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# Spectroscopy and Structure of Lanthanide Acetates and Propionates

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*Spectral intensities of solutions of the $Nd^{3+}$, $Ho^{3+}$ and $Er^{3+}$ acetates and propionates have been investigated for different M:L ratios and lanthanide ion concentrations at 21 °C, 40 °C and 60 °C. These results, together with the previously spectroscopically determined sets of stability constants, enabled us to make some conclusions about the possible mechanism of the hypersensitivity phenomenon of f–f transitions and about the possible structures of the consecutive complex species of lanthanide acetates and propionates existing in solutions.*

## Introduction

In our previous papers [1–6], spectral intensities of f–f transitions in aqueous solutions of lanthanide complex compounds have been reported. We have applied the Judd-Ofelt equation which relates the experimental oscillator strength value of the particular f–f transition to the $\tau_2$, $\tau_4$, $\tau_6$ parameters as follows:

$$P = \sum_{\lambda} \tau_\lambda \sigma (f^N \psi_J \| U^{(\lambda)} \| f^N \psi'_{J'})^2 / 2J + 1 \qquad (1)$$

$$\lambda = 2, 4, 6$$

where $\sigma$ is the wave number in $[cm^{-1}]$, $U^{(\lambda)}$ are the matrix elements of the unit tensor operator calculated by Carnall *et al.* [7] in the intermediate coupling scheme, $f^N\psi_J$, $f^N\psi'_{J'}$ are the initial and final states of electronic transitions and J is the total quantum number.

It was found [1, 2] that the value of the $\tau_2$ Judd-Ofelt parameter increases significantly with increasing ligand concentration in the aqueous solution, whereas the $\tau_4$ and $\tau_6$ parameter values are constant (within experimental error). These results encouraged us to apply the intensity parameter $\tau_2$ to the inspection of the complexation equilibria of lanthanide ions with different ligands. The oscillator strength of the 'hypersensitive' transition of lanthanide ions measured directly in the experiment [1, 2] proved to be more sensitive than did $\tau_2$. For such a hypersensitive transition the matrix element $U^{(2)}$ in eqn. (1) has a high non-zero value [7], so that the $U_2 \cdot \tau_2$ term contributes significantly to the oscillator strength value of the transition. If the mechanism of all f–f transitions, including the hypersensitive ones, is the same, the linear relation of $P_{exp}$ of the hypersensitive transition to the $\tau_2$ parameter should be obeyed. Some authors [8–14] have suggested however that the mechanism of the hypersensitive transition is different from those of f–f transitions which do not exhibit hypersensitivity. Recent data [1, 2] suggested that some differences between those two quantities may exist. It has been concluded that even in this case the linearity between P and $\tau_2$ could be preserved if the $U_2 \cdot \tau_2$ terms for non-hypersensitive f–f transitions are small in the fitting procedure and do not affect significantly the evaluation of the $\tau_2$ parameter. The fitting procedure also depends on the relations between the $\tau_2$, $\tau_4$ and $\tau_6$ values. In the Ln–L system in aqueous solutions with different free ligand concentrations, different complex species can exist [1–6]. Generally, the increase in the $\tau_2$ parameter value is determined by the particular complex equilibrium establishing in the solution between different complex species at a particular M:L ratio. High values of the $\tau_2$ parameter for a particular complex species reflected in the increase of this parameter for the whole solution may result in different conditions of the fitting procedure. Application of the oscillator strength of the hypersensitive transition to the investigation of complex equilibria of lanthanide ions enabled the determination of the stability constant sets for several lanthanide ions with different ligands [3–6]. The stability constants calculated at different temperatures were used for the determination of the thermodynamic functions of complexation: ΔG, ΔH and ΔS [5, 6].

The relation between the $\tau_2$ parameter value and that of the oscillator strength of the hypersensitive transition should also be considered. Generally, when the variation of $\tau_2$ depends on the variation of the oscillator strength values, each complex species

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TABLE I. $\tau_\lambda$ Parameter Values for $Nd^{3+}$–Acetate at 21 °C, 40 °C and 60 °C.

