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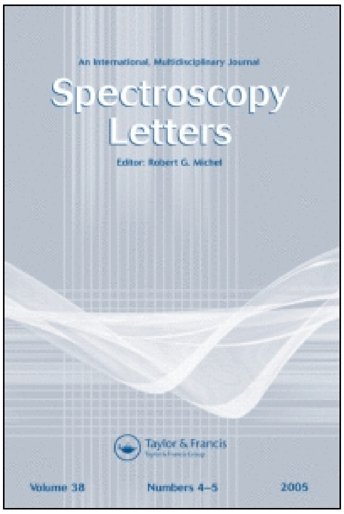

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Toward an Optimal Paramagnetic Relaxation Agent for ^{31}P NMR Spectroscopy

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TOWARD AN OPTIMAL PARAMAGNETIC RELAXATION AGENT FOR ^{31}P NMR SPECTROSCOPY

Key Words:

Phosphorus, Relaxation, Paramagnetic Relaxation Agents, T_1 Studies, ^{31}P NMR

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Abstract:

The dynamics of the use of relaxation agents for ^{31}P NMR spectroscopy were investigated. It was found that non-lability of the associated ligand is essential, in order for line broadening to be prevented. Thus, chelates were found to be most suitable. In addition, evidence was accumulated that indicates an outer sphere coordination is significant for effective reduction of spin-lattice relaxation times (T_1's). Finally, the magnitude of the magnetic moment, as pertains to Gd^{+3} and Fe^{+3}, was examined and related to effective reduction of T_1's.

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Introduction

Nuclear magnetic resonance (NMR) is a technique that has demonstrated considerable effectiveness for the analysis of species in dilute solution. Among its advantages are the non-destructiveness of the method and the specificity provided by the presence of distinct chemical shifts. The pulse-Fourier Transform technique, with signal averaging, has greatly lowered the concentration limits able to be observed.

However, long spin-lattice relaxation times (T_1's) present practical difficulties with respect to demands on instrument usage time. To some extent, this problem can be alleviated by the choice of solvent (1). Solvent viscosity is a factor in determining the rate of reorientation of a molecule and, accordingly, the effectiveness of this reorientation as a relaxation mechanism (2). However, there are financial, solubility and practical considerations. Another method of circumventing the problem is through the increased sensitivity provided by instrument modification. For example, Bertrand achieved this through cross polarization of liquids for ^{13}C and ^{15}N spectroscopy (3). A third less expensive and easily performed experimental procedure is to add paramagnetic materials to the solution under study (4). These paramagnetic materials, or relaxation agents, reduce the spin-lattice relaxation times so that more pulses may be effected within a given period of time without saturation, thus improving sensitivity.

In this laboratory, research efforts have been directed toward the analysis of phosphorus compounds in dilute solution. Relaxation agents

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are an important part of this work. Effort has been expended toward the accumulation of a body of information that would lead to the optimum use of these species and, possibly, to the synthesis of new and more effective relaxation agents. Contained herein are the results of some investigations into the dynamics of the use of relaxation agents.

Theory

In order for the combined techniques of time averaging and the pulse-Fourier Transform method to be most effective, there must be the complete loss of magnetization energy by the Boltzmann excess of NMR active nuclei. Since spontaneous emission is a negligible process, this loss of energy must be effected by interactions with fluctuating magnetic fields generated by the environment and, hence, is termed spin-lattice relaxation. Spin-lattice relaxation is an exponential decay process, which is characterized by the first order time constant, T_1, called the spin-lattice relaxation time. To avoid deleterious effects of saturation, one generally waits a period of 5 T_1's or longer between pulses.

Some of the physical processes by which nuclei exchange energy with the lattice are, as follows (5):

1. Magnetic dipole-dipole interactions among nuclei.
2. Internuclear electric quadrupole interactions.
3. Chemical shift anisotropic interactions.
4. Scalar coupling interactions.
5. Spin-rotation interactions.

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Often, however, the aforementioned mechanisms are inefficient at causing nuclei to relax. For example, dipolar interactions are distance dependent and this is described by the following (6):

$$R \propto r^{-6}, \qquad (1)$$

in which R is the relaxation rate and r is the internuclear distance. Thus, as a relaxation mechanism, dipolar interaction among nuclei are usually of great importance only in cases where the nuclei of interest are directly bonded to nuclei or of comparable proximity with strong magnetic moments like ^{1}H or ^{19}F. For phosphorus, an example of a species where this is an important mechanism is the PFO_3^{-2} ion (7). The other mechanisms are generally very effective only under rather stringent conditions (8). An example of this is provided by the PBr_3 molecule, for which scalar coupling is a significant mechanism (9). Because of this, one often encounters nuclei with rather long T_1's. Thus, the observation of nuclei which are dilute or insensitive requires long periods of instrument time.

However, this problem can be overcome by the addition of a relaxation agent to the solution under study. Relaxation may be induced by magnetic dipolar interaction between unpaired electrons and the nuclei of interest -- a process that is analogous to inter-nuclear dipolar interactions. Although the distances between the unpaired electrons of the relaxation agent and the nuclei of interest are greater than inter-nuclear distances, the magnetic moment of the unpaired electron is over 600 times greater than that of the proton. This intense magnetic moment, when modulated by molecular motion, becomes a very effective mechanism by which relaxation occurs. (10).

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The type of performance that one would like to obtain from the use of a relaxation agent is twofold. One is the reduction of spin-lattice relaxation times without the peak broadening that leads to reduced signal intensity and sensitivity. The other is minimal shifting of the resonance lines. Ideally, these criteria may be fulfilled by species which possess a high magnetic moment and does not interact chemically with NMR sample. In practice, good results have been obtained with chelates of transition metal ions. Examples of these are $Cr(acac)_3$, $Fe(acac)_3$ and $Gd(fod)_3$. All of these metal ions possess multiple unpaired electrons and, hence, have rather high magnetic moments. Furthermore, these complexes are characterized by high stability constants and are non-labile. Presumably, it is this strength of co-ordination that is a determing factor in the usefulness of a relaxation agent (11).

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Experimental:

Diethyl ethylphosphonate (DEP) and triphenyl phosphate (TPP) were obtained from the Aldrich Chemical Company and triethyl phosphate (TEP) and triethyl thiophosphate were obtained from Eastman Kodak Company. All metal salts mentioned were reagent grade chemicals from Fisher Scientific Company, except for the vanadium halides, which were obtained from Alfa Inorganics. Iron (III) acetylacetonate was obtained from ICN and gadolinium (III) $(fod)_3$ was obtained from the Norell Chemical Company. Co(II) $(acac)_2$ and Co(III) $(acac)_3$ were prepared in the laboratory (12). Aldrich supplied the acetylacetone that was used and the ethylenediamine was from Matheson, Coleman and Bell. All solutions examined were made with HPLC grade methanol from Burdick and Jackson and degassed by bubbling nitrogen gas, from Matheson Gas Products, through them.

