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NMR STUDIES OF ORGANOPHOSPHORUS EXTRACTANTS

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I. INTRODUCTION

During the past several years, nuclear magnetic resonance (nmr) has become increasingly important in the study of organophosphorus solvent extraction systems. The purpose of this review is to describe the principles involved in these studies and to summarize the most important results thus far reported.

The ^1H and ^{31}P nuclei of organophosphorus extractant molecules occur in almost 100% isotopic abundance and both nuclei give rise to sharp nmr signals. However, because of the much greater ease in signal detection and the wider availability and utilization of instrumentation, proton nmr (pmr) has been used far more extensively than ^{31}P nmr in studies of organophosphorus extractants.

The nmr studies of organophosphorus extraction systems can be categorized as follows: (1) studies of extractant molecules in an attempt to correlate their structural and electronic properties with their extractant abilities, and (2) studies of the interactions occurring in extraction systems.

This review is limited to neutral organophosphorus molecules that are extractants or are closely related to extractants. For further references to these and other types of organophosphorus compounds, the reader is referred to two recent reviews.^{1,2}

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II. PROTON MAGNETIC RESONANCE OF TYPICAL EXTRACTANTS

A. Monophosphoryl Compounds

Characteristic ^{31}P -H coupling constants and chemical shifts of some representative monophosphoryl extractants are tabulated in Table I.³⁻⁸ The decrease of the $\text{P-OCH}_2\text{-R}$ coupling constant in trialkylphosphates with increasing electron-releasing ability of the R group was first noted by Axtmann et al,³ and further investigated by Dudek.⁹ The same effect was noted in phosphonates and phosphinates.⁸ For the trialkylphosphates, Dudek found that for electron-releasing R groups a good correlation exists between $J(\text{P-OCH})$ and the Taft σ^* constant, but that electron withdrawing R groups have very little effect.⁹ It was concluded that the R group exerts its effect by changing the electronic environment of the methylene group rather than that of the phosphoryl group.⁹ This conclusion is consistent with the lack of correlation between $J(\text{POCH})$ and complexing ability.⁸

The ^{31}P -H coupling is rapidly attenuated by intervening atoms; thus, $J(\text{P-OCH})$ values are ~ 5 to 12 Hz, $J(\text{P-OCCH})$ values are usually < 1 Hz, and coupling through more than four bonds is not observable.

In compounds containing the $\text{P-CH}_2\text{CH}_2\text{R}$ fragment, the three-bond coupling constant, $J(\text{P-CCH})$, is usually larger than the two-bond coupling constant, $J(\text{P-CH})$. This anomalous effect has been explained theoretically by Klose.¹⁰

In homologous series of compounds, the proton chemical shifts are governed by the inductive effect of substituents.¹ The shifts are relatively insensitive to solvents.¹

B. Alkylenediphosphoryl Compounds, $R^1 \overset{\text{O}}{\parallel} \text{P} (\text{CH}_2)_x \overset{\text{O}}{\parallel} \text{P} - \text{R}''_2$

1. Methylenediphosphonates. The general features of the pmr spectra of diphosphonates, such as chemical shifts and proton-proton coupling constants, are similar to those of monophosphonates. However, in methylenediphosphonates, additional spectral complexity may arise from two sources: magnetic nonequivalence of chemically equivalent protons and the effects of ^{31}P - ^{31}P coupling. Siddall¹¹ has discussed the origin of magnetic nonequivalence in diphosphonates and has given several examples of its effects upon the pmr spectra. The effect is most noticeable when magnetically anisotropic groups are present near the nonequivalent protons.

Most neutral methylenediphosphonates give simple first-order pmr spectra. In tetramethylmethylenediphosphonate, a methyl triplet is observed at $\delta = 3.48$ ppm with $J_{\text{P-H}} = 11$ Hz, and a bridge-methylene triplet is observed at $\delta = 2.50$ ppm with $J_{\text{P-H}} = 22$ Hz.¹² In the tetraethyl compound, the chemical shifts and coupling constants are CH_3 : $\delta = 1.23$ ppm, $J_{\text{H-H}} = 6.9$ Hz, $J_{\text{P-H}} = \infty$; $-\text{CH}_2-\text{C}$: $\delta = 4.05$ ppm, $J_{\text{H-H}} = 6.9$ Hz, $J_{\text{P-H}} = 8.3$ Hz; and $\text{P}-\text{CH}_2-\text{P}$: $\delta = 2.29$ ppm, $J_{\text{P-H}} = 20.3$ Hz.¹³ In both compounds, $J_{\text{P-P}}$ is less than 1 Hz. In the tetraethyl compound, the methylene protons within an ethoxy group are magnetically nonequivalent, but this nonequivalence is not evident in the pmr spectrum.

In the anionic forms of the latter diphosphonates, $[\overset{\text{O}}{\parallel} \text{P}]_2^- - \text{CH}_2$, $J_{\text{P-P}}$ increases to about 25 Hz and the phenomenon of "Virtual Coupling" produces a complex alkoxy α -proton absorption.¹³

2. Ethylenediphosphonates. The pmr spectrum of tetraethylethylene-diphosphonate $[(\text{CH}_3\text{CH}_2\text{O})_2\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{P}(\text{O})(\text{OCH}_2\text{CH}_3)_2]$ is surprisingly complex.¹²⁻¹⁴ The absorptions of the bridge ethylene protons and the ethoxy methylene protons show broadened peaks. The origin of the broadening has not been determined, but long-range proton-proton coupling between the bridge and ethoxy methylene protons and hindered rotation have been shown not to cause the broadening.¹⁴

3. Carbamylmethylenephosphonates, $(\text{RO})_2\text{P}(\text{O})\text{C}(\text{R}')\text{C}(\text{R}'')\text{NR}_1\text{R}_2$. These compounds can be regarded as amides with a phosphoryl-containing substituent; thus because of slow rotation around the amide C-N bond, one usually observes separate signals for the protons in R_1 and R_2 , even if $\text{R}_1 = \text{R}_2$. If $\text{R}' \neq \text{R}''$, the R groups are nonequivalent, as are the geminal protons within the R-groups; the α -geminal protons in R_1 and R_2 are also nonequivalent and often exhibit complex patterns.¹¹⁻¹⁵

4. Carbamylphosphonates, $\text{R}_3\text{O} \text{---} \text{P}(\text{O})\text{C}(\text{O})\text{N}(\text{R}_1)\text{R}_2$. Carbamylphosphonates also may exhibit slow amide rotation. The presence of the phosphoryl group enhances the chemical shift difference between protons in the N-substituents by factors of 3 to 5 over the corresponding amide.¹⁶ If $\text{R}_3 \neq \text{R}_4$, geminal protons in the amide substituents are nonequivalent and may give rise to additional spectral structure. Geminal protons in the phosphorus substituents are also nonequivalent as long as amide rotation is slow.

