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ABSORPTION SPECTRA AND STRUCTURE OF LANTHANIDE COORDINATION COMPOUNDS IN SOLUTION

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CONTENTS

ABBREVIATIONS

H_2(tart)	tartaric acid, $HOOC(CHOH)_2COOH$
H_2(oda)	oxydiacetic acid, $(HOOCCH_2)_2O$
H_4(edta)	ethylenediamine tetraacetic acid, $(CH_2)_2N_2(CH_2COOH)_4$

dipy	dipyridyl, $(C_5H_4N)_2$
phen	phenanthroline, $(C_6H_4N)_2$
DMF	dimethyl formamide, $HCON(CH_3)_2$
DMSO	dimethyl sulfoxide, $SO(CH_3)_2$
TBP	tributyl phosphate, $PO(C_4H_9O)_3$
HMPA	hexamethyl phosphoramide, $PO[(CH_3)_2N]_3$
H(aca)	acetylacetone, $H_3CCOCH_2COCH_3$
H(bac)	benzoylacetone, $H_5C_6COCH_2COCH_3$
H(dbm)	dibenzoylmethane, $H_5C_6COCH_2COC_6H_5$
H(dpm)	dipivaloylmethane, $(CH_3)_3CCOCH_2COC(CH_3)_3$
H(hfa)	hexafluoroacetylacetone, $F_3CCOCH_2COCF_3$
H(tta)	thenoyltrifluoroacetone, $C_4H_3SCOCH_2COCF_3$
H(fod)	2,2-dimethyl-6,6,7,7,8,8,8-heptafluoroctandione-3,5, $(H_3C)_3CCOCH_2COC_3F_7$
H(pdm)	2,2-dimethyl-6-trifluoromethoxy-6,6-difluorohexandione-3,5, $(H_3C)_3CCOCH_2COCF_2OCF_3$
H(tdm)	1-(α-thienyl)-4-trifluoromethoxy-4,4-difluorobutandione-1,3 $C_4H_3SCOCH_2COCF_2OCF_3$
H(tdpf)	1-(α-thienyl)-4-(α-perfluorotetrahydrofuroyl)-4,4-difluorobutandione-1,3, $C_4H_3SCOCH_2COCF_2C_4OF_7$

A. INTRODUCTION

As early as 1930—1940 the theoretical possibility of studying the structure of lanthanide coordination compounds, in particular coordination compounds of europium, in solution by analysing their absorption and luminescence spectra in the region of *f—f* transitions of the Ln^{3+} ions was demonstrated by Freed et al. [1—4]. Nevertheless, to date spectroscopy has not been widely applied to study the coordination compounds of lanthanides in solution. This is attributed both to conventional difficulties encountered in the spectroscopy of coordination compounds in solution (the broadening of spectral lines resulting from the electron-vibronic interaction with a solvent, chemical equilibria between species of different composition and structure present in solution) and specific features of the absorption spectra of lanthanide ions which have complex fine structure, low intensity and relative inertness towards changes in the lanthanide ion environment. The latter suggests high requirements for experimental equipment and theoretical analysis of the spectra obtained. The theoretical interpretation is, in particular, difficult to make because of the lack of experimental data on the energy levels in the free lanthanide (3^+) ions (except for Ce^{3+}, Pr^{3+} and Er^{3+} ions).

Meanwhile during the last 10—15 years, new fields of application have been found for lanthanide coordination compounds in solution, concerned with specific features of Ln^{3+} spectra. They are used in the construction of liquid lasers, in studying transuranium elements as unique "spectral models", in examining the structure and functions of biosystems involving metal ions as "spectral probes", etc. The development of this research requires information on the composition and structure of species existing in the systems under investigation, their spectral, thermodynamic and kinetic parameters. Recent progress in the theory of lanthanide spectra and spectral procedure permits one to believe that some of these problems may be solved by optical spectroscopy.

This article presents an up-to-date survey of the spectroscopy of lanthanide ions in solution. The first part (section B) treats general theory, i.e. the determination of the level schemes for tripositive lanthanide ions and description of the ligand field effects. A comprehensive consideration of all these problems is beyond the scope of the present paper. However we outline the subject and present some references.

Section C gives a brief interpretation of the absorption spectra for separate lanthanide ions in crystals and solution.

Section D deals with some specific features of the analysis of the absorption spectra for lanthanide ions in solution.

Spectroscopic evidence on different types of coordination compounds in solution, solvato-complexes, compounds with halogenide ions, carboxylic acids and β-diketones are given in Section E. This survey does not discuss in any detail the spectroscopy of lanthanide compounds with polyaminopolycarboxylic acids (complexones). These will be considered elsewhere.

B. THEORY

(i) Energy levels of $4f^q$-configurations in Ln^{3+} free ions

The f—f transitions cannot be observed in the gaseous Ln^{3+} spectra [5] as they are parity forbidden. The energy levels of the $4f^q$ configurations may be determined from the parity allowed $4f^{q-1}\,5d \leftarrow 4f^q$ transitions observed in the near and vacuum ultraviolet regions. So far, they have been identified only for Ce^{3+} ($4f^1$) [6], Pr^{3+} ($4f^2$) [7,8] and, partially, for Er^{3+} ($4f^{11}$) [9].

The procedure for theoretical calculation of the energy levels and the analysis of Ln^{3+} spectra have been developed [10—14]. To a first approximation, the energy level structure of the $4f^q$ configuration arises from electrostatic and spin—orbit interactions between $4f$ electrons.

$$E = \sum_k f^k F_k + A_{SO}\zeta_{4f} \tag{1}$$

where f^k and A_{SO} are the angular parts of the electrostatic and spin—orbit interactions, respectively. They can be precisely calculated using tensor operator techniques [12]. F_k and ζ_{4f} are the radial integrals. Only terms with $k = 0, 2, 4, 6$ are significant for configurations with equivalent f-electrons. The term with $k = 0$ is constant for all levels of a given configuration and, therefore, is neglected while considering the configuration structure.

Thus, to define the energy-level scheme of the $4f^n$ configuration it is necessary to have four radial integrals: F_2, F_4, F_6 and ζ_{4f}.

They may be theoretically evaluated by the Hartree—Fock method. There exist two sets of the Hartree—Fock radial $4f$-functions. One of these has been calculated by Rajnak for Pr^{3+} and Tm^{3+} [15] and the other by Freeman and Watson [16] for Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, Dy^{3+}, Er^{3+} and Yb^{3+}.

However, F_k and ζ_{4f} are usually considered as empirical parameters and derived from a least-squares fit of the experimental energy levels of a Ln^{3+} ion which is either free or complexed. In the latter case the baricentres of the Stark-splitting components are used as "free-ion" levels. The estimated values of F_k and ζ_{4f} for all the Ln^{3+} ions have been tabulated [13]. The empirical parameters F_k and ζ_{4f} have the same order of magnitude as those calculated using the Hartree—Fock method but are less by 20—40%. As a rule, the sets of four parameters describe the spectra with considerable mean deviations as high as some hundred cm^{-1}.

Some ten years ago the theory was improved by involving second-order electrostatic interactions, i.e. configuration interaction, in defining the energy-level schemes. Generally configuration interaction is taken into account by introducing the three additional parameters, α, β and γ into parametrization [13,17]. The most systematic calculations based on "the expanded parametrization model" have been carried out by Carnall et al. for lanthanide aquo-ions [18—21]. The sets of seven parameters obtained satisfactorily described the spectra for Ln^{3+} aquo-ions. The mean deviation between the calculated and experimental levels do not exceed some ten cm^{-1}.

It has also been shown [22—24] that the theoretical analysis of the spectra for Ln^{3+}-free ions can be improved further by taking into account higher magnetic interactions such as a spin—spin coupling (E_{SS}) and spin-of-one-electron with the orbit-of-the-other-one coupling. The energy of these interactions is not higher than 1/10 part of that for a configuration interaction.

(ii) Ligand field effects

(a) Splitting of terms

In the lanthanide free ion with spherical symmetry each J-level is $(2J + 1)$-fold degenerate. The crystal field distorts the ion symmetry and the degeneracy is broken partly or completely depending on the crystal field symmetry, resulting in levels split by the crystal field. The total value of the Ln^{3+} J-level splitting is comparatively small and does not usually exceed 100—200 cm^{-1}.

Until recently the level splitting of lanthanide ions in crystals was thought to be mainly due to the electrostatic fields generated by the surrounding ions in the crystals, and described by crystal field theory [25]. To a first approximation the theory assumes that the crystal field affects only the orbitals of the metal ion open shell. The Hamiltonian for an electron in the crystal field may be written as

$$\mathcal{H} = \mathcal{H}_{\mathrm{fi}} + V_{\mathrm{cf}} \tag{2}$$

where $\mathcal{H}_{\mathrm{fi}}$ is the Hamiltonian for a free ion and V_{cf} represents the crystal field potential. The latter is expanded as a series

$$V_{\mathrm{cf}} = \sum_{n,m} B_n^m (C_n^m) \tag{3}$$

where C_n^m are tensor operators transforming as spherical harmonics and B_n^m are the crystal field coefficients. The coefficients with $n = m = 0$ denote a spherical part of the potential. To a first approximation, it gives equal shifts for all levels of a given configuration and can be neglected. All other parameters with $n > 6$ and odd n for the configurations of the equivalent f electrons equal zero. Their number depends on the crystal field symmetry. To characterize the crystal field potential of a cubic symmetry one requires two coefficients, the C_{3h} symmetry — four, the C_{3v} symmetry — six, the C_{2v} symmetry — nine, etc. [13, p. 164].

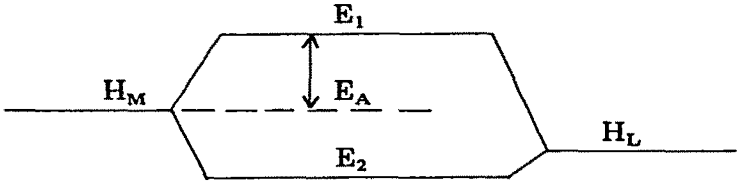
The crystal field coefficients, B_n^m are generally considered to be empirical parameters and determined from the spectral data using a least-squares fit. These have been calculated for lanthanide ions in different crystals. It has been shown that using the crystal field parameters one can define experimental levels with an average deviation as low as a few cm^{-1}.

This remarkable success of the parametrization scheme has led to a belief that the crystal field theory adequately describes the actual physical picture of lanthanide ion split levels. However, further studies on the subject have proved such concepts to be erroneous. All attempts to calculate theoretically the crystal field parameters from charge distribution data have met with failure. In the framework of an electrostatic model, these parameters may be expressed as

$$B_n^m = A_n^m (1 - \sigma_n) \langle r^n \rangle_{4f} \tag{4}$$

where A_n^m is determined by the sum of the crystal field static charges, $\langle r^n \rangle_{4f}$ are the even powers of a radial part of the $4f$-function, σ is a linear screening factor for f-electrons from the crystal field full potential (mainly, with closed $5s^2p^6$ shells). Although the calculations of the crystal field parameters involve some approximations, the discrepancy between theory and experiment is so high that there is no doubt that the concepts are invalid. Numerous attempts to improve calculation procedures by taking into account the additional electrostatic effects such as those of the $5s^2p^6$ shell polarization [26], configuration interaction [27—30], and the charge penetration [31,32], have given no satisfactory results.

On the other hand, Jørgensen et al. [33] have shown the possibility of interpreting the lanthanide crystal field in the framework of another distinct approach. They proposed to describe the lanthanide ion split levels in the crystal-fields on the basis of an "angular overlap model" (AO-model) which is one of the simplest approaches of the MO LCAO method. By the MO method, the magnitude of the level splitting is measured by the antibonding energy, E_A, equal to the difference in the energies of the atomic, H_M and antibonding, E_1 orbitals (both orbitals localizing mainly on the metal ion).



In accordance with the AO-model, the antibonding energy of the nl-orbital of the metal in the complex is proportional to the square of its overlap integral with the ligand orbitals.

$$E_A \simeq \frac{H_L^2}{H_M - H_L} S^2 \tag{5}$$

where H_M and H_L are the Coulomb integrals of the atomic orbitals of the metal and the ligand, respectively, S is an overlap integral. The latter is assumed to be the product

$$S = \Xi S_R^* \tag{6}$$

where Ξ and S_R^* are parameters depending on the angular and radial parts of interacting orbitals, respectively. If in the complex all ligands are identical and located at the same distance from the metal, then

$$E_A = e_\lambda^* \cdot \Xi_\lambda^2 \tag{7}$$

where

$$e_\lambda^* = \frac{H_L^2}{H_M - H_L} (S_R^*)^2 \tag{8}$$

λ denotes the type of overlap (σ or π). The angular parameters Ξ_λ can be accurately calculated if one knows the coordination number and symmetry of a given complex.

The angular parameters of the overlap integrals of f-orbitals, Ξ_σ in the chromophores having O_h and D_{3h} symmetry have been calculated by Jørgensen et al. [33]. The authors of the present survey have extended these calculations to other point-group symmetries and estimated the angular parameters for π-overlap integrals, Ξ_π [34]. The results obtained are summarized in Figs. 1 and 2.

The coefficients, e_λ^* are assumed to be empirical parameters and evaluated from spectral data. On the basis of the AO-model using only one empirical

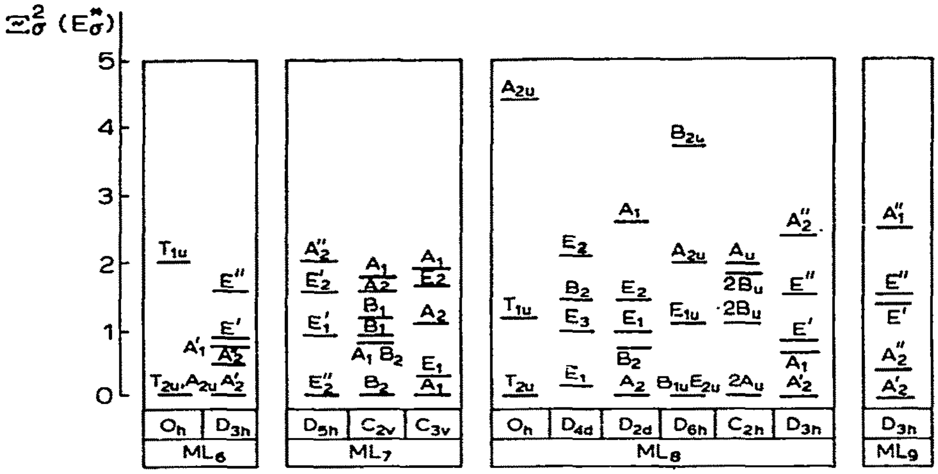


Fig. 1. Angular parameters, Ξ_σ^2 of *f*-orbital overlap integrals in complexes of various composition and symmetry (in $E_\sigma^* = 7\ l_\sigma^*$ units) [34].

parameter e_σ^* (i.e. taking into account only σ-overlap) the crystal fields have been successfully interpreted for a series of lanthanide ions in ethylsulphates [33], for Er^{3+} in orthovanadate and orthophosphate [35] and hydroxides [36]

Axe and Burns [37] using a semi-empirical MO-method have calculated the ground level splitting for Tm^{2+} (f^{13}) in the cubic field of CaF_2 taking into account σ- and π-interactions. The covalent contribution in the ground level splitting of Tm^{2+} was found to be near 50%.

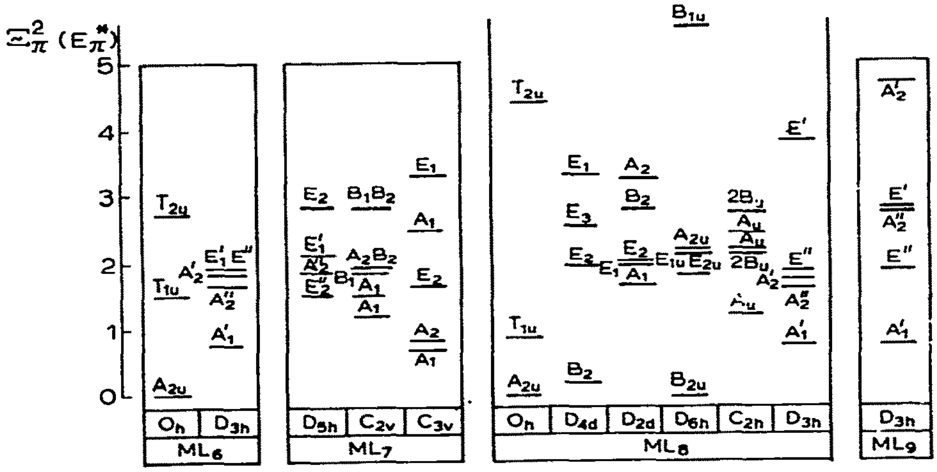


Fig. 2. Angular parameters, Ξ_π^2 of *f*-orbital overlap integrals in complexes of various compo sition and symmetry (in $E_\pi^* = 168\ e_\pi^*$ units) [34].