^{31}P NMR spectroscopy was performed on a multi-nuclear Varian XL-100 15 spectrometer, equipped with a Varian 620-L computer and Sykes Compucorder. Magnet homogeneity was initially obtained using a sample of methyl alcohol d_1 from the Norell Chemical Company, employing the internal deuterium lock, and maintained afterwards by an external fluorine lock. The probe temperature was regulated at 30^oC. T_1's were measured, using the P/N 20309-M inversion recovery program from Varian, with the 180^o pulse equal to 64 usec and the 90^o pulse equal to 32 usec.

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Results and Discussion

To obtain insight into the importance that the degree of coordination may have on relaxation agent usefulness, a number of phosphorous containing compounds with various structural features was used. These are illustrated in Figure 1, including ^{31}P chemical shifts (13) and typical T_1's in dilute (1% v/v) methanol solution. Triphenyl phosphate (TPP) was selected for the steric hindrance provided by the bulkiness of the phenyl groups. Triethy phosphate (TEP) and diethyl ethylphosphonate (DEP) are two sterically accessible compounds that differ structurally. Triethyl thiophosphate (TTP) was used because of the presence of the sulfur atom. The effectiveness of the reduction of the long relaxation times of these compounds by a relaxation agent was evaluated by the inversion-recovery (14) method of T_1 measurement.

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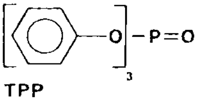
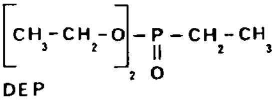
PHOSPHORUS COMPOUND	^{31}P CHEMICAL SHIFT (85% $H_3PO_4 = 0.0$ ppm)	T_1 (sec.) in methanol
TRIPHENYL PHOSPHATE  TPP	+18	27.0
TRIETHYL PHOSPHATE $[CH_3-CH_2-O]_3-P=O$ TEP	+ 1	20.0
DIETHYL-ETHYL PHOSPHONATE  $[CH_3-CH_2-O]_2-\underset{\underset{O}{\parallel}}{P}-CH_2-CH_3$ DEP	-32	18.3
TRIETHYL THIOPHOSPHATE $[CH_3-CH_2-O]_3-P=S$ TTP	-67	13.8

FIGURE 1
Selected Phosphorus Compounds
and Relevant Data

Figure 2 shows a proton decoupled ^{31}P spectrum of a mixture of the aforementioned compounds. Since TEP and TPP appear more than 30 ppm upfield of DEP, their signals are placed in the center of the illustration for convenience of representation. The concentration of each of the phosphorus compounds in 1% v/v and the spectrum was obtained over a period of approximately an hour.

Since most effective relaxation agents have tightly held ligands, e.g., Fe(III)(acac)$_3$, initial studies were made to see the effect that

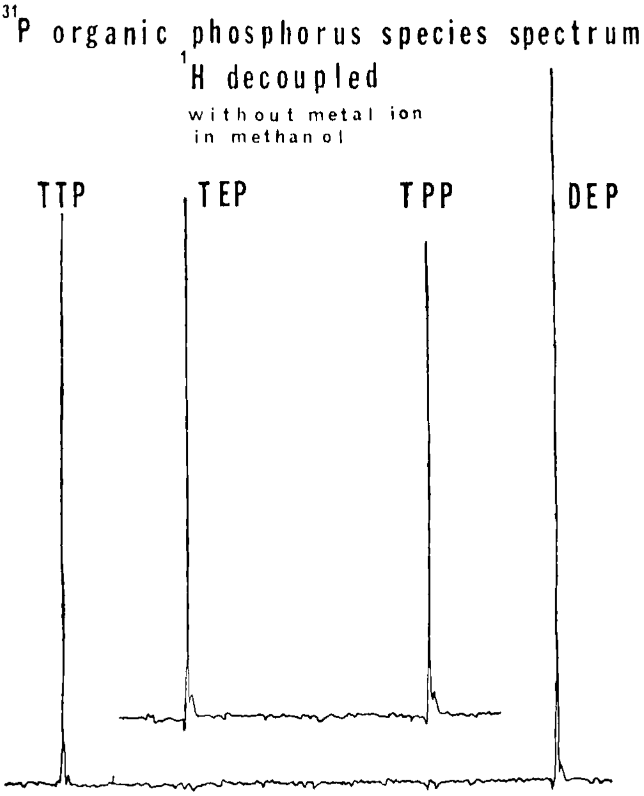


FIGURE 2

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a relatively exposed metal ion would have. For this, iron (III) nitrate was chosen because of the paramagnetism of the iron and the known poor coordinating ability of the nitrate. The results of the addition of iron nitrate to a mixture of the four organic phosphorus compounds are illustrated in Figure 3.

The peaks of the sterically accessible compounds are not observed. A number of attempts were made to find possible shifting of these resonance lines, but none was observed. We conclude from the observa-

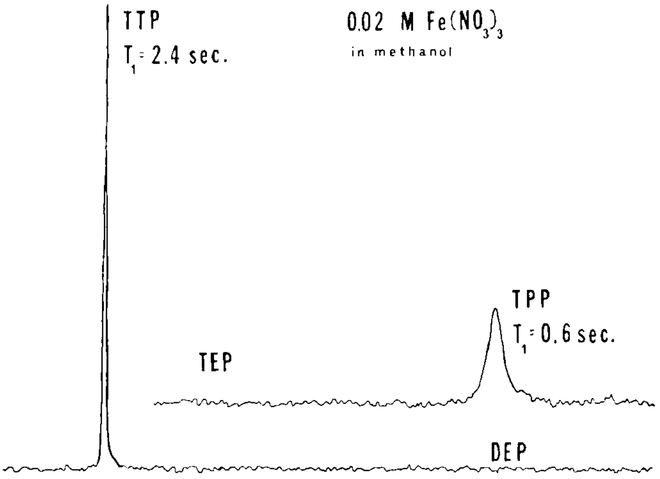

FIGURE 3

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tion that the signals for TEP and DEP have been broadened into the base line. As a result of previous work conducted in this laboratory, it was proposed that if the observed species migrated into the inner coordination sphere of the relaxation agent ion, signal broadening would occur (11). Such broadening would result from the migration of the TEP and DEP molecules into the inner coordination sphere of the iron ion. A coordination complex would then form with a definite geometry and orientation of the sterically accessible phosphorus compounds. A locally inhomogenous magnetic field would then induce broadening. In TPP, a broadened but observable signal is obtained. Presumably, the bulkiness of the phenyl rings would prevent the phosphorus atom from entering the iron inner coordination sphere. In TTP, the poorer coordinating ability of the sulfur atom hinders coordination and a sharp signal results. Similar results were obtained when these compounds were examined separately.