The principles of magnetic nonequivalence were used to assign amide isomers in several carbamylphosphonates of the type $(\text{R O})_2\text{P}(\text{O})\text{C}(\text{O})\text{N}(\text{R})(\text{aryl})$.¹¹ The pmr spectra of these compounds showed the presence of amide isomers in a 5:1 ratio below 100°C. The spectra of the major isomers showed doubling of the signals from the phosphoryl substituents, but the spectra of the minor isomers showed only single signal sets. From these observations, it was concluded that in the minor isomers the anisotropic aryl group was *trans* to

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the phosphoryl group and its substituents and thus was unable to provide the field gradient necessary to make the nonequivalence observable. In the major isomer, the aryl group would be *cis* to phosphoryl and the anisotropic effect upon the phosphoryl substituents would be great enough to produce observable nonequivalence.

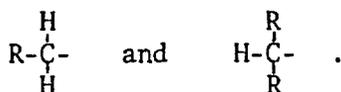
An unusual feature observed in carbamylphosphonates is the existence of ^{31}P -H coupling through four bonds and five bonds in the framework $\text{P}-\overset{\text{O}}{\parallel}{\text{C}}-\text{N}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\overset{\text{H}}{\text{C}}$.¹⁷ Coupling through three bonds, $\text{P}-\overset{\text{O}}{\parallel}{\text{C}}-\text{N}-\text{H}$, is too small to be observable. In N,N-dimethyl compounds, the ^{31}P -methyl proton coupling generally ranges from 0.9 to 1.2 Hz with extreme variations from 0.0 to 1.4 Hz. Coupling between ^{31}P and the highfield N-methyl is usually slightly larger than to the lowfield N-methyl.

In N-N-diethyl compounds, five-bond P-H coupling is larger than four-bond P-H coupling.¹⁷ Typical values are: $J(^{31}\text{P}-\text{C}-\text{N}-\underline{\text{CH}_2}) = 0$ Hz (lowfield set) and <0.5 Hz (highfield set); $J(\text{P}-\text{C}-\text{N}-\underline{\text{C}}-\text{CH}_3) = 0$ Hz (lowfield set) and 1 Hz (highfield set).

In N-N-di-2-propyl compounds, the coupling constant ranges are: $J(\text{P-highfield methine proton}) = 3.5$ to 5.2 Hz; $J(\text{P-lowfield methine proton}) = 1.0$ to 1.8 Hz; $J(\text{P-lowfield methyl proton}) = 0.5$ to 1.3 Hz; and $J(\text{P-highfield methyl proton}) = \sim 0$ Hz.¹⁷

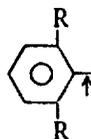
III. SYMMETRY EFFECTS ON THE SPECTRA

Frequently, two atoms of the same species (usually protons) or two radicals or substituent groups of the same kind may be joined to the same central atom (I). The question arises as to when these two geminal atoms (or groups) will be equivalent in a nmr sense and yield only one set of signals, or there will be nonequivalence between the geminal species with two sets of nmr signals. Most common among situations of this type are:



(I)

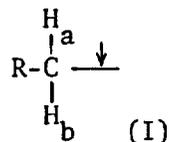
A similar situation is illustrated with



(II)

Still further complications may result when the organic molecule is bonded to a central metal atom.

The necessary conditions for observable nonequivalence have been stated.¹¹ First, there must not be any molecular motions that correspond to symmetry operations for the protons or groups that are completed in a time that is short compared to the nmr signal width. These are the familiar symmetry operations¹⁸ of stereochemistry. Note that rotation around the bond



does not constitute a symmetry operation. No matter whether this rotation is

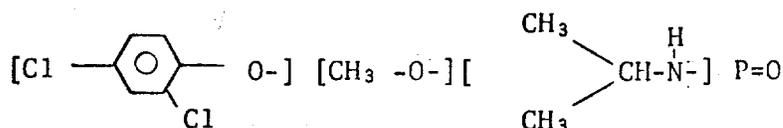
free or hindered, it does not of itself interchange the identities of H_a and H_b . On the other hand, reflection through a symmetry plane does effect such an interchange. In general, if (i) there is a molecular symmetry plane (ii) that can bisect the angle between H_a and H_b at some angle of rotation around the bond \downarrow then $H_a \equiv H_b$, and there will be only one signal set. If such a molecular symmetry plane is missing even though there may be other symmetry planes not fulfilling condition (ii), then $H_a \neq H_b$, and there may be two signal sets. (However, rotation around the bond by 180° in situation II does interchange R groups in that situation.)

There is, as specified above, a time element to be considered. For example, an asymmetry center in the molecule might be the basic reason for the absence of a symmetry plane. However, if this asymmetry center were to invert rapidly on the nmr time scale (commonly in the order 1 to 10 milliseconds), then in effect H_a and H_b would be reflected back and fourth so rapidly through a symmetry plane that only one averaged set of signals would result.

A second condition for observable nonequivalence is that there must be a field gradient (magnetic or electric) between the protons or groups. There might be geometrical nonequivalence, but if the internal fields at the two sites are not sufficiently different, then only one signal set would be observable.

A third condition is that there be no internal motion or set of motions that average out the field gradient. Even though not true symmetry operations, such motions could have the same net effect on the spectrum.

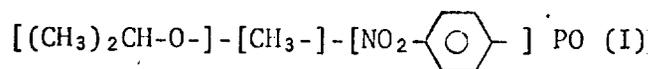
The first condition is in effect a rigorous set of selection rules, and its application follows in a straightforward manner. However, the second and third conditions lack any such precision in concept or prediction. In many organophosphorous compounds such as in the general molecule $[R_2CH-O-]_2P(O)R'$, the first condition is fulfilled. (There is no molecular symmetry plane between the two R groups of a R_2CHO- group even though there is such a plane between the two R_2CHO- groups). In fact, if the R groups are to give two signal sets, R' must be, or must contain, a benzene ring(s) or some other group with a large anisotropic internal magnetic field.⁵ Note that the observation of nonequivalence can be solvent dependent, possibly because hydrogen bonding affects rotamer preference,¹⁹ as in the case of the molecule



So far it has always been possible to account for doubled sets of resonances in organophosphorous extractant molecules by symmetry arguments or because of the coexistence of diastereoisomers. In particular, it has not been necessary to suppose that such doubling is due to any slow site exchange within the molecule.

