Interactions of Some Nitrogen, Oxygen, and Sulphur Heterocycles with Gadolinium and Nickel Chelates. A Carbon-13 Nuclear Magnetic Resonance Spin–Lattice Relaxation Study

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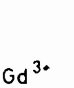
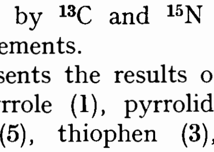
Electron–nuclear spin–lattice relaxation times for ^{13}C in natural abundance are determined for six saturated and aromatic heterocyclic compounds containing nitrogen, oxygen, and sulphur in the presence of the metal chelates $[Gd(tmhd)_3]$ and $[Ni(tmhd)_2]$ (tmhd = 2,2,6,6-tetramethylheptane-3,5-dionate). The measurements provide evidence of complex formation between $[Gd(tmhd)_3]$ and pyrrolidine and tetrahydrofuran, and between $[Ni(tmhd)_2]$ and pyrrolidine, tetrahydrofuran, and tetrahydrothiophen. The relative affinities of the metal chelates for different ligands have been studied in a series of competition experiments, yielding the affinity order N > O > S for $[Gd(tmhd)_3]$ and N > O ≈ S for $[Ni(tmhd)_2]$. For the case of $[Ni(tmhd)_2]$ complexes it is found that the relaxation rates deviate largely from the predictions of the Solomon–Bloembergen equation. Comparisons with contact shifts are employed in order to rationalize these deviations.

TRIS(2,2,6,6-TETRAMETHYLHEPTANE-3,5-DIONATO)GADOLINIUM(III) and bis(2,2,6,6-tetramethylheptane-3,5-dionato)nickel(II), $[Gd(tmhd)_3]$ and $[Ni(tmhd)_2]$, are known to interact readily with many organic bases, especially amines.[1-6] In most of the earlier work the authors focused little on the interaction of amines with these metal chelates, while little attention was paid to the behaviour of oxygen and particularly sulphur bases. Comparison of the interaction of different bases with these metal chelates has also been restricted to different amines, with no systematic comparison of the interaction of N, O, and S types of base with both of the metal chelates. In earlier investigations of base adduct interaction with $[Ni(tmhd)_2]$, the approach has been calorimetric,[6] spectrophotometric,[3,6] or based on ^{1}H n.m.r. measurements,[4,5] while the interaction of $[Gd(tmhd)_3]$ with some oxygen compounds[1] and a wide variety of amines[2] has been studied by ^{13}C and ^{15}N n.m.r. spin–lattice relaxation measurements.

(1) X = NH
(2) X = O
(3) X = S



(4) X = NH
(5) X = O
(6) X = S



(7) $R = C(CH_3)_3$, $M^{n+} = Gd^{3+}$
(8) $R = C(CH_3)_3$, $M^{n+} = Ni^{2+}$

This paper presents the results of our study of the interaction of pyrrole (1), pyrrolidine (4), furan (2), tetrahydrofuran (5), thiophen (3), and tetrahydrothiophen (6) with $[Gd(tmhd)_3]$ (7) and $[Ni(tmhd)_2]$ (8) using ^{13}C n.m.r. spin–lattice relaxation and contact-shift measurements.

The nuclear spin–lattice relaxation time (T_1) in molecules in a paramagnetic system has been widely used to study the structure of paramagnetic metal complexes in solution,[7] and as a tool for analyzing ^{13}C n.m.r. spectra.[8] Nuclear spin–lattice relaxation in a paramagnetic metal complex is due to a dipolar interaction of the nuclear spin with the unpaired electron spin of the metal atom. (In this paper we shall neglect any contribution due to a scalar interaction between the nuclear spin and the electron spin.[2]) If the electron spin is treated as a point dipole centred on the metal atom, this dipolar contribution to T_1^{-1} is given by Solomon[9] and Bloembergen[10] as in equation (1).

$$T_{1,M}^{-1} = \frac{2S(S+1)\gamma_I^2\gamma_S^2\hbar^2}{15r^6}\left(\frac{3\tau_c}{1+\omega_I^2\tau_c^2}+\frac{7\tau_c}{1+\omega_S^2\tau_c^2}\right) \quad (1)$$

Equation (1) is valid if $\omega_S \gg \omega_I$. γ_S and γ_I are the magnetogyric ratios of the nuclear spin I and the electron spin S, ω_I and ω_S are the Larmor frequencies, r is the distance between the nucleus and the metal ion, and τ_c is a correlation time. Under certain assumptions[2] it can be shown that τ_c is proportional to the macroscopic solution viscosity. Therefore, to be able to compare T_1 measurements from different paramagnetic solutions it is desirable to keep the viscosity constant.