Further progress in theoretical studies providing a better insight into the nature of the lanthanide ion crystal fields was, to a great extent, promoted by the Newman "superposition model" [38] which simplified the calculations of different contributions to the crystal field parameters and facilitated their analysis. This model corresponds to the assumption that the crystal field can be built up from separate contributions from each of the ions in the crystal. Each contribution may be represented as a cylindrically symmetrical field which is described by the three parameters, $A_2\langle r^2\rangle$, $A_4\langle r^4\rangle$ and $A_6\langle r^6\rangle$. To distinguish them from experimentally obtained parameters, the special notation is used, $\bar{A}_2(R)$, $\bar{A}_4(R)$, $\bar{A}_6(R)$, and they are usually referred to as "intrinsic parameters". The relationship between "intrinsic" and experimental parameters can be expressed as

$$A_n^m\langle r^n\rangle = \sum_i k_{nm}(i)\bar{A}_n(R_i) \qquad (9)$$

where k_{nm} is a coordination factor which depends on the angular position of a single ion at a distance R_i from the paramagnetic ion. In practice, it is assumed that only the coordinated ions, i.e. "ligands", contribute significantly to the crystal field. If ligands are at the same distance eqn. (9) takes the form.

$$A_n^m\langle r^n\rangle = k_{nm}\bar{A}_n(R) \qquad (10)$$

Newman [38] summarized the modem data on the origin of lanthanide crystal fields, and showed that the overlap and covalency (charge transfer) make dominant contributions to crystal field parameters with $n = 4$ and $n = 6$. Analysis of the results obtained for $PrCl_3$ has revealed that the experimental parameters $A_6^0\langle r^6\rangle$ and $A_4^0\langle r^4\rangle$ are in good agreement with the sum of the calculated electrostatic and covalent contributions. For $A_2^0\langle r^2\rangle$, the agreement is much poorer.

(b) Band shifts

The energy levels of lanthanide "free-ions" in crystals and solutions determined from the absorption spectra differ somewhat from those of gaseous Ln^{3+} ions and depend on the environment [7,9,39,40]. In ligand fields, the whole $4f^q$ structure turned out to be shortened compared to that of a gaseous ion. The mean J-level shift value amounts to 5% for Pr^{3+} [7] and ~1% for Er^{3+} [9]. The approach of the energy levels observed in the absorption spectra due to red shifts has been called the nephelauxetic effect [41]. The problem of nephelauxetic band shifts in the absorption spectra of lanthanide ions has been discussed in detail by Jørgensen [39,42,43] and, therefore, we confine ourselves to a summary outline of the subject.

The phenomenon of the nephelauxetic effect cannot be interpreted in the framework of an electrostatic model which takes into account exclusively the first-order effects of the crystal field. The shifts in the level could be due to second-order crystal field effects. However theoretical values of the latter are of the order $\sim 10\ \text{cm}^{-1}$ [24,44], and therefore, cannot account for experimentally observed band shifts which, in some cases, are as high as 10^2—$10^3\ \text{cm}^{-1}$.

At present most investigators are agreed that the nephelauxetic effect in the spectra of lanthanide compounds is analogous to that observed in the spectra of *d*-transition element compounds. It cannot be quantitatively interpreted by neglecting the covalent interaction of lanthanide ions with the neighbouring ligands. This concept has been put forward by Jørgensen [39]. He has also proposed two possible mechanisms of the interaction [42]: (1) direct participation of the 4*f*-orbitals in the formation of molecular orbitals ("symmetry-restricted covalency"); (2) transfer of some part of the ligand electron density to the unfilled 6*s* and 6*p* orbitals of the lanthanide ("central field covalency").

The nephelauxetic effect is quantitatively described by a nephelauxetic parameter, β, equal to the ratio of the interelectron repulsion parameters (either Slater's integrals F_k, or Racah's parameters, E^k) in the complex and in the free ion.

$$\beta = \frac{(F_k)_c}{(F_k)_f} \text{ or } \beta = \frac{(E^k)_c}{(E^k)_f} \tag{11}$$

As the nephelauxetic effect value $(1-\beta)$ is small in the lanthanide complexes it can be, to a fairly good approximation, defined from the ratio of the wave numbers of *f*—*f* transitions in the spectra of the complex and the free ion [39].

$$\beta \approx \frac{\nu_c}{\nu_f} \tag{12}$$

Since, in the general case, the energy levels in the lanthanide free ions are unknown the relative nephelauxetic effects, β', are usually determined from the experimental data using the spectra of the lanthanide aquo-ions as standards.

$$\beta' \approx \frac{\nu_c}{\nu_{aq}} \tag{13}$$

To define the nephelauxetic effect Jørgensen et al. [45] proposed an equation which takes into account the ground level stabilization in the complex compared to the aquo-ion.

$$\sigma_c - \sigma_{aq} = d\sigma - (d\beta)\sigma_{aq} \tag{14}$$

where σ_c and σ_{aq} stand for spectral band baricenters in the complex and the aquo-ion, respectively, $d\sigma$ is the ground level stabilization, $d\beta$ is a variation of the nephelauxetic parameter. The $d\sigma$ and $d\beta$ values are usually determined from a plot of $\sigma_c - \sigma_{aq}$ against σ_{aq} utilising as great a number of levels as possible. It has been shown [46,47] that the experimentally obtained plots of $\sigma_c - \sigma_{aq}$ against σ_{aq} can deviate from straight lines due to a relativistic nephelauxetic effect (the ratio of the Landé parameters in the complex and the free ion, $\beta_{rel} = \xi(4f)_c/\xi(4f)_f$) and equal contributions of spin—orbital coupling to the energies of the ground and excited states.

Carnall [48] proposed using the energy levels of lanthanide ions in LaF_3 as standards in defining β' and pointed out their advantages in comparison with the aquo-ions.

The dependence of the nephelauxetic effect upon the nature of coordinated ligands can be expressed by the nephelauxetic series of ligands. For light lanthanides (Pr, Nd), according to their $1-\beta'$ value, ligands can be arranged in the order: $F^- < H_2O <$ tart$^{2-} <$ aca$^- <$ bac$^- <$ edta$^{4-} <$ dipy $<$ phen $< Cl^- < Br^- < I^- < O^{2-}$, which, in general, coincides with the ligand nephelauxetic series for ions of *d*-transition elements. The highest nephelauxetic effect values were found to be in sulfides [49], tricyclopentadienides [50] and oxides [45,51]. However, attempts to obtain a common nephelauxetic series for all lanthanide ions have met with failure, at any rate, using aqua-ions of the corresponding lanthanides as standards. When complexing in aqueous solutions with the same ligands, the bands in the absorption spectra of light and heavy lanthanides can shift in different directions. This phenomenon may be due to differences in the structure of both initial aquo-ions and the complexes obtained.

For spectral studies on the structure of the lanthanide coordination compounds in solutions any evidence of the relationship between the nephelauxetic band shift and the structure is of special interest. The dependence of the nephelauxetic effect upon the coordination numbers has been noticed in early investigations by Jørgensen [39] and Ryan and Jørgensen [52]. It was suggested that the phenomenon may be due to the shortening of the metal—ligand distance with a decrease in the coordination number. Laughlin and Conway [53] studied the absorption spectra for Pr^{3+} in isostructural crystals: $CeCl_3$, $NdCl_3$, $SmCl_3$, $GdCl_3$. The data obtained show that with the identical structure of the complexes (the coordination number 9 and D_{3h} symmetry) there exists a linear dependence between the wave numbers of the ${}^3P_{0,1,2} \leftarrow {}^3H_4$ transitions in the spectra of Pr^{3+} and the praseodymium—ligand distance R. If R increases the bands shift towards the short-wave region.

We have pointed out [54—56] the close to linear correlation between $\bar{R}$(Ln—O) and the wave numbers of some f—f transitions in the absorption spectra of some Pr(III) and Nd(III) complexes having different coordination numbers and symmetry ($\bar{R}$(Ln—O) is the mean lanthanide—oxygen distance in the complexes with the ligands coordinated via oxygen atoms). To interpret this correlation an analysis of the relationship between nephelauxetic effect, geometric and energetic parameters have been carried out for complex compounds using an angular overlap model. The value of η proportional to the nephelauxetic effect

$$\eta = (1-\beta^{1/2})/\beta^{1/2} \qquad (15)$$

is shown to be expressed as

$$\eta \approx \frac{H_L^2}{(H_M - H_L)^2}(S_R^*)^2 N \qquad (16)$$

where N is the coordination number. For complexes with the ligands coordinated through identical donor atoms the first term of eqn. (16) is a constant.

$$\frac{H_L^2}{(H_M - H_L)^2} = \text{const.} \tag{17}$$

and hence

$$\eta = \text{const.}\ (S_R^*)^2 N \tag{18}$$

Equation (18) represents the nephelauxetic effect as a function of the two variables, S_R^* and N which vary with changes in the lanthanide—ligand distance in the opposite directions. However, any variations in R have led to much greater changes of $(S_R^*)^2$ compared to N. As a result, the nephelauxetic effect increases when the coordination number decreases (the lanthanide—ligand distances are shortened) in spite of the additive nature of β and the decrease in the number of coordinated ligands.

(c) Intensities

The f—f transitions in the lanthanide ions can absorb electric—dipole, magnetic—dipole and even higher electric—multipole radiations. The electric—dipole transitions in the f^q configurations are parity forbidden. In crystals and solutions, however, there arise weak (the oscillator strength is within 10^{-6}—10^{-5}) so called "forced" electric—dipole transitions. Their appearance has been interpreted by mixing the different configurations of opposite parity into the $4f^q$ configuration through the odd parity terms of the expansion of the crystal field potential [13].

The magnetic—dipole f—f transitions are parity allowed and in the Russell—Saunders coupling scheme follow the selection rules: $\Delta L = 0$, $\Delta S = 0$, $\Delta l = 0$, $\Delta J \leqslant 1$ (but not $0 \not\rightleftharpoons 0$). In accordance with the latter only the transitions between J-levels of the ground term are not forbidden. Yet, strong spin—orbit coupling in the lanthanide ions weakens the selection rules on L and S and, as a result, magnetic—dipole transitions are also observed between other levels, for example ${}^5D_1 \leftarrow {}^7F_0$ in the spectra of Eu(III). Their oscillator strengths are less by one or two orders of magnitude than those of the induced electric—dipole transitions. The calculated oscillator strengths of all the magnetic—dipole transitions in the spectra of lanthanide ions are tabulated in ref. 64.

The electric—quadrupole f—f transitions are also parity allowed. Their oscillator strengths were estimated to be $\sim 10^{-11}$. Accordingly, they have never been detected experimentally. Calculations have shown that higher electric—multipole transitions are still less intense.

In 1962 Judd [57] and, independently, Ofelt [58] developed an electrostatic model to calculate the intensities of the forced electric—dipole transitions in the Ln^{3+} ion spectra. The model supposes that these transitions arise from mixing the $4f^{q-1}5d$ and $4f^{q-1}ng$ states into the $4f^q$-states via the odd terms of the crystal field (both static or dynamic). The oscillator strength, P, of the $\psi J \rightarrow \psi' J'$ transition is given by the equation

$$P_{\text{E.D.}} = \bar{\nu} \sum_{\lambda} T_{\lambda} \langle f^q \psi J \| u^{(\lambda)} \| f^q \psi' J' \rangle^2 \qquad (19)$$

where $\bar{\nu}$ is the energy of transition, the expression in brackets is a matrix element connecting the initial $\langle f^q \psi J|$ and final $|f^q \psi' J'\rangle$ states of the transition by the unit tensor operator of the rank $\lambda = 2, 4, 6$. The sets of reduced matrix elements for aquo-ions of all lanthanides have been calculated by Carnall at al. [18—21]. It has been shown [59] that the matrix element values for the Ln^{3+} ion are practically independent of the environment and, therefore, can be useful in studying the intensity of the spectra of lanthanide ions in different crystals and solutions.

The T_2, T_4 and T_6 values are the functions of the refraction index of the medium, the radial wave functions of the initial and final states and the perturbation mechanism parameters. All attempts to calculate the T_{λ} values on the basis of an electrostatic point-charge model [57,60] have failed. In general, T_{λ} is considered as an empirical parameter and calculated from the experimental intensities.

Although the Judd-Ofelt theory is not able to elucidate the nature of T_{λ}, it has proved to be a very useful working tool to make it possible to discuss the intensities of numerous absorption bands using only three parameters. The appearance of this theory led to numerous studies on intensities measured in the lanthanide ion spectra. The references and the data analysis obtained are reported in two recent reviews by Peacock [61] and Henrie et al. [62] and in the article by Mason et al. [84].

The most systematic sets of T_{λ} * were determined by Carnall et al. [63,64] for lanthanide aquo-ions. It was found that the intensities in the spectra of all lanthanide ions from Nd(III) to Yb(III) are satisfactorily described by three parameters. The theory inadequately interprets the intensities in Pr(III) spectra. This phenomenon has not yet received satisfactory explanation.

T_4 and T_6 are slightly changed in the lanthanide ion series (not greater than by an order of magnitude) and are rather insensitive to variations in the environment.

T_2 is of significance only for the transitions corresponding to $|\Delta J| = 2$ and varies sharply if the environment changes. A high sensitivity of transitions to any variations in the environment has been reported in [68—71]. Such transitions have been called "hypersensitive".

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* Carnall et al. [63,64] in solution spectra studies have used J_{λ} independent of multiplicity of the ground state.

$$J_{\lambda} = T_{\lambda}(2J + 1) \qquad (20)$$

Axe [65] studying crystals has used Ω_{λ} independent of the refraction factor.

$$\Omega_{\lambda} = \frac{J_{\lambda}}{\chi[8\pi^2 mc/3h]} \qquad (21)$$

Jørgensen and Judd [72] have stated that "hypersensitive" transitions obey the selection rules for quadrupole transitions: $|\Delta J| = 2$, $|\Delta L| \leqslant 2$, $\Delta S = 0$, and, therefore, called them "pseudoquadrupole". They have considered a number of plausible mechanisms and come to the conclusion that "hypersensitivity" may by due to non-homogeneity of the medium (of the dielectric) surrounding the lanthanide ion.

Judd [73] has assigned the hypersensitivity to the changes in the symmetry of the lanthanide ion environment. He has pointed out that the variations in T_2 at constant T_4 and T_6 can be obtained by involving A_{1m} parameters in the expansion of the crystal field potential which can be made for the following point groups: C_s, C_1, C_2, C_3, C_4, C_6, C_{2v}, C_{3v}, C_{4v} and C_{6v}.

However, some experimental evidence can be accounted for neither by nonhomogeneity of the medium, nor by symmetry arguments. In the first place, hypersensitivity is observed in the absorption spectra of lanthanide trihalides, $LnHal_3$ in the gaseous state having the D_{3h} symmetry [74,75], in some hexacoordinated complexes of the O_h symmetry [52,76—78] and of Eu^{3+} ions substituted into site lattices with the $\sim D_{2d}$ or $\sim D_{3h}$ symmetry [79,80]. Moreover, a correlation was found to exist between the intensities of hypersensitive transitions, on the one hand, and the nephelauxetic effect [81,82], the basicity of ligands [75,82] and the number of coordinated (more basic) ligands [83], on the other hand.

To intepret these findings Mason et al. [84] developed a "dynamic coupling mechanism" model involving the mutual perturbation of the metal ion and ligands. According to the model the oscillator strengths of hypersensitive transitions are due to the Coulomb correlation between transient induced dipoles of ligands and quadrupole moments of metal ions. The mechanism proposed is expected to give a non-zero effect for the electric—dipole transition moment in the complexes belonging to the point groups D_p and C_p (with any p) and C_{3h}, D_{3h} and T_d and their subgroups. It is forbidden when the complex has a centre of inversion or belongs to the S_p point groups (when $p \geqslant s$). The model can describe quantitatively the intensities of hypersensitive transitions in the spectra of lanthanide tris-β-diketonates and gaseous $LnHal_3$. The calculated and observed intensities were found to be in good agreement.