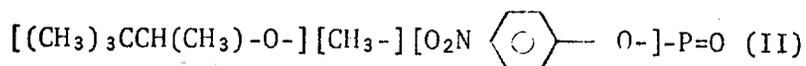
However, one investigation has yielded data that are very difficult to understand except on the basis of slow site exchange.²⁰ These authors examined the pmr spectra of three organophosphorous compounds and their uranyl nitrate adducts in detail.

The compound

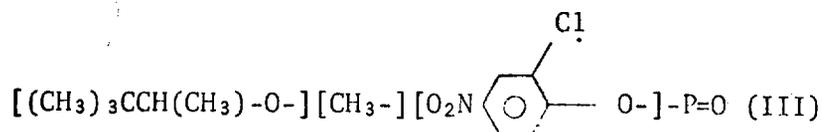


showed the doubled sets (two doublets of resonances to be expected on symmetry grounds alone for the methyl groups of $[(\text{CH}_3)_2\text{CH-O}]$). However, the methine proton of this group did not give the expected A_6BX pattern, but closely resembled an $A_6A_6'BB'X$ pattern. Such a pattern is consistent only with the coexistence of two molecular species. The authors believed these species to be the "up" and "down" rotamers of the $[(\text{CH}_3)_2\text{CHO}]$ group.

The other two compounds were



and



Compound II shows doubled resonances for the $(\text{CH}_3)_3\text{C}$ protons as well as for the $\beta\text{-CH}_3$ protons of the $[(\text{CH}_3)_3\text{CCH}(\text{CH}_3)\text{-}]$ group, but only one doublet (J_{PH}) for the methyl group directly attached to phosphorus ($\text{CH}_3\text{-P}$). The methine proton signals gave an $A_3A_3'BB'X$ pattern. At about 150°C in diphenyl ether, the doubled sets of resonances coalesced. In ethylene tetrachloride, the spectrum was appreciably broadened as the temperature was raised to the boiling point of the solvent. On complexing with uranyl nitrate, the doubling of resonance sets disappeared. Compound (III) behaved in a similar manner.

The behavior of compounds II and III does not necessarily require each to exist as two molecular rotameric species. Both molecules possess two asymmetry centers, and therefore can, and very probably do, exist in two diastereomeric forms. In principle, each of two diastereoisomers can possess

its own separate and distinctly different nmr spectrum. The coalescence of separate signal sets could be due to increased rate of inversion at one of the centers (if so, more likely the phosphorous). It is also possible that complex formation with uranyl nitrate so favors one diastereoisomer that the other disappears.

It is seen then that the behavior of Compounds II and III does not require "up"- "down" rotamers of relatively long life. However, these reviewers cannot provide a specific, satisfactory alternative explanation for the $A_6A_6'BB'X$ pattern obtained for the methine $(CH_3)_2-CH-O$ proton of Compound I. More work with similar compounds would be of great interest.

IV. ^{31}P CHEMICAL SHIFTS

Because of its smaller magnetic moment, the sensitivity of the ^{31}P nucleus at a given field strength is only 6.63% of that of an equal number of hydrogen nuclei. In organophosphorus compounds, the ^{31}P nucleus is usually surrounded by a number of interacting nuclei, and thus the ^{31}P resonance is usually a complex multiplet. As a result of these two factors, the minimum detectable concentration is much higher for ^{31}P nmr. However, these limitations can be partially offset by signal averaging and heteronuclear decoupling. A thorough discussion of these various aspects of ^{31}P nmr is available.²

^{31}P chemical shifts of phosphoryl compounds >P=O , with which we are chiefly concerned in this review, cover a range of about 75 ppm. In the phosphoryl derivatives, the bonding consists of four sp^3 -hybridized σ -bonding orbitals and one $p_{\pi}-d_{\pi}$ bond orbital which gives rise to multiple bond character that is capable of resonating between several of the bonds to the phosphorus atom.² ^{31}P chemical shifts depend for the most part on (1) the total occu-

pation of the phosphorus d_{π} orbitals; (2) the unbalance of the σ -bonds caused by the difference in electronegativities of the substituents; and (3) the bond angles.² The ^{31}P shifts are not as responsive to the effects of distant groups as are hydrogen shifts.²

In a series progressing from $(\text{RO})_3\text{P}=\text{O}$ to $\text{R}_3\text{P}=\text{O}$, the ^{31}P shielding decreases as shown by the results given in Table 2.⁸ These changes were attributed to decrease in occupation of the phosphorus d_{π} orbitals (or increase in $\overset{+}{\text{P}}-\overset{-}{\text{O}}$ character) in going through the series $(\text{RO})_3\text{P}=\text{O}$ to $\text{R}_3\text{P}=\text{O}$.⁸ The effect of substituent electronegativity can be seen in Table 2 by comparing the shifts of the dialkylphenylphosphonates with the other phosphonates. Thus, replacement of an alkyl group with a phenyl group causes a 15 ppm upfield shift of the ^{31}P resonance as a result of the increased π character of the $\text{P}=\text{O}$ bond.⁸

Large downfield shifts are produced by complexation with uranyl ion, as may be seen from the results given in Table 2. Part of the complexation shift is due to change in the nature of the $\text{P}=\text{O}$ bond, but the extent of this change cannot be measured because the ligands lie in the paramagnetic region of the uranyl ion.²¹ (See discussion of uranyl paramagnetism in Section V). The complexation shifts do, however, correlate with the extracting ability of the organophosphorus compound.^{8,22,23}

The effect upon the ^{31}P chemical shift of complexation with a diamagnetic ion is evident from the results given in Table 3 for the equilibrium $\text{Zn}(\text{TTA})_2 + \text{TOPO} = \text{TOPO}:\text{Zn}(\text{TTA})_2$ (TTA = thenoyltrifluoroacetone anion, TOPO = tri-*n*-octylphosphine oxide).²⁴ Thus, increasing complexation causes a downfield shift of up to 543 Hz, due entirely to decreasing population of the phosphorus d_{π} orbitals. When tri-*n*-butoxyethylphosphate (TBEP) is substituted for TOPO, no downfield shift is caused by adding $\text{Zn}(\text{NO}_3)_2$. The lack of a downfield

shift indicates that the interaction between TBEP and Zn^{2+} is very weak, in agreement with other evidence.²⁴

In complexes in which the organophosphorus molecule is bonded to the metal ion through the phosphoryl oxygen, the ^{31}P nucleus, being nearer the site of the interaction, may serve as a more sensitive probe than the protons. Thus, in lanthanide-triamylphosphate adducts, the paramagnetic shifts are much larger for ^{31}P than for the α protons, as may be seen by the results given in Table 4.²⁵

V. EFFECT OF COMPLEXING TO METAL SALTS IN EXTRACTANT COMPLEXES

Bonding to a metal ion in an extractant complex will have relatively small effect on the proton magnetic resonance spectrum of the extractant molecule if the metal ion is diamagnetic, but bonding to paramagnetic ions may produce large effects.^{26,27} With lanthanides and actinides, there may be a shift of 10 ppm or more of the resonance position before and after bonding. It is useful to define a quantity called the paramagnetic shift: $\Delta\sigma(\text{ppm}) = \delta_p$ (proton bound in paramagnetic complex) - δ_d (proton bound in diamagnetic complex).