| t [°C] | $C_{Nd^{3+}} \cdot 10^2$ [*M*] | $C_A \cdot 10^2$ [*M*] | $\tau_2 \cdot 10^9$ | $\tau_4 \cdot 10^9$ | $\tau_6 \cdot 10^9$ |
|---|---|---|---|---|---|
| 21 | 1.997 | 2.700 | 3.36 ± 0.63 | 5.08 ± 0.57 | 10.55 ± 0.82 |
| | | 9.695 | 4.94 ± 0.61 | 5.49 ± 0.56 | 10.89 ± 0.80 |
| | | 19.692 | 6.81 ± 0.61 | 4.90 ± 0.56 | 10.57 ± 0.80 |
| | | 29.691 | 7.74 ± 0.55 | 4.56 ± 0.49 | 9.96 ± 0.71 |
| | | 39.690 | 8.09 ± 0.66 | 4.82 ± 0.60 | 10.26 ± 0.87 |
| 40 | 1.988 | 2.688 | 3.68 ± 0.75 | 4.98 ± 0.68 | 10.45 ± 0.98 |
| | | 9.653 | 5.50 ± 0.63 | 5.26 ± 0.57 | 11.14 ± 0.82 |
| | | 19.606 | 7.12 ± 0.51 | 5.14 ± 0.46 | 10.57 ± 0.67 |
| | | 29.561 | 7.86 ± 0.65 | 4.75 ± 0.59 | 10.16 ± 0.86 |
| | | 39.516 | 8.38 ± 0.46 | 4.87 ± 0.42 | 10.42 ± 0.60 |
| 60 | 1.964 | 2.655 | 4.03 ± 0.63 | 4.82 ± 0.57 | 9.96 ± 0.83 |
| | | 9.535 | 5.95 ± 0.70 | 5.11 ± 0.63 | 10.65 ± 0.91 |
| | | 19.367 | 7.67 ± 0.63 | 4.89 ± 0.63 | 10.52 ± 0.92 |
| | | 29.200 | 8.56 ± 0.63 | 4.48 ± 0.57 | 10.08 ± 0.82 |
| | | 39.034 | 9.11 ± 0.61 | 4.97 ± 0.55 | 10.22 ± 0.80 |

existing in the solution should be characterised by a particular $\tau_2$ value. Moreover, a constant $\tau_2$ value at a particular M:L ratio should be preserved within the temperature range considered if intensity changes are determined exclusively by the complexation effect. On the other hand, this condition cannot be obeyed when the mechanism of the hypersensitive transition is different from those of other transitions of f–f type. These considerations however are applicable to systems for which all intensity changes are related only to the changes of the $\tau_2$ parameter values. Diluted aqueous solutions of lanthanide perchlorates ($c \sim 10^{-2}$ *M*) with different ligand concentrations are good examples of a behaviour of this type. It was proved previously that even within the considered temperature range (21 °C–60 °C), $\tau_4$ and $\tau_6$ are constant within the experimental error limits.

These aspects of spectral intensities will be exemplified by the $Nd^{3+}$, $Ho^{3+}$ and $Er^{3+}$ acetates and propionates. In this article, we shall focus our attention on the evaluation of the Judd-Ofelt parameters $\tau_2$, $\tau_4$ and $\tau_6$, for solutions of different M:L ratios at different temperatures, (21 °C, 40 °C, 60 °C).

On the other hand we have recently calculated the $\beta_n$, $\Delta H_n$ and $\Delta S_n$ values for the above mentioned systems [3–6], basing on the variation of the oscillator strength of hypersensitive transitions with varying metal and ligand concentrations.

## Experimental

### *Reagents*

The stock solutions of lanthanide perchlorates were prepared from 99.9% lanthanide oxides (Merck) by a method described previously [1]. The concentration of the $Ln^{3+}$ ion was determined gravimetrically. The buffered ligand solutions were prepared by the half neutralization method.

### *Measurements and Calculations*

Spectral measurements were made on the Cary 14 – Spectrophotometer. All details concerning the preparation of solutions and pH measurements have already been published in previous papers [1–6].

The oscillator strengths of f–f transitions of lanthanide ions in the investigated solutions were calculated using a graphical method of band integration and an appropriate computer program (ICH-31). The stability constant values ($\beta_n$) at different temperatures for the systems under test are listed in [3–6].

The $\tau_\lambda$ parameter values for solutions with different M:L ratios at different temperatures were computed using the usual fitting procedure [1, 2].

It should be emphasized that in the evaluation of the Judd-Ofelt parameters for all the lanthanide ions studied the same fit of the experimental oscillator strengths values for f–f transitions was taken into account.

The $\tau_2$ parameters for the particular complex species ($ML_n$) were calculated using the assumption:

$$\tau_{2\,\mathrm{sol}} = \sum_{n=0}^{N} k_n \tau_{2\,ML_n} \tag{2}$$

where: $k_n$ = molar ratio of the $ML_n$ complex species; $\tau_{2ML_n}$ = value of the $\tau_2$ parameter for the particular complex species.

