LnCl_3 \cdot 3hmpa$	4.68	1.14	0.768	0.942	2.97
$Ln(NCS)_3 \cdot 3hmpa$					7.54

All parameters are described in the text; $\tau_\lambda/10^{-9}$.

Judd–Ofelt parameters

Although the Judd–Ofelt theory does not elucidate the nature of the τ_λ parameters, it has been useful due to the fact that the intensities of several bands can be discussed with the use of only three parameters. In the literature, the τ_2 parameter has been related to the hypersensitivity, being more dependent on the covalent metal–ligand interactions, while τ_4 and τ_6 have been considered more dependent on the coordination cluster symmetry [6, 9, 18]. From the results shown in Table 1 it can be observed that hypersensitivity, taken as the τ_2 parameter, decreased in the order: $Nd(NO_3)_3 \cdot 4hmpa > Nd(NCS)_3 \cdot 4hmpa > Nd(ClO_4)_3 \cdot 6hmpa > Nd(ClO_4)_3 \cdot 4hmpa > Nd(PF_6)_3 \cdot 6hmpa > NdCl_3 \cdot 3hmpa > NdBr_3 \cdot 4hmpa$. This is the same order observed for the variation of intensities (P values) of the hypersensitive bands as shown in Fig. 1.

The large variation in τ_4 and τ_6 should be associated with the presence of different complex structures in solution. Although the transition intensity enlargement has sometimes been associated with ligand

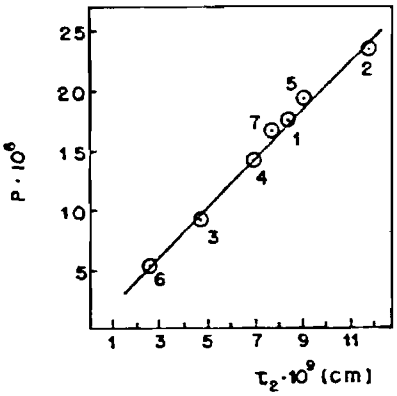

Fig. 1. Oscillator strength of the $^2G_{7/2}$, $^4G_{5/2} \leftarrow {}^4I_{9/2}$ transition as a function of the Judd–Ofelt τ_2 parameter. 1, $Nd(ClO_4)_3 \cdot 6hmpa$; 2, $Nd(NO_3)_3 \cdot 4hmpa$; 3, $NdCl_3 \cdot 3hmpa$; 4, $Nd(PF_6)_3 \cdot 6hmpa$; 5, $Nd(NCS)_3 \cdot 4hmpa$; 6, $NdBr_3 \cdot 4hmpa$; 7, $Nd(ClO_4)_3 \cdot 4hmpa$.

basicities [19], the Judd–Ofelt parameters, as described by Stephens *et al.* [20], must include all ligand dependent effects, except for J-mixing. Thus, τ_λ variations can be assigned to several ligand field effects such as coordination number and geometry, bond lengths and ligand basicities. In fact, this is of great importance when one try to correlate hypersensitivity with covalency only. As an example, the plot of δ as a function of τ_2, Fig. 2(a), shows an increase in τ_2 with the corresponding increasing in δ values within the series: $Nd(PF_6)_3 \cdot 6hmpa$, $Nd(ClO_4)_3 \cdot 4hmpa$, $Nd(ClO_4)_3 \cdot 6hmpa$, and $Nd(NCS)_3 \cdot 4hmpa$. Nevertheless, regarding the series $NdCl_3 \cdot 3hmpa$, $NdBr_3 \cdot 4hmpa$ and $Nd(NO_3)_3 \cdot 4hmpa$, an increase in δ seems to be associated with a decrease in τ_2. In Fig. 2(b) and (c) the plots of δ versus τ_2/τ_4 and τ_2/τ_6, respectively, show that $NdBr_3 \cdot 4hmpa$ can be included in the first series above.

Two conclusions can be drawn from these observations. It should be obvious that other effects like symmetry and the coordination number are as important as the covalency degree when discussing transitions intensities for these systems. Secondly, it must be pointed out that, from the definition of the nephelauxetic effect itself, we can see that $\bar{\beta}$, $b^{1/2}$ and δ are not the best parameters for covalency evaluation in the Ln–ligand interactions.

η_{21} *Parameter*

The luminescent transitions ${}^5D_0 \rightarrow {}^7F_J$ ($J = 0,1,2$) of Eu^{3+} occur in the 580–620 nm region. Although absolute intensities are difficult to obtain, the ${}^5D_0 \rightarrow {}^7F_1$ transition can be used as a reference, since it is purely magnetic dipolar in nature and should be independent of the chemical environment [21]. The relationship between the intensities of the ${}^5D_0 \rightarrow {}^7F_2$ hypersensitive transition and that of the ${}^5D_0 \rightarrow {}^7F_1$ transitions gives information about the hypersensitive degree. In the literature there are some correlations between emission intensities and ligand properties that can account for some covalent contribution in the Ln–ligand interaction. In aqueous solution, a straight correlation seems to exist between anion polarizabilities and emission intensities [22–24].