In practice, because bonding to a diamagnetic ion has relatively small effect on the proton shifts, it is usually a good approximation to substitute the resonance position of the uncomplexed extractant for δ_d . (However, note that with uranyl compounds this is generally not true; $\Delta\sigma$ is relatively small, usually ≤ 1 ppm, and the effects of coordination alone are competitively large in some cases.²⁸)

The origin of the paramagnetic shift lies in either or both of two phenomena. First, unpaired electron spin density may actually be propagated from the paramagnetic ion through delocalized electrons to the resonating nucleus. The finite spin density at the nucleus produces an internal magnetic field at the nucleus and causes the nuclear resonance to shift; this is known as the contact shift. The second phenomenon is a through-space effect, often called a pseudocontact effect or dipolar effect. The unpaired electron(s) is considered to act as a dipole that interacts directly with the nuclear dipole through space.

In any given situation, it may well be that both of these phenomena are operative. The factoring of the total paramagnetic shift into contact and pseudocontact contributions is now under rather active discussion. However, it seems likely that for lanthanide and actinide complexes the pseudocontact effect dominates. It is important to note that a pseudocontact shift will occur only if there is lower than cubic symmetry (O_h , T_d , or eight-coordinate) around the magnetic ion, because the magnetism must be anisotropic to produce the shift.

It should be noted that for an nmr spectrum to be observable in a paramagnetic molecule, certain conditions must be fulfilled. The first condition is a very short electronic relaxation time (time to change back and forth between electronic states). These conditions are discussed in the literature.²⁹

In general, these conditions are fulfilled in varying degree for all the lanthanide and actinide ions (so far tested). The most difficult situation is with Gd(III). Because Gd(III) is in an S state, the electronic relaxation time is long, even at room temperature, and nmr resonances, if observed at all, will be very broad. The sharpest pmr spectra for paramagnetic species are

generally obtained for complexes of Ce(III), Pr(III), Nd(III), Sm(III), Eu(III), and U(IV). The pmr spectra of U(IV) complexes may approach the quality of their thorium (diamagnetic) analogues. Complexes of the lanthanide (III) ions heavier than Gd usually give rather badly broadened signals from which all fine structure is lost. The situation improves again with Yb(III).

Among the ions considered in this review, UO_2^{2+} is unique. In the ground state there are no unpaired electrons or any 5f electrons. Nevertheless, after correction for the diamagnetism of the ligands, UO_2^{2+} is paramagnetic. This paramagnetism is due to the second-order Zeeman effect (sometimes called temperature independent paramagnetism, TIP) and is discussed on a theoretical basis by Eisenstein and Pryce.³⁰ The paramagnetic shifts are then entirely due to the pseudocontact effect. The uranyl ion is generally conceded to be linear in its ground state. The magnetic field surrounding this ion is anisotropic.

This simple situation allows for a simple equation for $\Delta\sigma$ ³¹

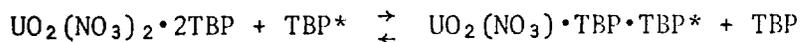
$$\Delta\sigma = \frac{\Delta\chi (1-3 \cos^2\gamma)}{3R^3}$$

where $\Delta\chi = \chi_{\parallel} - \chi_{\perp}$. χ_{\parallel} and χ_{\perp} are the molecular susceptibilities ($\text{cm}^3/\text{molecule}$) parallel and perpendicular to the UO_2 bond axis, respectively; γ is the angle between the uranyl axis and a line drawn from the proton to the uranium atom; and R is the distance between the proton and the uranium atom. (Strictly speaking, this equation applies only to the case of axial symmetry; there must be at least a C_3 axis). The UO_2^{2+} ion itself, of course, has axial symmetry. Complexing of the ion can reduce the symmetry to lower than C_3 ; however, the U-O bond length is 1.9 Å in UO_2^{2+} as compared to 2.4 to

2.5 Å for the U-O bond length for oxygen-bearing ligands complexed to UO_2^{2+} . On that basis, it might be assumed that non-axial components of the magnetic field are a minor perturbation on the axial component.

Equation (1) with $\Delta\chi_{\text{atomic}} = 2.74 \times 10^{-28} \text{ cm}^3$ has been used to calculate $\Delta\sigma$ in the neighborhood of a uranyl ion.²¹ These calculations are reproduced as Fig. 1. The bonding to UO_2^{2+} occurs in (or very nearly in) a plane through the uranium atom and perpendicular to the UO_2^{2+} axis. One conspicuous feature of this figure is the nodal plane at $\gamma = 54^\circ 40'$. With relatively few exceptions,¹¹ and these small in magnitude, $\Delta\sigma \leq 0$ (downfield). From this observation, it is inferred that the average position of protons in ligands joined to UO_2^{2+} is almost always within 35° of the ligation plane (or the "latitude" of the protons averages less than 35°).

The larger values for $\Delta\sigma$ are typically about 0.5 ppm. Such relatively large shifts are for α protons. The value of $\Delta\sigma$ falls off rapidly (as it should from equation (1)) on moving out on the alkyl chain. The effect is illustrated in Fig. 2. At low temperature, exchange for



is slow enough that separate signals can be observed for free TBP and for TBP bound to $\text{UO}_2(\text{NO}_3)_2$.³² However, there is a clear separation only for the α protons.

