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ISOTOPE EFFECTS IN NUCLEAR MAGNETIC RESONANCE SPECTRA OF POLYGLYCOLDIMETHYLEThERS, COMPLEXED WITH RARE-EARTH SHIFT REAGENTS.

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Recently (1,2) we observed an interesting isotope effect in the NMR spectrum of
$\text{CH}_2\text{OCH}_2\text{CD}_2\text{OCH}_2\text{CH}_2\text{OCH}_3$ (d$_2$-glyme-4) complexed with tris(dipivalomethanato)europium
(Eu(DPM)$_3$) (3) or praseodymium (Pr(DPM)$_3$) (4). All lines, detected in the spectrum of the
non-deuterated glyme-4 lanthanide (Ln) complex, were doubled in the spectrum of the deuterated
d$_2$-glyme-4 lanthanide complex (see ref. 1, fig. 2 and fig. 5). Smith et al. (5) also reported
such an effect for the adducts formed by complexation of Eu(DPM)$_3$-2 pyridine to deuterated and
non-deuterated trans-verbanol. They explained this phenomenon by a greater association constant
between the deuterium substituted compound and the metal complex than between the non-deuterated
compound and the metal complex. In this paper we like to present further evidence for the
correctness of this interpretation. We will show that the isotope effect, observed in the spectra
of Ln(DPM)$_3$-d$_2$-glyme-4, is caused by an intramolecular exchange reaction of the lanthanide
complex. Furthermore we will demonstrate that in the spectra of Ln(DPM)$_3$, complexed with a
mixture of non-deuterated glyme-5 and symmetrically deuterated d$_2$-glyme-5 ([CH$_3$OCH$_2$CD$_2$OCD$_2$CH$_3$]$_2$O),
intermolecular exchange reactions of the lanthanide complex give rise to isotope effects,
similar to those observed in the spectra of Ln(DPM)$_3$-d$_2$-glyme-4.

Intramolecular exchange

A spectrum of a solution containing equivalent amounts of Pr(DPM)$_3$ and d$_2$-glyme-4
in CCl$_4$ has been given in an earlier publication (1, fig. 5). Compared with the NMR pattern
of Ln(DPM)$_3$ with non-deuterated glyme-4, which consists of one singlet for the CH$_3$ group and
two unresolved triplets and one singlet for the CH$_2$ groups (1, fig. 2), the spectrum of
Pr(DPM)$_3$-d$_2$-glyme-4 clearly shows a doubling of the CH$_3$, C$_3$ and C$_1$ signals, the shift difference
between the two methyl peaks being 19Hz. However, in the NMR spectrum of a solution of d$_2$-
 glyme-4 in the presence of a 2.5 times excess of Pr(DPM)$_3$, this doubling was absent.

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We already pointed out (2) that in an Ln(DPM)$_3$-d$_2$-glyme-4 (1 : 1) mixture the following equilibrium exists:

\[
\begin{align*}
\text{(A)} & : & \quad \text{CH}_3\text{OCH}_2\text{CD}_2\text{OCH}_2\text{CD}_2\text{OCH}_3 \quad \quad \rightleftharpoons \quad \text{CH}_3\text{OCH}_2\text{CD}_2\text{OCH}_2\text{CH}_2\text{OCH}_3 \\
\text{(B)} & : & \quad \text{Ln} \quad \quad \quad \quad \quad \quad \text{Ln}
\end{align*}
\]

In the fast exchange limit the recorded NMR spectrum will be a statistical average of the spectra of A and B.

If the complexation constant between the metal complex and the -OCH$_2$CD$_2$O- moiety is greater than between the metal complex and the -OCH$_2$CH$_2$O- moiety a doubling of all NMR signals will occur because of this exchange reaction (except for the C$_2$ peak). The most shifted peak of each couple arises from those protons, situated in that half of the molecule which contains the CD$_2$ group. As reported before (2), when the lanthanide/glyme ratio exceeds unity, a second lanthanide complex binds to the glyme. In this situation the intramolecular reaction is blocked and the doubling of the peaks must disappear, as has in fact been observed.

The equilibrium constant K for this exchange reaction may be obtained in the following way. In the fast exchange limit the resonances of, for instance, the two CH$_3$ groups, indicated by $\bar{\omega}_p$ and $\bar{\omega}_q$ (see reaction scheme), are given by

\[
\begin{align*}
\bar{\omega}_p &= f_A \omega_A + f_B \omega_B \\
\bar{\omega}_q &= f_A \omega_A + f_B \omega_B
\end{align*}
\]

where $f_A$ and $f_B$ are the fractions of species A and B, respectively, $\omega_p$ is the resonance frequency of the methyl group p in species A (as resonance frequency of the methyl group q in species B), and $\omega_B$ is the resonance frequency of the methyl group p in species B (as resonance frequency of the methyl group q in species A).

