

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

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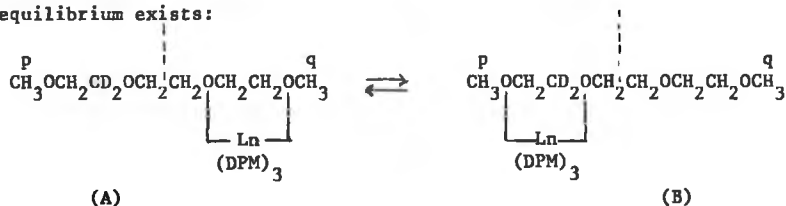
Recently (1,2) we observed an interesting isotope effect in the NMR spectrum of $\text{CH}_3\text{OCH}_2\text{CD}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3$ (d_2 -glyme-4) complexed with tris(dipivalomethanato)europium ($\text{Eu}(\text{DPM})_3$) (3) or -praseodymium ($\text{Pr}(\text{DPM})_3$) (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 $\text{Eu}(\text{DPM})_3 \cdot 2$ 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 $\text{Ln}(\text{DPM})_3$ - d_2 -glyme-4, is caused by an intramolecular exchange reaction of the lanthanide complex. Furthermore we will demonstrate that in the spectra of $\text{Ln}(\text{DPM})_3$, complexed with a mixture of non-deuterated glyme-5 and symmetrically deuterated d_4 -glyme-5 ($[\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCD}_2\text{CH}_2]_2\text{O}$), intermolecular exchange reactions of the lanthanide complex give rise to isotope effects, similar to those observed in the spectra of $\text{Ln}(\text{DPM})_3$ - d_2 -glyme-4.

Intramolecular exchange

A spectrum of a solution containing equivalent amounts of $\text{Pr}(\text{DPM})_3$ and d_2 -glyme-4 in CCl_4 has been given in an earlier publication (1, fig. 5). Compared with the NMR pattern of $\text{Ln}(\text{DPM})_3$ 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 $\text{Pr}(\text{DPM})_3$ - 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 $\text{Pr}(\text{DPM})_3$, this doubling was absent.

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



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 $-\text{OCH}_2\text{CD}_2\text{O}-$ moiety is greater than between the metal complex and the $-\text{OCH}_2\text{CH}_2\text{O}-$ 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^x. 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

$$\begin{aligned}
 \bar{\omega}_p &= f_A \omega_A + f_B \omega_B \\
 \bar{\omega}_q &= f_B \omega_A + f_A \omega_B
 \end{aligned}$$

where f_A and f_B are the fractions of species A and B, respectively, ω_A is the resonance frequency of the methyl group p in species A (= resonance frequency of the methyl group q in species B), and ω_B is the resonance frequency of the methyl group p in species B (= resonance frequency of the methyl group q in species A).

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

$$K = \frac{(\omega_A - \omega_B) + (\bar{\omega}_q - \bar{\omega}_p)}{(\omega_A - \omega_B) - (\bar{\omega}_q - \bar{\omega}_p)}$$

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

^xThis 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.

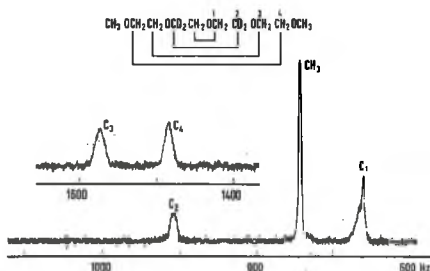


Fig. 1. 1H NMR spectrum (60 MHz) of a 2.5 : 1 mixture of $Eu(DPM)_3$ and glyme-5/ d_4 -glyme-5 (glyme-5 in slight excess) in CCl_4 at $37^\circ C$ ($[Eu(DPM)_3] = 0.15 M$). Peak positions are given relative to TMS.