Nuclei in a paramagnetic solution which are not directly co-ordinated to the paramagnetic centre will be subject to relaxation by a mechanism which is known as outer-sphere relaxation.[11] According to the approximate formulation given by Abragam[12] this contribution is proportional to the viscosity and to the number of paramagnetic ions per unit volume in the solution.

A co-ordinatively unsaturated metal chelate such as $[Gd(tmhd)_3]$ or $[Ni(tmhd)_2]$ can easily extend its co-ordination number by bonding to a basic portion of a substrate molecule. For practical purposes, in most cases there will be an excess of substrate molecules present in the solution. Consequently the nuclei of the substrate can be in either of two different chemical environments: in the co-ordination sphere of the paramagnetic metal chelate or in the free solvent. For the type of complexes studied in this work, there will be a rapid exchange of substrate molecules between these two environments at room temperature.[2,5] This will, for a given ^{13}C nucleus, result in a single line in the n.m.r. spectrum. The relaxation rate of that nucleus will then be a weighed average of the relaxation rates in the two environments. If there is a considerable excess of nuclei in the free solvent, the expression for the paramagnetic contribution to the spin–lattice relaxation rate of the observed line is given by Bloembergen and Morgan [13] and Luz and Meiboom [14] as in equation (2).

$$(T_{1,P})^{-1} = (T_1)^{-1} - (T_1^{0})^{-1} = \frac{qp}{T_{1,M} + \tau_M} + \frac{1}{T_{1,A}} \qquad (2)$$

The number of substrate ligands in the co-ordination sphere of the metal is given by q, p is the ratio of the concentration of complex-bound metal chelate to the concentration of free substrate, $(T_{1,P})^{-1}$ is the paramagnetic contribution to the observed relaxation rate $(T_1)^{-1}$, $(T_1^{0})^{-1}$ is the diamagnetic contribution due to other relaxation mechanisms, $T_{1,M}$ is the relaxation time for a nucleus in the co-ordination sphere of the metal chelate, given by equation (1), $T_{1,A}$ is the relaxation time for a nucleus in the free solvent, and τ_M is the mean residence time of the substrate in the co-ordination sphere of the metal chelate. For the type of complexes studies in the work, τ_M is assumed to be very small compared to $T_{1,M}$, and can thus be neglected.[2,4,5]

EXPERIMENTAL

All chemicals of the best grade available were purchased from Fluka AG. Solvent and liquid compounds were dried and distilled by standard methods prior to use. The complex [Gd(tmhd)$_3$] was synthesized according to the method of Eisentraut and Sievers [15] and purified by vacuum sublimation at 180 °C; [Ni(tmhd)$_2$] was synthesized according to method D of Hammond *et al.*[16] and purified by repeated vacuum sublimation at 120 °C until no residue was observed. The purified complexes were stored over P_2O_5 in a vacuum desiccator. All samples of heterocyclic compounds were 1 mol dm^{-3} solutions in methylcyclopentane. Samples containing [Gd(tmhd)$_3$] and [Ni(tmhd)$_2$] were prepared by dilution of stock solutions with methylcyclopentane as solvent. The samples of furan and pyrrole with [Ni(tmhd)$_2$] were degassed by several freeze–pump–thaw cycles and sealed under vacuum. This was necessary to avoid nickel-catalyzed oxidation of these heterocycles. In all other cases the samples were not degassed.

