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Solvent Effects on the Isotropic Shifts and Magnetic Susceptibility of the Shift Reagent Tris(dipivaloylmethanato)europium(III)

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The solution magnetic susceptibilities of the shift reagent $Eu(DPM)_3$ (DPM = 2,2,6,6-tetramethyl-3,5-heptanedione) are reported. The susceptibility is lower in solution than in the solid state and decreases with increasing coordinating ability of the solvent or added solute. The isotropic shift of the ligand *tert*-butyl protons increases as the solvent basicity increases. The magnetic properties are dependent on the presence or absence of dimers in solution and the coordination number and geometry. 1-Adamantanamine is used as a substrate molecule to show that the dipolar shift mechanism is dominant but that a substantial scalar mechanism may contribute to the shift of protons close to the source of unpaired spin density.

In 1969 Hinckley reported the successful nmr analysis of cholesterol using the dipyridine adduct of $Eu(DPM)_3$ as a shift reagent.[1] Further studies showed that the pyridine-free complex produced much larger shifts.[2] Many recent papers have appeared describing the applications of $Eu(DPM)_3$ and other lanthanide complexes, but the mechanism by which they act is not yet fully understood.[3] Isotropic shifts arise from two separate mechanisms: the scalar (or contact) and the dipolar (or pseudocontact). The relationship between magnetic susceptibility and isotropic shifts is well known.[4-7] The lanthanide induced shifts are in the directions predicted by available magnetic anisotropy data as would be expected if the dipolar contribution to the shift is dominant.[3a] Since the total isotropic shift is proportional to the magnetic susceptibility and to the susceptibility anisotropy, a direct correlation between the magnitude of the magnetic susceptibility of the lanthanide complex and the isotropic shift would be expected.

In order to assess the importance of the magnetic properties of $Eu(DPM)_3$ on its action as a shift reagent, we have examined the magnetic susceptibility of the complex in solvents of varying Lewis basicity. The largest induced isotropic shifts occur in molecules which have the strongest Lewis bases as functional groups.[8] We report here the first measurements of the changes in magnetic properties of $Eu(DPM)_3$ in the presence of potentially coordinating Lewis bases and the concomitant changes in effectiveness of its ability to act as a shift reagent.

Experimental Section

Preparation of $Eu(DPM)_4$.—$Eu(DPM)_3$ was prepared by the method of Eisentraut and Sievers.[9] The europium complex was purified by recrystallization from chloroform and by vacuum sublimation. Dipivaloylmethane was obtained from Eastman Organic Chemicals and used without further purification. *Anal.* Calcd for $C_{33}H_{57}O_6Eu$: C, 56.48; H, 8.19. Found: C, 56.42; H, 8.17.

Preparation of $Eu(DPM)_3 \cdot 2py$.—$Eu(DPM)_3 \cdot 2py$ was obtained by dissolving $Eu(DPM)_3$ in 10 ml of hot pyridine until a saturated solution was obtained. A slight excess of pyridine was added and the solution was refrigerated overnight. Colorless crystals were collected, air-dried, and stored in a desiccator. *Anal.* Calcd for $C_{43}H_{67}N_2O_6Eu$: C, 60.06; H, 7.85. Found: C, 60.14; H, 7.78.

Magnetic Susceptibilities.[10]—The susceptibilities of $Eu(DPM)_3$ and $Eu(DPM)_3 \cdot 2py$ in solution were measured by the Evans nmr method.[11] The magnetic susceptibilities obtained in most solvents qualitatively agree with those calculated by Van Vleck,[12] using eq 1 which describes the case of multiplet intervals comparable to kT. The energy levels W^0 and the temperature-independent paramagnetism α are indexed by the total quantum number J. The energy of the first excited state ($^7F_1$) of europium(III) is only approximately 200 cm^{-1} above the ground state ($^7F_0$). The factor kT = 210 cm^{-1} at 300°K.

$$\chi = \frac{N \sum_{J=L-S}^{L+S} \{[g_J{}^2\beta^2 J(J+1)/3kT] + \alpha_J\} \times (2J+1)e^{-W_J{}^0/kT}}{\Sigma(2J+1)e^{-W_J{}^0/kT}} \tag{1}$$

Isotropic Shift Studies.—All magnetic resonance studies were carried out using a Varian A-60D spectrometer. Deuterated solvents were used as obtained without further purification or drying. All other solvents were dried over molecular sieves. The test molecule, 1-adamantanamine, was used as obtained from Aldrich Chemical Co., Inc.