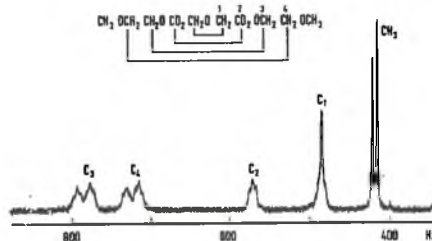


Fig. 2. 1H NMR spectrum (60 MHz) of a 1 : 1 mixture of $Eu(DPM)_3$ and glyme-5/ d_4 -glyme-5 (glyme-5 in slight excess) in CCl_4 at $37^\circ C$ ($[Eu(DPM)_3] = 0.15 M$). Peak positions are given relative to TMS.

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_3 , C_3 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 CH₂ 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.

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ESR STUDIES ON THE $[\text{Ag}(\text{dtc})_2]_2$ DIMER; THE FIRST TRIPLET SPECIES CONTAINING SILVER

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A single crystal ESR study of silver di-isopropylthiocarbamate 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 $\text{Ag}(\text{dtc})_2\text{-Zn}(\text{dtc})_2$ system (dtc = di-isopropylthiocarbamate). When $\text{Ag}(\text{dtc})_2$ is built into the dimeric $\text{Zn}(\text{dtc})_2$ [5] at low concentrations all the $\text{Ag}(\text{dtc})_2$ occurs in the form of $\text{Zn}(\text{dtc})_2\text{-Ag}(\text{dtc})_2$ 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 $\text{Ag}(\text{dtc})_2\text{-Ag}(\text{dtc})_2$ pairs are formed giving rise to triplet spectra ($S = 1$), which are the subject of this paper.

2. Experimental

Single crystals of $\text{Zn}(\text{dtc})_2$ containing about 25% $\text{Ag}(\text{dtc})_2$ 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:

$$g^2(H)D(H) = \sum_{p,q} l_p (\mathbf{g} \cdot \mathbf{D} \cdot \mathbf{g}^t)_{pq} l_q \quad (p,q = k,y,z),$$

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 \mathbf{g}^t 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 $\mathbf{g}(H)$ and $\mathbf{D}(H)$ were corrected for second order effects, which for some orientations reached the values of 0.05 and 0.0015 cm^{-1} for $\mathbf{g}(H)$ and $\mathbf{D}(H)$, 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 $\text{Ag}(\text{dtc})_2\text{-Zn}(\text{dtc})_2$ 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

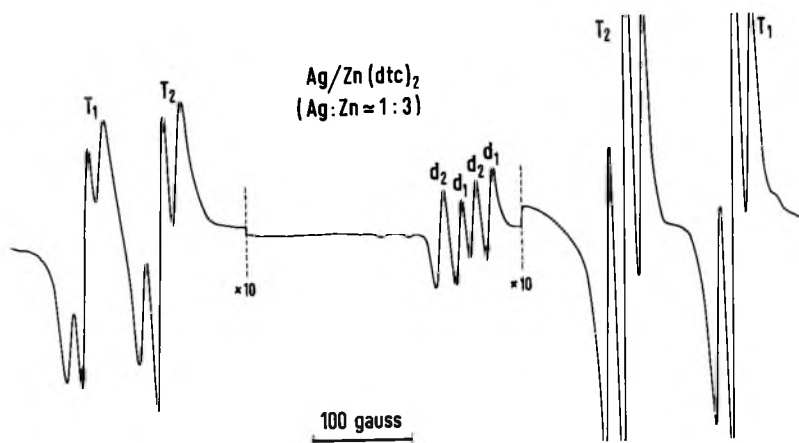


Fig. 1. ESR spectrum of silver dithiocarbamate magnetically diluted in the analogous zinc complex. The inner part of the spectrum refers to the doublet monomer, the outside parts, recorded with a 10 fold increase in amplification with respect to the inner part, to the triplet dimer.

were also observed for the $\text{Cu}(\text{dtc})_2\text{-Zn}(\text{dtc})_2$ 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 $[\text{Cu}(\text{dtc})_2]_2$. The hyperfine coupling parameters can be determined most reliably from the 'forbidden' $\Delta M_S = 2$ transition, which for all orientations of the crystal gives the best resolved hyperfine pattern.