To define "hypersensitivity" Henrie et al. [62] proposed a semi-quantitative "covalent model", in which the covalency effects are involved in the Judd—Ofelt theory via charge-transfer states. A physical interpretation of T_λ parameters treats T_2 as dependent upon covalency while T_4 and T_6 are considered to be mainly functions of symmetry of the complex.

They have also admitted that their "covalent model" and the "dynamic coupling model" developed by Mason et al. have much in common as both involve the polarization of ligands, a charge transfer being the extreme case of polarization.

Peacock [61] has briefly considered the "covalent model" and pointed out that the mechanism proposed should have lead to the hypersensitivity of T_4 which is not observed experimentally.

C. ABSORPTION SPECTRA OF LANTHANIDE IONS

The absorption spectra of each of the thirteen lanthanide ions having an unfilled $4f$-shell will be briefly described in this section. Table 1 lists some data on the energy level schemes for Ln^{3+} ions. The configurations f^q and f^{14-q} are characterized by identical sets of terms. The configuration becomes rapidly complicated in the transition from $f^1(f^{13})$ to f^7.

In the absorption spectra of Ln^{3+} ions the $4f$—$4f$ transitions lie in the near infrared, visible and near ultraviolet regions and correspond to transitions from the ground to excited levels of the configurations. Only for Eu^{3+} and Sm^{3+} can one also observe the transition from the first and second excited levels of the ground multiplet, having low energy values and populated at room temperature.

(i) $Ce^{3+}(4f^1)$

In the Ce^{3+} free ion the single $4f$ electron can exist in two states differing by spin direction: ${}^2F_{5/2}$ (ground state) and ${}^2F_{7/2}$. Their energy difference obtained from the spectrum of gaseous tripositive cerium is 2257 cm^{-1} [6]. Thus, f—f transitions for Ce^{3+} fall into the infrared region. As the absorption bands of H_2O lie in this region it is impossible to observe the above transitions

TABLE 1

Terms of f^q configurations of Ln^{3+} free ions

Configuration	Ln^{3+}	Terms	Number of terms	Number of levels with different J
f^1, f^{13}	Ce^{3+}, Yb^{3+}	${}^2F$	1	2
f^2, f^{12}	Pr^{3+}, Tu^{3+}	${}^1SDGI$ ${}^3PFH$	7	13
f^3, f^{11}	Nd^{3+}, Er^{3+}	${}^2PDFGHIKL$ ${}^4SDFGI$ 2222	17	41
f^4, f^{10}	Pm^{3+}, Ho^{3+}	${}^1SDFGHIKLN$ ${}^3PDFGHIKLM$ ${}^5SDFGI$ 24 423 2 3243422	47	107
f^5, f^9	Sm^{3+}, Dy^{3+}	${}^2PDFGHIKLMNO$ ${}^4SPDFGHIKLM$ ${}^6PFH$ 457675532 2344332	73	198
f^6, f^8	Eu^{3+}, Tb^{3+}	${}^1SPDFGHIKLMNQ$ ${}^3PDFGHIKLMNO$ 4 648473422 659796633 ${}^5SPDFGHIKL$ ${}^7F$ 32322	119	295
f^7	Gd^{3+}	${}^2SPDF\ G\ HIKLMNOQ$ ${}^4SPDFGHIKLMN$ 25710 10997542 22657 5533 ${}^6PDFGHI$ ${}^8S$	119	327

in aqueous solutions and crystallohydrates. The *f*—*f* transitions in Ce^{3+} were examined in the infrared spectra activated by Ce^{3+} crystals transparent in this region [85—89]. At room temperature the *f*—*f* transitions occur as an unresolved band with the maximum at about 2200—2300 cm^{-1} and a half-width of 250—300 cm^{-1}. At low temperature this band splits into some lines which are due to both pure electronic *f*—*f* transitions between sublevels of ^2F term splittings in the crystal field and electron—vibronic transitions.

The Ce^{3+} ion is characteristic of the absorption in the near ultraviolet due to 4*f*—5*d* transitions. In solution spectra these transitions occur as broad, intense bands (the half-width is 1000—2000 cm^{-1}, ϵ is of the order 10^2—10^3 l mol cm^{-1}).

In the free Ce^{3+} ion the energy of two doublet terms corresponding to the [Xe] $5d^1$ configuration equals 49735 cm^{-1} ($^2D_{3/2}$) and 52226 cm^{-1} ($^5D_{5/2}$). As a result of the *D*-term splitting the number and location of bands corresponding to *f*—*d* transitions strongly depend upon the strength and symmetry of the ligand field surrounding the Ce^{3+} ion [39,90]. At low temperature the bands have a fine structure i.e. involve a series of narrow lines resembling the analogous *f*—*f* transitions. Most of these are of vibronic origin [36].

(ii) $Pr^{3+}(4f^2)$

The f^2 configuration of a free Pr^{3+} ion involves 13 energy levels. Their location is found experimentally by analysis of the spectra for a gaseous Pr^{3+} [7,8]. The ground term appears to be $^3H_4$. Figure 3 gives the energy level scheme for a free Pr^{3+} ion. All the lines observed in the absorption spectra for Pr(III) in solutions and crystals in the near infrared and visible spectral regions correspond to the transitions from the ground state. The transition to the highest $^1S_0$ level which lies in the near ultraviolet region cannot be observed as it is masked by the *f*—*d* transition in the same region of the spectrum [91,92].

The absorption spectra of Pr^{3+} in crystals have been extensively studied [14, 24, 93 and refs. therein]. At low temperature bands in these spectra display the fine structure induced by *J*-level splitting in the crystal fields. For two pairs of levels, $^1I_6$—$^3P_1$ and $^3F_4$—$^3F_3$ the splitting components may be overlapped.

The absorption spectra of Pr(III) in solutions in the visible region involve four bands due to the transitions from the ground level to $^3P_2$, $^3P_1$ + $^1I_6$, $^3P_0$ and $^1D_2$ levels. More complete absorption spectra of Pr(III) in liquid media have been observed in diluted $DClO_4$, ethylacetate and a molten $LiNO_3$—KNO_3 mixture [63,94]. Crystal-field components in the absorption spectra of Pr(III) in solution are unresolved.

(iii) $Nd^{3+}(4f^3)$

Because of the great number of energy levels for the f^3 configuration (41 levels) the absorption spectra of Nd(III) in crystals and solutions contain

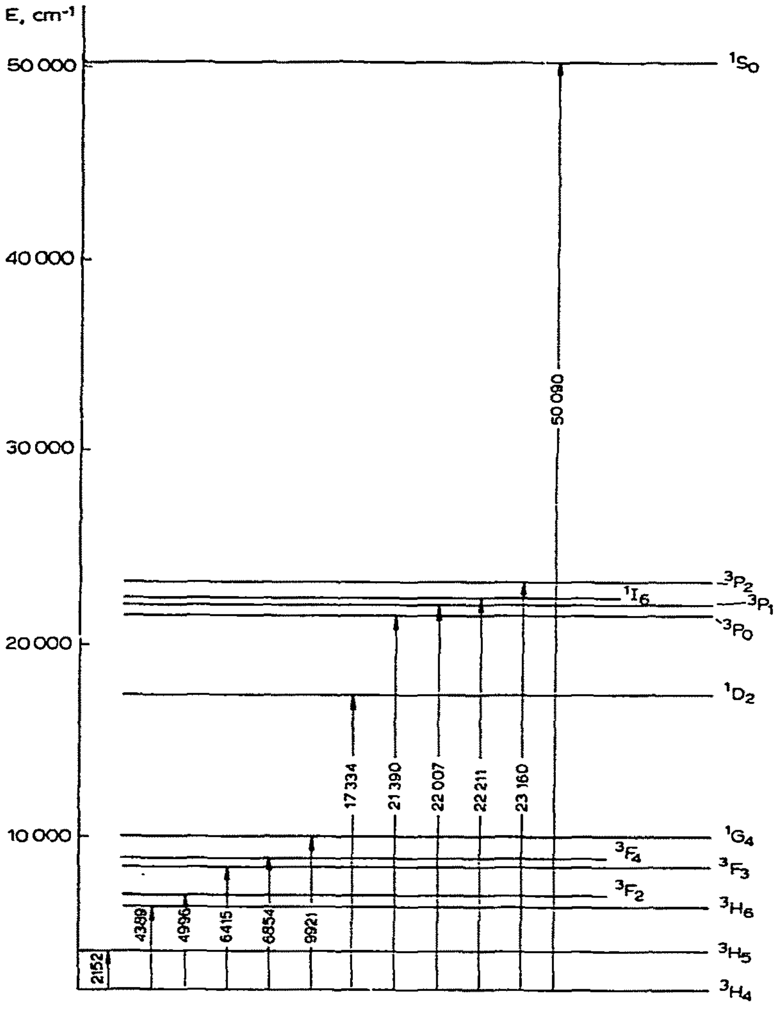


Fig. 3. Energy-level diagram for Pr^{3+} free ion [7].

many bands due to transitions from the ground level $^4I_{9/2}$ to the excited levels of the configuration [101—103].

Figure 4 represents the assignment of transitions in the near IR, visible and near UV regions of the Nd^{3+}_{aq} absorption spectrum [18].

The spectra of Nd(III) in solutions taken on spectrographs of high resolving power reveal fine structure. However, the splitting components belonging to different *J*—*J* transitions and the various complex species present in solution in equilibrium, as a rule, overlap. As a result, the analysis of the ligand field spectrum for Nd(III) is complicated. The simplest interpretation appears to be for the fine structure of the line corresponding to the $^2P_{1/2} \leftarrow {^4I_{9/2}}$ transition (~23400 cm^{-1}). The upper level of this transition does not split in the ligand

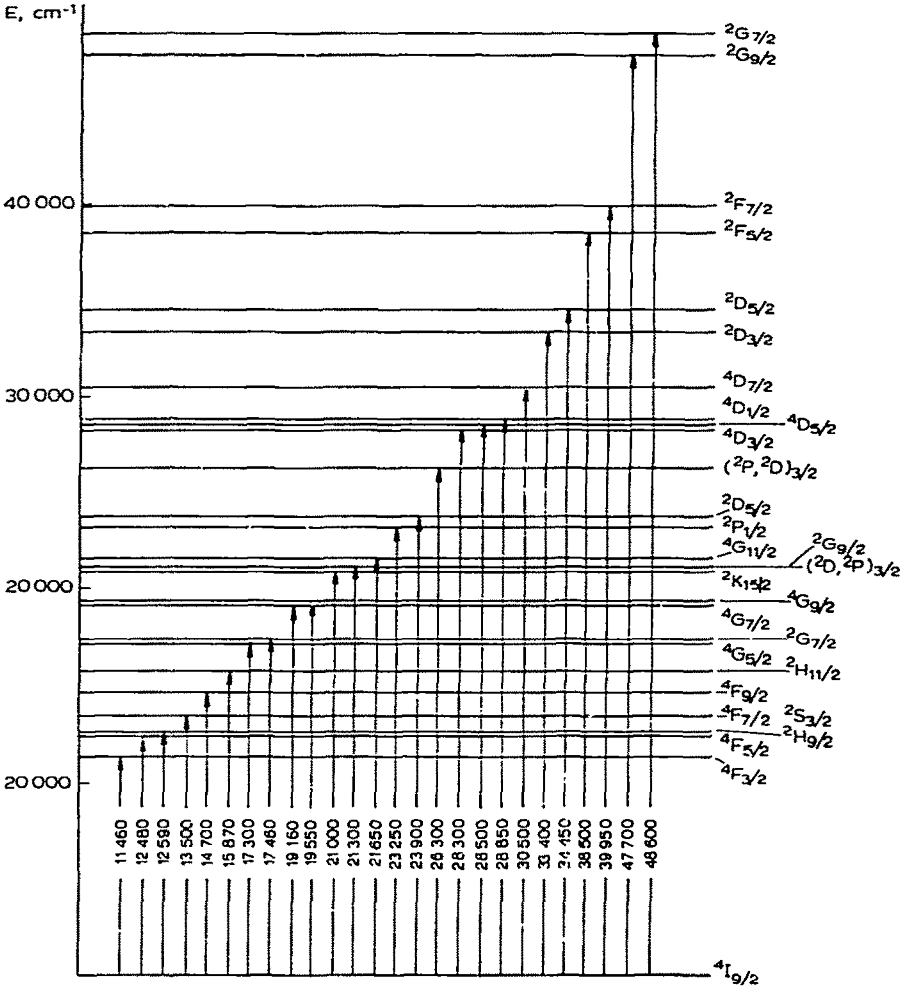


Fig. 4. Assignment of transition in near-IR, visible and near-UV regions of Nd$^{3+}_{aq}$ absorption spectra [18].

field of any symmetry (Kramers' doublet) and the observed picture of splitting corresponds to that of the ground level. For an individual species the maximum number of the Nd(III) ground level splitting equals five. All investigations on the fine structure of bands in the spectra of Nd(III) in solutions have been carried out for this transition.

The intensities in the absorption spectra of neodymium compounds can be reasonably described by the Judd—Ofelt theory even at marked variations in the band intensities [63,66,95,97,99,100,104—108]. The transition $^4G_{5/2} \leftarrow {}^4I_{9/2}$ located in the visible region of the spectrum (~17500 cm^{-1}) is hypersensitive. It is overlapped by a less intense transition to the level $^4G_{7/2}$ (~17460 cm^{-1}). The $^4G_{5/2,7/2} \leftarrow {}^4I_{9/2}$ band intensity is commonly used in determining the composition and the stability constants of neodymium complexes using various spectrophotometric methods.

(iv) $Pm^{3+}(4f^4)$

Promethium is the only lanthanide that lacks stable isotopes. For chemical investigation the isotope ^{147}Pm with a half-life of $\tau = 2$ years is usually employed.

The absorption spectra for Pm(III) in aqueous solutions at 3000—10 000 Å were first obtained in 1950 [109,110]. Later Gruber and Conway [111] recorded the absorption spectra of Pm(III) in 0.023 M DCl in a wider spectral region. Carnall et al. [112] examined the absorption spectra of Pm(III) in diluted $DClO_4$ and in molten $LiNO_3$ and assigned bands up to 30 000 cm^{-1}. The transitions $^5I_8 \leftarrow {}^5I_4$ (6670 cm^{-1}) and $^5I_7 \leftarrow {}^5I_4$ (4990 cm^{-1}) have been observed for the first time in the nitrate eutectic [112]. The analysis of the Pm^{3+} aquo-ion absorption spectrum has been carried out [18]. The bands at ~25 000 cm^{-1} are overlapped by absorption due to the radiolysis products of solutions. The experimental intensities of the bands which can be observed correlate well with those calculated with the help of the Judd—Ofelt theory [64]. The bands at ~17700 cm^{-1} and ~18 260 cm^{-1} corresponding to the transitions to the $^5G_2$ and $^5G_3$ levels, respectively, are hypersensitive.

(v) $Sm^{3+}(4f^5)$

The number of multiplet terms for the f^5 configuration equals 73, the number of levels with various J is 198, the ground level is $^6H_{5/2}$.

In spite of the high density of energy levels for Sm^{3+}, the intensity of only a small number of transitions is sufficient to make it possible to observe them in the absorption spectra of Sm(III) in solution [64]. The visible region of the spectrum also lacks the transitions sensitive to the environment. Some more intense bands corresponding to transitions to the ^6F multiplet are observed in the infrared region. The $^6F_{1/2} \leftarrow {}^6H_{5/2}$ transition (6400 cm^{-1}) is hypersensitive. Analysis of the intensities in Sm(III) spectra has been carried out [66,67,95, 100].

