THE SPECTROSCOPY AND STRUCTURE OF SOME LANTHANIDE CHLORIDES IN AMIDE SOLUTIONS

By

JANINA LEGENDZIEWICZ, KRYSYNA BUKIETYNSKA

and

BOGUSŁAWA JEZOWSKA-TRZEBIATOWSKA

INSTITUTE OF CHEMISTRY, UNIVERSITY OF WROCLAW, WROCLAW, POLAND

(Received 14. III. 1973)

The spectral properties of Pr, Nd, Ho and Er anhydrous and hydrated chlorides in amide solutions have been investigated. The Judd–Oefelt method of intensity analysis and determination of nepheloauxetic effect allowed to establish the first coordination sphere of lanthanide ion and approximate symmetry of amide solvates of anhydrous and hydrated lanthanide chlorides. The difference between symmetry and coordination numbers of light and heavy lanthanide solvates has been found. The relation between the structure of lanthanide solvates and structure of amide molecules have been established.

In recent papers [1, 2, 3, 4, 5, 6, 7, 8] several authors have considered the possibility of applying the JUDD-OEFELT method to the analysis of the spectra of lanthanide compounds. An attempt was also made to determine the nepheloauxetic effect and to relate it to the type of bonding of lanthanide systems.

In previous papers we have considered the spectral intensities of lanthanide chloride systems in amide solvents, in terms of the JUDD-OEFELT theory. These data, together with those previously obtained, enabled us to apply the experimentally determined $\tau_2$ JUDD-OEFELT parameter as an indication of symmetry for these systems. Several authors, however, are still arguing about the mechanism of the hypersensitivity lanthanide $f^\rightarrow f$ transition on the environment of the lanthanide ion, relating this sensitivity not to the symmetry changes alone.

It was expected that some steps towards explaining this problem would be made, if it were possible to find a system in which a small nepheloauxetic effect were accompanied by a significant intensity increase and by changes in $\tau_\lambda$ parameter values. The amide solutions of lanthanide chlorides seemed to be particularly convenient systems for such investigations. The amides are very polar solvents, so in such a system the nepheloauxetic effect has to be rather small. From the analysis of the charge-transfer spectra it follows that, as stated by us, no chloride ions exist in the first coordination sphere of the systems investigated [1, 9]. In such circumstances in amide solutions of lanthanide chlorides only pure amide solvates are present. If hypersensitivity
is related to the covalency effect one could not expect any significant intensity changes in such a system in comparison with aquoion. In a recent paper [1], however, we have calculated the $\tau_2$ parameters for Pr, Nd and Ho chloride systems in formamide, methylformamide, dimethylformamide and diethylformamide, where much higher $\tau_2$ parameters than for aquo ion have been found. We have suggested the symmetry of amide species and possible coordination numbers of lanthanide solvates. In the present paper we have correlated the nepheloauxetic effect for lanthanide chloride—amide systems with intensity analysis data. To ensure that the character of the intensity changes is reasonable for heavy and lighter lanthanides, it was necessary to perform an additional intensity analysis for another heavy lanthanide ion. We have chosen erbium, because of the large number of $f-f$ transitions, which resulted in a smaller error in the determination of the $\tau_2$ parameter.

**Experimental part**

*Reagents*

The hydrated chlorides were obtained by dissolving oxides in concentrated hydrochloric acid. 99.99% of the oxides were provided by Fluka. A. G. The chlorides were crystallized from water. The anhydrous chlorides PrCl$_3$, NdCl$_3$, HoCl$_3$ and ErCl$_3$ were prepared by the Freeman method [10]. The absence of the OH group frequency at 1000 cm$^{-1}$ and 3600 cm$^{-1}$ was considered as evidence of the complete dryness of the chloride. Cl$^-$ ions in the chlorides were analysed by the usual method. The lanthanides were determined as oxalates [11].

*Solvents*

Formamide (analytical grade) was purified by the method given by Verhock and Hobbs [12]. After drying over anhydrous Na$_2$SO$_4$ the product was distilled under vacuum. The medium fraction was removed and subjected to fractional crystallization. Formamide was considered as pure, when the freezing point was not higher than 2.55 °C.

Methylformamide, dimethylformamide and diethylformamide were purified by the method given by Dawson, Golben and Zimmerman [12]. The purified and dried solvents were characterized by $n_20^D = 1.4310$, $n_25^D = 1.4294$ and $n_20^D = 1.4340$, respectively.

*Absorption spectra measurements*

Absorption spectra measurements in the range examined (8000--42000 cm$^{-1}$) were recorded on a Cary 14 spectrophotometer. The respective solvents