Since $K = f_B / f_A$, it is easy to show that

\[
K = \frac{(\bar{\omega}_A - \bar{\omega}_B) + (\bar{\omega}_q - \bar{\omega}_p)}{(\bar{\omega}_A - \bar{\omega}_B) - (\bar{\omega}_q - \bar{\omega}_p)}
\]

$\bar{\omega}_q - \bar{\omega}_p$ can be measured directly from the spectra of the Ln(DPM)$_3$-d$_2$-glyme-4 (1 : 1) mixtures. A good estimate for $\omega_A$ and $\omega_B$ can be obtained from the spectrum of a 1 : 1 mixture of Ln(DPM)$_3$ and ethyleneglycol methyl, n-octylether (CH$_3$OCH$_2$CH$_2$O(CH$_2$)$_7$CH$_3$), a compound containing one complexation site of two oxygen atoms. This results in a value for K of 1.030 ± 0.005 for both Eu(DPM)$_3$ and Pr(DPM)$_3$, which seems to be a reasonable value for such an isotope effect.

$^\ddagger$This can be derived from the two peaks originating from the C$_3$ protons (see fig. 5, ref. 1). The peak with the smallest linewidth is shifted most. Since the linewidth is mainly determined by the spin-spin interactions with the neighbouring group, the narrowest peak must be assigned to the CH$_2$ group adjacent to the CD$_2$ group.
Intermolecular exchange

Another system, which has been investigated by us is a mixture of glyme-5 and d$_4$-glyme-5, glyme-5 being present in slight excess. A solution of a small amount of this mixture in CCl$_4$ with a 2.5 times excess of Eu(DPM)$_3$ yields the NMR pattern, shown in figure 1.

The structural formula of the deuterated species is given in this figure, together with the peak assignments, which were reported before (2). The spectrum shows one set of NMR signals and is almost identical to that of Eu(DPM)$_3$ and non-deuterated glyme-5 (ratio 2.5 : 1). However, the same mixture but with a Eu(DPM)$_3$ concentration equal to the total glyme concentration (ratio 1 : 1) gives rise to the NMR pattern, shown in figure 2.

Now the CH$_j$, C$_j$ and C$_4$ signals are doubled. The most shifted member of each couple, having the lowest intensity, must be assigned to the deuterated glyme-5, in accordance with our earlier findings that deuteration enhances the association constant between the rare earth complex and the glyme oxygens.

This observation can not be explained by intramolecular exchange because of the symmetry of the glyme molecules involved. One is forced to postulate the presence of a small percentage of diassociated lanthanide/glyme adduct ([Ln(DPM)$_3$]$_2$-glyme) in the 1 : 1 mixture of lanthanide and glyme-5/d$_4$-glyme-5. The stronger binding of Ln(DPM)$_3$ to the deuterated species than to the non-deuterated species leads to a slight excess of [Ln(DPM)$_3$]$_2$-d$_4$-glyme-5 with respect to [Ln(DPM)$_3$]$_2$-glyme-5. Intermolecular Ln exchange reactions between the various species, e.g. mono- and diassociated lanthanide/glyme complexes, will then produce the extra set of peaks, observed in the spectrum which is shown in figure 2. This explanation is supported by the observation that the chemical shift differences disappear when the Ln/total glyme ratio is 2.5 : 1 (fig. 1).
It is tempting to speculate about the origin of these kinetic isotope effects. The observed effects seem to indicate that not only the oxygen atoms are involved in the binding of the metal complex, but also some protons (deuterons). This view is supported by the observation that the shifts of the protons of the terminal and penultimate CH\textsubscript{2} groups not only originate from contributions of pseudo-contact interactions but also contain a Fermi contact shift contribution (2).

The experiments were performed on a Varian A60A and a Varian T60 spectrometer.

Acknowledgement

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ESR STUDIES ON THE [Ag(dtc)₂]₂ DIMER;
THE FIRST TRIPLET SPECIES CONTAINING SILVER

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A single crystal ESR study of silver di-isopropyldithiocarbamate diluted in the corresponding zinc complex has provided evidence for spin–spin interaction between two silver atoms within isolated dimers. The directions of the principal axes of the zero field splitting tensor point to a large spin–orbit interaction.