(vi) $Eu^{3+}(4f^6)$

The assignment of the bands in the absorption spectrum of Eu^{3+}_{aq} is given in Fig. 5. The ground multiplet of Eu^{3+}, ^7F, is very deep and its levels do not overlap with those of the next multiplet, ^5D. The $^5D \leftarrow {}^7F$ transitions are located in the visible region, the transitions between the ground multiplet levels correspond to the infrared region of the spectrum. The excited levels of the ground multiplet, $^7F_1$ and $^7F_2$ are only 360 cm^{-1} and 1000 cm^{-1} above the ground level and are also populated at room temperature. Thus, the number of possi-

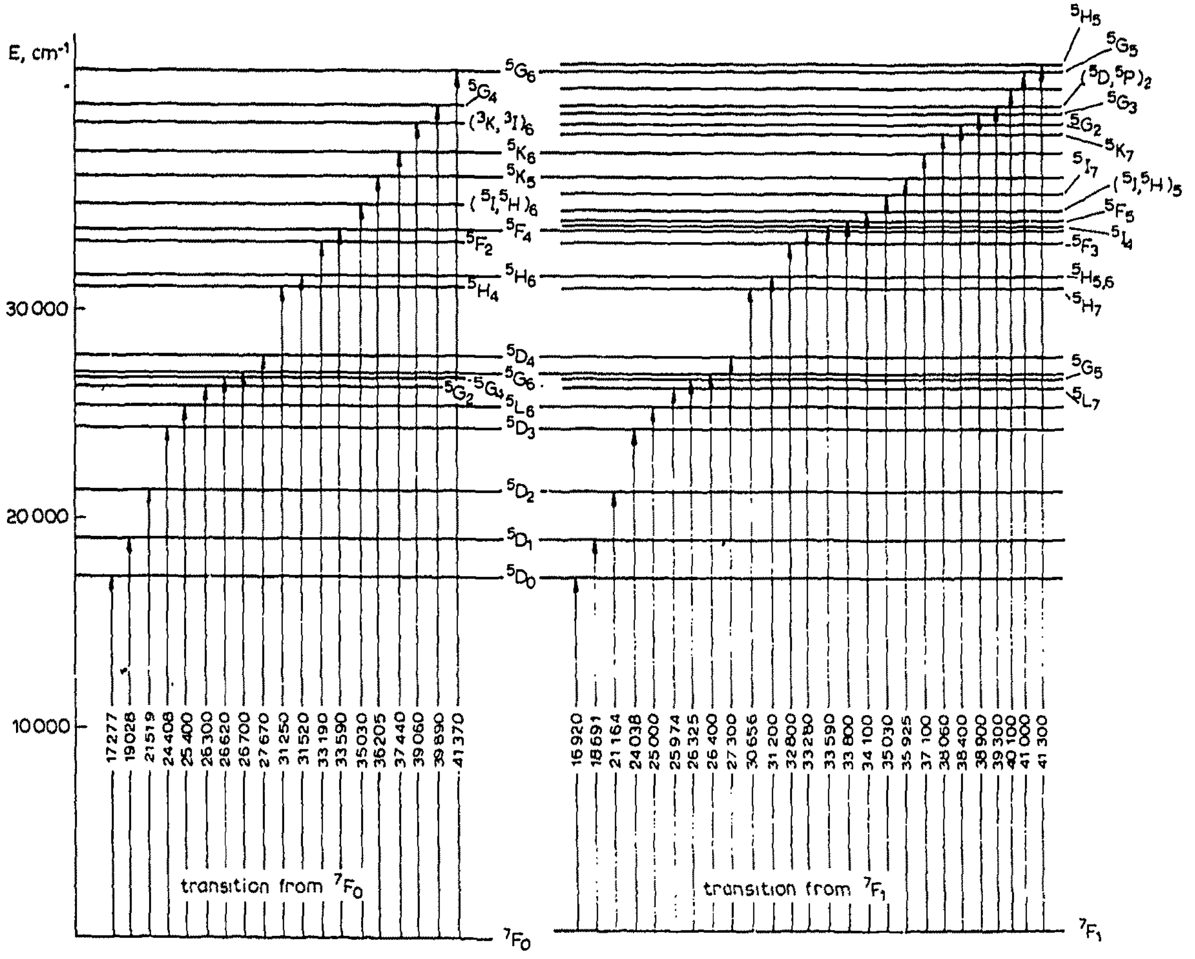


Fig. 5. Assignment of transitions in visible and near-UV regions of Eu^{3+}_{aq} absorption spectra [21].

ble transitions in the visible and ultraviolet regions of the absorption spectra of Eu^{3+} is very high. However, many of them are forbidden by selection rules on $\Delta J (\Delta J \neq \text{odd})$.

The ground level of Eu^{3+}, $^7F_0$ cannot split in the ligand fields and the transitions from it arise as narrow bands. The transitions from $^7F_1$ and $^7F_2$ levels are observed as diffuse bands. In some cases, the transitions from the $^7F_0$ level are overlapped and observed in the spectra as a sharp peak superimposed upon a diffuse absorption band. For example, in the aquo-ion spectrum the $^3H_4 \leftarrow {}^7F_0$ transition at 31250 cm^{-1} is superimposed upon the absorption arising from the $^5H_5 \leftarrow {}^7F_1$ transition (31162 cm^{-1}), while the $^5F_2 \leftarrow {}^7F_0$ transition (33190 cm^{-1}) overlaps the $^5F_4$, $^5I_4 \leftarrow {}^7F_1$ transition (33400 cm^{-1}).

The $^5D_0 \leftarrow {}^7F_0$ transition is strictly electric-dipole forbidden by selection rules on ΔJ ($0 \nleftrightarrow 0$). The $^5D_1 \leftarrow {}^7F_0$ transition is also electric—dipole forbidden and occurs mainly by a magnetic—dipole mechanism (at ~21520 cm^{-1} in the aquo-ion spectra). The $^5D_2 \leftarrow {}^7F_0$ transition is hypersensitive. The $^5D_0 \leftarrow {}^7F_0$, $^5D_1 \leftarrow {}^7F_1$ and $^5D_2 \leftarrow {}^7F_1$ transitions are also hypersensitive [113].

(vii) $Gd^{3+}(4f^7)$

The absorption spectra of a Gd^{3+} ion in crystals have been interpreted [114—118]. Carnall et al. [19] discussed the spectrum of $Gd(ClO_4)_3$ in dilute aqueous solution.

A Gd^{3+} ion has a half-filled 4*f*-shell and, to a first approximation, neither its ground, nor the excited states must split in ligand fields. The ground term, $^8S_{7/2}$ is located very deeply and far from the excited states. Therefore, the absorption spectrum of Gd^{3+} lies entirely in the ultraviolet region and consists of a variety of narrow bands corresponding to transitions to the components of ^6PIDG multiplets.

Analysis of the intensities in the absorption spectrum of the gadolinium aquo-ion have been reported [64]. The most intense group of narrow bands correspond to the transitions to the levels of the ^6I multiplet (36000—37000 cm^{-1}). The less sharp intense bands at ~51000 cm^{-1} and ~50000 cm^{-1} correspond to the transitions to the ^6G multiplet levels. The intensity of weak bands in the range 32000—33000 cm^{-1} (transitions to $^6P_{7/2}$ and $^6P_{5/2}$ levels) arises almost entirely by a magnetic—dipole mechanism [64]. The bands corresponding to the transitions to ^6D multiplet levels (39000—40000 cm^{-1}) are less intense.

(viii) $Tb^{3+}(4f^8)$

The ground term of Tb^{3+} is similar to that of Eu^{3+}but has a reverse order of levels. Therefore, the ground state is characterized by the maximum number of *J*, $^7F_6$. The highest component of the ground multiplet term is separated from the lowest component of the first excited states by more than 16000 cm^{-1}. Unlike Eu^{3+} the distance between the ground, $^7F_6$, and the first excited,

$^7F_5$, components of the ground multiplet amounts to 2080 cm^{-1} and the excited components of the ground multiplet are unpopulated at room temperature.

The absorption bands of Tb^{3+} in crystals are assigned up to ~26000 cm^{-1} [119,120]. They belong to transitions from the ground level, $^7F_6$, to other levels of the same multiplet and the first two levels of the first excited multiplet, i.e. $^5D_4$ and $^5D_3$.

Carnall et al. [20] assigned bands in the terbium aquo-ion absorption spectrum up to ~40000 cm^{-1}. The *f—f* transitions with energy value higher than 36000 cm^{-1} are superimposed by more intense and broad bands centred at ~38000 and ~46000 cm^{-1} and resulting from *f—d* transitions.

The intensities in the Tb(III) absorption spectra were investigated [64,113].

(ix) Dy^{3+}(4f^9)

A set of multiplet terms (73 in all) for f^9 Dy^{3+} is similar to that for Sm^{3+} The ground state of Dy^{3+} is $^6H_{15/2}$.

Interpretation of the Dy^{3+} crystal spectra have been reported [121—123]. Carnall et al. [18] have theoretically analysed the dysprosium(III) aquo-ion absorption spectrum and assigned spectral bands up to ~40000 cm^{-1}.

The *f—f* transitions of Dy^{3+} with energy higher than 36000 cm^{-1} are superimposed by more intense absorption due to the *f—d* transitions. The oscillator strengths of bands in the absorption spectra of Dy(III) in solutions have been given [64,67,95,113]. In the visible region of the spectrum hypersensitive transitions are not observed. A hypersensitive band has been revealed [124] in the infrared region of the Dy^{3+} spectrum at 7700 cm^{-1}. It is assigned [64] to the $^6F_{11/2} \leftarrow {}^6H_{15/2}$ transition.

(x) Ho^{3+}(4f^{10})

47 multiplet terms arise from the f^{10} configuration. They form 107 levels with different *J* due to spin—orbit coupling. The ground state of Ho^{3+} is $^5I_8$. Although the spectrum of Ho^{3+} is complex its theoretical analysis has been carried out. It has been interpreted mainly on the basis of the absorption spectra of Ho^{3+} in crystals. A full list of references can be found [125]. A theoretical analysis of the $\mathrm{Ho}^{3+}_{\mathrm{aq}}$ absorption spectrum has been made [18]. The absence of strong absorption in the near ultraviolet region has permitted the assignment of bands up to 50000 cm^{-1}.

The band intensities in the absorption spectra of Ho^{3+} have been studied [64,66,67,100,106—108]. The bands at 22100 cm^{-1} ($^5G_6 \leftarrow {}^5I_8$ transition) and at 27700 cm^{-1} ($^3G_6 \leftarrow {}^5I_8$ transition) are hypersensitive.

(xi) Er^{3+}(4f^{11})

The f^{11} configuration is characterized by 17 multiplet terms which result in 41 levels due to spin—orbit coupling. The *J* energy levels in Er^{3+} are more separated than in Nd^{3+} having the same set of terms (f^3). The structure of the spectrum for Er^{3+} is relatively simple. It is given in Fig. 6. The transitions from the ground level ($^4I_{15/2}$) to $^2H_{11/2}$ (19200 cm^{-1}) and $^4G_{11/2}$ (26500 cm^{-1}) are hypersensitive [63]. The intensities in the erbium coordination compounds were studied [63,66,95—98,100,107,108].

(xii) $Tm^{3+}(4f^{12})$

The electronic f^{12} configuration is characterized by the same states as the f^2 configuration for Pr^{3+}. However, according to Hund's rule the levels of the ground multiplet are reversed and the lowest lying level is $^3H_6$. Both in crys-

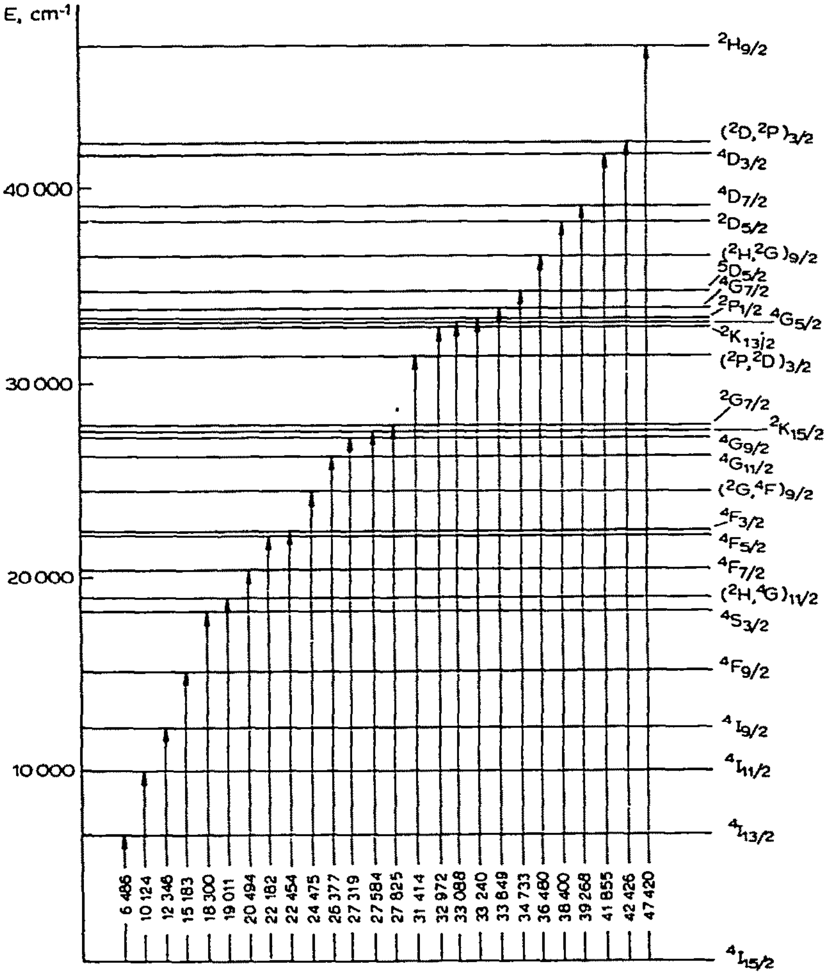


Fig. 6. Energy-level diagram for Er^{3+} free ion [9].

tals and solutions, the transitions from the ground level to all excited levels but the highest (>70000 cm^{-1}) $^1S_0$ have been observed in absorption spectra of Tm^{3+}. A thorough theoretical analysis of the absorption spectrum for Tm^{3+} in crystal matrices of LaF$_3$ with allowance for electric and magnetic interactions of the higher orders has been carried out by Carnall et al. [23]. One can find the references on all previous works dealing with the analysis of the Tm^{3+} ion spectra in crystals in the latter work [23]. Theoretical analysis of the absorption spectrum for thulium aquo-ion has been reported [18].

The intensities in the absorption spectrum of Tm(III) in liquid media are discussed [63,66,95,108]. The $^3F_4 \leftarrow {}^3F_6$ transition is hypersensitive.

(xiii) Yb^{3+}(4f^{13})

The energy level scheme for Yb^{3+} is similar to that for a Ce^{3+} ion having electronic configuration f^1. Yb^{3+} has the doublet term ^2F. The ground level is $^2F_{7/2}$. The distance between the doublet components is fairly large (10300 cm^{-1}) and the corresponding transition can be observed both in absorption and luminescence.

In liquid media the absorption spectra of ytterbium(III) has been examined in deuterated perchloric acid, in molten LiNO$_3$—KNO$_3$ and ethylacetate [63]. The oscillator strength of the $^2F_{5/2} \leftarrow {}^2F_{7/2}$ transition in these media is of the order (2—8) · 10^{-7}. According to the calculations its intensity is appreciably affected by a magnetic dipole contribution.

D. SOME SPECIFIC FEATURES OF THE SPECTROSCOPY OF LANTHANIDE COORDINATION COMPOUNDS IN SOLUTION

The spectroscopy of coordination compounds in solution is known to be complicated by the presence of chemical equilibria. In contrast to crystals two or more complex species resulting from dissociation, solvolysis, polymerization and isomerization reactions of a dissolved coordination compound can exist in equilibrium.

Therefore, one of the problems of primary importance is how to obtain the individual spectra of these species.

The individual absorption spectra of coordination compounds with given stoichiometric metal-to-ligand ratios, ML$_n$, can be derived from the overall spectra of solutions containing mixtures of consecutive complexes by a routine procedure, i.e. solving linear equations of the type

$$\bar{\epsilon}^{(\lambda)} = \sum_n \alpha_n \epsilon_n^{(\lambda)} \tag{22}$$

where $\bar{\epsilon}^{(\lambda)}$ is the mean molar extinction coefficient of solution at the wavelength λ, α_n are molar fractions of the metal in complexes ML$_n$, $\epsilon_n^{(\lambda)}$ are unknown molar extinction coefficients. However, for coordination compounds of lanthanides the ϵ_n values are low (seldom exceed 10 l mol cm^{-1}) while the band shifts in stepwise complexing are not high (within a few ten cm^{-1}) and the absorption spectra of consecutive complexes generally overlap. Therefore the calculation of the absorption spectra of the individual coordination compounds of the lanthanides can be correctly carried out only in cases where their solution spectra are taken with a fairly high resolution and highly accurate absorbance measurements.

In most cases the spectroscopy of lanthanide coordination compounds in solution is limited by systems in which only one, (maximum two) species exist. For some systems, however, the absorption spectra of individual species were derived from the overall spectra of their mixtures. They are mono-, bis- and tris-oxydiacetates of Pr(III), Nd(III), Eu(III) and Er(III) [127], mono- bis- and tris-benzoyiacetonates of Eu(III) [128], mono-β-diketonates of Eu(III) with various β-diketones [129]. As an example Fig. 7a shows same absorption spectra of solutions involving mixtures of Pr(III) oxydiacetate complexes of various composition while Fig. 7b represents the individual spectra which have been calculated with the help of eqn. (22).