TABLE II. $\tau_\lambda$ Parameter Values for $Nd^{3+}$–Propionate at 21 °C, 40 °C and 60 °C.

| t [°C] | $C_{Nd^{3+}}\cdot 10^2$ [*M*] | $C_A\cdot 10^2$ [*M*] | $\tau_2\cdot 10^9$ | $\tau_4\cdot 10^9$ | $\tau_6\cdot 10^9$ |
|---|---|---|---|---|---|
| 21 | 1.997 | 2.695 | 4.39 ± 0.59 | 4.77 ± 0.53 | 9.28 ± 0.77 |
| | | 9.693 | 5.75 ± 0.63 | 5.12 ± 0.57 | 10.14 ± 0.82 |
| | | 19.692 | 7.22 ± 0.61 | 5.09 ± 0.55 | 10.21 ± 0.80 |
| | | 29.691 | 8.55 ± 0.62 | 4.74 ± 0.56 | 10.23 ± 0.82 |
| | | 39.690 | 9.30 ± 0.63 | 4.91 ± 0.57 | 9.99 ± 0.83 |
| 40 | 1.988 | 2.683 | 4.27 ± 0.73 | 4.35 ± 0.66 | 10.90 ± 0.95 |
| | | 9.651 | 6.17 ± 0.58 | 4.95 ± 0.52 | 10.22 ± 0.76 |
| | | 19.606 | 7.66 ± 0.46 | 5.03 ± 0.42 | 10.18 ± 0.61 |
| | | 29.561 | 8.75 ± 0.59 | 4.80 ± 0.53 | 10.24 ± 0.77 |
| | | 39.516 | 9.49 ± 0.67 | 4.61 ± 0.60 | 10.29 ± 0.87 |
| 60 | 1.964 | 2.651 | 4.75 ± 0.48 | 4.80 ± 0.44 | 9.14 ± 0.63 |
| | | 9.533 | 6.85 ± 0.60 | 5.17 ± 0.55 | 10.46 ± 0.79 |
| | | 19.367 | 8.41 ± 0.58 | 5.15 ± 0.53 | 10.22 ± 0.77 |
| | | 29.201 | 9.34 ± 0.53 | 5.13 ± 0.48 | 10.08 ± 0.69 |
| | | 39.034 | 9.80 ± 0.54 | 5.03 ± 0.49 | 9.99 ± 0.71 |

TABLE III. $\tau_\lambda$ Parameter Values for $Ho^{3+}$–Acetate at 21 °C, 40 °C and 60 °C.

| t [°C] | $C_{Ho^{3+}}\cdot 10^2$ [*M*] | $C_A\cdot 10^2$ [*M*] | $\tau_2\cdot 10^9$ | $\tau_4\cdot 10^9$ | $\tau_6\cdot 10^9$ |
|---|---|---|---|---|---|
| 21 | 2.014 | 3.020 | 2.60 ± 0.27 | 3.62 ± 0.34 | 4.18 ± 0.33 |
| | | 10.016 | 5.50 ± 0.33 | 3.57 ± 0.42 | 4.12 ± 0.41 |
| | | 20.013 | 7.61 ± 0.37 | 3.73 ± 0.46 | 3.86 ± 0.46 |
| | | 30.011 | 8.51 ± 0.28 | 3.55 ± 0.36 | 3.89 ± 0.35 |
| | | 40.007 | 8.79 ± 0.37 | 3.68 ± 0.27 | 3.83 ± 0.27 |
| 40 | 2.006 | 3.007 | 2.88 ± 0.26 | 3.75 ± 0.32 | 4.05 ± 0.32 |
| | | 9.972 | 5.75 ± 0.30 | 3.99 ± 0.38 | 3.88 ± 0.37 |
| | | 19.925 | 7.86 ± 0.36 | 3.66 ± 0.45 | 3.81 ± 0.44 |
| | | 29.879 | 8.89 ± 0.33 | 3.81 ± 0.41 | 3.79 ± 0.41 |
| | | 39.832 | 9.29 ± 0.35 | 3.88 ± 0.44 | 3.66 ± 0.43 |
| 60 | 1.981 | 2.970 | 3.45 ± 0.31 | 3.70 ± 0.39 | 4.03 ± 0.38 |
| | | 9.851 | 6.26 ± 0.35 | 4.19 ± 0.43 | 3.69 ± 0.43 |
| | | 19.685 | 8.25 ± 0.39 | 3.84 ± 0.49 | 3.92 ± 0.48 |
| | | 29.514 | 9.18 ± 0.36 | 3.68 ± 0.45 | 3.90 ± 0.44 |
| | | 39.346 | 9.76 ± 0.33 | 3.90 ± 0.42 | 3.80 ± 0.41 |

TABLE IV. $\tau_\lambda$ Parameter Values for $Ho^{3+}$–Propionate at 21 °C, 40 °C and 60 °C.