Natural-abundance, ^1H noise-decoupled, ^{13}C n.m.r. spectra were obtained in the Fourier-transform mode with a Varian XL 100 spectrometer operating at 25.2 MHz ^{13}C resonance frequency. Measurements were made using 12-mm n.m.r. tubes with 10-mm n.m.r. tubes containing the sample and with D_2O placed in the annulus between the 10- and the 12-mm tubes for field-frequency stabilization. The spin–lattice relaxation times were measured using the fast-inversion recovery method [17] and the non-linear three-parameter fitting of line intensities.[18] Each T_1 was measured at least twice, with mean values of T_1 reported. The standard deviations of the obtained T_1 values were 2—8%. The T_1 experiments were carried out completely under computer control, using the Varian disk system software $(T_{1,P})^{-1}$, the contribution to the observed relaxation rate due to the presence of unpaired electrons in the solution, was obtained as the difference between the relaxation rates measured in the presence and absence of relaxation reagent, $(T_{1,P})^{-1} = (T_1)^{-1} - (T_1^{0})^{-1}$. In this way any contribution due to the presence of dissolved oxygen in the solutions was subtracted. Chemical shifts were measured relative to the α-carbon of the solvent, methylcyclopentane. Unless specified, all measurements were made at 29 ± 2 °C.

RESULTS AND DISCUSSION

Experimental Conditions and Diamagnetic T$_1$ *Data.*—All data are for 1 mol dm^{-3} solutions of the heterocyclic compounds with methylcyclopentane as the solvent. At this concentration the viscosity could be taken as approximately the same in all experiments. The choice of methylcyclopentane as the solvent is motivated by the assumption that this molecule is inert towards [Gd(tmhd)$_3$] and [Ni(tmhd)$_2$] and by its structural resemblance to the heterocyclic compounds. The $T_{1,P}$ for methylcyclopentane will thus be controlled by the outer-sphere mechanism only and will give a good estimate of the contribution from this mechanism to the observed $T_{1,P}$ values for the heterocycles. With these experimental conditions (approximately constant viscosity and presence of an internal probe of the outer-sphere contribution), observed $T_{1,P}$ values will give a direct qualitative measure of the nature of the interaction between the metal chelate and the heterocyclic compound.

Diamagnetic ^{13}C n.m.r. spin–lattice relaxation times for pyrrole, pyrrolidine, furan, tetrahydrofuran, thiophen, and tetrahydrothiophen, and for the solvent methylcyclopentane are given in Table 1. The headings C_α, C_β, and C_γ are used to denote carbons successively remote from the substituent. Except for pyrrole, these T_1^{0} are *ca.* 20 s for all of the five-membered rings.

TABLE 1

Diamagnetic ^{13}C spin–lattice relaxation times (T_1^{0}/s) for 1 mol dm^{-3} solutions of heterocyclic compounds in methylcyclopentane

Molecule	C_α	C_β	C_γ
Pyrrole	14	13	
Pyrrolidine	20	*a*	
Furan [b]	21	24	
Tetrahydrofuran	23	24	
Thiophen	22	23	
Tetrahydrothiophen	19	20	
Methylcyclopentane			22 (21) [b]

[a] Not measurable, due to overlapping solvent line. [b] Measured at 15 °C.

This discrepancy from an expected $T_1^{CH}/T_1^{CH_2}$ value of 2 may tentatively be assigned to ring puckering in the saturated five-membered rings,[19] resulting in a shorter effective correlation time.[20] The relatively short T_1^{0} for pyrrole is probably caused by some kind of self-aggregation between pyrrole molecules.

[Gd(tmhd)$_3$].—In Table 2 the paramagnetic contribution to the observed spin–lattice relaxation times for the six heterocycles and methylcyclopentane in the presence of 5×10^{-4} mol dm^{-3} [Gd(tmhd)$_3$] are given. Inspection of the $T_{1,P}$ values for the saturated heterocycles clearly shows that in the case of pyrrolidine and tetrahydrofuran a complex is formed with [Gd(tmhd)$_3$]. For these compounds, the short values of $T_{1,P}$ relative to the inert methylcyclopentane and the difference between α- and β-carbon in the case of tetrahydrofuran indicate that the spin-dipolar interaction between the nuclear spin and the unpaired electron spin of the gadolinium atom is the dominating relaxation mechanism. The shorter $T_{1,P}$ value of 0.6 s for the α-carbon of pyrrolidine, compared to 1.3 s for the same carbon of tetrahydrofuran, indicates that a stronger complex, resulting in a shorter gadolinium–carbon bond, is formed between [Gd(tmhd)$_3$] and pyrrolidine. Tetrahydrothiophen, on the other hand, shows a behaviour much the same as that observed for the unsaturated oxygen and sulphur compounds furan and thiophen. For all three compounds there is no significant difference between observed $T_{1,P}$ values for α- and β-carbons. The absolute values, all *ca.* 30 s, do not differ much from the value of 51 s observed for methylcyclopentane. These observations show that no complex formation occurs between tetrahydrothiophen, thiophen, or furan and [Gd(tmhd)$_3$]. These observations are consistent with the fact that gadolinium, being a ' hard ' metal, is not likely to bind to sulphur, and that the free electron pair in furan, being delocalized in a π-electron system within the ring, is not likely to take part in a chemical bond. The $T_{1,P}$ values for pyrrole, on the other hand, indicate that this compound most likely forms a complex with [Gd(tmhd)$_3$]. The relatively long absolute values for both carbons of pyrrole as compared to tetrahydrofuran and pyrrolidine indicate that only a fraction of the present [Gd(tmhd)$_3$] molecules are bound to pyrrole, while in the case of the other two molecules all the [Gd(tmhd)$_3$] is probably present as the adduct.