Analysis of individual absorption spectra is usually made to obtain the crys-

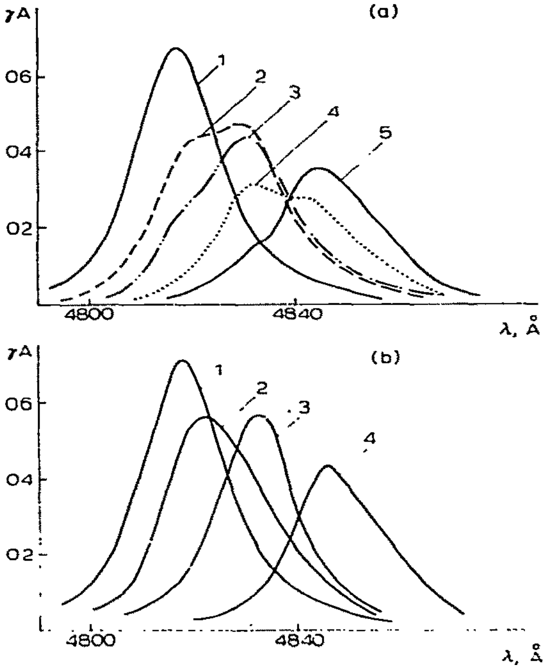


Fig. 7. (a) Absorption spectra of solutions involving Pr$_{aq}^{3+}$, Pr(oda)$^+$, Pr(oda)$_2^-$ and Pr(oda)$_3^{3-}$ at ratios: (1) 1 : 100 : 0 : 0; (2) 5 : 61 : 34 : 0; (3) 1 : 34 : 61: 4; (4) 0 : 2 : 54 : 44; (5) 0 : 0 : 11 : 89. (b) Absorption spectra of Pr$_{aq}^{3+}$ (1) and calculated spectra of Pr(oda)$^+$ (2), Pr(oda)$_2^-$ (3) and Pr(oda)$_3^{3-}$(4) [127]. ($^3P_0 \leftarrow {}^3H_4$ transition; γ is the coefficient of contrast for the photographic plate).

tal field (B_n^m), nephelauxetic (β) and intensity (T_λ) parameters for a given coordination compound. Then, using known relationships of spectroscopic, energy and geometric parameters one can get information on the structure of a complex compound.

Studying the structures of lanthanide coordination compounds in crystals one commonly uses band splittings. The band splitting components correspond to the transitions between the splitting sublevels of the lower and upper J-levels of a given transition. As the level splitting of lanthanides is not high at room temperature, the ground and some excited ligand—field sublevels of the ground J-levels can be populated according to the Boltzmann distribution law. Thus, the number of transitions may be very high. In the absorption spectra, however, one can observe only those transitions which are symmetry allowed. Their number is calculated by group theory [130]. Comparing the number of experimentally observed transitions with those allowed for various point-groups one can determine the symmetry of the lanthanide ion environment in the complex.

Unfortunately, the identification and analysis of ligand field spectra for lanthanide coordination compounds in solution often proves to be impossible. The fine structure of the absorption bands in the spectra is either unresolved or resolved incompletely because of small ligand—field splitting and broadening of bands due to an electron—vibronic interaction with a solvent. Karraker [160,161] proposed to study the overall shapes of unresolved bands comparing them with the shapes of the bands in the absorption spectra of the compounds of known structure.

In principle, the ligand—field spectra can be revealed by a mathematical resolution of bands into separate components but it is not possible without some assumption (about the shape, number, intensity of individual ligand—field bands). Therefore, the analysis of the fine structure of bands is limited, as a rule, by the "simplest bands", i.e. those which are split into the minimum number of ligand—field components. A list of such bands is given [131] but most of them are of very low intensity and are not observed in absorption spectra.

Analysis of the fine structure of the absorption bands corresponding to ${}^5D_{0,1,2} \leftarrow {}^7F_0$ transitions in the Eu(III) absorption spectra proves to be the simplest. Transitions from a non-degenerate ground level, ${}^7F_0$, arise in spectra as narrow bands. As the ground state does not split in the fields of any symmetry, the observed splitting can be unambiguously attributed to that of excited states. Table 2 lists data on ${}^5D_{0,1,2}$ level splitting and the activity of ${}^5D_{0,1,2} \leftarrow {}^7F_0$ transitions in ligand fields of various symmetry. The splitting of these bands in the absorption spectra was used in determining the symmetry of the environment of Eu(III) in solutions of its various complexes [127,132, 133].

The detection of the "extra" bands permits one to assume the existence, in solution, of more than one species of the coordination compound under examination ("spectral isomers"). The existence of isomeric species of complexes

TABLE 2

The splitting of $^5D_0$, $^5D_1$ and $^5D_2$ levels and the activity of $^7F_0 \to {^5D_{0,1,2}}$ transitions in the spectra of Eu(III) in ligand fields of different symmetry (according to the selection rules on symmetry only)

Symmetry	$^5D_0$			$^5D_1$			$^5D_2$		
	Sublevel splitting	Active as[a]		Sublevel splitting	Active as[a]		Sublevel splitting	Active as[a]	
		ED	MD		ED	MD		ED	MD
C_s	A'	A'	A'	$A'\ 2A''$	$A'\ 2A''$	$A'\ 2A''$	$3A'\ 2A''$	$3A'\ 2A''$	$3A'\ 2A''$
C_2	A	A	A	$A\ 2B$	$A\ 2B$	$A\ 2B$	$3A\ 2B$	$3A\ 2B$	$3A\ 2B$
C_{2v}	A_1	A_1	—	$A_2\ B_1\ B_2$	$B_1\ B_2$	$A_2\ B_1\ B_2$	$2A_1\ A_2\ B_1\ B_2$	$2A_1\ B_1\ B_2$	$A_2\ B_1\ B_2$
C_{2h}	A_g	—	A_g	$A_g\ 2B_g$	—	$A_g\ 2B_g$	$2A_g\ 3B_g$	—	$2A_g\ 3B_g$
C_3	A	A	—	$A\ E$	$A\ E$	$A\ E$	$A\ 2E$	$A\ 2E$	$A\ 2E$
C_{3v}	A_1	A_1	—	$A_2\ E$	E	$A_2\ E$	$A_1\ 2E$	$A_1\ 2E$	$2E$
C_{3h}	A'	—	A'	$A'\ E''$	—	$A'\ E''$	$A'\ E'\ E''$	E'	$A'\ E''$
C_4	A	A	A	$A\ E$	$A\ E$	$A\ E$	$A\ 2B\ E$	$A\ E$	$A\ E$
C_{4v}	A_1	A_1	—	$A_2\ E$	E	$A_2\ E$	$A_1\ B_1\ B_2\ E$	$A_1\ E$	E
C_{4h}	A_g	—	A_g	$A_g\ E_g$	—	$A_g\ E_g$	$A_g\ 2B_g\ E_g$	—	$A_g\ E_g$
D_2	A	—	—	$B_1\ B_2\ B_3$	$B_1\ B_2\ B_3$	$B_1\ B_2\ B_3$	$2A\ B_1\ B_2\ B_3$	$B_1\ B_2\ B_3$	$B_1\ B_2\ B_3$
D_{2h}	A_g	—	—	$B_{1g}\ B_{2g}\ B_{3g}$	—	$B_{1g}\ B_{2g}\ B_{3g}$	$2A_g\ B_{1g}\ B_{2g}\ B_{3g}$	—	$B_{1g}\ B_{2g}\ B_{3g}$
D_{2d}	A_1	—	—	$A_2\ E$	E	$A_2\ E$	$A_1\ B_1\ B_2\ E$	$B_2\ E$	E
D_3	A_1	—	—	$A_2\ E$	$A_2\ E$	$A_2\ E$	$A_1\ 2E$	$2E$	$2E$
D_{3h}	A'_1	—	—	$A'_2\ E''$	—	$A'_2\ E''$	$A'_1\ E'\ E''$	E'	E''
D_{3d}	A_{1g}	—	—	$A_{2g}\ E_g$	—	$A_{2g}\ E_g$	$A_{1g}\ 2E_g$	—	$A_{1g}\ E_g$
D_4	A_1	—	—	$A_2\ E$	$A_2\ E$	$A_2\ E$	$A_1\ B_1\ B_2\ E$	E	E
D_{4h}	A_{1g}	—	—	$A_{2g}\ E_g$	—	$A_{2g}\ E_g$	$A_{1g}\ B_{1g}\ B_{2g}\ E_g$	—	E_g
D_{4d}	A_1	—	—	$A_2\ E_3$	—	$A_2\ E_3$	$A_1\ E_1\ E_2$	E_1	—
T_d	A_1	—	—	T_1	—	T_1	$E\ T_2$	T_2	—
O_h	A_{1g}	—	—	T_{1g}	—	T_{1g}	$E_g\ T_{2g}$	—	—

[a] ED = Electric dipole; MD = Magnetic dipole.

with the same metal-to-ligand ratio can be clearly concluded on investigating the spectra of Eu(III) in the region of the $^5D_0 \leftarrow {}^7F_0$ transition, where only one band is possible for each species. The presence of more than one band within the *O*—*O* transition was observed, for example, in the solution spectra for Eu(III) complexes with EDTA [134,135] and β-diketones [128].

The nephelauxetic parameter β is considered to be a spectroscopic covalency parameter of the metal—ligand bonds in the complex. The values of β for Pr(III) and Nd(III) complexes with various ligands were determined from their solution spectra with the help of eqn. (13) [249—254].

However, it is necessary to have in mind that a nephelauxetic series of ligands for any metal ion is valid only if the complexes under investigation have the same structure. This condition must be more strictly checked while constructing the nephelauxetic series for lanthanide ions as the latter can have various coordination numbers easily changed in the substitution of ligands. Moreover the nephelauxetic band shifts due both to ligand substitution and coordination number change have the same order of magnitude and cannot be differentiated without special investigation.

The correlation relationship between the energy of some *J*—*J* transitions (ν, cm^{-1}) and the mean metal—ligand distances ($\bar{R}$, Å) were suggested for use in determining R and estimating the coordination numbers of lanthanide ions in complexes from spectral data [54,55]. Figures 8 and 9 illustrate the procedure for Pr(III) and Nd(III) complexes. The X-ray ($\bar{R}$) and spectral (ν) data

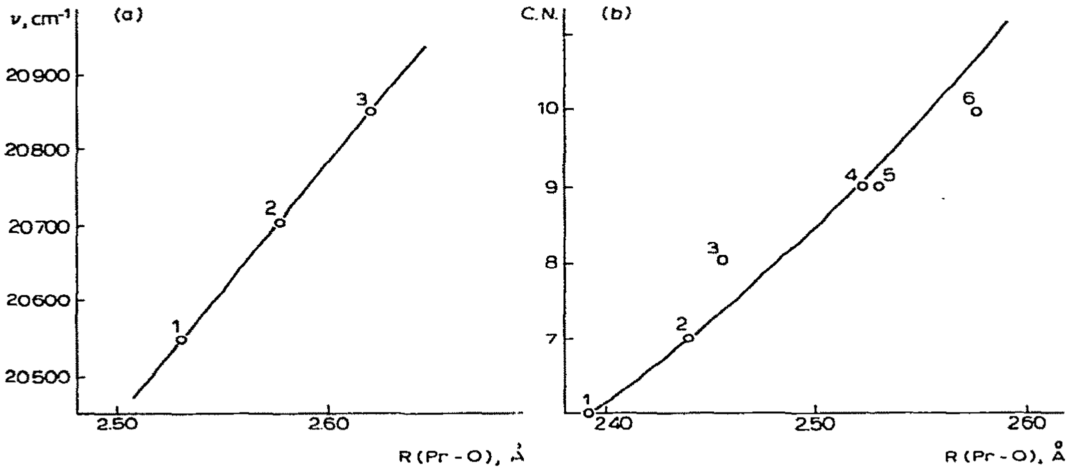


Fig. 8. (a) Dependence of $^3P_0 \leftarrow {}^3H_4$ transition energy (ν) in the absorption spectra for Pr(III) complexes on mean Pr—O distances in PrO_x chromophores: (1) $Pr(C_2H_5SO_4)_3 \cdot 9\ H_2O$ [142]; (2) $Pr(NO_3)_3 \cdot 6\ H_2O$ [143]; (3) $Pr_2Mg_3(NO_3)_{12} \cdot 24\ H_2O$ [144]; ($R_{Pr—O}$ is determined by extrapolation from $Ce_2Mg_3(NO_3)_{12} \cdot 24\ H_2O$ [145]. (b) Interrelation between praseodymium coordination numbers (CN) and $\bar{R}$(Pr—O): (1) C-Pr_2O_3 [146]; (2) Pr_2 (dpm)$_6$ [137]; (3) $NH_4Pr(tta)_4$ [138]; (4) $Pr_2(C_2O_4)_3 \cdot 10\ H_2O$ [139]; (5) $Pr(C_2H_5SO_4)_3 \cdot 9\ H_2O$ [140]; (6) $Pr(NO_3)_3 \cdot 6\ H_2O$ [141].

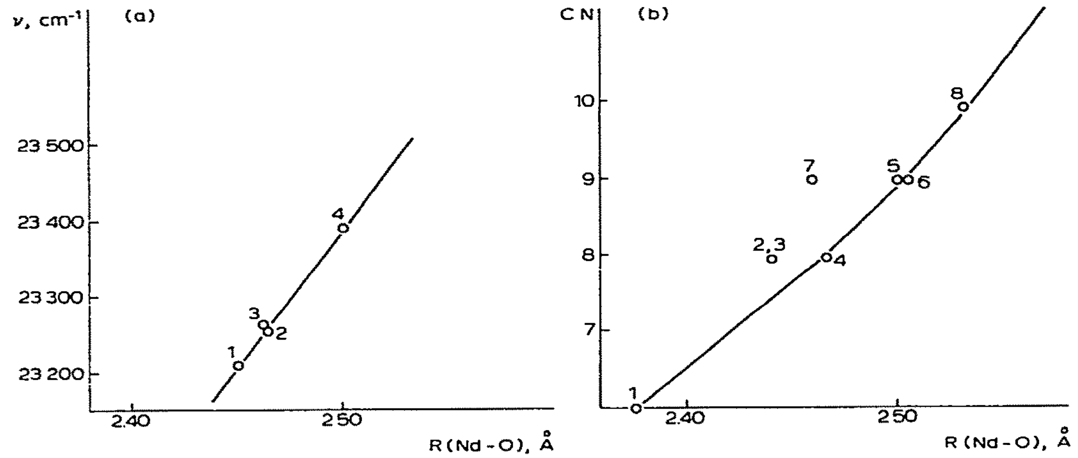


Fig. 9. (a) Dependence of $^2P_{1/2} \leftarrow {}^4I_{9/2}$ transition energy in absorption spectra for Nd(III) complexes on mean Nd—O distances in NdO_x chromophores: (1) $Nd(BrO_3)_3 \cdot 9\ H_2O$ [153]; (2) $Nd(aca)_3 \cdot 3\ H_2O$ [55]; (3) $K_3Nd(oda)_3 \cdot 2\ NaClO_4 \cdot 6\ H_2O$ [127]; (4) $(C_5H_{11}N)$ [Nd(bac)$_4$] [55]. (b) Interrelation between neodymium coordination numbers and $\bar{R}$(Nd—O): (1) C-Nd_2O_3 [146]; (2) $Nd(tta)_3 \cdot 2$ TPPO [147]; (3) (C_5H_6N) [Nd(tta)$_4$] [148]; (4) $Nd(aca)_3 \cdot 3\ H_2O$ [149]; (5) $Nd(BrO_3)_3 \cdot 9\ H_2O$ [150]; (6) $Nd_2(C_2O_4)_3 \cdot 10\ H_2O$ [139]; (7) $Na_3Nd(oda)_3 \cdot 2\ NaClO_4 \cdot 6\ H_2O$ [151]; (8) $Nd(NO_3)_3 \cdot 4$ DMSO [152].

for the same lanthanide compounds in crystal states are necessary to obtain the plots shown in Figs. 8a and 9a. The curves in Figs. 8b and 9b represent the theoretical dependences between R and coordination numbers (CN) [136], the points are put in accordance with the X-ray evidence for various crystals. Thus using the experimental ν value one can determine $\bar{R}_{\mathrm{Ln—O}}$ from Figs. 8a and 9a and then evaluate CN from the dependence shown in Figs. 8b and 9b.