| t [°C] | $C_{Ho^{3+}}\cdot 10^2$ [*M*] | $C_A\cdot 10^2$ [*M*] | $\tau_2\cdot 10^9$ | $\tau_4\cdot 10^9$ | $\tau_6\cdot 10^9$ |
|---|---|---|---|---|---|
| 21 | 1.988 | 2.970 | 2.87 ± 0.33 | 3.50 ± 0.41 | 4.21 ± 0.41 |
| | | 9.694 | 6.30 ± 0.46 | 3.44 ± 0.57 | 4.11 ± 0.56 |
| | | 19.954 | 8.05 ± 0.44 | 4.13 ± 0.55 | 4.07 ± 0.54 |
| | | 29.980 | 8.93 ± 0.38 | 3.95 ± 0.48 | 3.71 ± 0.47 |
| | | 39.970 | 9.48 ± 0.33 | 4.15 ± 0.41 | 3.82 ± 0.41 |
| | | 2.957 | 3.24 ± 0.23 | 3.56 ± 0.49 | 4.06 ± 0.48 |

*(continued overleaf)*

TABLE IV. *(continued)*

| t [°C] | $C_{Ho^{3+}}\cdot 10^2$ [*M*] | $C_A\cdot 10^2$ [*M*] | $\tau_2\cdot 10^9$ | $\tau_4\cdot 10^9$ | $\tau_6\cdot 10^9$ |
|---|---|---|---|---|---|
| 40 | 1.979 | 9.920 | 6.56 ± 0.37 | 3.68 ± 0.47 | 3.71 ± 0.46 |
| | | 19.867 | 8.45 ± 0.36 | 4.00 ± 0.45 | 3.88 ± 0.44 |
| | | 29.849 | 9.64 ± 0.33 | 3.99 ± 0.42 | 3.76 ± 0.41 |
| | | 39.795 | 10.08 ± 0.33 | 4.04 ± 0.41 | 3.67 ± 0.40 |
| 60 | 1.955 | 2.921 | 3.57 ± 0.34 | 3.50 ± 0.43 | 3.95 ± 0.42 |
| | | 9.799 | 6.73 ± 0.31 | 3.92 ± 0.38 | 3.57 ± 0.38 |
| | | 19.624 | 8.97 ± 0.28 | 3.86 ± 0.35 | 3.81 ± 0.34 |
| | | 29.485 | 10.01 ± 0.21 | 3.92 ± 0.26 | 3.72 ± 0.25 |
| | | 39.310 | 10.67 ± 0.30 | 3.78 ± 0.38 | 3.34 ± 0.37 |

TABLE V. $\tau_\lambda$ Parameter Values for $Er^{3+}$–Acetate at 21 °C, 40 °C and 60 °C.

| t [°C] | $C_{Er^{3+}}\cdot 10^2$ [*M*] | $C_A\cdot 10^2$ [*M*] | $\tau_2\cdot 10^9$ | $\tau_4\cdot 10^9$ | $\tau_6\cdot 10^9$ |
|---|---|---|---|---|---|
| 21 | 2.003 | 3.013 | 2.67 ± 0.33 | 4.57 ± 0.24 | 1.53 ± 0.44 |
| | | 10.009 | 5.52 ± 0.38 | 4.67 ± 0.27 | 1.45 ± 0.50 |
| | | 20.006 | 7.35 ± 0.41 | 4.85 ± 0.29 | 1.57 ± 0.54 |
| | | 30.002 | 8.60 ± 0.35 | 4.40 ± 0.25 | 1.44 ± 0.46 |
| | | 40.001 | 9.18 ± 0.43 | 4.31 ± 0.31 | 1.71 ± 0.56 |
| 40 | 1.994 | 3.000 | 2.85 ± 0.28 | 4.87 ± 0.20 | 1.57 ± 0.36 |
| | | 9.965 | 5.98 ± 0.31 | 4.69 ± 0.23 | 1.72 ± 0.41 |
| | | 19.918 | 7.93 ± 0.38 | 4.61 ± 0.27 | 1.65 ± 0.50 |
| | | 29.871 | 8.94 ± 0.39 | 4.33 ± 0.28 | 1.69 ± 0.51 |
| | | 39.826 | 9.41 ± 0.44 | 4.29 ± 0.32 | 2.08 ± 0.58 |
| 60 | 1.970 | 2.963 | 3.28 ± 0.26 | 4.75 ± 0.19 | 1.55 ± 0.34 |
| | | 9.844 | 6.60 ± 0.26 | 4.40 ± 0.19 | 1.75 ± 0.34 |
| | | 19.675 | 8.60 ± 0.31 | 4.22 ± 0.22 | 1.79 ± 0.41 |
| | | 29.506 | 9.58 ± 0.34 | 4.05 ± 0.24 | 1.89 ± 0.45 |
| | | 39.340 | 9.89 ± 0.36 | 4.14 ± 0.26 | 2.03 ± 0.47 |

TABLE VI. $\tau_\lambda$ Parameter Values for $Er^{3+}$–Propionate at 21 °C, 40 °C and 60 °C.