Observation of these separate signal sets was the first direct evidence that the stoichiometry found for the $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}$ complex in the solid phase isolated by Healy and McKay³³ is the same in solution. It was also possible to estimate roughly that in solution of about equal amounts of free and bound TBP, the TBP exchange time is about 10^{-3} sec at -10°C . These experiments also demonstrated

that $\text{UO}_2(\text{NO}_3)_2$ has a greater affinity for extractants with branched alkyl chains than it does for those with straight chains. The extractant exchange rate is also slower for the extractants with branched chains. This last observation suggests that exchange occurs by an SN_2 mechanism. TBP exchange was also observed to be slow on the nmr time scale for the following binary mixtures of metal nitrate-TBP complexes with no excess TBP present: $\text{UO}_2(\text{NO}_3)_2\text{-Pr}(\text{NO}_3)_3$; $\text{Th}(\text{NO}_3)_4\text{-Pr}(\text{NO}_3)_3$; and $\text{La}(\text{NO}_3)_3\text{-Pr}(\text{NO}_3)_3$.

No systematic exploitation of $\Delta\sigma$ has yet been made. Obviously in the region of slow and intermediate ligand exchange rates, many kinetic and thermodynamic studies are possible.

R. V. Ammon and coworkers²⁸ have investigated TBP and also TOPO (tri-octylphosphine oxide) extraction systems with both pmr and ^{31}P magnetic resonance. Their general technique involved measuring the shifts of $\alpha\text{-CH}_2$ proton resonances and of ^{31}P resonance as functions of extractant, water, HNO_3 , and uranyl nitrate concentration in n-dodecane. Their nmr studies support the results of studies by other methods and earlier workers. For example, they have shown that the prominent extracting species of uranyl nitrate is $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{P}$ (where P is the extractant molecule) and that $\text{HNO}_3 \cdot \text{TBP}$ is an important species.

Interesting results were also obtained in support of the existence of additional species such as $\text{H}_2\text{O} \cdot 2\text{TOPO}$ and $\text{UO}_2(\text{NO}_3)_2 \cdot \text{TOPO} \cdot \text{H}_2\text{O}$. The authors concluded that $\Delta\sigma$ for the uranyl nitrate complexes that were studied were always due to two different effects: the magnetic anisotropic field of the UO_2^{2+} group; and the inductive effect, which changes the electron density over the whole phosphoryl group (and presumably at least the α protons as well). The inductive effect always produces a low field shift.

Much larger values of $\Delta\sigma$ are observed for U(IV) and lanthanide (III) extractant complexes. Shifts of 5 to 10 ppm are quite common, and the effects are sufficiently large to affect the shifts of alkyl protons on β , γ , and δ carbon atoms. This effect is illustrated in Fig. 3. The spectrum for $\text{La}(\text{NO}_3)_3 \cdot [\text{C}_4\text{H}_9\text{-}]_3 \text{P=O}$ (diamagnetic) is compared with the spectrum for the corresponding Ce(III) (paramagnetic) adduct. For the La adduct, the α , β , and γ signals overlap. For the Ce(III) compound, separate groups of signals are observed for α , β , γ , and δ protons. Furthermore, there is even some evidence of coupling fine structure for the α signals. For the corresponding UCl_4 adduct, the shifts are much larger, $\Delta\sigma(\delta) = -0.52$ (ppm); $\gamma = -1.23$; $\beta = -5.0$; and $\alpha = -8.5$. Commonly for TBP (and related complexes), $\Delta\sigma < 0$. However, it is very likely that for Eu(III), $\Delta\sigma$ will be > 0 (though the reviewers know of no experiment); this is true of many other lanthanide complexes. Evidently $\Delta\chi_{\text{atomic}}$ reverses sign for Eu(III). Possibly this is due to the fact that χ is identically zero for the ground state of Eu(III) (${}^7\text{F}_6$) (see Wybourne's³⁴ equation 5-35).

VI. STOICHIOMETRY IN SOLUTIONS

When excess ligand is added to a solution of an inorganic complex, separate signal sets for the bound ligand and free ligand may be observed if the ligand exchange rate is sufficiently slow. The exchange rate may sometimes be sufficiently reduced by lowering the temperature of the solution, as illustrated in

Fig. 2.³² As may be seen in the figure, at -50°C exchange is slow enough to allow the observation of separate $\alpha\text{-CH}_2$ proton sets in bound and unbound TBP. As the temperature is raised, both resonances broaden and merge into a single resonance which is the average of the bound and unbound resonances. Using the known concentrations of complex and free ligand, the stoichiometry of the complexing reaction can be determined if separate signal sets are observable. Thus in the example given in Fig. 2, it was determined that only two molecules of TBP are coordinated to uranium in a solution containing excess TBP. The free energy of the exchange process is about 10 kcal/mole. Similar results were obtained for uranyl nitrate adducts of tri-2-propylphosphate and tris(4-methyl-3-amy)phosphate except that much slower ligand exchange rates were observed.

Separate resonances were also observed for free TBP and TBP bound to praseodymium nitrate or thorium nitrate in CDCl_3 . The exchange rates in these complexes are much more rapid than in the uranyl nitrate case.³²

VII. RELATIVE LIGAND AFFINITIES

The relative affinities of a given metal ion for different ligands can be determined if the ligand exchange rates are sufficiently slow at low temperature, i.e., one can obtain equilibrium constants for the ligand exchange process

$$\text{ML}_n + mL' \rightleftharpoons \text{ML}_{(n-m)}L'_m + mL.$$

This method has been used to determine the relative affinities of TBP and tri-2-propylphosphate (TPP) for uranyl nitrate.³² At -60°C , a mixture of $\text{UO}_2(\text{NO}_3)_2 \cdot (\text{TBP})_2$ and TPP gave four sets of α -proton signals (bound and free TBP and bound and free TPP). No signal that could be attributed to the mixed adduct $\text{UO}_2(\text{NO}_3)_2 \cdot \text{TBP} \cdot \text{TPP}$ was observed, but the expected signals could have been obscured by signal overlap. By integrating these signals, the equilibrium constant for ligand exchange was determined:

$$K = \frac{[\text{UO}_2(\text{NO}_3)_2(\text{TPP})_2][\text{TBP}]^2}{[\text{UO}_2(\text{NO}_3)_2(\text{TBP})_2][\text{TPP}]^2} = 4$$

where it is assumed that no mixed adduct was present. Thus it was shown that TPP has a greater affinity for $\text{UO}_2(\text{NO}_3)_2$ than does TBP, even though TPP has steric disadvantages.