The dependence of band intensities in the absorption spectra of transition metal ions on the ligand concentration is commonly used to study chemical equilibria in solutions of complex compounds. The absorption in the region of *f*—*f* transitions in determining the composition and stability constants for lanthanide complexes was first applied by Sonesson in his investigation on Er(III) acetate [154] and Nd(III) glycolate [155] complexes. For lanthanide complexes of low stability a differential approach [156] enables one to work with high concentrations of metal ions. A so-called "spectrographic" procedure [157] is based on measuring the intensities of individual band splitting components depending upon the ligand concentration by spectrographs of high resolution. It is a visual working tool which permits one to obtain data on the composition, conditions of existence and stability of complexes.

To calculate the stability constants of lanthanide complexes Bukietinska et al. [158] make use of integrated band intensities.

An application of intensities to the study of structure of lanthanide complexes in solution has, so far been limited and, in most cases, is based upon empirical correlations. It has been pointed out [132] that very low intensities of forced electric—dipole transitions, sometimes lower than those of magnetic—dipole transitions, may indicate that the ligand field belongs to a point-group symmetry with a centre of inversion. They have used this criterion in determining the ligand field symmetry for a Eu(III) aquo-ion. Ryan and Jørgensen [52] have made use of such an intensity ratio to prove the octahedral structure of hexahalide complexes, LnHal_6^{3-}.

Choppin et al. [159] have applied the intensity of the Nd(III) hypersensitive transitions to distinguish inner- and outer-sphere complexing. Karraker [160] determined the coordination numbers for Nd(III), Ho(III) and Er(III) ions in solutions of their complexes with β-diketones using a comparison of intensities (and band shapes) of hypersensitive transitions with those of crystalline β-diketonate complexes of known structure.

It has been suggested [162] that the intensity of the hypersensitive transition in the spectrum of Nd(III) may be employed in determining whether the metal ion is bound to protein by a carboxylic or an amino-carboxylic group.

E. APPLICATION OF SPECTROSCOPY TO THE INVESTIGATION OF LANTHANIDE COORDINATION COMPOUNDS IN SOLUTION

(i) Solvato-complexes

(a) Aquo-complexes

So far, the composition and the structure of lanthanide aquo-complexes are, in many respects, open to question. Chemists are not agreed upon the magnitudes of the coordination numbers of lanthanides involved in aquo-complexes, their constancy or variation in the lanthanide series and existence, for each given lanthanide, of one or several equilibrium species of aquo-complexes differing by their composition and/or structure.

In 1966 Spedding et al. [163—166] in interpreting their thermodynamic and kinetic data measured for dilute aqueous solutions of lanthanide inorganic salts, put forward a hypothesis that the coordination numbers of lanthanides in aquo-ions were changed from 9 for light to 8 for heavy lanthanides. For elements occupying the middle position in the lanthanide series, they suggested the existence of the two equilibrium species, $\mathrm{Ln(H_2O)_9^{3+}}$ and $\mathrm{Ln(H_2O)_8^{3+}}$. To verify and prove their hypothesis Spedding and co-workers have carried out many investigations [126,167—173]. This hypothesis is often used to account for the thermodynamic parameters, ΔH and ΔS [174—178], and the rates [179—181] in complexing of lanthanides in aqueous solution.

Karraker [161] has pointed out that the coordination numbers of lanthanides in aquo-complexes can vary if the concentration is changed and the coordination number of Nd(III), in particular, varies from 9 to 8 when the concentration of chloride in solution is increased. The assumption was confirmed by Nakamura and Kawamura's [182] data on the nuclear magnetic relaxation rate for ^{139}La in aqueous salt solutions. In accordance with the latter in aqueous lanthanum perchlorate solutions there exists the equilibrium

$$La(H_2O)_9^{3+} \rightleftharpoons La(H_2O)_8^{3+} + H_2O \qquad (23)$$

which shifts to the right if the concentration of the solution is increased.

However, some other investigators, on the basis of the dissolution heat measurements for hydrated chlorides [183], partial molar heat capacity measurements [184] and NMR spectra of ^{17}O [185] for rare earth perchlorates have concluded that the coordination numbers for all lanthanide ions in aquo-complexes are identical. Using NMR-spectroscopy Reuben [186] has stated that La^{3+} is nine-coordinated both in dilute and concentrated aqueous $LaCl_3$ solutions. Nevertheless, X-ray spectral studies [187,188] show that the dominating species in concentrated aqueous $LaCl_3$ and $LaBr_3$ solutions is octaaquo—lanthanum (III).

The absorption spectra in the region of *f—f* transitions of Ln^{3+} ions have also been used to determine the composition and the structure of lanthanide aquo-complexes. Comparing the absorption spectra of dilute aqueous neodymium perchlorate solutions with those of neodymium inorganic salt crystallohydrates of known composition and structure Krumholz [189] has revealed a marked similarity between the absorption spectra for Nd_{aq}^{3+} and $Nd(BrO_3)_3 \cdot 9H_2O$. In accordance with Helmholz' X-ray data [150] the environment of the neodymium ion in this crystallohydrate involves nine water molecules located at the vertices of a three-capped trigonal prism (D_{3h} symmetry). The similarity of the absorption spectra for Nd_{aq}^{3+} and $Nd(BrO_3)_3 \cdot 9\ H_2O$ proved to be the most convincing evidence for the coordination number 9 and D_{3h} symmetry for neodymium(III) aquo-ion.

A comparative spectroscopy procedure has been extended to aquo-ions of other lanthanides [190,191]. The absorption spectra of neodymium, europium and erbium perchlorates in dilute solutions have been compared with those for isostructural (for these elements) crystallohydrates of the corresponding lanthanides, $LnCl_3 \cdot 6\ H_2O$ and $Ln(BrO_3)_3 \cdot 9\ H_2O$. It has been shown that the absorption spectrum for a Nd(III) aquo-ion in the position and fine structure of the bands is fairly close to that for bromate, but differs from the spectrum for chloride. At the same time, the absorption spectrum for an erbium(III) aquo-ion reveals a close resemblance with that for $ErCl_3 \cdot 6\ H_2O$ but differs from $Er(BrO_3)_3 \cdot 9\ H_2O$. The absorption spectrum for a europium(III) aquo-ion proved to be different from those for $EuCl_3 \cdot 6\ H_2O$ and $Eu(BrO_3)_3 \cdot 9\ H_2O$. These findings agree with the assumption that the different lanthanides have different structures for their aquo-ions.

The absorption spectrum for a europium(III) aquo-ion has been examined in detail [132,192,193]. In the visible region it is of low intensity. Under the usual experimental conditions, the $^7F_0 \leftarrow {}^5D_0$ transition does not manifest itself and can be observed only at a path length of absorption of about 11 m [192]. Sayre et al. [132] have shown that the intensity of the magnetic—dipole transition, $^5D_1 \leftarrow {}^7F_0$ is close to that of the forced electric—dipole transition, $^5D_2 \leftarrow {}^7F_0$. They pointed out that such a relationship of intensities is, in accordance with the selection rules, possible only in fields having a centre of inversion. The number of maxima of these spectral bands (3 and 5) is identical with the splitting component number of the $^5D_1$ and $^5D_2$ levels in fields of low symmetry. Taking these facts into account and assuming, for europium, a coordination number of 8, the authors have suggested that the spectrum for Eu^{3+}_{aq} can be assigned only to the europium aquo-ion species with D_{2h} symmetry. Analogous interpretation of the absorption spectrum for Eu^{3+}_{aq} has been reported [193].

In order to find out whether the equilibrium europium(III) aquo-ion species having different coordination numbers exist, Geier and Karlen [194] studied the temperature dependence of the absorption spectrum of dilute aqueous $Eu(ClO_4)_3$ solution in the region of the $^5L_6 \leftarrow {}^7F_0$ transition. They revealed no changes in the spectrum within a temperature range of 25 to 91°C and also suggested that only one europium(III) aquo-ion species exists. However, Lugina and Davidenko [191] have observed that a fairly distinct temperature dependence in the Eu^{3+}_{aq} spectrum can be observed in the region of the magnetic dipole $^5D_1 \leftarrow {}^7F_0$ transition, which manifests itself in the redistribution of relative intensities of long-wave and short-wave bands (Fig. 10). The influence of outer-sphere complexing with Cl^-, ClO_4^-, BrO_3^- and SCN^- anions upon the absorption spectrum for Eu^{3+}_{aq} in the $^5D_{0,1,2} \leftarrow {}^7F_0$ transitions has also been investigated. Some of the spectra obtained are given in Fig. 11. The outer-sphere bonding of the above inorganic anions results in a marked increase in the integrated intensity of the hypersensitive $^5D_2 \leftarrow {}^7F_0$ transition and a change in the relative intensities of its separate components. In the $^5D_0 \leftarrow {}^7F_0$ transition two low intensity bands appear simultaneously and their intensities depend upon the nature and the concentration of the ligand involved in the outer-sphere complexing. Changes in the $^5D_1 \leftarrow {}^7F_0$ transition due to outer-sphere complexing are similar to those which occurred with temperature variation. Neither band shifts nor new absorption bands are observed in this case

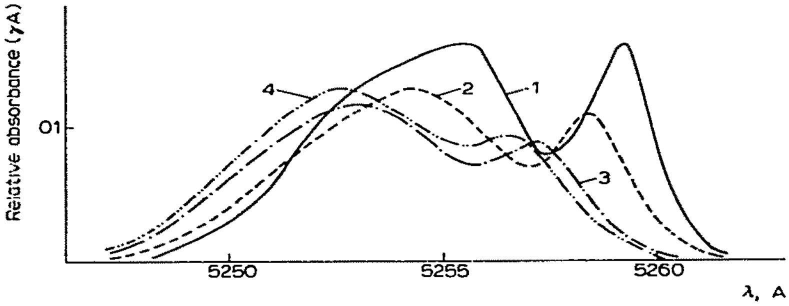


Fig. 10. Absorption spectra of 0.064 M $Eu(ClO_4)_3$ solution in $^5D_1 \leftarrow {}^7F_0$ transition at 3° (1), 25° (2), 55° (3) and 80° (4) [191].

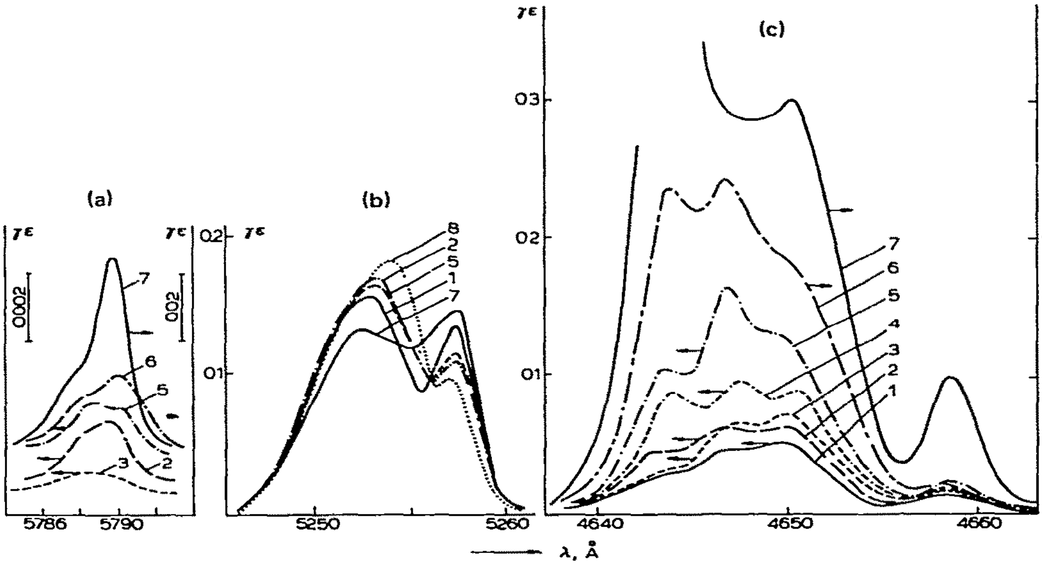


Fig. 11. Absorption spectra of Eu(III) salt solutions in transitions: (a) ${}^5D_0 \leftarrow {}^7F_0$; (b) ${}^5D_1 \leftarrow {}^7F_0$; (c) ${}^5D_2 \leftarrow {}^7F_0$ [191]. (1) 0.036 M $Eu(ClO_4)_3$; (2) 1 M $EuCl_3$; (3) 1 M $Eu(ClO_4)_3$; (4) 0.10 M $Eu(ClO_4)_3$ in 5 M LiCl; (5) 1 M $Eu(BrO_3)_3$; (6) 0.10 M Eu $(ClO_4)_3$ in 0.4 M KCNS; (7) 0.10 M $Eu(ClO_4)_3$ in 10 M LiCl; (8) 0.10 M $Eu(ClO_4)_3$ in 8 M $NaClO_4$.

which confirms the absence of the inner-sphere complexing under given conditions. These findings can be satisfactorily interpreted only on the basis of the hypothesis that there exist more than one europium(III) aquo-ion species and that the equilibrium between them shifts according to outer-sphere complexing. An attempt has also been made to resolve the bands in the region of the ${}^5D_1 \leftarrow {}^7F_0$ transition into the individual ligand field components. In spite of the approximations used the resolution has invariably resulted in more than three (6—7) components which is also indirect evidence in favour of the existence of two or a greater number of europium(III) aquo-ion species.

The existence of the "extra" bands in the absorption spectra for aquo-ions have been indicated for other lanthanides as well, in particular, for neodymium [189] and cerium [195]. It has been accounted for by a small quantity of aquo-ions with smaller coordination numbers present in solution alongside the dominating aquo-ion species of these lanthanides.

(b) Non-aqueous and mixed solvato-complexes

Information on the composition and structure of lanthanide ion solvato-complexes with non-aqueous solvent molecules is scarce and has been obtained mainly from spectroscopic studies. The luminiscence and absorption spectra for alcoholic and mixed alcohol—aqueous solutions of lanthanide chlorides have been investigated in detail [132,196—207]. The absorption spectra of $LnCl_3$ in the region of *f—f* transitions of Ln^{3+} ions in aquo—alcoholic solutions containing less than 80—85% of alcohol are largely similar to those for aquo ions of the corresponding lanthanides. A further increase in the alcohol concentration of the solvent results in shifts of the absorption bands and changes in their shapes and, also, increase in the intensity of hypersensitive transitions. These changes have been attributed [196—202] to resolvation, i.e. the substitution of the water molecules in the nearest environment of the lanthanide ion by alcohol molecules. The number of the alcohol molecules in alcoholic solvato-complexes of Pr(III) and Nd(III) [198,202,206] was found to be six. The possibility of the coordination of chlorine ions to a lanthanide ion in alcohol solutions has not been taken into account.

Sayre et al. [132] have accepted the coordination number for Eu(III) of 8 and examined the fine structure of bands due to $^5D_{0,1,2} \leftarrow {}^7F_0$ transitions. They have assigned the symmetry of alcoholic europium solvate to the C_{2v} point group.

According to another viewpoint [203—205,207,213] the discrepancies observed in the absorption spectra of aqueous and alcoholic $LnCl_3$ solutions are, in the first place, due to the presence of chloride complexes in alcoholic solutions. The evidence of the existence of inner-sphere halogenide complexes with lanthanide ions in $NdCl_3$ and $LaCl_3$ methanol solutions was obtained recently by X-ray diffraction [226,237]. The composition and stability constants of lanthanide halogenide complexes in alcoholic and alcohol—aqueous solutions have been determined by spectrophotometry [208—212].

Davidenko et al. [204] have shown that the absorption spectra for methanolic solutions of lanthanide inorganic salts depend upon the nature of the dissolved salt anion and that the differences observed in the absorption spectra for alcohol solutions from those for aqueous solutions of the same salts increase in the series of lanthanides: Er < Eu < Nd and anions: $ClO_4^- < BrO_3^- < Cl^-$.

The existence of chloride complexes in $EuCl_3$ solutions in 80—100% methanol is indicated by the presence of the band due to the charge-transfer from chlorine to europium. At lower methanol concentration, this band is not observed. Meantime, the band due to the charge transfer from methanol to europium has already appeared in the absorption spectra of solutions containing ~30% methanol. Thus, a substitution of H_2O molecules in the nearest environment of the europium ion by methanol molecules does not markedly affect the *f—f* transitions. The differences observed in the absorption spectra of aqueous and alcohol $LnCl_3$ solutions are due to the coordination of chlorine ions and, perhaps, simultaneous change in the geometry of a chromophore.