If a poorly coordinating ligand allows such coordination of sterically accessible molecules and resultant broadening of signals, the presence of a more tightly held ligand would prevent migration of these compounds into the inner coordination sphere of a relaxation agent ion. Therefore, the effect of the addition of a suitable chelate should be the reappearance of the TEP and DEP signals. Acetylacetone is such a substance and it forms an immediate blood red complex with ferric iron.

Figure 4 illustrates the results that the addition of acetylacetone has on the spectrum of the mixture of the organic phosphorus compounds with ferric nitrate. As expected, the signals for TEP and

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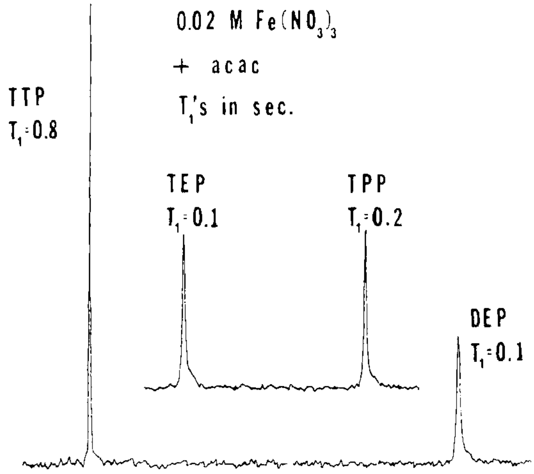

FIGURE 4

DEP have reappeared with good line shape and signal-to-noise ratio and considerably reduced T_1's. Again, similar results were obtained when the phosphorus compounds were examined individually which indicates that the relaxation agent functions the same, whether the species of interest is isolated or part of a mixture with other similar species. From these results, it appears that an important function of the chelate ligand is to prevent signal broadening by keeping the phosphorus-containing species of interest from occupying a place in the inner coordination sphere of the relaxation agent ion.

To test this idea further, similar experiments using copper (II) ion were performed. The addition of copper (II) nitrate to solutions of the phosphorus compounds in methanol gave results very similar to those obtained with iron (III) nitrate. This is shown in Figure 5. Copper has a strong affinity for nitrogen (15) and so ethylenediamine

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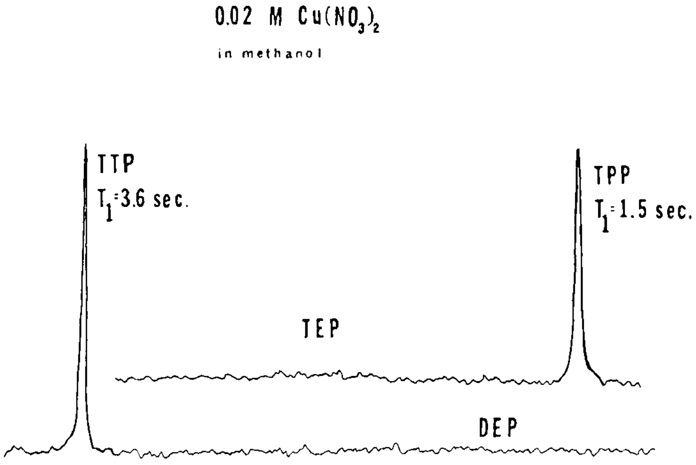

FIGURE 5

was added to the solution and the results are shown in Figure 6. As in the case of iron and acetylacetone, the signals for TEP and DEP have reappeared with good signal-to-noise and line shape. The TTP signal is virtually unaffected. However, the triphenylphosphate signal is severely broadened. In addition, a methanol solution of TTP, $Cu(NO_3)_2$ and ethylenediamine is green in color, as opposed to the distinct blue of similar solutions of the other phosphorus compounds. This suggests that a distinct chemical species is being formed--a coordination complex with the TPP present in the copper inner coordination sphere. If such is the case, it would be a further indication that exclusion of the phosphorus species from the inner coordination sphere of the metal ion is essential for relaxation agent effectiveness.

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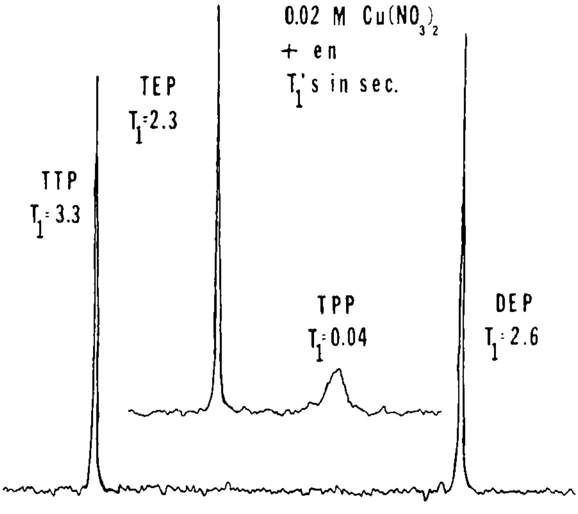

FIGURE 6

To investigate this further, the principle of hard and soft acids and bases (HSAB) (16) was considered. For example, an oxygen (small and unpolarizable) containing ligand will bond more strongly to a small, unpolarizable cation than to a larger more polarizable cation. Thus, if the theory applies, then improved signal-to-noise should be obtained with Co(III)$(acac)_3$, as opposed to Co(II)$(acac)_2$. Figure 7 shows that such is the case, which further strengthens the argument that if the phosphorus