The observed shifts are caused by the unpaired electrons on the Eu^{3+} ion. The contact shift[13-15] is directly related to the amount of unpaired electron spin density at the nucleus and is given for rare earth ions[15] by eq 2 where $\Delta\nu_c$ is the contact shift, A_i is the electron–nucleus hyperfine coupling constant, and g_L is the Lande

$$\Delta\nu_c = \left[\frac{J(J+1)\beta^2}{3kT}\right]\frac{A_i}{g_n\beta_n}g_L(g_L - 1) \tag{2}$$

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[9] K. J. Eisentraut and R. E. Sievers, *Inorg. Syn.*, **11**, 94 (1970).

[10] P. W. Selwood, "Magneto Chemistry," Wiley-Interscience, New York, N. Y., 1956.

[11] The susceptibility was calculated from the equation $\chi = (3\Delta f/2\pi fm) + \chi_0$: D. F. Evans, *J. Chem. Soc.*, 2003 (1959). Values of χ_0 were obtained from standard tables.

[12] J. H. Van Vleck, "The Theory of Electric and Magnetic Susceptibilities," Oxford University Press, London, 1932, Chapter IX.

[13] H. M. McConnell and D. B. Chestnut, *J. Chem. Phys.*, **28**, 107 (1958).

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g factor. The other symbols have their usual meanings.

The pseudocontact through-space coupling is represented by eq 3[16] where $\Delta\nu_p$ is the shift due to the pseudocontact mechanism, r_i is the distance from the nucleus of the paramagnetic ion to the

$$\Delta\nu_p = -\left[\frac{J(J+1)\beta^2}{3kT}\right]\left[\frac{3\cos^2\theta_i - 1}{r_i^3}\right]f(g) \quad (3)$$

ith proton, θ_i is the angle between the distance vector and the principal molecular axis, assuming at least a threefold symmetry axis, and $f(g)$ describes the magnetic anisotropy of the molecule.

Both $\Delta\nu_c$ and $\Delta\nu_p$ as well as the expression for χ are directly dependent on the same term, $J(J + 1)\beta^2/3kT$. A decrease or increase of the magnetic susceptibility should cause a corresponding decrease or increase of the observed nmr shifts if the change in magnetic susceptibility is a major factor influencing the isotropic shifts in solution.

Results and Discussion

1. Solvent Effects on Eu(DPM)$_3$.—The solid-state gram-susceptibility for Eu(DPM)$_3$, χ_g, has been found to be 7.88×10^{-6} cgsu corresponding to an effective magnetic moment, μ_{eff}, of 3.47 BM at 22°.[17] This value agrees qualitatively with Van Vleck's calculated values of 3.4–3.5 BM for the Eu^{3+} ion. The solution-state magnetic susceptibilities are given in Table I.

TABLE I

MAGNETIC GRAM-SUSCEPTIBILITIES OF Eu(DMP)$_3$ AND THE ISOTROPIC PMR SHIFTS OF THE COMPLEXED DIPIVALOYLMETHANATO LIGAND IN VARIOUS SOLVENTS