VIII. SYNERGISTIC COMPLEXES

The extraction of metal ions from an aqueous phase by charged anionic species such as β -diketones or alkylphosphoric acids is greatly enhanced by the presence of neutral organophosphorus reagents in the organic phase. For example, extraction of Nd^{3+} by TTA is enhanced by a factor of 350 when TBP is added to the organic phase.³⁵ This enhanced extraction by TBP is due to the "synergistic effect" of the TBP. In some cases, the synergistic complexes, e.g., $\text{Zn}(\text{TTA})_2 \cdot \text{TOPO}$, have been isolated.²⁴

Li and coworkers with pmr and ^{31}P nmr, have studied the structures of synergistic complexes and the equilibria involved in their formation. The systems studied were $\text{Zn}(\text{TTA})_2 \cdot \text{TBP}$;³⁴ $\text{Zn}(\text{TTA})_2 \cdot \text{TBEP}$;^{24, 36} $\text{M}(\text{TTA})_2 \cdot \text{TOPO}$ ($\text{M} = \text{Zn}^{2+}, \text{Cu}^{2+}$);²⁴ MX_2S_X ($\text{M} = \text{UO}_2^{2+}, \text{Cu}^{2+}, \text{Zn}^{2+}, \text{Ni}^{2+}, \text{Co}^{2+}$; $\text{X} = \text{TTA}$; $\text{S} = \text{TBP}, \text{TBEP}, \text{TOPO}, 4\text{-me-py}, \text{TPPO}$);³⁷ $\text{Zn}(\text{HFacac})_2(\text{TOPO})_2$;³⁷ $\text{Cu}(\text{HFacac})_2\text{TOPO}$;³⁷ $\text{Co}(\text{acac})(4\text{-me-py})_2$;³⁷ $\text{UO}_2(\text{acac})_2 \cdot 4\text{-me-py}$;³⁷ $\text{UO}_2(\text{acac})_2(\text{TPPO})_3$;³⁷ $\text{Zn}(\text{BTA})_2 \cdot \text{TOPO}$;³⁸ $\text{Zn}(\text{HFacac})_2 \cdot (\text{TOPO})_2$;³⁹ $\text{Zn}(\text{TTA})_2\text{TOPO}$;⁴⁰ $\text{UO}_2(\text{TTA})_2 \cdot \text{TBP}$;⁴⁰ $\text{Zn}(\text{BTA})_2 \cdot \text{TOPO}$;⁴⁰ and $\text{Zn}(\text{TFA})_2(\text{TOPO})_2$.^{40*} From

* TTA = thenoyltrifluoroacetone anion
 TBP = tributylphosphate
 TBEP = tri-n-butoxyethylphosphate
 TOPO = tri-n-octyl phosphine oxide
 TPPO = triphenyl phosphine oxide

4-me-py = 4-methylpyridine
 HFacac = hexafluoroacetylacetone anion
 acac = acetylacetone anion
 BTA = benzoyltrifluoroacetone anion
 TFA = trifluoroacetylacetone anion

these studies, Li concluded that the synergistic agent, S, is directly bonded to the metal ion and that the synergistic effect involves both the stability and the solubility of the ternary complex in the organic phase.

When excess S is added to the extraction system, the enhancement of extraction is destroyed; this effect has been termed the antisnergistic effect. Li, who prefers to call the phenomenon, "destruction of synergism", obtained evidence which suggests that the effect is due to the decomposition of the synergic species, e.g., $\text{Zn}(\text{HFA})_2 \cdot (\text{TOPO})_2$ to form $\text{Zn}(\text{HFA})_2 \cdot 2\text{H}_2\text{O}$ followed by its acid-catalyzed hydrolysis to Zn^{2+} and $\text{HHFA} \cdot 2\text{H}_2\text{O}$ in the aqueous phase and subsequent extraction of $\text{HHFA} \cdot 2\text{H}_2\text{O}$ into the organic phase by excess TOPO as the species $\text{HHFA} \cdot 2\text{H}_2\text{O}(\text{TOPO})_2$.³⁹

Below 20°C in CDCl_3 solution, two signal sets are observed for the TBP α -protons in a solution of $\text{UO}_2(\text{TTA})_2 \cdot \text{TBP}$ plus excess TBP.⁴¹ The chemical shift between the bound and free TBP α -protons and the coalescence of the two signal sets are very similar to that observed for $\text{UO}_2(\text{NO}_3)_2 \cdot \text{TBP}$ -TBP solutions. This behavior has been cited as evidence for direct bonding between TBP and metal in the synergistic complex. In $\text{UO}_2(\text{TTA})_2 \cdot \text{TOPO}$ -TOPO solutions, separate signals were not observed, because of lack of resolution of the complex signal patterns. The ^{31}P spectrum, however, shows three ^{31}P signals, with two of the signals arising from bound TOPO and the third signal arising from free TOPO.

At -38°C in CDCl_3 with no excess TBP present, two ^{31}P signal sets are observed in the $\text{UO}_2(\text{TTA})_2 \cdot \text{TBP}$ complex. Similar results were observed for the $\text{UO}_2(\text{TTA})_2 \cdot \text{TOPO}$ complex. In addition, the pmr spectrum of the TTA ligand in the complex showed multiple signal sets at low temperatures. These results showed that for a given complex there are two different kinds of ligand, S, in roughly equal amounts but that there are three different kinds of TTA. These results

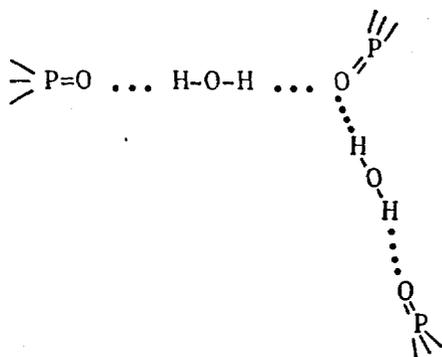
were explained as indicating that two of the three possible isomers shown in Fig. 4 are present.⁴¹

IX. WATER-TBP INTERACTIONS

In the TBP solvent extraction process in which TBP with or without an organic diluent is contacted with an aqueous phase containing metal ions, an appreciable amount of water is extracted along with the metal ions. The nature of the interaction of TBP and water has thus received a great deal of study, and among the methods used to study the interaction, pmr has played a prominent role.

When water is diluted with an inert solvent, the water proton resonance peak shifts upfield as a result of the breaking of water hydrogen bonds.³¹ The shift between pure water and monomeric water (water at infinite dilution in CCl_4)⁴² is about 4 ppm. Similarly, the water proton resonance in TBP- H_2O solutions shifts linearly upfield as the water content is reduced, but the infinite dilution shift is only 2 ppm.⁴³ The smaller infinite dilution shift in the latter case indicates, in agreement with other evidence,⁴⁴ that a rather strong hydrogen-bonding interaction occurs between water and TBP.