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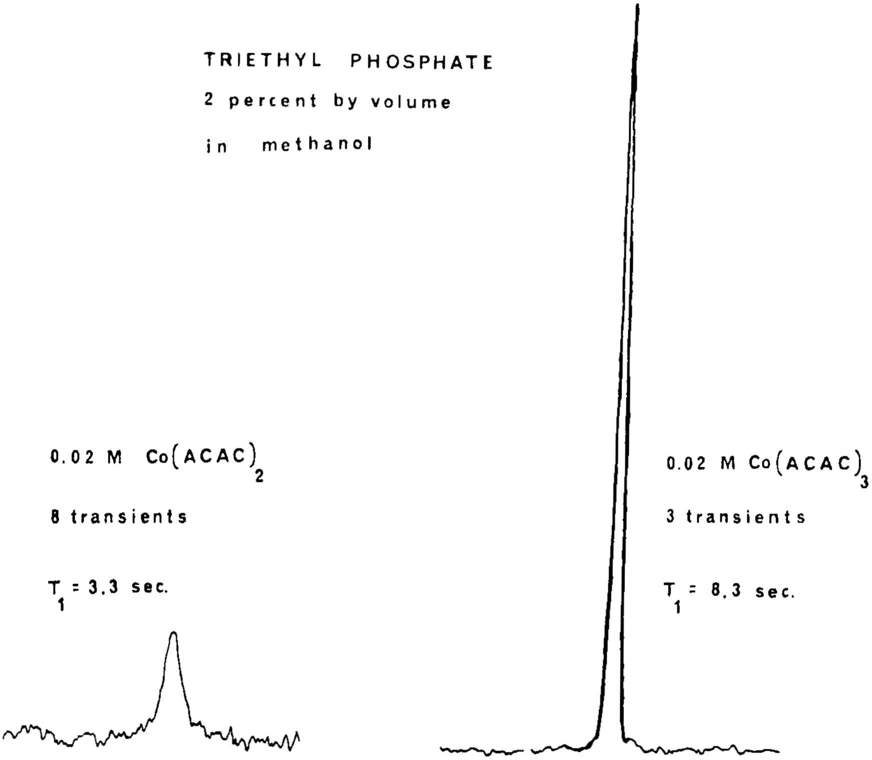

FIGURE 7

atom is kept outside of the inner coordination sphere of the relaxation agent ion, effective relaxation without excessive broadening will result.

Additional evidence for this comes from experiments using vanadium (III) ion as a relaxation agent. Figure 8 clearly demonstrates that the effectiveness of a relaxation agent ion is very dependent on the anion associated with it. Superior signal-to-noise results for both TEP and TPP when VF_3 is used. This is in contrast to the broader signals obtained with an equivalent concentration of VCl_3. This is expected

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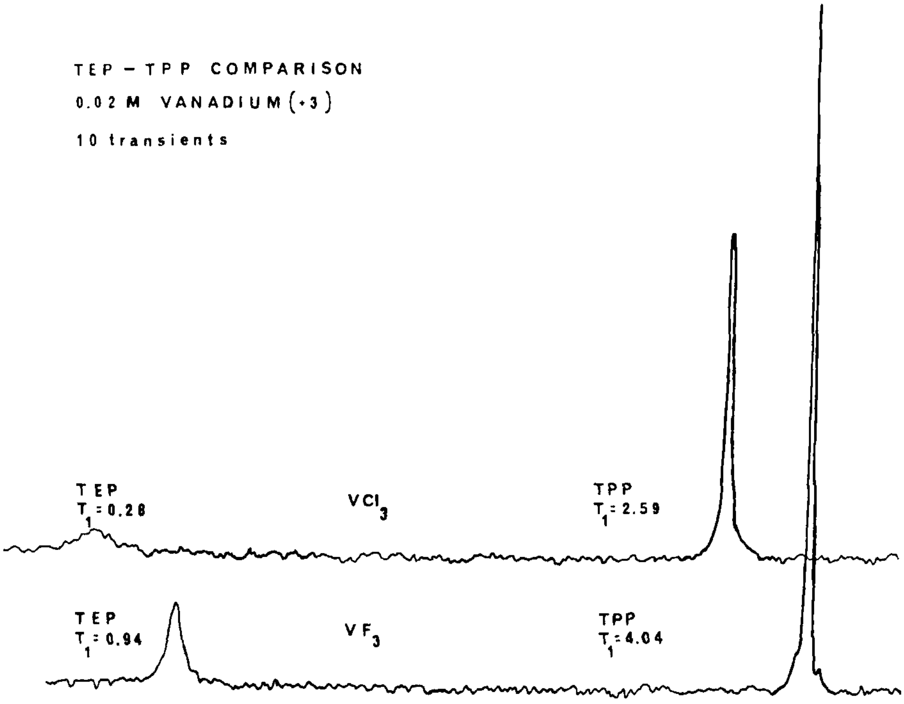

FIGURE 8

as a consequence of a stronger assocation of the small and unpolarizable vanadium (III) ion with the small, unpolarizable fluoride, than with the larger, more polarizable chloride ion. This trend was observed in other systems; examples of which are shown in Table 1. For a given first row transition metal ion, its effectiveness as a relaxation agent was observed to be dependent on the type of halide ion associated with it. In addition, it appears that increased signal-to-noise is related to increased magnitude of the stability constant of the relaxation agent in solution. Such behavior was observed for all four phosphorus compounds.

It seems, then, that for a relaxation agent to be effective, the ligand must function to exclude the phosphorus containing species of interest from the inner coordination sphere of the metal ion. If the observed species migrate into the inner coordination sphere, severe broadening results. If it is prevented from doing so, effective T_1 reduction with minimum broadening results.

The effectiveness of a relaxation agent may be affected by other factors. From a contact model of hard shell spheres, an expression, developed initially by Abragam (17) and later modified by Levy (18) and Gurley (19), may be derived that relates the effectiveness of a given relaxation, as measured by R_1^e, the electron-nuclear dipolar relaxation rate, to solution viscosity (v) and the molar concentration of the paramagnetic species ($\underline{M}$), in the following manner:

$$R_1^e = ((2.59)\ T_1^e (v)(\underline{M}))^{-1} \qquad (2)$$

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Table

The Effect of Halides on Metal

Phosphorus Compound	Metal Halide	Conc. Moles/Liter	T_1 (sec)
TEP	$CuCl_2$	0.02	—[b]
TEP	$CuBr_2$	0.02	—[b]
TEP	$CoCl_2$	0.01	0.14
TEP	$CoBr_2$	0.01	0.10
TPP	$CuCl_2$	0.02	1.93
TPP	$CuBr_2$	0.02	1.58
TPP	$CoCl_2$	0.01	3.20
TPP	$CoBr_2$	0.01	2.95
DEP	$CrCl_3$	0.02	1.50
DEP	$CrBr_3$	0.02	0.36
TTP	$CrCl_3$	0.02	2.29
TTP	$CrBr_3$	0.02	1.64

a) Values from Stability Constants of Metal-ion
The Chemical Society, Burlington House, W. I.,

b) Signal not observed.