The triplet spectra can be described with the spin hamiltonian

$$\begin{aligned} \mathcal{H} = & \beta_e \mathbf{H} \cdot \mathbf{g} \cdot \mathbf{S} - g_N \beta_N \mathbf{H} \cdot (\mathbf{I}_1 + \mathbf{I}_2) \\ & + \mathbf{S} \cdot \mathbf{A} \cdot (\mathbf{I}_1 + \mathbf{I}_2) - \mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S}, \end{aligned}$$

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 $\text{S}(1)\text{-Ag-C}(1)$ 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° 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-

Table 1
Spin hamiltonian parameters for $\text{Ag}(\text{dtc})_2$ and $[\text{Ag}(\text{dtc})_2]_2$, with $\text{R} = i\text{-C}_3\text{H}_7$, both in $\text{Zn}(\text{dtc})_2$.
 A and D values in 10^{-4} cm^{-1}

	$\text{Ag}(\text{dtc})_2$	$[\text{Ag}(\text{dtc})_2]_2$
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		$\pm (683 \pm 2)$
D_2		$\mp (154 \pm 5)$
D_3		$\mp (529 \pm 1)$

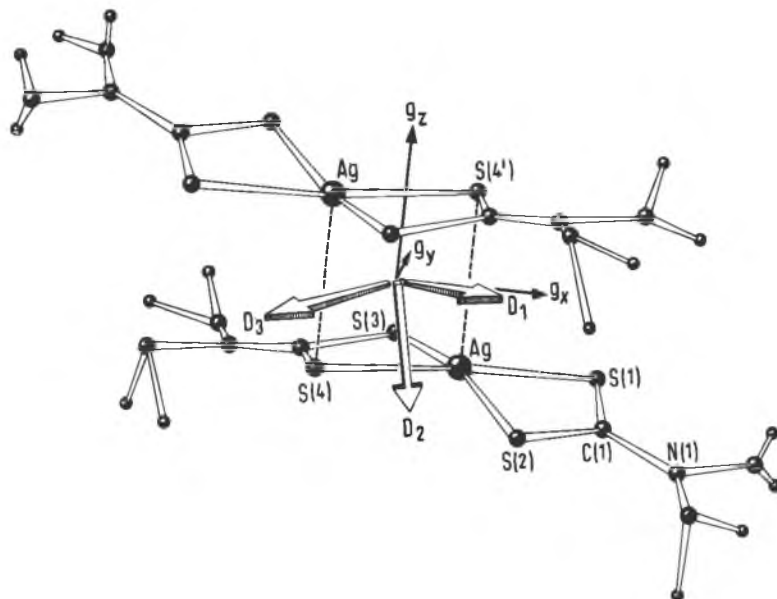


Fig. 2. Sketch of the directions of the g and D tensor components indicated in the structure diagram for the triplet dimer $[\text{Ag}(\text{dtc})_2]_2$.

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 $[\text{Ag}(\text{dtc})_2]_2$ and $\text{Ag}(\text{dtc})_2\text{-Zn}(\text{dtc})_2$ have the same structure (at least with respect to the surroundings of the Ag atom). ESR single crystal studies on silver diethyldithiocarbamate, 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 , $\mp 0.0092 \text{ cm}^{-1}$ found for the $\text{Cu}(\text{dtc})_2\text{-Zn}(\text{dtc})_2$ 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 $\langle r_{12}^{-3} \rangle$, 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 $\text{Ag}(\text{dtc})_2$ 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 2
Direction angles (in degrees) of the principal axes of the D tensor relative to those of the g tensor, for $[\text{Ag}(\text{dtc})_2]_2$ in $\text{Zn}(\text{dtc})_2$, with $\text{R} = i\text{-C}_3\text{H}_7$, (accuracy 1°)

	D_1	D_2	D_3
g_x	52	65	132
g_y	132	100	135
g_z	65	153	100

$[\text{Ag}(\text{dtc})_2]_2$ 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 [10].

From ref. [5] we calculated that the shortest distance between two metal atoms in two different $[\text{Zn}(\text{dtc})_2]_2$ 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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