| t [°C] | $C_{Er^{3+}}\cdot 10^2$ [*M*] | $C_A\cdot 10^2$ [*M*] | $\tau_2\cdot 10^9$ | $\tau_4\cdot 10^9$ | $\tau_6\cdot 10^9$ |
|---|---|---|---|---|---|
| 21 | 2.006 | 2.563 | 2.89 ± 0.23 | 4.06 ± 0.16 | 1.67 ± 0.30 |
| | | 9.554 | 5.62 ± 0.26 | 4.02 ± 0.19 | 1.52 ± 0.34 |
| | | 19.544 | 7.82 ± 0.30 | 3.96 ± 0.22 | 1.72 ± 0.40 |
| | | 29.569 | 8.69 ± 0.40 | 3.86 ± 0.29 | 1.72 ± 0.53 |
| | | 39.561 | 9.39 ± 0.34 | 3.45 ± 0.25 | 1.76 ± 0.45 |
| 40 | 1.997 | 2.552 | 3.35 ± 0.28 | 4.11 ± 0.20 | 1.47 ± 0.36 |
| | | 9.512 | 6.44 ± 0.34 | 4.35 ± 0.25 | 1.21 ± 0.45 |
| | | 19.458 | 8.44 ± 0.46 | 4.12 ± 0.33 | 1.45 ± 0.60 |
| | | 29.439 | 9.30 ± 0.40 | 3.92 ± 0.29 | 1.37 ± 0.53 |
| | | 39.388 | 9.84 ± 0.41 | 3.91 ± 0.29 | 1.42 ± 0.54 |
| | | 2.521 | 3.79 ± 0.27 | 4.17 ± 0.20 | 1.59 ± 0.36 |

*(continued on facing page)*

TABLE VI. *(continued)*

| t [°C] | $C_{Er^{3+}} \cdot 10^2$ [*M*] | $C_A \cdot 10^2$ [*M*] | $\tau_2 \cdot 10^9$ | $\tau_4 \cdot 10^9$ | $\tau_6 \cdot 10^9$ |
|---|---|---|---|---|---|
| 60 | 1.973 | 9.396 | 6.88 ± 0.40 | 4.22 ± 0.29 | 1.44 ± 0.53 |
|  |  | 19.221 | 8.80 ± 0.38 | 4.41 ± 0.28 | 1.39 ± 0.51 |
|  |  | 29.081 | 9.58 ± 0.42 | 4.42 ± 0.30 | 1.45 ± 0.55 |
|  |  | 38.907 | 10.09 ± 0.39 | 3.97 ± 0.28 | 1.71 ± 0.52 |

The molar ratios of the complex species in the solution at a particular M:L ratio were calculated from the set of stability constants determined spectroscopically [3–6]. This procedure was performed for solutions at different M:L ratios and temperatures within the 21 °C–60 °C range (taking into consideration an appropriate set of stability constants for a given temperature).

## Results and Discussion

The $\tau_\lambda$ values evaluated using the Judd-Ofelt equation from the spectra of solutions of different M:L ratios at different temperatures are presented at Tables I–VI for $Nd^{3+}$, $Ho^{3+}$ and $Er^{3+}$ acetates and propionates, respectively. All the results prove that under these conditions the $\tau_4$ and $\tau_6$ parameters remain constant within the limit of the experimental error. A significant increase in the $\tau_2$ parameter values with increasing M:L ratio is observed. Moreover, the character of the increase of the $\tau_2$ parameter values is similar for a given ligand at different temperatures.

Typical $\tau_2 = f(C_A)$ curves, (where $C_A$ is total ligand concentration and $C_M$ = const) are presented in Fig. 1 for the $Nd^{3+}$–acetate system at 21 °C, 40 °C and 60 °C. $\tau_2$ values of particular complex species for the $Nd^{3+}$ acetates and propionates are presented in Table VII. For the $Nd^{3+}$–acetates a reasonable set of $\tau_2$ parameter values was achieved only when the formation of three complex species was taken into account. In comparison with the $\tau_2$ value of the aquoion, the $\tau_2$ parameters of the complex species are significantly larger. Species ML and $ML_2$ are characterised by comparable values of this parameter, whereas for $ML_3$ a distinctly higher $\tau_2$ value is observed.

Considering the $\tau_{2ML_n}$ values for $Nd^{3+}$ propionates listed in Table VII, similar behaviours can generally be observed. Some differences exist still, because the $\tau_{2ML_2}$ values of propionate species increase with increasing temperature.