TABLE 2

$T_{1,P}$ values(s) for 1 mol dm^{-3} solutions containing 5×10^{-4} mol dm^{-3} [Gd(tmhd)$_3$]

Molecule	C_α	C_β	C_γ
Pyrrole	5.4	8.0	
Pyrrolidine	0.6	*a*	
Furan [b]	28	32	
Tetrahydrofuran	1.3	5.2	
Thiophen	22	27	
Tetrahydrothiophen	27	28	
Methylcyclopentane			51 (41) [b]

[a] Not measurable due to overlapping solvent line. [b] Measured at 15 °C.

In order to get a direct comparison of the affinity of both pyrrolidine and tetrahydrofuran for [Gd(tmhd)$_3$], the paramagnetic contributions to the observed spin–lattice relaxation times were evaluated in a solution containing an equimolar amount of both heterocycles. $T_{1,P}$ for the α-carbon of pyrrolidine in the mixture is 0.6 s, the same as in the solution with only pyrrolidine in the presence of [Gd(tmhd)$_3$]. $T_{1,P}$ for the α-carbon of tetrahydrofuran on the other hand is 28 s, much longer than in the single-component system. It is noteworthy that the value of $T_{1,P}$ for tetrahydrofuran is the same as that observed for the α-carbon of furan in the presence of [Gd(tmhd)$_3$]. These data clearly show that the affinity for [Gd(tmhd)$_3$] is much stronger for pyrrolidine than it is for tetrahydrofuran. In the equimolar solution this results exclusively in the formation of [Gd(tmhd)$_3$]–pyrrolidine complexes. Finally, it should be pointed out that within experimental accuracy no paramagnetic induced shifts were observed for any of the compounds in the presence of [Gd(tmhd)$_3$].

[Ni(tmhd)$_2$].—In a solution containing no molecules capable of co-ordinating to [Ni(tmhd)$_2$] this metal chelate has a singlet ground state and is diamagnetic. As shown by Cotton and Fackler,[21] this is due to the monomeric state of the square-planar [Ni(tmhd)$_2$] in solution. On the other hand, in a solution containing molecules which form an octahedral complex with [Ni(tmhd)$_2$], the metal chelate is paramagnetic with a triplet ground state.[16,21] These extraordinary magnetic properties of [Ni(tmhd)$_3$] make it unusually suitable for applying the method of spin–lattice relaxation measurements to study the interaction of organic bases with this metal chelate. If the relaxation time for a potential substrate is shortened in a solution containing [Ni(tmhd)$_2$], this directly shows that the substrate forms a paramagnetic octahedral bis complex with [Ni(tmhd)$_2$].