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Ions as Relaxation Agents

Stability Constant Typical K_1[a] (in sol'n, logarithm)	# Transients	S/N Ratio
0.1	10	—[b]
-0.6	10	—[b]
3.1	15	5
2.5	15	5
0.1	10	112
-0.6	10	38
3.1	15	59
2.5	15	38
-1.0	8	346
-2.5	8	19
-1.0	8	450
-2.5	8	74

Complexes, Special Publication No. 17, London, Metcalfe and Cooper 670 (1964).

T_1^e, in turn, is the relaxation time due to election-nuclear dipolar interactions and is able to be calculated from the following equation:

$$\frac{1}{T_1^e} = \frac{1}{T_1} - \frac{1}{T_1^*} \qquad (3)$$

In Equation 3, T_1 is the relaxation time measured for the species of interest with the relaxation agent and T_1^* is the relaxation time measured for the species of interest without the relaxation agent. By substitution of Equation 3 into Equation 4, one may obtain the following expression that relates concentration of relaxation agent to the inverse of T_1:

$$\frac{1}{T_1} = [(2.59)\ R_1^e\ v\ \underline{M}] + \frac{1}{T_1^*} \qquad (4)$$

From Equation 3, it is clearly seen that the only parameters that effect the observed T_1 are the viscositv of the solution under study and the concentration of the relaxation agent. Thus, the observed T_1 of a phosphorus species should be invariant with respect to concentration of the phosphorus species, at constant relaxation agent concentration and solution viscosity. To test this point, a series of methanol solutions with varying TEP concentrations were prepared. All contained a constant concentration of $Fe(acac)_3$ and were found to possess negligible variations in viscosity. The measured T_1's for the series were found to be relatively invariant and this is shown in Figure 9.

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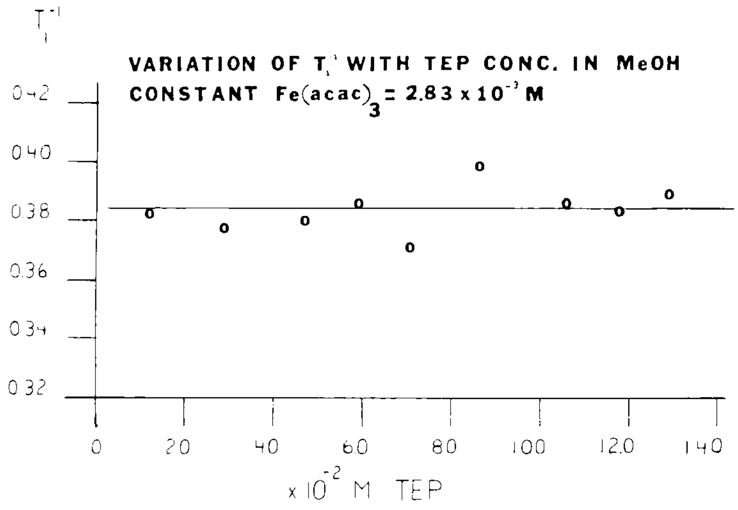

FIGURE 9

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Other useful information may be obtained from Equation 4. The y-intercept provides the inverse of the T_1, without the presence of the relaxation agent. From the slope of equation, the electron-nuclear relaxation rate, R_1^e, may be calculated. However, Equation 4 needs to be used with care, as the effectiveness of a relaxation agent may be affected by parameters, other than the viscosity and the limitations imposed by solubility (20).

It was of interest to see if there is an optimum concentration for a relaxation agent. The T_1's of a series of 2% (v/v) solutions of TEP in methanol with varying $Fe(acac)_3$ concentrations were measured. Figure 10 shows a plot of $Fe(acac)_3$ concentration vs. the measured T_1's for the solution. A linear plot is indeed obtained; however, there is a point of inflection at 4.7×10^{-3} M.

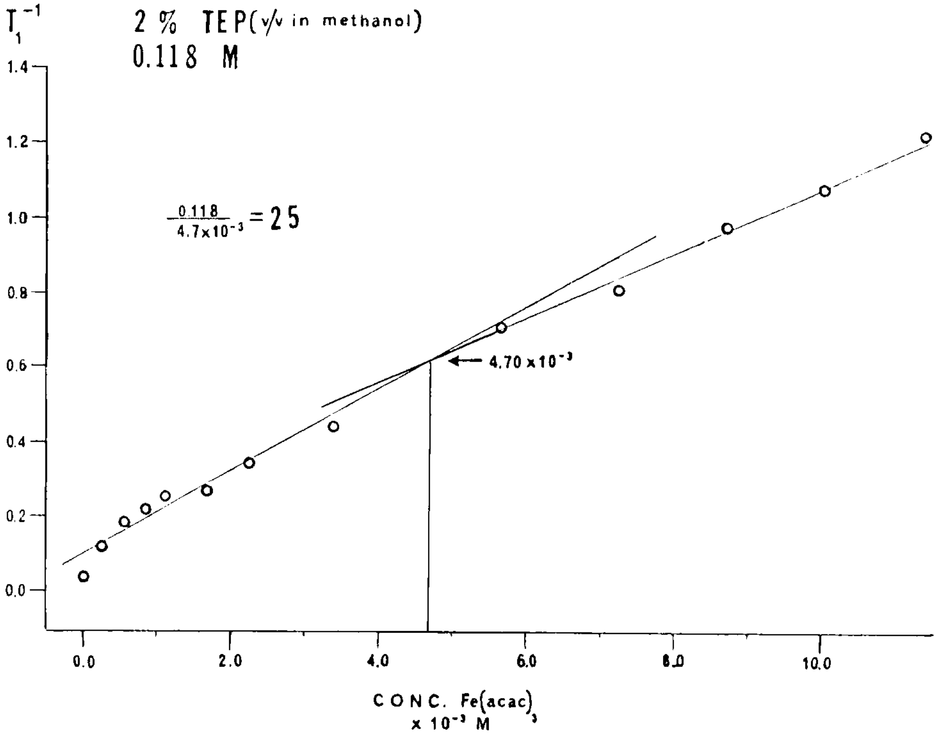

FIGURE 10

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The lower segment has a slope of 115, from which an R_1^e value of 87 is calculated for the viscosity of methanol at 30°C, 0.51 cp (21). The upper segment has a slope of 88, from which an R_1^e value of 66 is calculated, which is in relatively close agreement with the literature value of 50 (20) obtained from ^{13}C NMR data. Furthermore, the concentration ratio of TEP to Fe(acac)$_3$ at the point of inflection is approximately 25. A similar plot for a series of 1% (v/v) TEP solution is shown in Figure 11. This plot has an inflection point at 2.2 x 10^{-3}M and a resultant concentra-