In our opinion, this could be caused by the greater formation of the $ML_4$ species for propionates than for acetates of light lanthanides. This should be observed especially at higher temperatures, where the formation of the polynuclear species is less probable. In our earlier investigations the higher values of $\beta_4$ for propionates at different temperatures ($\beta_4^{21}$ = 3300 $M^4$, $\beta_4^{40}$ = 8900 $M^4$, $\beta_4^{60}$ = 20500 $M^4$) than for acetates ($\beta_4^{21}$ = 1900 $M^4$, $\beta_4^{40}$ = 3800 $M^4$, $\beta_4^{60}$ = 7600 $M^4$) were observed. Moreover, for the propionates, the $\beta_4^{60}$ exceeds the $\beta_3^{60}$, and $\beta_4/\beta_3$ ratio for propionates is significantly higher than for acetates. All $\beta_4$ values in these cases were evaluated with poor accuracy and should be treated very carefully.

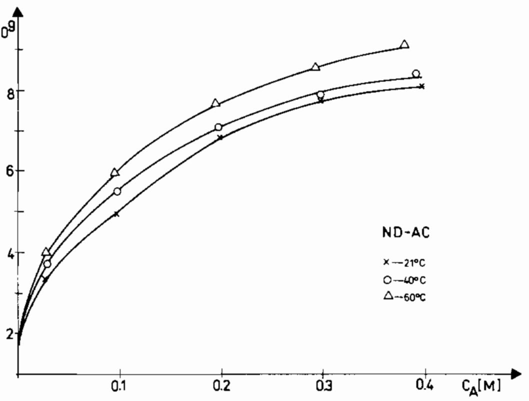

Fig. 1. $\tau_2$ parameter for $Nd^{3+}$–acetate at 21 °C, 40 °C and 60 °C as function of ligand concentration ($C_A$).

The $\tau_2$ parameter values of the $ML_n$ species of $Ho^{3+}$ acetates and $Ho^{3+}$ propionates are collected in Table VIII. In this case, a distinct increase in the $\tau_2$ parameter value in comparison with the aquoion is also observed. In the case of $Ho^{3+}$ acetates however, only the consideration of four species $ML_1, \cdots, ML_4$ led to a consistent set of values. This means that for this ion, the concentration of the $ML_4$ species is too significant to be neglected. As for $Nd^{3+}$, the $\tau_{2ML_3}$ value for $Ho^{3+}$ is significantly higher than $\tau_{2ML}$ and $\tau_{2ML_2}$.

For acetates and propionates of $Er^{3+}$ (Table IX) the $\tau_2$ for all $ML_n$ species are significantly higher than $\tau_2$ for the aquoion; however the $\tau_2$ values increase in the sequence: $\tau_{2ML} < \tau_{2ML_2} < \tau_{2ML_3}$. Those results should be discussed in terms of the possible mechanisms responsible for the appearance and intensities of the f–f transitions. Acetate and

TABLE VII. $\tau_{2ML_n}$ Parameter Values for $Nd^{3+}$ Acetates and Propionates at 21 °C, 40 °C and 60 °C.

| System | Temperature [°C] | $\tau_{2M^{3+}} \cdot 10^9$ | $\tau_{2ML^{2+}} \cdot 10^9$ | $\tau_{2ML^{2+}} \cdot 10^9$ | $\tau_{2ML_3} \cdot 10^9$ |
|---|---|---|---|---|---|
| $Nd^{3+}$–Ac | 21 | 1.69 ± 0.53 | 4.19 ± 0.51 | 5.58 ± 1.11 | 10.52 ± 0.81 |
| | 40 | | 4.70 ± 0.20 | 5.73 ± 0.41 | 10.32 ± 0.28 |
| | 60 | | 5.23 ± 0.17 | 5.59 ± 0.33 | 11.39 ± 0.22 |
| $Nd^{3+}$–Prop | 21 | 1.69 ± 0.53 | 6.59 ± 0.16 | 2.98 ± 0.31 | 13.37 ± 0.23 |
| | 40 | | 5.81 ± 0.16 | 4.69 ± 0.33 | 12.06 ± 0.21 |
| | 60 | | 6.19 ± 0.11 | 6.06 ± 0.19 | 11.88 ± 0.12 |

TABLE VIII. $\tau_{2ML_n}$ Parameter Values for $Ho^{3+}$ Acetates and Propionates at 21 °C, 40 °C and 60 °C.