Solvent	$10^6\chi_g$, cgsu	Temp, °C	Resonance freq,[a] Hz	Isotropic shift,[b] Hz
Chloroform-d_1	5.41 ± 0.17	36.3	−12[c]	57
CCl$_4$	5.34 ± 0.13	30.2	−27[d]	40
Methanol-d_4	5.25 ± 0.07	30.0	43	112
Ethyl acetate	5.10 ± 0.11	29.4	56	125
Ethanol	5.03 ± 0.10	37.2	25	94
Acetone-d_6	4.77 ± 0.03	29.4	47	116
Benzene-d_6	4.56 ± 0.09	29.0	−16	48
Pyridine-d_5	3.03 ± 0.10	30.5	113	182

[a] The 60-MHz spectra of the ligand *tert*-butyl protons relative to TMS. A negative sign indicates downfield from TMS. [b] The shift is measured from the proton resonance of the uncomplexed ligand in the appropriate solvent. All shifts are to high field. [c] The *tert*-butyl resonance was concentration dependent in CDCl$_3$ ranging from a shift from +10 Hz at 6.5 mg/ml to the reported value +57 Hz with ~30 mg/ml. The resonance frequency was not significantly concentration dependent in any of the other solvents. [d] N. Ahmad, N. S. Bhacca, J. Selbin, and J. D. Wander, *J. Amer. Chem. Soc.*, **93,** 2546 (1971).

The same susceptibility is obtained in pyridine as solvent when either Eu(DPM)$_3$ or Eu(DPM)$_3$·2py is added.

In all solvents the ligand *tert*-butyl protons were shifted to high field relative to the free ligand. The magnitudes of the upfield shifts relative to the free ligand in the same solvent are given in Table I. The isotropic shifts of the *tert*-butyl protons are plotted against the magnetic susceptibility of the complex in Figure 1. Three groups of points are observed which qualitatively correspond to noncomplexing, weakly complexing, and strongly complexing solvents. These resonances do not appear to be concentration dependent except for those measured in deuteriochloroform.

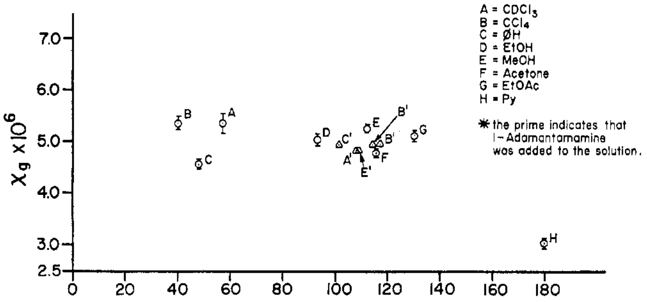

Figure 1.—Magnetic gram-susceptibilities of Eu(DPM)$_3$ *vs.* the isotropic shifts of the complexed dipivaloylmethanato ligands as a function of solvent.

In the noncomplexing solvents, two or three weak additional resonances attributable to coordinated ligand are observed. In CDCl$_3$ they occur at 212, 203, and 160 Hz, in benzene-d_6 at 227, 215, and 151 Hz, and in CCl$_4$ at 217 and 167 Hz. These additional resonances are assigned to *tert*-butyl protons on [Eu(DPM)$_3$]$_2$ dimers. The integrated intensity of all the dimer peaks is smaller by a factor of 10 than the monomer *tert*-butyl peak.

In the solid state, Eu(DPM)$_3$ has been shown to be dimeric with the europium atoms equally sharing two of the twelve oxygen atoms.[18] Considering the oxygen atoms as point negative charges, the crystal field corresponds to seven-coordinate distorted trigonal-prismatic (1:4:2) geometry.[18] Two of the dipivaloylmethanato ligands act as simple bidentate ligands providing four of the seven oxygens. Two additional oxygens are contributed from the third DPM ligand with one of these oxygens simultaneously acting as a bridge to the second europium atom. The seventh oxygen is provided as a bridge from a DPM ligand on the second metal atom. At least three magnetically nonequivalent *tert*-butyl groups are present in the dimer: the *tert*-butyl on the bridging ligand closest to the bridging oxygen, the one farthest from the bridging oxygen, and the four *tert*-butyl groups on the nonbridging ligands. Nonequivalence among the latter groups is not resolved. The nmr results are consistent with the existence of dimers in solution. The dimeric form of the complex occurs in solution only in noncoordinating solvents.[17] The resonances attributed to the dimer are observed only in these solvents. No dimer signals were observed in methanol, acetone, or pyridine. Furthermore, when Lewis bases were added to the chloroform solution, the dimer resonances disappeared.