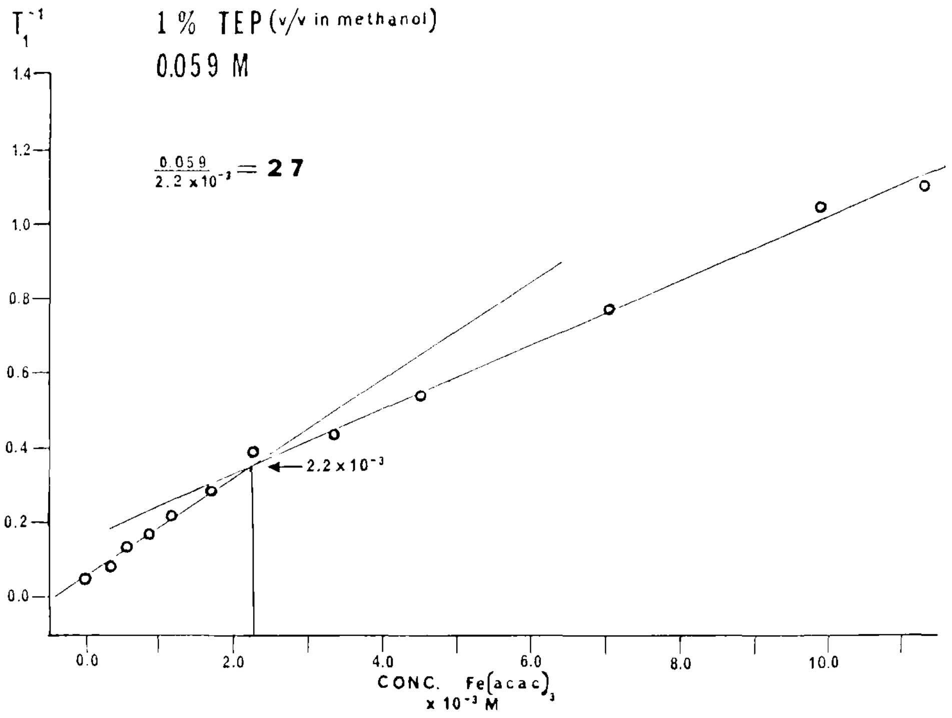

FIGURE 11

tion ratio of TEP to Fe(acac) of approximately 27. The lower segment has a slope of 130, from which an R_1^e of 98 is calculated and the upper segment has a slope of 80, from which an R_1^e of 61 is calculated. Both of these R_1^e values are in good agreement with their counterparts from the 2% plot.

The point of inflection indicates that, for TEP, the effectiveness of the Fe(acac)$_3$ is diminished after a certain concentration limit is reached. The significance of this may be realized from a calculation that shows that 32 molecules of the dimensions of a

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TEP molecule may fit around a molecule of the size of an Fe(acac)$_3$ molecule, if one uses the Abragam's hard sphere model. From this, we theorize that a labile outer sphere coordination may be taking place between the observed phosphorous species and the relaxation agent. As the Fe(acac)$_3$ concentration increases, there is an increased number of coordination sites for the TEP molecules to assume and so T_1 is reduced with greatest effectiveness. After a certain concentration of Fe(acac)$_3$ is reached there are more coordination sites than TEP molecules to occupy them. Additional Fe(acac)$_3$ molecules are able to interact with the TEP molecules only at greater intermolecular distances. As dipolar interactions fall off rapidly with distance, the reduction in T_1 is not as large at these higher levels of Fe(acac)$_3$ concentration. If this is a valid model, the optimal relaxation agent would be a physically large molecule, so that more of the observed species could fit around it.

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Additional evidence for the outer sphere coordination model was provided by experiments that measured the T_1's of a series of 2% (v/v) solution of TTP in methanol with varying concentrations of Fe(acac)$_3$. From HSAB, it is expected that TTP would have a smaller degree of interaction with Fe(acac), due to the presence of the sulfur atom. An outer sphere coordination complex would not be as likely to form in this case. A plot of Fe(acac)$_3$ concentration vs. T_1^{-1} would therefore show no point of inflection. Figure 12 shows that such is the case. Due to the weakness of the interaction, the degree to which the spin-lattice relaxation

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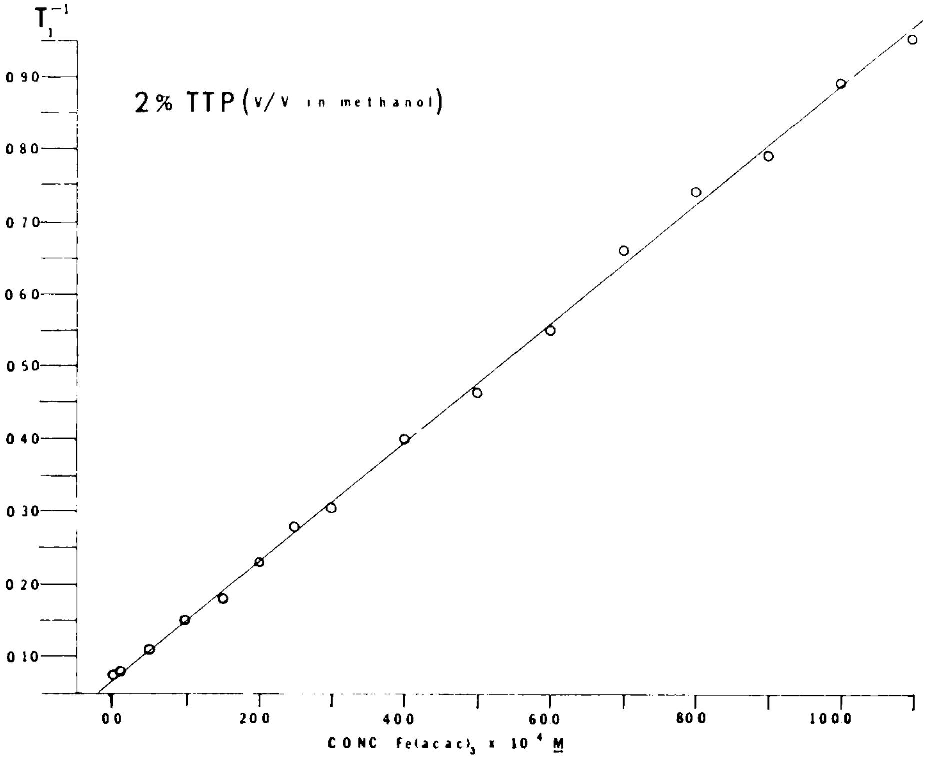

FIGURE 12

time is reduced would be smaller for TTP than TEP, at a given concentration of Fe(acac)$_3$. This is observed, as shown in Table 2. Over an equivalent concentration range of Fe(acac)$_3$, the degree to which the phosphorus T_1 is reduced is indeed smaller for TTP than for TEP. The slope of the line is 80, and the resultant R_1^e value is 61. Thus, the greater degree of intertness with TTP results in an R_1^e value, consistent with those calculated from the upper segments of the TEP plots.