Jezowska-Trzebiatowska and co-workers have studied the absorption spectra for $PrCl_3$ and $NdCl_3$ in the visible [203,207] and near UV [213] regions. From the data obtained on the position and intensities of the spectral bands due to *f—f*, *f—d* and charge-transfer transitions they have made some conclusions about the composition and the symmetry of chloride—alcohol complexes present in these solutions.

Abrahamer and Marcus [214] have studied the absorption spectra of neodymium and europium nitrates in different organic solutions. By comparing the shape and intensity of spectral bands they have obtained the following relative affinity series of the nitrate anion and solvent molecules towards lanthanide ions: DMF > TBP > NO_3^- > H_2O > C_2H_5OH > dioxan.

The intensity of ${}^5D_{0,2} \leftarrow {}^7F_0$ bands has been used by Haas and Stein [215] as a measure of relative tendency for NO_3^- and ClO_4^- anions towards complexing with a europium ion in different solvents. The complexing with a nitrate anion was found to be decreased in the solvent sequence: acetonitrile > methanol > water. With a perchlorate anion it was observed only in acetonitrile, and an ionic pair is expected to be formed in this case.

To determine the state of lanthanide salts in amide and nitrile solvents Bukietinska et al. [205] have analysed the intensities based on the Judd—Ofelt theory. A considerable increase in the T_2 parameter (compared to aqueous solutions) was assumed as an indication of anion penetration into the inner coordination sphere.

Lugina et al. [217] have examined the absorption spectra for Nd(III) in the ${}^2P_{1/2} \leftarrow {}^4I_{9/2}$ transition in DMSO, DMF and mixed H_2O—DMSO and H_2O—DMF neodymium perchlorate solutions. From electroconductivity data it follows that $Nd(ClO_4)_3$ is completely dissociated in such solutions. Figure 12 shows a number of spectra of 0.05 M $Nd(ClO_4)_3$ in solvents with various ratios of DMSO: H_2O and, also, the reflection spectra of crystallosolvates, $Nd(ClO_4)_3 \cdot 8$ DMSO. In solution spectra one can observe two bands the relative intensity of which depends upon the solvent composition. These bands have been assigned to NdO_9 and NdO_8 chromophores based on their genesis, the comparison with crystallosolvate spectra and the known [54,55] relationship between nephelauxetic band shifts, Nd—O distances and Nd(III) coordination

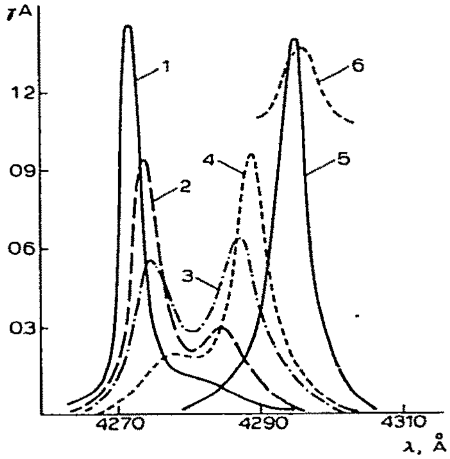


Fig. 12. Absorption spectra of 0.05 M $Nd(ClO_4)_3$ in H_2O (1), DMSO (5) and in mixed H_2O—DMSO solvents at ratios (vol); 10 : 1 (2); 6 : 1 (3); 3.5 : 1 (4) and reflectance spectrum of $Nd(ClO_4)_3 \cdot 8$ DMSO (6) [217]. (${}^2P_{1/2} \leftarrow {}^4I_{9/2}$ transition).

numbers (see Fig. 9). It follows that in the anhydrous DMSO there exists one solvate species, $Nd(DMSO)_8^{3+}$, and in anhydrous DMF along with the dominating species $Nd(DMF)_8^{3+}$ a small quantity of $Nd(DMF)_9^{3+}$ is also present. In mixed solvents the equilibrium has been found to exist between the aqueous–organic mixed solvato-complexes with the Nd(III) coordination number 9 and 8. This equilibrium shifts towards eight-coordinated solvato-complexes if the portion of non-aqueous solvent is increased. The substitution of H_2O molecules by the DMSO (DMF) molecules in both eight- and nine-coordinated solvatocomplexes is accompanied by a longwave shift in the corresponding spectral bands. These shifts have been used to estimate the stepwise formation constants for H_2O—DMSO (DMF) solvato-complexes.

Lanthanide dimethyl formamide and hexamethyl phosphoramide complexes in nitromethane have been studied by a spectroscopic procedure [218]. The absorption spectra for hydrated lanthanide perchlorates in nitromethane are identical to those of the corresponding lanthanide aquo-ions. The addition of DMF to the solution results in the shift of spectral bands which indicates the substitution of H_2O molecules, in the nearest environment of the lanthanide ion, by DMF molecules. The coordination numbers of lanthanides in DMF and in mixed H_2O—DMF complexes (in nitromethane) have been determined by comparing the data on the dependence of the band shift upon the DMF concentration with those obtained by IR-spectroscopy. For Er(III), the coordination number was found to be 6. For Pr(III) and Nd(III), equilibrium was found to exist between solvato-complexes with the coordination numbers 8 and 9. It was also found that the maximum number of HMPA molecules which can be directly coordinated to a neodymium ion does not exceed 6, but the overall coordination number of Nd(III) in these solvato-complexes is 8 due to additional coordination of water molecules or inorganic anions present in solution.

Barraclough et al. [219] have examined the spectra for Pr(III) and Nd(III) in anhydrous HF solution and found that the position and intensity of their spectral bands are similar to those for Pr(III) and Nd(III) in aquo-ion spectra and in crystalline LnF_3. They suggested that metal ions are present in the HF solution simply as solvated cations with the coordination type identical to that in water.

(ii) Lanthanide coordination compounds with halogenide ions

From the data obtained by various physico-chemical methods the inner-sphere of lanthanide chloride complexes is not formed in aqueous solutions [159,185,220—225]. This conclusion contradicts the recent X-ray diffraction data [216,226] which suggest that in the concentrated $LnCl_3$ solution in 10 M HCl the Ln^{3+} ions are coordinated by seven H_2O molecules and a Cl^- ion.

The absorption spectra for Ln(III) ions in aqueous solutions of HCl and alkali chlorides have been examined within a wide range of the chloride concentration. The absorption spectra for Nd(III) in solutions containing less than 5—6 M of chloride do not differ from those for Nd(III) aquo-ion which indicates the absence of the inner-sphere chloride complexes. However, if the concentration of chloride in solution is increased one can observe longwave band shifts and changes in the shape and intensity of the bands [156,161, 227,228]. These changes have been attributed [156,227] to the formation of inner-sphere chloride complexes.

Karraker [161] has interpreted these changes as being due to a decrease in the coordination number of Nd(III) retaining only the nearest aqueous environment.

The absorption spectrum of Eu(III) is somewhat more sensitive to an increase in the concentration of the Cl^--ions involved in solution. Figure 11 shows that the spectrum for Eu(III), even in 5 M LiCl, markedly differs from that for the europium aquo-ion: the intensity of the $^5D_2 \leftarrow {}^7F_0$ transition increases, the relative intensity of short- and longwave components of the $^5D_1 \leftarrow {}^7F_0$ transition is redistributed and two weak bands appear at the $^5D_0 \leftarrow {}^7F_0$ transition. At higher chloride concentration these differences increase. However, up to 13—14 M LiCl no appreciable longwave band shifts have been observed which might have indicated the formation of inner-sphere complexes. It has been suggested that these changes in the spectrum can be interpreted by a shift in the equilibrium between different species of europium aquo-ions due to the outer-sphere complexing of a chloride ion.

The absorption spectra of heavier lanthanide ions (Er^{3+}, Ho^{3+}) are not changed up to a chloride concentration as high as 13—14 M. It follows that neither inner-sphere coordination of chloride ions nor changes in the coordination numbers of heavy lanthanides take place in aqueous solutions [161].

Ryan and Jørgensen [52] have obtained, for the first time, inner-sphere hexahalogenide complexes of lanthanides in non-aqueous solutions and have examined their absorption spectra in the *f*—*f* and charge-transfer regions. They have developed a special procedure for isolation of lanthanide hexahalogenide complexes as phosphonium salts, $[PH(C_6H_5)_3]_3[LnHal_6]$ (where $Hal^- = Cl^-$, Br^-) and studied the conditions of the existence of hexahalogenide complexes, $LnHal_6^{3-}$ in nitrile solvents. The absorption spectra of lanthanide hexahalogenide complexes exhibit some special features which allow one to assign complexes both in the solid state and in solutions to an octahedral structure. In the first place, there is a very low intensity for all bands corresponding to the *f*—*f* transitions, the intensity of which except for hypersensitivity has remained approximately the same as in the absorption spectra of the aquo-ions. Moreover, the vibronic structure of these bands is typical of octahedral complexes. The nephelauxetic effects, $d\beta$ for $LnHal_6^{3-}$ exceed the known values $d\beta$ for lanthanide ions in the $LaCl_3$ lattice, but are less than those for oxides. Some parameters for charge-transfer bands (energy, molar extinction coefficients) have been determined in the absorption spectra for Sm(III), Eu(III), Tm(III), Yb(III) and Ce(IV). The origin of the bands has been discussed. The apparent optical electronegativities for lanthanide ions have also been calculated.

The optical evidence indicates the existence of mono-, di- and tert-chloride complexes of lanthanides in anhydrous alcohols (see E. 1b). Lanthanide hexachloride complexes exist in anhydrous ethanol solutions containing more than 2 M HCl [229,230]. The Eu(III) ions are completely bound into the hexahalogenide complexes at a HCl concentration of 5.5 M while Pr(III) and Nd(III) ions require concentrations of HCl higher than 8 M. The absorption spectra for Ln(III) in such solutions are identical to those for $LnCl_6^{3-}$ studied in nitrile solvents by Ryan and Jørgensen. The octahedral structure of these complexes has been confirmed by qualitative analysis of Stark splitting levels and intensities.

(iii) Lanthanide coordination compounds with carboxylic and oxycarboxylic acids

There is little information on the structure of lanthanide carboxylate complexes received from the absorption spectra for Ln(III). The longwave shift of the $^3P_0 \leftarrow {}^3H_4$ transition band in the spectrum for Pr(III) in complexing with the anions of malic, tartaric and trioxyglutaric acids has been investigated [231]. The data reveal an approximate additivity of the shift in the band examined, i.e. each group coordinated towards a praseodymium ion contributes to the overall shift. In this case it was possible to attribute nearly equal shift increments to the similar groups (carboxylic, alcoholic) resulting from different acids. The possibility of taking advantage of such increments for studying structure has been suggested.

The approach has been applied in studying the structure of the nearest environment of lanthanide ions in their complexes with β-diketones [232] and polyaminopolycarboxylic acids [233].

However, the regularities of the shift in absorption band proved to be more complicated and, in particular, one should take into account the possibility of changing the coordination number of the lanthanide ion in complexing.

The absorption spectra of aqueous solutions containing the Nd(III) [234] and Er(III) [235] glycolate complexes and Nd(III) citrate complexes [236] have also been studied. The assignments of bands in the spectra to complexes with different metal-to-ligand ratios have been made on the basis of the equilibrium diagram. It was pointed out [235] that the formation of a chelate grouping, in particular, in complexing with erbium can bring about a shortwave band shift.

Choppin et al. [159] examined the absorption spectra of acetate complexes of neodymium in solution. They found that in the formation of a monoacetate complex the band intensity due to a hypersensitive transition for Nd(III) remained unchanged and only a small longwave band shift in the spectrum had taken place. The formation of a diacetate complex is followed by a sharp increase in the intensity of this band and a marked longwave shift. Such changes in the absorption spectrum have been accounted for by the fact that the penetration of a second acetate anion into the inner coordination sphere, unlike the first one, causes significant alterations in the structure of a NdO_x chromophore.

The absorption spectra of lanthanide (Pr, Nd, Eu and Er) oxydiacetate complexes have been studied in greater detail [127]. Good resolution of the fine structure of the ($^5D_2 \leftarrow {}^7F_0$) band has been obtained in the absorption spectra of Eu(III) oxydiacetate complexes. Analysis of the fine structure of the band based on the selection rules of symmetry-allowed transitions made it possible to obtain information on the ligand field symmetry in Eu(III) oxydiacetate complexes in solution. In the spectra of Pr(III), Nd(III) and Er(III) oxydiacetates the fine structure has remained unresolved. It has been found that stepwise complexation of Pr(III) and Nd(III) is followed by a steady longwave band shift indicating a decrease in the mean Ln—O distances in their LnO_9 chromophores on substituting the H_2O molecules in the aquo-ions by oxydiacetate acid anions. The values of $\bar{R}$(Ln—O) in oxydiacetate complexes of Pr(III) and Nd(III) and effective coordination numbers of lanthanides, CN_{eff}, evaluated from the position of spectral bands are given in Table 3. Stepwise complexation of Eu(III) and Er(III) with oxydiacetate anions is followed by non-monotonic band-shift. Non-monotony has been accounted for by an overlap of the two effects: the increase in coordination number of lanthanide up to 9 (as the aquo-ions of these elements have smaller coordination numbers) results in band shifts to higher energy and the substitution of H_2O molecules by oxydiacetate anions gives rise to a longwave band shift. The coordination numbers of all lanthanides in tris-oxydiacetates in solution are equal to 9. This follows from the similarity of their spectra with those of crystalline salts of tris-oxydiacetates, $K_3[Ln(CO_2CH_2OCH_2CO_2)_3] \cdot 2\ NaClO_4 \cdot 6\ H_2O$ of known structure [151,238].

(iv) Lanthanide coordination compounds with β-diketones

The absorption and luminescence spectra of lanthanide β-diketonates were intensively studied in the sixties, particularly with the problem of creating liquid lasers. Most of the investigations deal with the determination of luminescent characteristics of tetrakis-β-diketonates and processes of intramolecular energy transfer at their excitation. We shall below quote only those works which were aimed at determining the state of β-diketonate complexes in solution and the structure of the species present.

It is known that there exist two series of crystalline lanthanide β-diketonates: tetrakis-diketonates, $C^+[Ln(\beta\text{-diket})_4]$ (where C^+ is an inorganic or organic cation) and tris-β-diketonates, $Ln(\beta\text{-diket})_3$. The latter are, from the viewpoint of coordination, unsaturated and easily take donor molecules (Lewis bases).

To define the state of lanthanide β-diketonate complexes in solution Karraker [160] used comparative spectroscopy, comparing the shape and relative intensity of bands in the absorption spectra for β-diketonates in crystals and solution. The absorption spectra for six-coordinate trichelates in polar

TABLE 3

Nephelauxetic effects $(1-\beta')$, mean lanthanide—ligand distances ($\bar{R}$(Ln—O)) and effective coordination numbers of lanthanides ($CN_{eff.}$) in Pr(III) and Nd(III) oxydiacetate complexes determined from baricentres (σ) of spectral bands

Complex	Pr(III)				Nd(III)			
	$\sigma(^3H_4 \leftarrow {}^3P_0)$ (cm^{-1})	$(1-\beta')$ 10^3	$\bar{R}$(Pr—O) (Å)	CN_{eff}	$\sigma(^2P_{1/2} \leftarrow {}^4I_{9/2})$ (cm^{-1})	$(1-\beta')$ 10^3	$\bar{R}$(Nd—O) (Å)	CN_{eff}
$Ln^{3+}(aq)$	20750	—	2.590	11.2	23393	—	2.500	9.0
$Ln(OOCCH_2OCH_2COO)^+$	20719	1.5	2.584	11.0	23348	1.9	2.486	8.6
$Ln(OOCCH_2OCH_2COO)_2^-$	20689	3.1	2.572	10.5	23313	3.4	2.476	8.3
$Ln(OOCCH_2OCH_2COO)_3^{3-}$	20621	6.2	2.552	10.0	23279	4.9	2.468	8.2
$Na_3Ln(OOCCH_2OCH_2COO)_3 \cdot 2\,NaClO_4 \cdot 6\,H_2O$	20582	8.1	2.540	9.5	23262	5.6	2.462	8.0

solvent solutions were found to approximate to eight-coordinate ones due to complexing of solvent molecules, and those of hydrated chelates in benzene approximate to six- and seven-coordinate chelates as a result of dehydration.