The isotropic shifts of the ligand *tert*-butyl protons are approximately +50 Hz in the noncoordinating solvents, approximately +110 Hz in the weakly coordinating solvents, and +175 Hz in pyridine. When 1-adamantanamine is added to solutions in the weak and noncoordinating solvents, the *tert*-butyl resonance appears at essentially the same value in all solvents (Figure 1).

The *tert*-butyl protons are affected by both the contact mechanism and a dipolar mechanism. As the coordination number of the europium changes from 6 to 8, the unpaired spin density at the *tert*-butyl protons, the position of the *tert*-butyl protons, and the

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[16] (a) H. M. McConnell and R. E. Robertson, *J. Chem. Phys.*, **29,** 1361 (1958); (b) E. R. Birnbaum and T. Moeller, *J. Amer. Chem. Soc.*, **91,** 7274 (1969).

[17] (a) M. K. Archer, D. S. Fell, and R. W. Jotham, *Inorg. Nucl. Chem. Lett.*, **7,** 1135 (1971); (b) S. Jaakkola and R. W. Jotham, *ibid.*, **8,** 639 (1972).

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anistropic g values all change. In the absence of detailed structural and anisotropic magnetic data for the complex in solution it is impossible definitively to assess the relative importance of the scalar or dipolar mechanisms. Some insight into the importance of the geometry changes may be obtained by considering a simple axially symmetric model. The *tert*-butyl protons in $Eu(DPM)_3$ are positioned on the average at an angle of approximately 50 ± 15°. Small changes in θ will cause large changes in the geometric factor and may even cause it to change sign. It is thus reasonable to ascribe the effect of the solvent on the observed shift primarily to changes in geometry, *vide infra*, although changes in $f(g)$ in eq 3 may also have a small effect. According to this model the change in shift from approximately 50 Hz in the noncoordinating solvents to approximately 115 Hz in the weakly coordinating solvents would require a change in angle of only 6° from the average value of 50°. The increase in shift to 182 Hz exhibited in pyridine would require a change in angle of only 12°. The equivalence of the shifts in all solvents in the presence of 1-adamantanamine is to be expected since the structures should be almost identical. A recent crystal structure[19] of the pyridine adduct of $Eu(DPM)_3$ confirms that geometry changes of the type and magnitude discussed here occur. The adduct has C_2 symmetry in the solid state. Thus, in the solid state the simple axial model does not strictly apply. However, in many quantitative computer fits of the observed nmr spectra, excellent results have been obtained using the axial model.[20,21] For example, the pyridine shifts can be fit to within 4% using this model.[21] Under the rapid-exchange conditions in solution it is possible that the average structure on the nmr time scale approaches axial symmetry.

The difference in magnetic susceptibility between solid state and solution arises from the intermolecular electrostatic field present in the solid state.[22] According to this explanation the intermolecular crystal field opposes the intramolecular ligand field in quenching the orbital angular momentum. The decrease of the susceptibility with increasing solvent-coordinating ability arises from increased orbital angular momentum quenching by the expanded, lower symmetry field in solution. In both cases the effects on the magnetic properties are predicted and found to be small since the filled 5s and 5p orbitals shield the 4f orbitals from the electrostatic fields.[23]

The experimental relationship between the magnitude of the observed shift and the magnetic susceptibility is opposite to that predicted by eq 2 and 3. The decrease in susceptibility with increasing solvent or substrate basicity is discussed above. Since the observed shift *increases* with increasing solvent and substrate basicity, the susceptibility change does not dominate the shift of the *tert*-butyl protons or the shifts induced in the substrate molecule. In the former case, the geometry changes are probably the dominating factor as discussed previously. In the latter, competition between solvent and substrate for a coordination site probably determines the magnitude of the shift although the magnetic susceptibility probably plays a small role.