In an attempt to determine the species present in TBP- H_2O solutions, Bullock and Tuck⁴⁵ made a more detailed pmr study of the system. A plot of water proton chemical shift vs TBP/ H_2O ratio taken from their paper is given in Fig. 5. Over the entire concentration range, only one resonance was observed for the water protons, indicating that water exchange between all species was rapid (on the pmr time scale). At low water concentration, Bullock and Tuck postulate a dimeric structure $\begin{array}{c} \diagup \\ \text{P}=\text{O} \end{array} \dots \text{H}-\text{O}-\text{H} \dots \text{O}=\text{P} \begin{array}{c} \diagdown \\ \end{array}$, in agreement with infrared results which show that most, if not all, -OH groups are hydrogen bonded at these concentrations.⁴⁶ As further water is added, the slope of the δ vs concentration curve decreases. Bullock and Tuck⁴⁴ postulated that at this point a trimer is formed

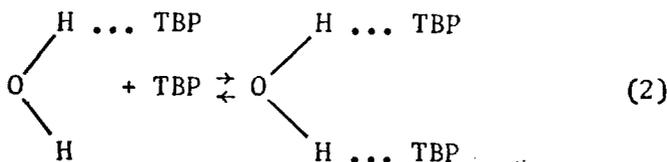
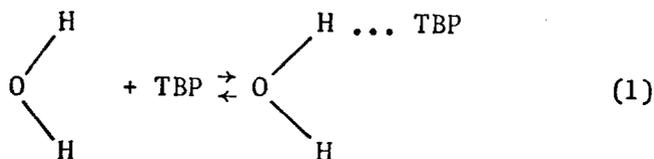


The lack of axial symmetry in this trimeric structure was believed to be responsible for the decreased slope.

At still higher water concentrations, a closed ring polymeric structure was postulated.⁴⁵

The systems TBP-H₂O-HNO₃,^{47,48} TBP-H₂O-HCl,^{48,49} and TBP-H₂O-HF⁵⁰ have been studied.

Studies of hydrogen bonding between water protons and TBP in CCl₄ solutions have been reported.⁴⁴ At water concentrations low enough to preclude water self-association (mol fraction water < 2.0 x 10⁻³) the following equilibria characterize the system:



The equilibrium constants were measured in the range 10 to 45°C, and the following thermodynamic parameters determined: $\Delta H_1 = -4.1 \pm 0.2$ kcal/mole; $\Delta S_1 = -5.5$ eu; $\Delta H_2 = -2.0 \pm 0.3$ kcal/mole; and $\Delta S_2 = -2.7$ eu.⁴⁴ These thermodynamic parameters must be treated with the usual caution necessary for values obtained from the temperature coefficients of equilibrium constants. A direct calorimetric determination of the heats of hydration of TBP indicates much smaller values for ΔH_1 .^{51*}

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PW/jh/bch/sce

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TABLE I

COUPLING CONSTANTS AND CHEMICAL SHIFTS FOR REPRESENTATIVE ORGANOPHOSPHORUS EXTRACTANTS

Compound	Coupling Constants, Hz				Chemical Shifts, ppm from TMS				Ref
	Alkoxy		Alkyl		Alkoxy		Alkyl		
	J(P-H α)	J(P-H β)	J(P-H α)	J(P-H β)	ν (H α)	ν (H β)	ν (H α)	ν (H β)	
(MeO) ₃ PO	11.2								3
(EtO) ₃ PO	8.4	0.7			4.0	1.3			3, 4, 8
(n-propyl O) ₃ PO	7.7								3
(n-butyl O) ₃ PO	7.7								3
(n-amyl O) ₃ PO	7.6								3
(2-propyl O) ₃ PO	7.4	<0.5							5
(i-butyl O) ₃ PO	6.6								3
(neopentyl O) ₃ PO	5.2								3
(MeO)PO[O-n-butyl] ₂	8.0(OCH ₂ -)								8
(MeO) ₂ PO(Me)	11.0		17.3		3.7		1.4		6
(EtO) ₂ PO(Me)	8.7		18.1		4.0	1.3	1.4		8
(EtO) ₂ P(O)(Et)	8.5		19.2	21.6	4.0	1.3	1.7	1.2	8
(2-propyl O) ₂ PO(C ₆ H ₅)	8.1				4.6	1.2, 1.3			8
(n-butyl O) ₂ PO(CH ₂ Cl)	8.2		11.2		4.1		3.5		8
(MeO)PO(n-butyl) ₂	10.9				3.6				8
(Me) ₃ PO			13.4				2.0		7
(Et) ₃ PO			11.9	16.3			2.3	1.2	7

TABLE 2

Phosphorus Chemical Shifts for Organophosphorus Compounds
and Their Uranyl Complexes* (From Reference 8)

Compound	Chemical shift, ppm		
	σ_{CCl_4}	$\sigma_{\text{UO}_2^{2+}, \text{CCl}_4}$	$\Delta\sigma$
$(\text{CH}_3\text{CH}_2\text{O})_3\text{PO}$	- 0.5	+ 0.2	+ 0.7
$[\text{CH}_3(\text{CH}_2)_3\text{O}]_2\text{PO}(\text{OCH}_3)$	+ 0.2	1.9	1.7
$(\text{CH}_3\text{O})_2\text{PO}(\text{H})$	9.8	17.3	7.5
$(\text{CH}_3\text{CH}_2\text{O})_2\text{PO}(\text{H})$	6.2	10.8	4.6
$[\text{CH}_3(\text{CH}_2)_3\text{O}]_2\text{PO}(\text{H})$	6.7	12.5	5.8
$(\text{CH}_3\text{CH}_2\text{O})_2\text{PO}(\text{CH}_3)$	29.4	37.6	8.2
$(\text{CH}_3\text{CH}_2\text{O})_2\text{PO}(\text{CH}_2\text{CH}_3)$	32.2	39.0	6.8
$[\text{CH}_3(\text{CH}_2)_3\text{O}]_2\text{PO}[(\text{CH}_2)_2\text{CH}_3]$	31.1	37.9	6.8
$[(\text{CH}_3)_2\text{CH-O}]_2\text{PO}(\text{C}_6\text{H}_5)$	15.7	20.0	4.3
$[\text{CH}_3(\text{CH}_2)_2\text{O}]_2\text{PO}(\text{C}_6\text{H}_5)$	17.8	22.6	4.8
$(\text{CH}_3\text{O})\text{PO}[(\text{CH}_2)_3\text{CH}_3]_2$	56.8	72.1	15.3
$[\text{CH}_3(\text{CH}_2)_7]_3\text{PO}$	42.0	74.1	32.1

* Chemical shifts are given in ppm and are relative to external 85% phosphoric acid. Positive values represent chemical shifts at lower applied field than the reference.