With the seeming importance of the ligand and the outer sphere

Table 2

Comparison of T_1 Reduction of TEP and TTP by (Fe(acac)$_3$ (2% (v/v Solutions)

Conc. Fe(acac)$_3$ x 10^{-4} M	TEP T_1 (sec)	$\frac{1}{T_1}$	Conc. Fe(acac)$_3$ x 10^{-4} M	T_1 (sec)	$\frac{1}{T_1}$
2.83	7.76	0.13	1.00	12.72	0.08
5.66	5.25	0.19	5.00	9.28	0.11
8.49	4.87	0.21	10.00	6.87	0.15
11.33	4.06	0.25	15.00	5.49	0.18
16.99	3.70	0.27	20.00	4.32	0.23
22.65	2.97	0.34	25.00	3.58	0.28
33.98	2.27	0.44	30.00	3.28	0.31
56.63	1.41	0.71	40.00	2.52	0.40
70.79	1.23	0.81	50.00	2.12	0.47
84.89	1.02	0.98	60.00	1.81	0.55
99.10	0.93	1.08	70.00	1.52	0.66
113.30	0.81	1.24	80.00	1.36	0.74
			90.00	1.26	0.79
			100.00	1.12	0.89
			110.00	1.05	0.95

coordination mechanism at hand, the possibilities afforded by the use of gadolinium(III) tris-1,1,1,2,2,3,3-tetra-fluoro-7,7-dimethyl-4,6-octanedionate(Gd)fod)$_3$) (22) as an ideal relaxation agent for ^{31}P NMR were explored. The complex as a whole is rather large

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(our calculation show it has a hydrodynamic radius of 9.65 Å, as compared to a claculated hydrodynamic radius of 6.16 Å for Fe(acac)$_3$), its fod ligand is tightly held, and the Gd(III) ions has a high, isotropic magnetic moment (as both Gd(III) and Fe(III) ions have S ground states (23), there is no orbital contribution to the magnetic moment and the magnetic moments for these ions may be conviently calculated by a "spin-only" formula: 7.9 B.M. for Gd(III) as opposed to 5.9 B.M. for Fe(III)). Figure 13 shows the results obtained with its use. Note the low concentration of the Gd(fod)$_3$ needed to effect significant relaxation. However, at higher con-

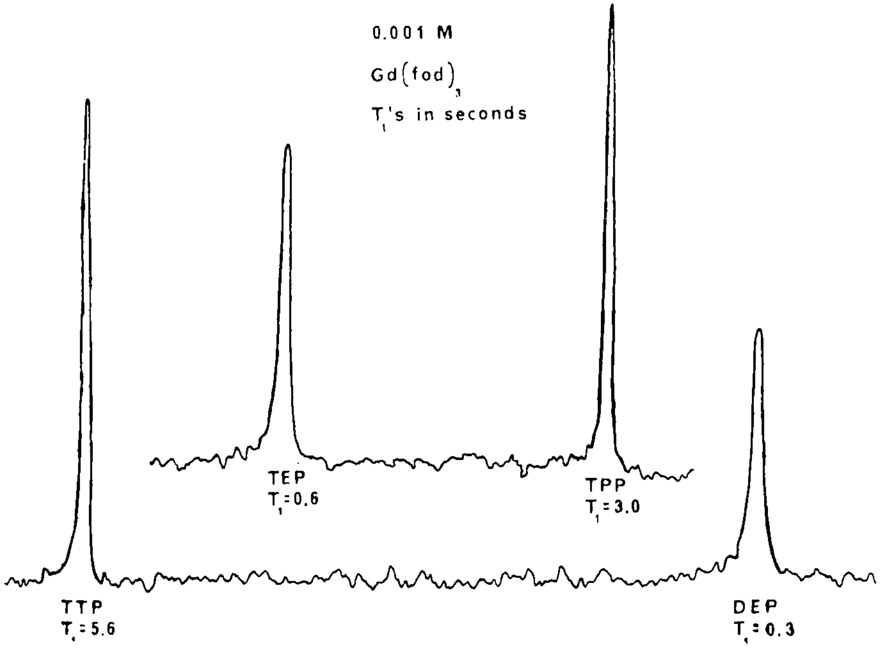

FIGURE 13

centrations, the DEP and TEP signals tend to be broadened into the baseline (24). In light of the presence of the P→O moiety in the DEP and TEP compounds and the high magnetic moment of the $Gd(fod)_3$ molecule, such broadening would be expected if an outer sphere coordination is taking place.

The T_1's of a series of 2% (v/v) TEP solutions in methanol with varying $Gd(fod)_3$ concentrations were measured. Figure 14 shows a plot of $Gd(fod)_3$ concentrations vs. T_1^{-1} for this series. As with the $Fe(acac)_3$ plots, a point of inflection is observed and it is at 2.0×10^{-4} <u>M</u> $Gd(fod)_3$ with a concentration ratio of TEP

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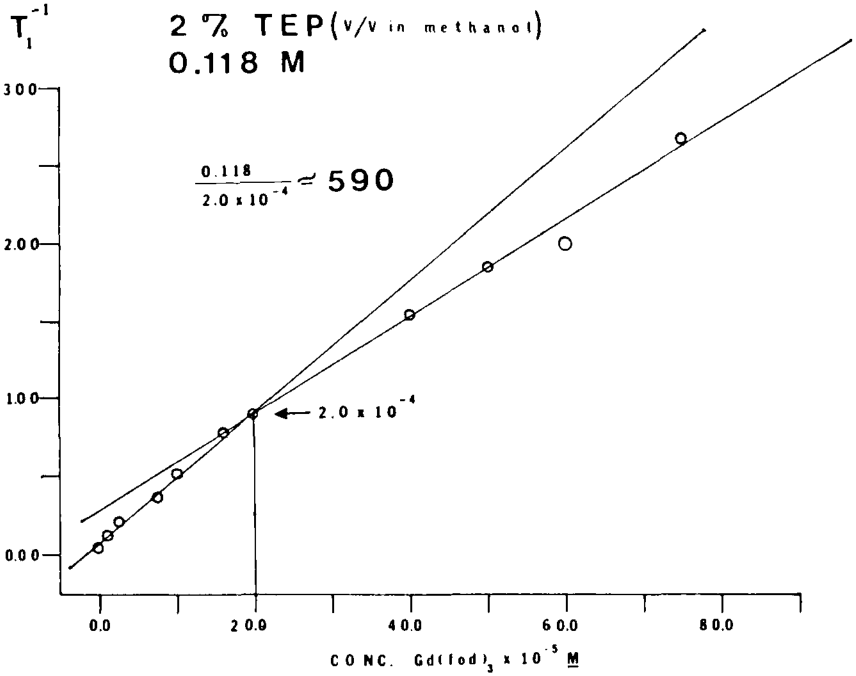