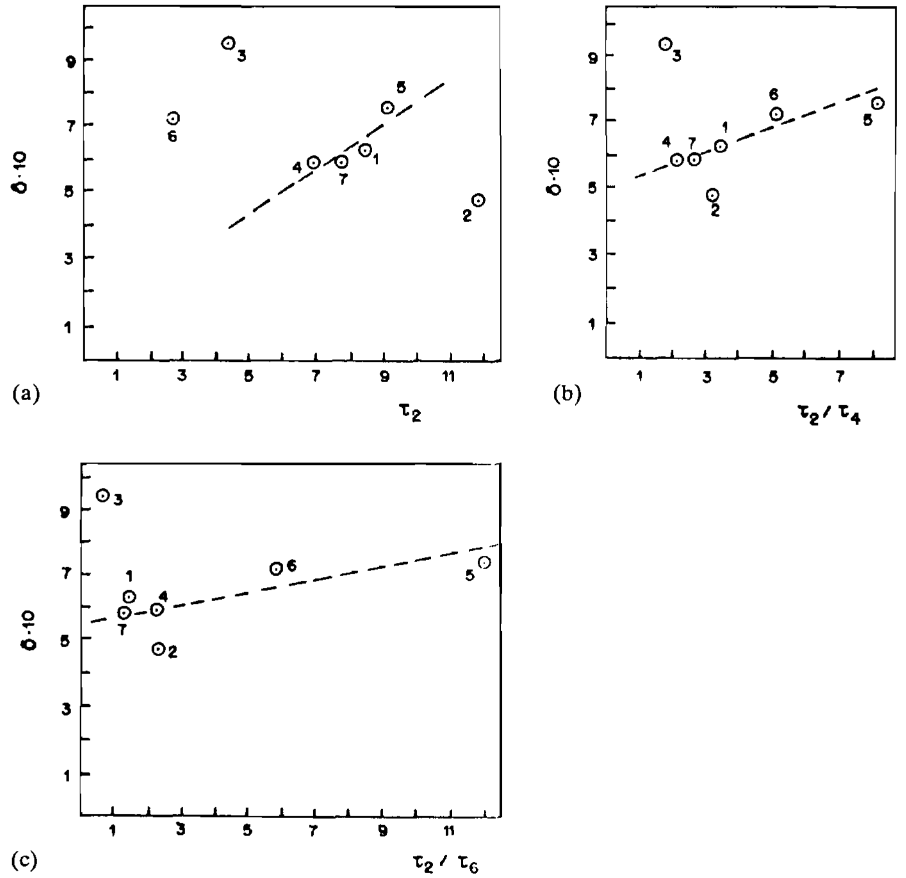

Fig. 2. Sinha's covalency parameter (δ) as function of: (a) τ_2; (b) τ_2/τ_4; (c) τ_2/τ_6. 1, $Nd(ClO_4)_3 \cdot 6hmpa$; 2, $Nd(NO_3)_3 \cdot 3hmpa$; 3, $NdCl_3 \cdot 3hmpa$; 4, $Nd(PF_6)_3 \cdot 6hmpa$; 5, $Nd(NCS)_3 \cdot 4hmpa$; 6, $NdBr_3 \cdot 4hmpa$; 7, $Nd(ClO_4)_3 \cdot 4hmpa$.

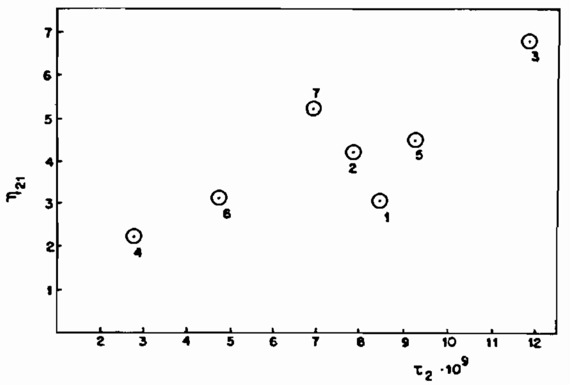

Fig. 3. Intensity parameter η_{21} obtained from emission spectra of Eu^{3+} compounds in solution as a function of the Judd–Ofelt τ_2 parameter obtained from absorption spectra of Nd^{3+} compounds in solution. 1, $Ln(ClO_4)_3 \cdot 6hmpa$; 2, $Ln(ClO_4)_3 \cdot 4hmpa$; 3, $Ln(NO_3)_3 \cdot 4hmpa$; 4, $LnBr_3 \cdot 4hmpa$; 5, $Ln(NCS)_3 \cdot 4hmpa$; 6, $LnCl_3 \cdot 3hmpa$; 7, $Ln(PF_6)_3 \cdot 6hmpa$. Ln = Nd^{3+}, Eu^{3+}.

Also, the importance of the symmetry effects becomes evident when the same ligand atom is attached to the central metal ion [25].

We have shown earlier [26] that non-radiative paths are predominant in the excited states relaxation processes for the series of Eu^{3+} solid complexes described here. In solution, there are also solvent molecules and relaxation processes must be more complicated. In spite of this, the same trend of ligand effects in the hypersensitivity distinguished from the excited state (Eu^{3+} emission) as from the ground state (Nd^{3+} absorption) can be observed as shown in the Fig. 3.

Conclusions

It is still a challenge to find correlations between covalency parameters and electronic transition intensities mainly because of the many factors that contribute to the observed intensities. In the literature, difficulties have also been found in the correlation between covalency and ligand field parameters [27].

The results show clearly that τ_2 reflects the hypersensitive transition intensities with fidelity (Fig. 1). The same can be said for η_{21}, as there is a good correlation between τ_2 from the Nd^{3+} compounds and η_{21} from the analogous Eu^{3+} compounds (Fig. 3).

Judd–Ofelt and covalency parameters both depend on the structure and chemical nature of the compounds, but the evaluation of the covalency is still a matter of discussion.

Supplementary material

Characterization results, absorption spectra of neodymium compounds in solution, tables with experimental and calculated oscillator strength values, and emission spectra of europium compounds in solution can be obtained from the authors on request.

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