| System | Temperature [°C] | $\tau_{2M^{3+}} \cdot 10^9$ | $\tau_{2ML^{2+}} \cdot 10^9$ | $\tau_{2ML_2^+} \cdot 10^9$ | $\tau_{2ML_3} \cdot 10^9$ | $\tau_{2ML_4^-} \cdot 10^9$ |
|---|---|---|---|---|---|---|
| $Ho^{3+}$–Ac | 21 | 0.58 ± 0.24 | 3.85 ± 0.13 | 5.68 ± 0.34 | 12.15 ± 0.51 | 6.60 ± 0.66 |
| | 40 | | 4.12 ± 0.13 | 5.59 ± 0.30 | 13.18 ± 0.62 | 8.30 ± 0.53 |
| | 60 | | 4.79 ± 0.19 | 6.08 ± 0.45 | 11.41 ± 0.89 | 10.46 ± 0.65 |
| $Ho^{3+}$–Prop | 21 | 0.58 ± 0.24 | 3.40 ± 0.10 | 9.51 ± 0.24 | 7.19 ± 0.44 | 13.49 ± 0.47 |
| | 40 | | 3.92 ± 0.50 | 7.95 ± 1.23 | 9.99 ± 2.57 | 11.91 ± 1.82 |
| | 60 | | 4.39 ± 0.23 | 6.73 ± 0.50 | 12.30 ± 1.18 | 11.54 ± 0.66 |

TABLE IX. $\tau_{2ML_n}$ Parameter Values for $Er^{3+}$ Acetates and Propionates at 21 °C, 40 °C and 60 °C. $\beta_n$ Values are Determined from the Oscillator Strength Values of (a) $^4G_{11/2} \leftarrow {}^4I_{15/2}$ Transition and (b) $^2H_{11/2} \leftarrow {}^4I_{15/2}$ Transition.

| System | Temperature [°C] | $\tau_{2M^{3+}} \cdot 10^9$ | | $\tau_{2M^{3+}} \cdot 10^9$ | $\tau_{2ML_2^+} \cdot 10^9$ | $\tau_{2ML_3} \cdot 10^9$ | $\tau_{2ML_4^-} \cdot 10^9$ |
|---|---|---|---|---|---|---|---|
| $Er^{3+}$–Ac | 21 | 0.88 ± 0.22 | a | 3.44 ± 0.56 | 7.76 ± 1.44 | 8.08 ± 3.08 | 12.30 ± 2.38 |
| | | | b | 3.24 ± 0.60 | 8.02 ± 1.51 | 7.81 ± 3.20 | 12.58 ± 2.57 |
| | 40 | | a | 3.32 ± 0.10 | 7.11 ± 0.20 | 11.67 ± 0.54 | 9.58 ± 0.37 |
| | | | b | 3.31 ± 0.21 | 7.30 ± 0.42 | 10.46 ± 0.99 | 10.48 ± 0.74 |
| | 60 | | a | 3.73 ± 0.30 | 7.43 ± 0.69 | 11.86 ± 1.50 | 10.03 ± 0.94 |
| | | | b | 3.73 ± 0.30 | 7.42 ± 0.68 | 11.94 ± 1.50 | 9.99 ± 0.95 |
| $Er^{3+}$–Prop | 21 | 0.88 ± 0.22 | a | 4.53 ± 0.59 | 6.16 ± 1.63 | 12.25 ± 3.30 | 9.24 ± 3.36 |
| | | | b | 4.55 ± 0.59 | 6.12 ± 1.59 | 12.43 ± 3.35 | 9.16 ± 3.26 |
| | 40 | | a | 4.72 ± 0.19 | 7.14 ± 0.51 | 11.20 ± 0.95 | 10.48 ± 0.88 |
| | | | b | 4.74 ± 0.20 | 7.12 ± 0.50 | 11.53 ± 1.05 | 10.31 ± 0.83 |
| | 60 | | a | 5.05 ± 0.24 | 6.70 ± 0.56 | 11.64 ± 1.38 | 10.48 ± 0.75 |
| | | | b | 4.98 ± 0.21 | 6.70 ± 0.57 | 11.07 ± 1.08 | 10.71 ± 0.70 |

propionate ligands form inner-sphere species with lanthanide ions. In comparison with the aquoion [1], the nepheloauxetic effect is extremely small. X-Ray data for solid $Ce^{3+}$ and $Er^{3+}$ acetates [15, 16] indicate evidently that one water molecule is preserved in the $Ce^{3+}$ coordination polyhedron and two water molecules in that of $Er^{3+}$. It should be stressed that no distinct differences are observed in the distances between $Ln^{3+}$ and the water oxygen atom and that of the acetate carboxylic group. In the case of $Er^{3+}$, for example, the $Er^{3+}$–$H_2O$ distance = 2.31 Å and the $Er^{3+}$–$H_2O$ distance = 2.30 Å are the shortest bond lengths in the lattice of $Er(CH_3COO)_3 \cdot 2H_2O$ [16].

On the other hand, thermodynamic data [2–6] indicate that lanthanide acetates and propionates are mainly enthropy-stabilised.

All these facts are in the opinion of the authors arguments against the covalency mechanism of the hypersensitivity of those systems. The significant increase in the $\tau_2$ parameter values for the particular complex species cannot be explained by this mechanism because there is no significant change in the bond character of the complex species when a water molecule is replaced by an oxygen atom of the acetate or propionate group in the first coordination sphere of the lanthanide ion.