It was shown [239—242] that the luminescence spectra for europium tetrakis-β-diketonates in crystals and solution differ from each other. Analysing the shape of the band corresponding to the $^5D_0 \rightarrow {}^7F_0$ transition Brecher et al. [239] attributed the observed difference to partial dissociation of the complexes in solution. They found that the extent of dissociation in ethanol is 37%. In dimethyl formamide dissociation is 7% and in the mixed solvent DMF and ethanol (1 : 3) 30% [240]. The dilution of the solution favours the dissociation which depends upon both the nature of the β-diketone and the solvent [241].

In the non-polar solvents, despite the nature of the β-diketone, tetrakis-β-diketonate dissociates to a neutral species, i.e. tris-β-diketonate and β-diketone salt.

The addition of water or other oxygenated ligands to the solution containing Nd(III) or Er(III) tris-β-diketonate with H(fod) results in marked changes in the shape and oscillator strength of hypersensitive transitions [255]. The spectral changes observed were considered to be due to the coordination of the ligands added. From a comparison of the absorption spectra the relative coordinating strength has been found to follow the order: $C_2H_5OH > H_2O > (C_2H_5)_2O$.

Change of luminescence spectrum for alcohol (HP) [Eu(bac)$_4$] (P is piperidine) solution acidified by anhydrous HCl have also been examined [242,243]. Four types of spectra have been assigned to tetrakis-, tris-, bis- and monobenzoylacetonates of Eu(III). The presence of a single band on the $^5D_0 \rightarrow {}^7F_0$ transition has been taken as a criterion for assignment of the spectrum to individual species. Using the band splitting corresponding to the $^5D_0 \rightarrow {}^7F_{1,2,3}$ transitions, the Eu(bac)$_4^-$ complex in anhydrous methanol was accorded C_3 symmetry, and Eu(bac)$_3$, Eu(bac)$_2^+$ and Eu(bac)$^{2+}$ complexes C_2 symmetry.

We have studied [128,129,232,244—248] the absorption spectra of Pr(III) ($^3P_0 \leftarrow {}^3H_4$ transition), Nd(III) ($^2P_{1/2} \leftarrow {}^4I_{9/2}$ transition) and Eu(III) ($^5D_0 \leftarrow {}^7F_0$ transition) with several β-diketones having alkyl and aryl radicals. The absorption spectra of mono-, bis-, tris- and tetrakis-β-diketonates have been calculated. With the help of the comparative spectroscopy of tris- and tetrakis-β-diketonates in crystals and solutions and the analysis of band shifts some information has been obtained about the state of β-diketonates in solution.

The changes in the nephelauxetic effect ($1 - \beta'$), the mean distance lanthanide—ligand ($\bar{R}$(Ln—O)) and the effective coordination number (CN$_{\text{eff.}}$) of lanthanides in stepwise complexing of Pr(III) and Nd(III) with acetylacetone can be seen from the data given in Table 4. The effective coordination numbers were determined from theoretical interrelations between CN and $\bar{R}$(Ln—O) shown in Figs. 8b and 9b. The values of CN obtained for Pr(III) seem to be too high and could not be completely interpreted at present.

The Nd(III) and Eu(III) ions in tetrakis-β-diketonates are eight-coordinate,

TABLE 4

Nephelauxetic effects $(1-\beta')$, mean lanthanide—ligand distances ($\bar{R}$(Ln—O)) and effective coordination numbers of lanthanide ($\mathrm{CN_{eff}}$) in Pr(III) and Nd(III) acetylacetonate complexes determined from baricentres (σ) of spectral bands [a]

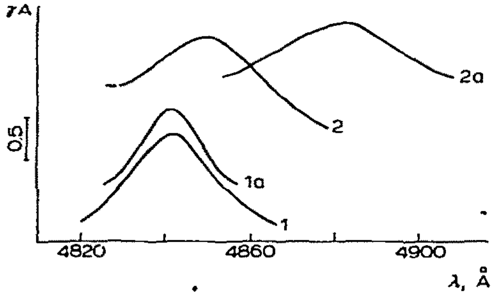
Complex	Pr(III)				Nd(III)			
	$\sigma(^3P_0 \leftarrow {}^3H_4)$ cm^{-1}	$(1-\beta')$ 10^3	$\bar{R}$(Pr—O) Å	$\mathrm{CN_{eff}}$	$\sigma(^2P_{1/2} \leftarrow {}^4I_{9/2})$ cm^{-1}	$(1-\beta')$ 10^3	$\bar{R}$(Nd—O) Å	$\mathrm{CN_{eff}}$
Ln^{3+} (solv)	20750	—	2.590	11.2	23385	0.3	2.498	8.9
$Ln(CH_3COCHCOCH_3)^{2+}$	20741	0.4	2.588	11.1	23320	3.1	2.482	8.5
$Ln(CH_3COCHCOCH_3)_2^+$	20681	3.3	2.570	10.5	23298	4.1	2.473	8.3
$Ln(CH_3COCHCOCH_3)_3$	20664	4.1	2.565	10.3	23244	6.4	2.457	7.9
$Ln(CH_3COCHCOCH_3)_4^-$	20596	7.4	2.542	9.8	23217	7.6	2.450	7.7

[a] In mixed solvent with H_2O: CH_3OH ratio 1 : 4.

independent of the nature of the β-diketone and the composition of the H_2O—CH_3OH mixed solvent. In tris-β-diketonates the lanthanide ions are also eight coordinate by six oxygen atoms from the three β-diketonate anions and two oxygen atoms of solvent molecules solvating the lanthanide ion.

The crystallization of tris-β-diketonate depending mainly upon the nature of the β-diketone may be accompanied by "knocking-out" of one or more solvent molecules from the inner coordination sphere. This results in a red shift in the spectrum of a crystalline β-diketonate compared to the solution spectrum, as can be seen in Fig. 13.

The composition of the H_2O—CH_3OH mixed solvent does not seriously



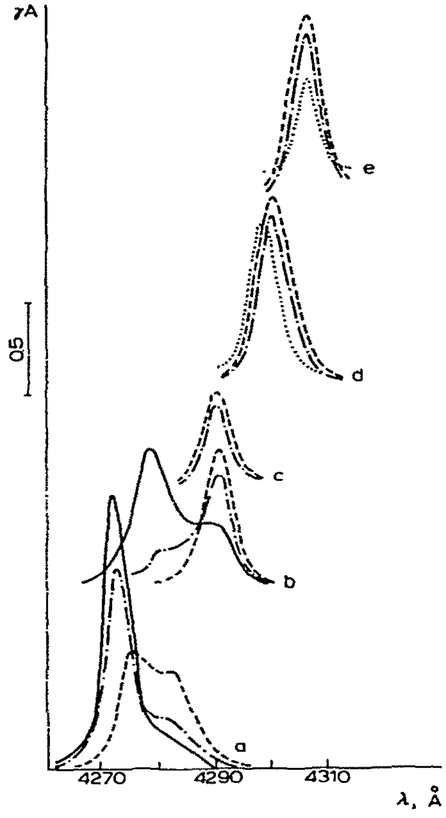


Fig. 13. Absorption spectra for Pr(III) tris-β-diketonates in solutions and crystals: (1) $Pr(bac)_3$ in CH_3OH; (1a) $Pr(bac)_3 \cdot 2\,H_2O$; (2) $Pr(dbm)_3$ in CH_3OH; (2a) $Pr(dbm)_3 \cdot H_2O$. ($^3P_0 \leftarrow {}^3H_4$ transition).

Fig. 14. Solution spectra for: (a) $Nd(ClO_4)_3$; (b) $Nd(aca)^{2+}$; (c) $Nd(aca)_2^+$; (d) $Nd(aca)_3$; (e) $Nd(aca)_4^-$ in water (———), H_2O—CH_3OH solvent (- - - - - -), anhydrous CH_3OH (-·-·-·-) and reflectance spectra for $Nd(aca)_3 \cdot 3\,H_2O$ and $KNd(aca)_4$ (···········) ($^2P_{1/2} \leftarrow {}^4I_{9/2}$ transition).

affect the absorption spectra for the tris-β-diketonates of Nd(III). On the other hand, absorption spectra for bis- and mono-β-diketonates depend markedly on solvent composition (Fig. 14).

For some complexes one can reveal, in solutions, the existence of equilibrium species, so called "spectral isomers", having identical metal-to-ligand ratios but characterized by different absorption spectra. The ratio of intensity of the bands assigned to different "isomers" may, depending upon the nature of the lanthanide, vary if the composition of the solvent changes. Thus, in the case of Nd(III) monoacetylacetonate the quantity of long-wave species which can be assigned to an eight-coordinate species increases with increasing methanol in the solvent, and vice versa, the portion of "long-wave" species with a higher coordination number (apparently, 9) decreases.

The relative quantity of bis-β-diketonates with coordination numbers 8 and 9 depends also on the nature of the β-diketone. This dependence was more thoroughly studied for Eu(III) bis-β-diketonates in 80% methanol. Figure 15 shows that in the absorption spectra for Eu(β-diket)$_2^+$ two bands appear some 15—19 Å from each other in the $^5D_0 \leftarrow {}^7F_0$ transition. The relative intensity of the shortwave band (corresponding to a higher Eu(III) coordination number) decreases in the series of β-diketones: aca$^-$ > bac$^-$ > dbm$^-$. It is not available in the spectra of bis-β-diketonates with fluorinated radicals. In the absorp-

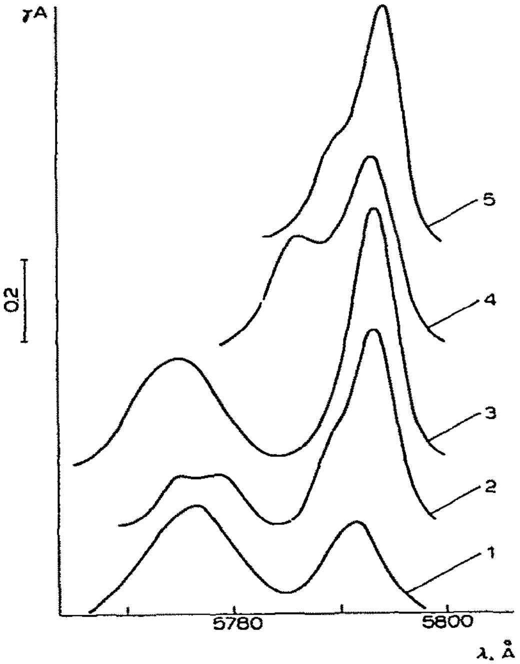


Fig. 15. Solution spectra for Eu(III) bis-β-diketonates: (1) Eu(aca)$_2^+$; (2) Eu(bac)$_2^+$; (3) Eu(dbm)$_2^+$; (4) Eu(tta)$_2^+$; (5) Eu(tdm)$_2^+$ in mixed H_2O—CH_3OH (1 : 4) solvent ($^5D_0 \leftarrow {}^7F_0$ transition).

tion spectra of Eu(III) bis-β-diketonates with β-diketones of a non-symmetrical structure, especially at low temperature, a doublet structure of both shortwave and longwave bands exists independent of the solvent composition. Its presence is accounted for by the existence of geometric isomers occurring due to the different mutual location of β-diketone R^I and R^{II} radicals in different configurations of both EuO_8 and EuO_9 chromophores.

The dependence of nephelauxetic band shifts in the solution absorption spectra for lanthanide β-diketonates upon the nature of a β-diketone has mostly completely been traced using the ${}^5D_0 \leftarrow {}^7F_0$ transition in the spectra of Eu(III) mono-β-diketonates [129]. A linear correlation was revealed between the sum of Taft's constant values, $\sigma^*_{R^I} + \sigma^*_{R^{II}}$ of the two β-diketone radicals and the nephelauxetic effect defined from the shift of the band examined (Fig. 16). This correlation has been used to determine Taft's constants of new fluorinated radicals.

Dutt et al. [251] studied the visible spectra of Nd(III) hydroxo-aquo-bis-benzoylacetonato complex, $Nd(bac)_2(OH)(H_2O)$ in methanol, acetone, benzene and chloroform. They found the nephelauxetic effect, $1 - \beta'$ equal $3 \cdot 10^{-2}$ in all the solvents. The high value of $1 - \beta'$ was attributed to the resonating effect of a β-diketone moiety. However we think that it also can be due to the small coordination number of the neodymium ion in this complex (six) and hence the short Nd—O distances (see Fig. 9).

The dependence of the absorption spectra of the Pr(III) and Nd(III) β-diketonate complexes upon the nature of inorganic anions present in solution has also been studied [243,248]. Lanthanide—mixed ligand coordination compounds involving β-diketone and inorganic anions in the inner sphere were formed in anhydrous methanol in the presence of Cl^- or NO_3^- ions.

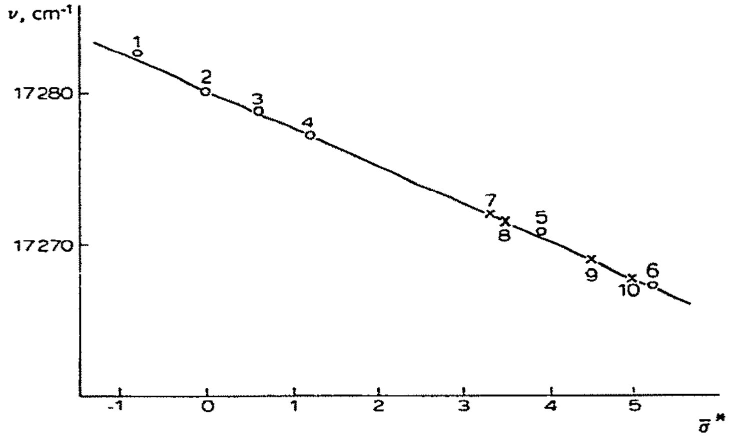


Fig. 16. Dependence of the ${}^5D_0 \leftarrow {}^7F_0$ transition energy in the absorption spectra for Eu(III) mono-β-diketonates on the sum of Taft's constants for R^I and R^{II} radicals in β-diketone: (1) $Eu(dpm)^{2+}$; (2) $Eu(aca)^{2+}$; (3) $Eu(bac)^{2+}$; (4) $Eu(dbm)^{2+}$; (5) $Eu(tta)^{2+}$; (6) $Eu(hfa)^{2+}$; (7) $Eu(fod)^{2+}$; (8) $Eu(pdm)^{2+}$; (9) $Eu(tdpf)^{2+}$; (10) $Eu(tdm)^{2+}$ [129].

F. CONCLUSION

During the last decade the theoretical interpretation of ligand field effects in the absorption spectra of lanthanide ions in crystals and solution has greatly changed. The effects are interpreted now not only on the basis of pure electrostatic concepts. Some models have been developed which take into account covalent contributions to these effects.

In general, present theory permits one to obtain much information on the structure of lanthanide coordination compounds in solution based on the analysis of their absorption spectra in the region of f—f transitions. In practice, however, the analysis of these spectra and the estimation of ligand—field parameters often encounter considerable difficulties. The most intricate and so far unresolved problem in the analysis of the absorption spectra of lanthanide ions in solution is to recognize the complete picture of band splitting. Sometimes one can obtain the resolved structure of bands directly from experiment. It is possible, however, only for some of the "simplest" bands, in particular, in absorption spectra of Eu(III). The information, as a rule, is not enough for the estimation of crystal field parameters, B_n^m, but in some cases it helps to determine the symmetry of ligand fields around Eu(III) ions and reveal the existence of isomeric forms for complexes.

The intensity parameters, T_λ can be calculated rather simply from experimental spectra of all Ln^{3+} ions. In recent years T_λ parameters have been determined in different coordination compounds and some attempts have been made to use them for determining the structure of the nearest environment for lanthanide ions in these compounds. Unfortunately, the relations between structural parameters and intensity parameters are not clear enough at present.

The application of the nephelauxetic parameter, β, to obtain information on the structure of lanthanide coordination compounds in solution is rather promising. The β (or β') values can be fairly easily obtained from the position of unresolved spectral bands and used to determine the lanthanide—ligand distances and to estimate coordination numbers of lanthanide ions in complexes on the basis of the empirical interrelationships established between these structural parameters and the nephelauxetic parameter. The application of this approach in combination with comparative spectroscopy of coordination compounds in crystals and solution permits one to obtain data on the structure of lanthanide solvato-complexes, complexes with β-diketones and some other complexes of praseodymium, neodymium and europium in solution. This approach needs, in our opinion, further verification and theoretical proof. Its extension to coordination compounds of all lanthanides is expedient.

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