1. Introduction

As part of our ESR studies on sulphur or selenium coordinated complexes of the coinage metals [1–4], we have investigated the Ag(dtc)₂—Zn(dtc)₂ system (dtc = di-isopropyldithiocarbamate). When Ag(dtc)₂ is built into the dimeric Zn(dtc)₂ [5] at low concentrations all the Ag(dtc)₂ occurs in the form of Zn(dtc)₂—Ag(dtc)₂ pairs, which give rise to \( S = \frac{1}{2} \) spectra. These doublet spectra will be discussed elsewhere [6]. At higher Ag:Zn ratios (e.g., 1:3) also Ag(dtc)₂—Ag(dtc)₂ pairs are formed giving rise to triplet spectra (\( S = 1 \)), which are the subject of this paper.

2. Experimental

Single crystals of Zn(dtc)₂ containing about 25% Ag(dtc)₂ were grown by slow evaporation of a solution of these compounds in dimethylformamide. In order to derive the principal values of the \( g \) and zero-field splitting (\( D \)) tensor ESR spectra were recorded every 15° in three arbitrary planes, usually taken almost mutually perpendicular. With the help of a computer program a transformation to an orthogonal axes system was accomplished. The angular variation of \( D \) is given by the expression:

\[
g^2(H)D(H) = \sum_{p,q} (g\cdot D\cdot g^\dagger)_{pq} l_p \quad (p,q = k,y,z),
\]

where \( l_x, l_y, \) and \( l_z \) are the direction coefficients of the external magnetic field \( H \) in a fixed reference frame \( x, y, z \) and \( g^\dagger \) is the transposed \( g \)-tensor. Since the electronic Zeeman term at 3kG and the spin–spin interaction of the two unpaired electrons are of about the same order of magnitude, the measured values of both \( g(H) \) and \( D(H) \) were corrected for second order effects, which for some orientations reached the values of 0.05 and 0.0015 cm⁻¹ for \( g(H) \) and \( D(H) \), respectively. All data were analysed using a least squares method.

A Varian V 4503 X band spectrometer was used to record the single crystal spectra. The klystron frequency was measured with a Hewlett-Packard 5246 L frequency counter. The magnetic field values were measured by means of an AEG nuclear magnetic resonance gaussmeter, in conjunction with the frequency counter mentioned above.

3. Results

In fig. 1 the ESR spectrum is shown of an Ag(dtc)₂—Zn(dtc)₂ single crystal with an Ag:Zn ratio of approximately 1:3. Since the unit cell contains two magnetically inequivalent sites, the spectrum consists of two \( S = \frac{1}{2} \) spectra (\( d_1 \) and \( d_2 \)) and two \( S = 1 \) spectra (\( T_1 \) and \( T_2 \)), showing hyperfine interaction with one and two Ag nuclei (\( I = \frac{1}{2} \)), respectively. Similar spectra
Fig. 1. ESR spectrum of silver dithiocarbamate magnetically diluted in the analogous zinc complex. The inner part of the spectrum refers to the doublet monomer, the outside parts, recorded with a 10 fold increase in amplification with respect to the inner part, to the triplet dimer.

were also observed for the Cu(dtc)$_2$—Zn(dtc)$_2$ system by Villa and Hatfield [7] and by Cowsik et al. [8]. The best resolved ESR spectra at X-band frequencies are measured below $T = 130\,^\circ\text{K}$; above this temperature the triplet lines become broader in contrast to what has been found for the triplet spectra of [Cu(dtc)$_2$]$_2$. The hyperfine coupling parameters can be determined most reliably from the ‘forbidden’ $A_{M_s} = 2$ transition, which for all orientations of the crystal gives the best resolved hyperfine pattern.

The triplet spectra can be described with the spin hamiltonian

$$
\hat{H} = \beta_e H \cdot g \cdot S - g_N \beta_N H \cdot (I_1 + I_2) + S \cdot A \cdot (I_1 + I_2) - S \cdot D \cdot S,
$$

where the first two terms stand for the Zeeman interactions of the two electron spins and the two nuclear spins and the third term for the hyperfine interactions. The last term describes the spin—spin interaction between the two unpaired electrons.

From the spectra we determined for the doublet species the $g$ and hyperfine tensor ($A$) and for the triplet species the $g$, $A$ and $D$ tensor. In table 1 the principal values of all these tensors are listed. Fig. 2 shows the directions of the $g$ and $D$ tensor for the triplet species, assuming that the Ag dimer has the same structure as the Cu dimer [9]. The direction of $g_z$ coincides with the normal to the least squares plane through the four sulphur atoms with the shortest Ag—S distances. The $g_x$ and $g_y$ axes lie in this plane with $g_x$ bisecting approximately the S(1)—Ag—C(1) angle. The angles between the principal axes of the $g$ tensor and the $D$ tensor are listed in table 2.