FIGURE 14

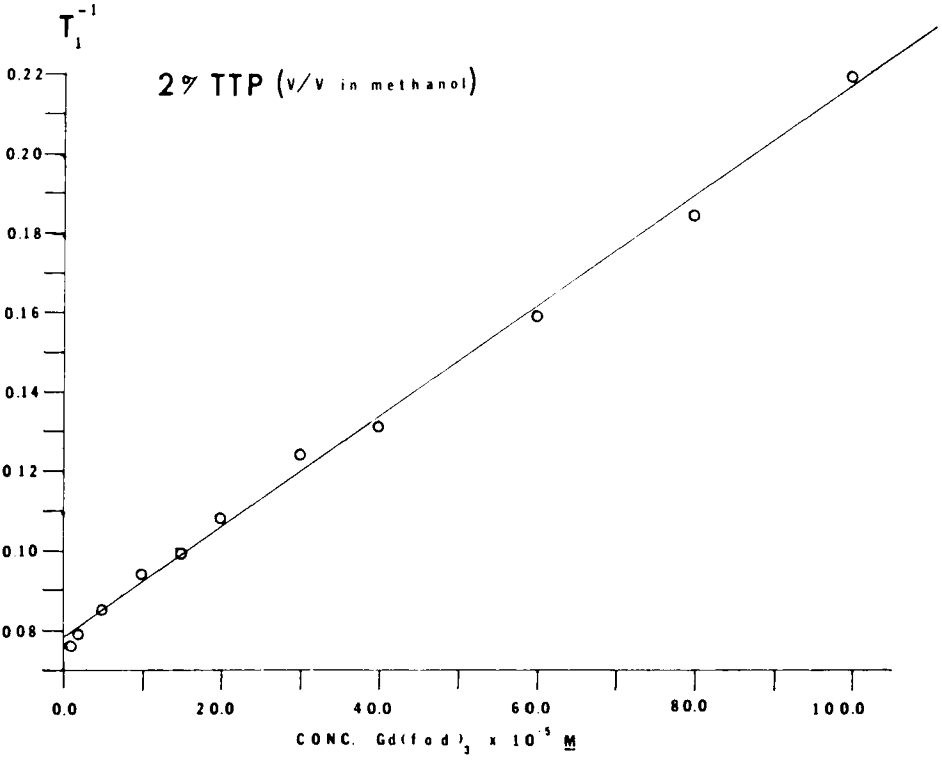

FIGURE 15

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to Gd(fod)$_3$ of 590. Calculations indicate that approximately 61 TEP molecules are able to fit around one Gd(fod)$_3$. Yet, this factor of almost 10 differences does not preclude an outer sphere coordination as a valid mechanism. Rather, it is the result of the high magnetic moment of Gd(fod)$_3$ effecting the relaxation of a large number of TEP molecules in rapid equilibrium. When compared to the magnetic moment of Fe(III), the magnetic moment of Gd(III) is larger by a factor of 1.34. As the r^{-6} dependence (25) of dipolar interactions defines an effective radius for Fe(III),

Table 3

Comparison of T_1 Reduction of TEP and TTP by $Gd(focl)_3$ (2% (v/v) solutions)

Conc. $Gd(focl)_3$ x 10^{-5} M	TEP T_1 (sec)	$\frac{1}{T_1}$	Conc. $Gd(focl)_3$ x 10^{-5} M	TTP T_1 (sec)	$\frac{1}{T_1}$
1.00	7.81	0.13	1.00	13.18	0.076
2.50	4.79	0.21	2.00	12.65	0.079
7.50	2.76	0.36	5.00	11.73	0.085
10.00	1.94	0.52	10.00	10.62	0.094
16.00	1.28	0.78	15.00	10.07	0.099
20.00	1.12	0.89	20.00	9.23	0.018
40.00	0.64	1.56	30.00	8.04	0.124
50.00	0.54	1.85	40.00	7.64	0.131
60.00	0.49	2.02	60.00	6.30	0.159
75.00	0.37	2.67	80.00	5.43	0.184
			100.00	4.57	0.219

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the effective distance for Gd(III) will be a factor of $(1.34)^6$ or 5.82 greater. Within the folume of the spherical shell described by this larger effective radius, a large number of TEP molecules may be included. Using Abragam's contact model, calculations show that 129 TEP molecules are able to fit into the second coordination sphere and that 222 TEP molecules are able to congregate in a tertiary coordination sphere. Thus, there are three concentric spheres which are able to contain a number of TEP molecules (61 + 129 + 222 = 412) that is a fair approximation of the 590 obtained from the point of inflection in the plot.

As in the case of $Fe(acac)_3$, a plot of $Gd(fod)_3$ concentration vs. T_1^{-1} for a series of 2% (v/v) TTP solutions in methanol shows no point of inflection. This is illustrated in Figure 15. In addition, the degree to which T_1 is reduced for TTP at a given $Gd(fod)_3$ concentration is considerably smaller than for TEP. This provides a further indication that the lack of interaction from the sulfur-containing species is a limiting factor in the ability of the $Gd(fod)_3$ to function as a relaxation agent. Table 3 contrasts the effect of a concentration range of $Gd(fod)_3$ on TEP and RRP in 2% (v/v) solutions.

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CONCLUSIONS

In summary, there appears to be a number of conditions for the optimal relaxation agent for phosphorus NMR:

a) to prevent broadening, a tightly bound ligand is necessary

b) an outer sphere coordination between the observed substrate and relaxation agent may be needed for maximum effectiveness

c) the size of the magnetic moment plays a significant role in the usefulness of the relaxation agent.

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