Apart from the effect on the relaxation time for nuclei in a paramagnetic nickel complex, the carbon-13 shifts are strongly influenced by the presence of the unpaired electrons of the nickel ion. For an octahedral base adduct with [Ni(tmhd)$_2$], the electronic ground state is $^3A_{2g}$,[3] with the consequence that the magnetic susceptibility of the complex is isotropic. For such a complex the observed paramagnetic shift is caused by the Fermi contact interaction between the nuclear spin and the delocalized unpaired electron spin, called the contact shift.[22] Under conditions of fast exchange the observed contact shift $\Delta\omega$ is given by Swift and Connick [23] as in equation (3) where p and q are defined as above. $\Delta\omega_M$ is

$$\Delta\omega = pq\Delta\omega_M \tag{3}$$

the contact shift for a nucleus in the paramagnetic complex and its relationship to the hyperfine coupling constant is given by Bloembergen [22] as in equation (4).

$$\frac{\Delta\omega_M}{\omega} = \frac{S(S+1)\gamma_S A}{kT\gamma_I} \tag{4}$$

ω is the resonance frequency of the observed nucleus, A is the hyperfine coupling constant (in energy units), k is the Boltzmann constant, and T is the temperature. S, γ_I, and γ_S are defined as above.

From the above discussion it follows that [Ni(tmhd)$_2$], in the presence of a ligand that binds to the metal chelate, behaves both as a shift and relaxation reagent.

Table 3 contains $T_{1,P}$ values for 1 mol dm^{-3} solutions of heterocyclic compound and for the solvent methylcyclopentane, in the presence of 10^{-2} mol dm^{-3} [Ni(tmhd)$_2$]. The data for pyrrole, furan, and thiophen clearly show that these compounds are inert towards [Ni(tmhd)$_2$]. This is obvious from the fact that observed spin–lattice relaxation times, in the solutions of these compounds with [Ni(tmhd)$_2$], are the same as in the absence of [Ni(tmhd)$_2$]. On the other hand, the 1 mol dm^{-3} solutions of pyrrolidine, tetrahydrofuran, and tetrahydrothiophen are paramagnetic. This fact, and the observation that the $T_{1,\mathrm{P}}$ values for these compounds are very short compared to that for methylcyclopentane, obviously show that pyrrolidine, tetrahydrofuran, and tetrahydrothiophen form octahedral bis complexes with [Ni(tmhd)$_2$]. A quick inspection of the $T_{1,\mathrm{P}}$ values for the α-carbons of these three compounds indicates that pyrrolidine forms the strongest complex with [Ni(tmhd)$_2$] while the interactions of tetrahydrofuran and tetrahydrothiophen with the chelate seem to be roughly equal. However, a closer inspection of the data in Table 3 reveals several facts the explanation of which is not trivial. First, the α- and β-carbon relaxation times in pyrrolidine are equal within the experimental error (which in this case is quite large due to significantly broadened lines). This is inconsistent with the r^{-6} dependence in the Solomon–Bloembergen equation (1). Secondly, $T_{1,\mathrm{P}}$ for the α-carbon in tetrahydrothiophen is shorter than $T_{1,\mathrm{P}}$ for the α-carbon in tetrahydrofuran. If the pq values for both compounds are assumed to be the same (see below), these data in connection with equations (1) and (2) would indicate that the nickel–sulphur distance is shorter than the nickel–oxygen distance. This is, however, inconsistent with the covalent radii of sulphur and oxygen. In order to explain these peculiarities we have turned to a determination of the contact shifts and to competition experiments.

TABLE 3

$T_{1,\mathrm{P}}$ values and observed contact shifts for 1 mol dm^{-3} solutions containing 10^{-2} mol dm^{-3} [Ni(tmhd)$_2$]

	$T_{1,\mathrm{P}}$/s			Δω/p.p.m.	
Molecule	C_α	C_β	C_γ	C_α	C_β
Pyrrole[a]				0	0
Pyrrolidine	0.2	0.2		−2	+3.2
Furan[a,b]				0	0
Tetrahydrofuran	0.9	2.6		+1.0	+2.1
Thiophen[a]				0	0
Tetrahydrothiophen	0.7	2.3		−4.1	+1.2
Methylcyclopentane			51[c]		

[a] Observed values of T_1 are the same as in the absence of [Ni(tmhd)$_2$]. [b] Measured at 15 °C. [c] Mean value from the paramagnetic solutions.