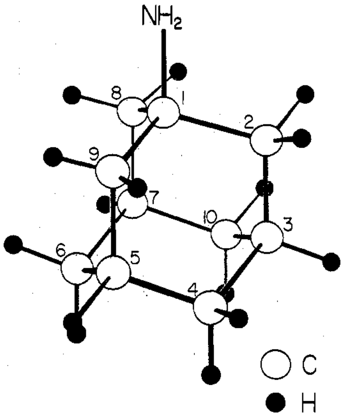

Figure 2.—Structure of 1-adamantanamine.

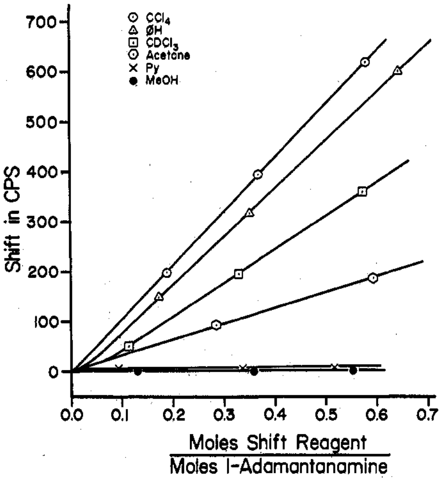

Figure 3.—Shifting ability of $Eu(DPM)_3$ as a function of solvent. Plotted are the proton resonances of the six 2, 8, and 9 protons of 1-adamantanamine.

2. Solvent-Dependent Isotropic Pmr Shifts of 1-Adamantanamine.—The magnitude of the lanthanide-induced shift of a proton on a base which is produced at a specified mole ratio of lanthanide shift reagent to base is highly solvent dependent. In general, the effectiveness of $Eu(DPM)_3$ as a shift reagent is greatest in noncoordinating solvents and decreases with increasing solvent-coordinating ability. The base 1-adamantanamine was used in this study of solvent effects because of its high symmetry and the large number of nonequivalent protons. The structure of 1-adamantanamine and the numbering system used in this paper are shown in Figure 2.

A typical plot of the observed shift *vs.* the ratio of shift reagent to base is shown in Figure 3. Europium is known to form labile complexes and to expand its coordination sphere easily.[24,25] A linear increase of the shift with increase in mole ratio of shift reagent was observed in all solvents in the mole ratio range shown in Figure 3. Because of the great preponderance of uncomplexed solvent molecules to complexed mole-

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(19) R. E. Cramer and K. Seff, *J. Chem. Soc., Chem. Commun.*, 400 (1972).

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cules, no shift in the resonance frequencies of the undeuterated bulk solvents was observed.

The smallest induced shifts on adamantanamine protons are observed in the solvents pyridine and methanol which can effectively compete with adamantanamine for coordination sites on the metal. Interaction between methanol or pyridine and $Eu(DPM)_3$ is indicated by the shift induced in protons on the solvents. Shifts induced in pyridine have been reported.[26] A 4:1 ratio of methanol to shift reagent in carbon tetrachloride produced a 780-Hz shift of the methyl resonance.

From Figure 3, it is seen that the solvents acetone and chloroform can also compete with adamantanamine but that their effectiveness is intermediate in magnitude between the strongly interacting solvents discussed above and the noncoordinating solvents carbon tetrachloride and benzene. Acetone and chloroform inhibit the shift reagent by different mechanisms. Acetone can coordinate directly to the metal. At a 4:1 acetone to shift reagent mole ratio in carbon tetrachloride the induced shift was 25 Hz. Because it is a weaker base than pyridine, it does not compete as effectively with adamantanamine for the metal. Chloroform, on the other hand, inhibits the shift reagent by hydrogen bonding. It can hydrogen bond to the nitrogen of the adamantanamine thus decreasing its coordinating ability. It can also hydrogen bond to the π system of the DPM[27] and sterically inhibit the approach of the base. Hydrogen bonding to the π system is probably responsible for the concentration dependence of the *tert*-butyl shifts reported in Table I.