On the other hand, the data are quite easy to explain if we assume another mechanism of hypersensitivity. Both the symmetry model [9] and the dynamic crystal field model [14] can be applied. According to the X-Ray data for solid $Ce^{3+}$ acetates [15], the coordination polyhedron of the $Ce^{3+}$ ion is a distorted Archimedian antiprism. One of the edges is occupied by two oxygen atoms of the acetate cyclic group. A water molecule is located in the first coordination sphere. The $Ce-H_2O$ distance is 2.59 Å. All three acetate groups form bridge bonds, however they differ in character. One of them is linked to 2 cerium atoms, *i.e.* the acetate group is bidentate bridge-bonded (Ce–O 2.45 Å, Ce–O 2.46 Å). The second acetate group forms three bonds, two of them are virtually equivalent (Ce–O 2.41 Å, Ce–O 2.47 Å), the third one is significantly weaker (Ce–O 2.69 Å). This means that the acetate group can be considered a tridentate cyclic group. The third acetate group is also cyclic, however, all three bonds are primarly equivalent (2.61 Å, 2.56 Å and 2.58 Å).

This low-symmetric structure of the solid acetate implies the symmetry of the species formed when water molecules are displaced by the acetate group in the lanthanide aquoion polyhedron. At first, the water molecules (generally with longer bond lengths for lanthanide aquoions) are displaced in the equatorial plane. In this case, the ML and $ML_2$ species should be of similar symmetry. The replacement of the next water molecules by acetate groups causes a further lowering of the symmetry. A symmetry group not higher than $C_{2v}$ should be expected for ML and $ML_2$. The $ML_3$ species should be of even lower symmetry. The contraction of the ionic radius ($Nd^{3+}$ –0.995 Å, $Ho^{3+}$ –0.894 Å, $Er^{3+}$ –0.881 Å) across the lanthanide series may be responsible for the changes of the structure of the solid acetates and propionates of heavy lanthanides.

The coordination number of the $Er^{3+}$ ion in the solid acetate lattice is 9 [16]. Two water molecules are preserved in the first coordination sphere of $Er^{3+}$ with Er–O distances given above. Two acetates are cyclic bidentate groups, the third one is a bidentate-bridge-cyclic group. Three oxygen atoms of the acetates form the triangle plane of the prism. Three further oxygen atoms are placed above the rectangular planes of the prism.

The second triangle plane of the prism is formed by two oxygen atoms of the water molecules and an oxygen atom of the bridge-bonded acetate cyclic group.

The approximate symmetry of the polyhedron, which is half of the dimeric species $Er_2(CH_3COO)_6\cdot 4H_2O$, is $C_3$. In the case of heavy lanthanide ions the structure of the aquoion polyhedron in solution is still unclear. The two most probable structures of the aquoion are species with a coordination number 9 (with possible symmetry $D_{3h}$ or $C_{3h}$) or species with coordination number 8 ($D_{4h}$ or $D_{2d}$). In both cases the displacement of water molecules in the lanthanide aquoion polyhedron by acetate groups leads to a consecutive lowering of the symmetry of the ML, $ML_2$ and $ML_3$ species, respectively. This is in good agreement with the consecutive increase in the $\tau_2$ parameter values (see Tables VIII and IX). The real existence of $ML_4$ species is very characteristic of heavy lanthanide ions.

It is easy to explain why the further displacement of two water molecules results in two possibilities. When the bridge-bonded cyclic acetate group is preserved in the structure of the dimeric species $Ln_2(Ac)_8$ and the acetate group displaces water molecules as a cyclic group, a symmetry similar as for $ML_3$ should be observed. When water molecules are substituted by a cyclic acetate group and the bridge bonding is broken, all acetate groups become cyclic, forming a higher symmetric coordination polyhedron.

The above discussion should be considered as an argument for the usefulness of the symmetry concept in consideration of the hypersensitivity phenomena in the lanthanide complex spectra, rather than as a well-defined method for the determination of the structure of species existing in solution.

Differences in the $\tau_2$ parameter values for different low-symmetric species were observed in spectra of several lanthanide compounds.

These results are beyond the framework of the simple Judd-crystal-field model since no significant differences in the $\tau_2$ parameter values should be observed for species with $C_n$ and $C_{nv}$ symmetry. More advanced considerations however suggest that such differences should be especially important for low symmetric species. It is hard to decide if these considerations should be treated quite generally as an argument against the covalency mechanism of hypersensitivity. To do this it is necessary to investigate more completely the spectral properties and thermodynamics of these lanthanide complexes in solution, for which more covalent character may be expected.

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