Table 3 includes the observed contact shifts for the six heterocycles in the presence of 10^{-2} mol dm^{-3} [Ni(tmhd)$_2$]. These data confirm that pyrrolidine, tetrahydrofuran, and tetrahydrothiophen all form complexes with [Ni(tmhd)$_2$]. A closer inspection, however, again reveals some remarkable features of the data. Thus, it is apparent from the higher absolute values of the observed contact shifts for the β-carbons of pyrrolidine and tetrahydrofuran that for these compounds the spin density of the delocalized electron spin of the nickel ion is greater on the β- than it is on the α-carbons. This implies that in the complexes between pyrrolidine and tetrahydrofuran with [Ni(tmhd)$_2$] the electron spin of the nickel ion is delocalized onto the ligand to such a great extent that the Solomon–Bloembergen treatment of the electron spin as a point dipole is not valid. The abnormally short $T_{1,\mathrm{P}}$ for the β-carbon of pyrrolidine is thus explained by the breakdown of this equation. The fact that the Solomon–Bloembergen treatment of the relaxation time for nuclei in a paramagnetic system is incomplete has recently been demonstrated both theoretically and experimentally.[24–27] For the [Ni(tmhd)$_2$] complexes with tetrahydrofuran and tetrahydrothiophen the validity can be approximately tested with the following procedure. The quotient $T_{1,\mathrm{M}}{}^{\mathrm{C}\alpha}/T_{1,\mathrm{M}}{}^{\mathrm{C}\beta}$ can be calculated from the experimental $T_{1,\mathrm{P}}$ values using equation (2), with the assumption that $\tau_\mathrm{M} \ll T_{1,\mathrm{M}}$, and with $T_{1,\mathrm{A}}$ given by the value of $T_{1,\mathrm{P}}$ for methylcyclopentane. This value is then compared with that calculated from the Solomon–Bloembergen equation (1), under the assumption that the correlation time is the same for all carbons within one molecule. If the nickel–sulphur and -oxygen bond lengths are taken from the crystal structure data for similar complexes, the nickel–carbon distances can be calculated under the assumption that the heterocyclic rings are planar (this is of course an approximation but the deviations are probably small). When the nickel–oxygen bond length is given the value 2.14 Å,[28] $T_{1,\mathrm{M}}{}^{\mathrm{C}\alpha}/T_{1,\mathrm{M}}{}^{\mathrm{C}\beta}$ takes the value 0.12 while the experimentally calculated value is 0.32. For tetrahydrothiophen, if the nickel–sulphur bond length is given the value 2.5 Å,[29] the quotient expected from the Solomon–Bloembergen equation is 0.19, while the experimentally calculated value is 0.26. The poor agreement between the calculated ratios, observed for tetrahydrofuran can be explained in the following way. The observed contact shift is approximately twice as large for the β- than for the α-carbon. This means that at the site of the nucleus the spin density is larger on the β- than on the α-carbon. This gives a larger non-Solomon–Bloembergen contribution for the β- than for the α-carbon, and the experimental value becomes larger than the Solomon–Bloembergen value. The experimental ratio between $T_{1,\mathrm{M}}$ for the α- and β-carbons in tetrahydrothiophen agrees reasonably well with the ratio expected from Solomon–Bloembergen theory. This is not surprising, since the observed contact shift is approximately four times larger for α than it is for β. This means that the non-Solomon–Bloembergen contribution for this complex is larger for the α- than for the β-carbon. Consequently, the agreement between the calculated ratios is fairly good.

The above discussion explains the shorter $T_{1,\mathrm{P}}$ for the α-carbon of tetrahydrothiophen as compared to tetrahydrofuran. It also shows that it is not possible to compare the data in Table 3 in terms of the Solomon–Bloembergen equation.

Table 4 contains $T_{1,\mathrm{P}}$ values and observed contact shifts for the two competition experiments: 1 mol dm^{-3} pyrrolidine with 1 mol dm^{-3} tetrahydrothiophen in the presence of 10^{-2} mol dm^{-3} [Ni(tmhd)$_2$], and 1 mol dm^{-3} tetrahydrofuran with 1 mol dm^{-3} tetrahydrothiophen in the presence of 10^{-2} mol dm^{-3} [Ni(tmhd)$_2$]. The competition experiment with pyrrolidine and tetrahydrothiophen has been done in order to determine whether the short $T_{1,\mathrm{P}}$ for the former compound is really due to a higher affinity of this base towards [Ni(tmhd)$_2$] or if the reason is to be sought in the spin delocalization and/or scalar relaxation (very broad lines for both carbons indicate that at least for T_2 this mechanism could be operative). Both $T_{1,\mathrm{P}}$ values and observed contact shifts are the same for pyrrolidine in this competition experiment as in the case without tetrahydrothiophen. On the other hand, there is no contact shift for tetrahydrothiophen and the $T_{1,\mathrm{P}}$ values are much longer and show no difference between α- and β-carbon, indicating an outer-sphere contribution only. This clearly shows that in this solution [Ni(tmhd)$_2$] binds solely to pyrrolidine and that the short $T_{1,\mathrm{P}}$ values for pyrrolidine as compared to tetrahydrofuran and tetrahydrothiophen in the single-substrate series are at least partly due to the formation of a stronger complex between pyrrolidine and [Ni(tmhd)$_2$].