3. The Mechanism of the Isotropic Shift.—1-Adamantanamine presents an ideal system from which the shift mechanism may be determined. First, it contains five sets of equivalent protons which, with the exception of the amine protons, obey a simple $(3 \cos^2 \theta - 1)/r^3$ pseudocontact model. Second, two of the sets of protons lie at about the same distance from the nitrogen but differ in the total number of bonds between them and the nitrogen.

The observed shifts of all of the CH protons fit a simple pseudocontact model with a maximum deviation of less than 10%. It was assumed in this calculation that the metal complex possessed axial symmetry with the symmetry axis along the metal–nitrogen bond, that all bonds were free to rotate, and that the bond angles about the nitrogen were tetrahedral. Accurate fits have been obtained previously assuming axial symmetry about the metal[20,21] even though the symmetry is probably lower. The amine proton resonances shift downfield much more rapidly than the dipolar model predicts. For example, at a shift reagent to adamantanamine concentration ratio of 0.225, the observed shift is 782 Hz downfield. The shift calculated on the same basis as all of the other protons should only be 659 ± 20 Hz. The discrepancy may arise from (1) errors in the measurement of the angle θ and (2) a contact shift mechanism which is important for protons a few bonds removed from the metal, but unimportant for protons many bonds removed. The observed shift of the amine protons is outside of the uncertainty introduced into the calculated shift by the estimated error in the $(3 \cos^2 \theta - 1)/r^3$ term by greater than 100 Hz. It is unlikely that a more complicated model would account for the total discrepancy between the observed and calculated amine shift. A contact mechanism implies that unpaired spin density is directly delocalized from the metal. Direct delocalization could arise from direct metal 4f orbital participation in the bonding or from indirect effects such as metal 6s mixing in the ground state with bonding between the metal 6s and ligand orbitals. Contact shift contributions have also been observed in molecules containing oxygen atoms as donor atoms.[28] This is the first reported system in which protons on an amine directly bonded to a metal are contact shifted downfield.

A direct experimental test of the dominance of the dipolar mechanism is provided by the existence of protons at about the same distance from the metal but separated from it by different numbers of bonds. The 4, 6, and 10 equatorial protons are 0.2 Å closer to the amine nitrogen than are the bridgehead 3, 5, and 7 protons. The $(3 \cos^2 \theta - 1)/r^3$ factor for the former set compared to the latter is larger by 13.4%. The shift differences of 13.4% predicted solely on the basis of a dipolar $(3 \cos^2 \theta - 1)/r^3$ mechanism compares favorably with the 12.9% larger observed shift of the 4, 6, and 10 equatorial protons compared to the bridgehead protons. The pseudocontact mechanism is thus the dominant shift mechanism for these protons. The contact mechanism might be expected to be small for protons more than four bonds removed in a σ system from the source of unpaired spin density.

From the above considerations, it is clear that the dominant shift mechanism for large organic molecules is dipolar. However, protons on the complexed dipivaloylmethanato ligand or a substrate molecule which are a small number of bonds removed from the metal are also shifted by a scalar mechanism. The larger downfield shift of the amine protons in excess of that expected on the basis of the $(3 \cos^2 \theta - 1)/r^3$ model implies that direct delocalization of unpaired spin density from the metal may occur in these systems.[29]

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(29) NOTE ADDED IN PROOF.—Subsequent to the submission of this paper, a report has been published confirming the existence of $[Eu(DPM)_3]_2$ dimers in solutions in noncoordinating solvents: J. K. M. Sanders, S. W. Hanson, and D. H. Williams, *ibid.*, **94**, 5325 (1972).