The principal axes of the $g$ tensor of the doublet species coincide within $5^\circ$ with those for the triplet species. The same coincidence has been found for the $g$ and $A$ tensor of both the doublet and triplet species. A comparison between the $A$ tensors for the doublet and triplet species shows that the $A_1$ components co-

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**Table 1**

| Spin hamiltonian parameters for Ag(dtc)$_2$ and [Ag(dtc)$_2$]$_2$ with $R = i$-C$_3$H$_7$, both in Zn(dtc)$_2$. $A$ and $D$ values in $10^{-4}$ cm$^{-1}$ |
|---------------------------------|-----------------|
|                                | Ag(dtc)$_2$     | [Ag(dtc)$_2$]$_2$ |
| $g_x$                          | 2.0094 ± 0.0001 | 2.0087 ± 0.0001   |
| $g_y$                          | 2.0157 ± 0.0001 | 2.0156 ± 0.0003   |
| $g_z$                          | 2.0493 ± 0.0001 | 2.0456 ± 0.0005   |
| $A_1$                          | 33.5 ± 0.2      | 17.7 ± 0.7        |
| $A_2$                          | 22.6 ± 0.7      | 13.2 ± 0.7        |
| $A_3$                          | 21.1 ± 0.1      | 12.5 ± 0.7        |
| $D_1$                          | ± (683 ± 2)     |                  |
| $D_2$                          | ± (154 ± 5)     |                  |
| $D_3$                          | ± (529 ± 1)     |                  |
incide, but the corresponding $A_2$ and $A_3$ components differ by 14° and 10° (accuracy = 2.5°).

4. Discussion

The close similarity between the principal $g$ values for the doublet and triplet species, together with the observed coincidence of their principal axes, suggest that the two dimers [Ag(dtc)$_2$)$_2$ and Ag(dtc)$_2$—Zn (dtc)$_2$ have the same structure (at least with respect to the surroundings of the Ag atom). ESR single crystal studies on silver diethylidithiocarbamate, diluted in the corresponding zinc complex [6] have shown that the structure of the Ag—Zn dimer closely resembles the structure of the Cu—Cu dimer in its own crystal lattice [9].

The $D$ tensor components are much larger than the values of ± 0.0184, ± 0.0092, ± 0.0092 cm$^{-1}$ found for the Cu(dtc)$_2$—Zn(dtc)$_2$ system [7, 8], which were completely ascribed to dipolar interactions between the two unpaired electrons. For the Ag compound the dipolar interaction cannot be larger than for the Cu compound, since it is proportional to $\langle r^{-3} \rangle$, where $r_{12}$ is the distance between the two spins, which is expected to be larger for Ag—Ag than for Cu—Cu. Moreover, if the dipolar interaction is the main mechanism one expects a $D$ tensor, which is axially symmetric around the line connecting the centers of the two Ag(dtc)$_2$ molecules. We think therefore, that the $D$ tensor must contain significant contributions from spin—orbit coupling. The peculiar orientations of the principal axes of the $D$ tensor also point to this.

From the fact that at 4° K a spectrum was still observed which had approximately the same intensity as the one recorded at 77°K, we conclude that

<table>
<thead>
<tr>
<th>$g_x$</th>
<th>$D_1$</th>
<th>$D_2$</th>
<th>$D_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>52</td>
<td>65</td>
<td>132</td>
<td></td>
</tr>
<tr>
<td>$g_y$</td>
<td>132</td>
<td>100</td>
<td>135</td>
</tr>
<tr>
<td>$g_z$</td>
<td>65</td>
<td>153</td>
<td>100</td>
</tr>
</tbody>
</table>
[Ag(dtc)$_2$]$_2$ must have a triplet ground state. At the moment experiments are being performed in order to determine the energy distance between the singlet and the triplet state.

In first order one expects that the hyperfine coupling parameters of the dimer are half those of the monomer. Inspection of table 1 shows that significant deviations from this ratio occur, which may be ascribed to supertransferred hyperfine fields$^4$. 

From ref. [5] we calculated that the shortest distance between two metal atoms in two different [Zn(dtc)$_2$]$_2$ dimers is about 6.7 Å. If these two metal positions are occupied by silver atoms the so formed triplet species will have a dipolar axial $D$ tensor with a largest component of about 0.0057 cm$^{-1}$. For some orientations of the crystal indeed additional triplet spectra were observed, with $D(H)$ values of this order of magnitude.

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