TABLE 4

$T_{1,\mathrm{P}}$ values and observed contact shifts for equimolar mixtures of pyrrolidine with tetrahydrothiophen and tetrahydrofuran with tetrahydrothiophen

	$T_{1,\mathrm{P}}$/s		Δω/p.p.m.	
Molecule	Cα	Cβ	Cα	Cβ
Pyrrolidine [a]	0.2	0.2	−2	+3.5
Tetrahydrothiophen [a]	39	37	0	0
Tetrahydrofuran [b]	1.4	4.4	+0.6	+1.2
Tetrahydrothiophen [b]	1.3	5.2	−2.0	+0.5

[a] Mixture of 1 mol dm^{-3} pyrrolidine with 1 mol dm^{-3} tetrahydrothiophen. [b] Mixture of 1 mol dm^{-3} tetrahydrofuran with 1 mol dm^{-3} tetrahydrothiophen.

The competition experiment with tetrahydrofuran and tetrahydrothiophen has been done as an attempt to quantify the relative affinities of these compounds towards [Ni(tmhd)$_2$]. If it is assumed that [Ni(tmhd)$_2$] forms only 1 : 2 complexes with these compounds, there is a possibility of the existence of three different complexes in the solution: with two tetrahydrofuran, two tetrahydrothiophen, or one tetrahydrofuran and one tetrahydrothiophen ligand respectively. This means that both of the two organic compounds can be in either of three different environments: (A) in the free solvent; (B) co-ordinated as one of two different ligands in a mixed complex; and (C) co-ordinated as one of two ligands of the same kind in a non-mixed complex. This has the consequence that the simple two-site exchange expression for the paramagnetic contribution to the observed spin–lattice relaxation time given in equation (2) is no longer valid. Instead, the three-site exchange model developed by Led and Grant [30] must be adopted. As shown by these authors, for a three-site exchange with no direct exchange between the two paramagnetic sites, the paramagnetic contribution to the observed spin–lattice relaxation rate is given by (5). [A] is the concentration of free ligand, [B] and [C] are the concentrations of the complexes B and C, the number of ligand molecules bound to the paramagnetic centre in a complex B or C is denoted q_B and q_C, $T_{1,\mathrm{B}}$ and $T_{1,\mathrm{C}}$ are

$$\frac{1}{T_{1,\mathrm{P}}} = \frac{q_\mathrm{B}[\mathrm{B}]/[\mathrm{A}]}{T_{1,\mathrm{B}} + \tau_\mathrm{B}} + \frac{q_\mathrm{C}[\mathrm{C}]/[\mathrm{A}]}{T_{1,\mathrm{C}} + \tau_\mathrm{C}} + \frac{1}{T_{1,\mathrm{A}}} \tag{5}$$

the relaxation times for the nucleus in the complexes B and C respectively, and τ_B and τ_C are the lifetimes of the nucleus in the two complexes. $T_{1,\mathrm{A}}$ is defined as above. In order to proceed, we now make three simplifying assumptions. First, it is assumed that $\tau_\mathrm{B} \ll T_{1,\mathrm{B}} = T_{1,\mathrm{C}} \gg \tau_\mathrm{C}$. Further, we assume that in the presence of a large excess of the ligand (which is the case in our experiments) only 2 : 1 complexes are formed with [Ni(tmhd)$_2$]. We then identify 'site' B as a mixed complex and 'site' C as a complex with two identical ligands. Equation (5) then becomes (6) where

$$\frac{1}{T_{1,\mathrm{P}}} - \frac{1}{T_{1,\mathrm{A}}} = \frac{[\mathrm{B}] + 2[\mathrm{C}]}{[\mathrm{A}]T_{1,\mathrm{C}}} = \frac{[\mathrm{L}]}{[\mathrm{A}]T_{1,\mathrm{C}}} \tag{6}$$

