USE OF LUMINESCENCE SPECTRA OF ADDUCTS OF EUROPIUM \( \beta \)-DIKETONATES WITH METHYL-SUBSTITUTED PYRIDINES IN INTERPRETING NMR DATA OBTAINED BY THE USE OF LANTHANIDE SHIFT REAGENTS

V. F. Zolin, L. G. Koreneva, A. E. Obukhov, V. P. Zvolinskii, and I. R. Kordova

Lanthanide shift reagents (LSR) [1] are widely used in interpreting the NMR spectra of complex molecules [1, 2] and in determining the structure of LSR–substrate adducts [3-12]. In nonpolar media, the most frequently used LSRs are lanthanide tris-\( \beta \)-diketonates \( \text{Ln(dpm)}_3 \) and \( \text{Ln(fod)}_3 \) (\( \text{Ln} = \text{Pr}^{3+}, \text{Eu}^{3+}, \text{Yb}^{3+} \)). The interpretation of experimental data obtained by the use of LSRs is based on a number of assumptions as to the interaction of the LSR with the substrate in solution: 1) Only one type of adduct exists; 2) the adduct has axial symmetry; 3) the contribution of contact interaction to the LSR-induced shift of the proton NMR is insignificant. If these assumptions are correct for a given system, the LSR-induced NMR shift can be described by the simplified formula of McConnell and Robertson [13],

\[
\Delta \nu_1/\nu = D_1 (3 \cos \theta - 1) r^{-3},
\]

where \( r_1 \) and \( \theta_1 \) are the spherical coordinates of the resonating nucleus; \( D_1 \) is an unknown coefficient. By examining the relative values of the NMR shifts of different nuclei of the substrate, we can eliminate the coefficient \( D_1 \). In this case, the induced shifts are functions of the relative location of the nucleus and the lanthanide ion, and this offers the possibility of determining the spatial structure of the LSR–substrate adduct.

However, as has been shown repeatedly [5, 6, 10, 14, 15], LSR adducts do not always have axial symmetry. In the absence of axial symmetry, the pseudocontact shifts are determined by the expression [10]

\[
\Delta \nu/\nu = D_1 (3 \cos \theta - 1) r^{-3} + D_2 \sin^2 \theta \cos 2\phi r^{-3},
\]

where \( \phi \) is the third spherical coordinate of the resonating nucleus; \( \chi_{x,y,z} \) are the principal values of the magnetic susceptibility of the adduct. The shift formula is generally not used in this form, since \( D_1 \) and \( D_2 \) are most often unknown. In the calculations, then, in addition to \( r_1 \), \( \theta_1 \), and \( \phi_1 \), which determine the conformation of the adduct, \( D_1 \) and \( D_2 \) also become variable parameters. If \( D_1 \) and \( D_2 \) are varied arbitrarily, the geometry of the complex is not determined unambiguously [9]. If the values of these coefficients are calculated from the results obtained in measurements of the anisotropy of magnetic susceptibility of crystalline compounds [5, 6], it then becomes necessary to seek a method of accounting for the change in anisotropy when the compound is dissolved.

It was pointed out previously [15-17] that the values of these coefficients might be estimated from optical spectra of the lanthanide ion. The estimate is based on the theory of Bleaney [18], who showed that under appropriate conditions, the coefficients \( D_1 \) and \( D_2 \) are proportional to the second-order crystal field parameters (CFP), \( B_{1}^{0} \) and \( B_{2}^{0} \),

\[
D_1 = C B_{1}^{0}, \quad D_2 = C B_{2}^{0},
\]

with the coefficient \( C \) for the europium ion at 300°C being equal to \(-3 \text{ ppm} \cdot \text{Å/cm} \) [16]. The CFPs \( B_{1}^{0} \) and \( B_{2}^{0} \) can be determined from the optical spectra of europium [19, 20], for example

\[
B_{2}^{0} = -2.5[E(B_1) + E(B_2)], \quad B_{1}^{0} = -2.5[E(B_1) - E(B_2)].
\]
Fig. 1. Densitograms of luminescence spectra of europium β-diketonate adducts: 1) adduct of Eu(fod)$_3$ with pyridine; 2) adduct of Eu(dpm)$_3$ with pyridine; 3) adduct of Eu(dpm)$_3$ with 2-methylpyridine; a) at 300°K; b) at 77°K.

where $E(B_1)$ and $E(B_2)$ are the Stark displacements of the half-levels of the $^7F_1$ level, the wavefunctions of which are transformed similar to representations of $B_1$ and $B_2$ of symmetry group $C_{2v}$.

It will be shown in the following material that, when we use the coefficients $D_1$ and $D_2$ calculated by the use of Eqs. (3) and (4), we can determine the geometric parameters of the adducts Eu(dpm)$_3$ and Eu(fod)$_3$ in those cases in which the symmetry of the adduct is not axial. Simultaneously, by means of optical and NMR spectroscopy, we can test the validity of the above-listed assumptions 1-3 for the adducts of these LSRs.

In order to resolve these problems, we selected the adducts of Ln(dpm)$_3$ and Ln(fod)$_3$ with alkyl-substituted pyridines, which may be considered as the simplest set of substrates. Although the adducts of these LCRs with certain substituted pyridines have been investigated by means of NMR [3-6, 10] or optical methods [15, 21], our work was different in that it constituted a systematic investigation of these adducts with simultaneous use of NMR and luminescence spectroscopy to obtain luminescence and NMR spectra on exactly the same adduct samples. Also, in comparison with the earlier studies [4, 6], our work has included a more thorough accounting for contact interaction of the lanthanide ions with the protons and carbon nuclei. We have determined repeatedly the position of the ion in certain adducts, both with and without axial symmetry of dipole-dipole interaction. The aim of the calculations, similar to that in [4], was to establish the influence of the different factors on the adduct parameters as obtained by calculation. Also, we have demonstrated the impossibility of using the axial approximation in cases in which the optical experiment indicates nonaxiality of the adduct.

In examining the luminescence spectroscopic data, it should be kept in view that the condition of fast exchange $\Delta \omega \Delta \tau \ll 1$ ($\Delta \omega$ is the shift between resonance frequencies of the complex participating in the exchange; $\Delta \tau$ is the characteristic time of exchange) can be fulfilled only for the NMR experiment. The influence of ligand exchange on the optical spectrum can be estimated by comparing the luminescence spectra at 300°K, i.e., with exchange, and in frozen solutions at 77°K in the absence of exchange. In Fig. 1 we show luminescence spectra of certain adducts of Eu(dpm)$_3$ and Eu(fod)$_3$ that were obtained at these temperatures. In the spectrum of the adduct of Eu(fod)$_3$ with pyridine that was obtained at 77°K (spectrum 1b), we observe five components of the $^5D_0-^7F_1$ transition, indicating the presence of more than one type of adduct. When the spectrum of the same sample is obtained at 300°K (spectrum 1a), only three narrow lines are observed in this transition. These changes in the spectrum, if the influence of transfer of excitation is eliminated (see below), indicate the