[L] is the total concentration of ligands bound in either B or C. Under the same assumptions, equation (2) becomes (7) where [M$_0$] is the concentration of [Ni(tmhd)$_2$] and 2[M$_0$] is the concentration of bound ligand.

$$\frac{1}{T_{1,\mathrm{P}}} - \frac{1}{T_{1,\mathrm{A}}} = \frac{2[\mathrm{M_0}]}{[\mathrm{A}]T_{1,\mathrm{M}}} \tag{7}$$

As the third assumption we set $T_{1,\mathrm{M}} = T_{1,\mathrm{C}}$. Now, the ratio between $T_{1,\mathrm{P}}^{-1} - T_{1,\mathrm{A}}^{-1}$ in the two kinds of experiments, corresponding to equations (6) and (7), becomes (8). $T_{1,\mathrm{A}}$ can be estimated from the relaxation

$$\frac{(T_{1,\mathrm{P}}^{-1} - T_{1,\mathrm{A}}^{-1})_{\mathrm{mixture}}}{(T_{1,\mathrm{P}}^{-1} - T_{1,\mathrm{A}}^{-1})_{\mathrm{single}}} = \frac{[\mathrm{L}]}{2[\mathrm{M_0}]} \tag{8}$$

rate of methylcyclopentane. Thus, equation (8) can be used to obtain the fraction of bound tetrahydrofuran and tetrahydrothiophen in the mixture. Similarly, from the expression for the observed contact shift in a three-site exchange system given by Led and Grant,[30] an expression for the ratio between the observed contact shifts in the two kinds of experiments can be derived. It is easily shown that under the same assumption as above this ratio is given by (9). Thus, the contact shift also

$$\frac{(\Delta\omega)_{\mathrm{mixture}}}{(\Delta\omega)_{\mathrm{single}}} = \frac{[\mathrm{L}]}{2[\mathrm{M_0}]} \tag{9}$$

gives the fraction of bound tetrahydrofuran and bound tetrahydrothiophen in the mixture.

The fractions of tetrahydrofuran and tetrahydrothiophen bound to [Ni(tmhd)$_2$] in the competition experiment can thus be calculated in four ways, using both the spin–lattice relaxation time and the observed contact-shift data for both carbons. The mean value of the fraction of bound tetrahydrofuran obtained from this set of data is 58% while that for tetrahydrothiophen obtained in the same way is 45%. The sum of these fractions should, under the given assumption that all $[\mathrm{Ni(tmhd)_2}]$ molecules are present as the adduct, equal 100%. The difference of 3% is well within the range of experimental error. The above results show that the affinity of tetrahydrofuran for $[\mathrm{Ni(tmhd)_2}]$ is slightly larger than that of tetrahydrothiophen, which agrees nicely with the classification of nickel as an intermediate case between the typical ' hard ' and ' soft ' metals.

Conclusions.—The results of this work clearly demonstrate the usefulness of the application of carbon-13 n.m.r. spin–lattice relaxation measurements to the study of the interaction of organic bases with paramagnetic metal chelates. The results obtained with $[\mathrm{Ni(tmhd)_2}]$ show that care should be taken in interpretation of spin–lattice relaxation time data in terms of the Solomon–Bloembergen equation. Comparison of the affinity of different substrates for a metal chelate can be done quite directly provided that not only single-component but also competition experiments are used. The results of the measurements for both $[\mathrm{Gd(tmhd)_3}]$ and $[\mathrm{Ni(tmhd)_2}]$ are in agreement with the ' hard–soft ' properties of the metals. For both chelates we note that the unsaturated ligands show no, or weak, interaction while for the saturated compounds we obtain the affinity order $\mathrm{N} \gg \mathrm{O} \gg \mathrm{S}$ for $[\mathrm{Gd(tmhd)_3}]$ and $\mathrm{N} \gg \mathrm{O} \simeq \mathrm{S}$ for $[\mathrm{Ni(tmhd)_2}]$.

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