TABLE 3

^{31}P Frequency of Tri-n-octyl Phosphine Oxide (TOPO)
in CCl_4 at 26°C (From Reference 23)

$C_{\text{TOPO}},$ M	$C_{\text{Zn(TTA)}_2},$ M	$\nu,$ Hz (downfield from TBP)
0.5	0	1110 = ν_f
0.5	0.05	1135
0.5	0.10	1200
0.5	0.20	1280
0.5	0.30	1361
0.4	0.10	1216
0.3	0.10	1243

$\nu_c - \nu_f = 543$ Hz, where ν_f = shift of uncomplexed TOPO and ν_c = shift of complexed TOPO.

TABLE 4

Chemical Shifts for Lanthanide-Triamylphosphate (TAP) Adducts (From Reference 24)

	<u>PMR Data at 25°C*</u>						
	<u>0.1M Adduct in CDCl₃</u>		<u>0.1M Adduct + 0.4M CHCl₃ in Hexane</u>		<u>0.1M Adduct + 0.1M CHCl₃ in Hexane</u>		<u>0.1M Adduct in Hexane</u>
	<u>CHCl₃</u>	<u>α Proton</u>	<u>CHCl₃</u>	<u>α Proton</u>	<u>CHCl₃</u>	<u>α Proton</u>	<u>α Proton</u>
Nd	7.2	4.58	7.15	4.1	7.20	4.10	3.95
Yb	7.54	+0.84	8.2		lost in hexane signals		lost in hexane
La	7.28	4.1	7.25	4.18	7.3	4.15	4.1
Pr	7.20	4.9	6.95	3.60	7.1	3.55	3.38
Tm	8.5	+5.6	10.0	+4.49	10.17	+3.91	+3.64

	<u>Chemical Shifts for ³¹P**</u>	
	<u>In CHCl₃</u>	<u>In Hexane</u>
La	+3.31	+3.95
Pr	-79.9	-71.7
Nd	-103.6	-100.3
Er	+262.47	+249.38
Tm	+162.6	+147.8
Yb	+49.88	+43.95

* Chemical shifts in ppm from TMS

** In ppm from external H₃PO₄ at 29°C. Obtained with a Varian HR-60 spectrometer.

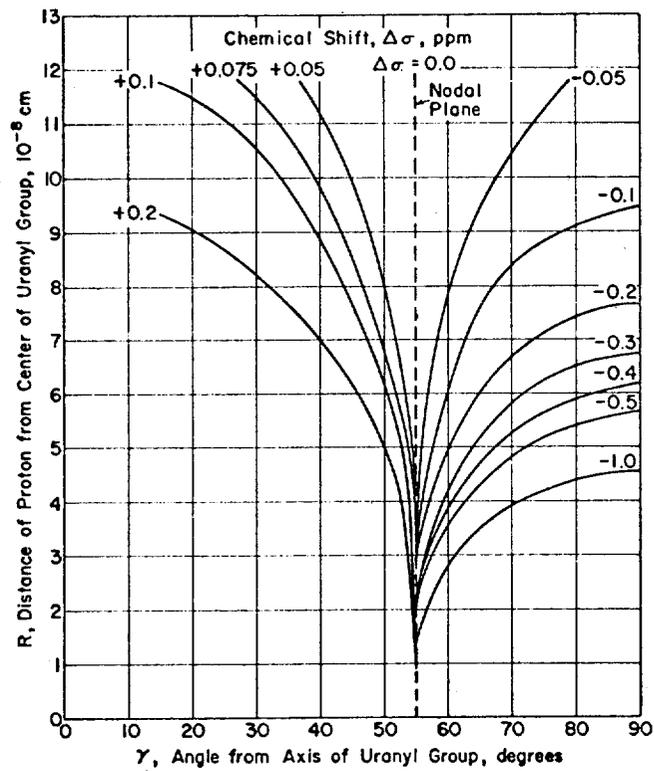


FIG. 1 MAGNETIC FIELD AROUND THE URANYL GROUP

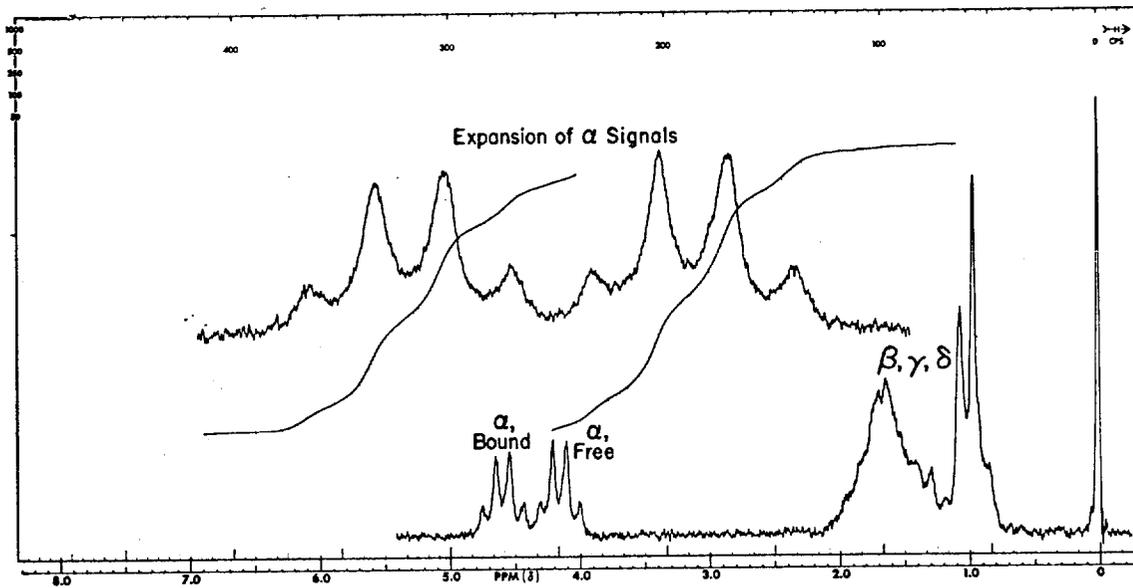


FIG. 2 PMR SPECTRUM AT -50°C OF 76 mg OF $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}$
 PLUS 48 mg OF TBP ($[\overset{\delta}{\text{CH}_3}\overset{\gamma}{\text{CH}_2}-\overset{\beta}{\text{CH}_2}-\overset{\alpha}{\text{CH}_2}\text{O}]_3\text{P}=\text{O}$)
 PER ml IN CDCl_3

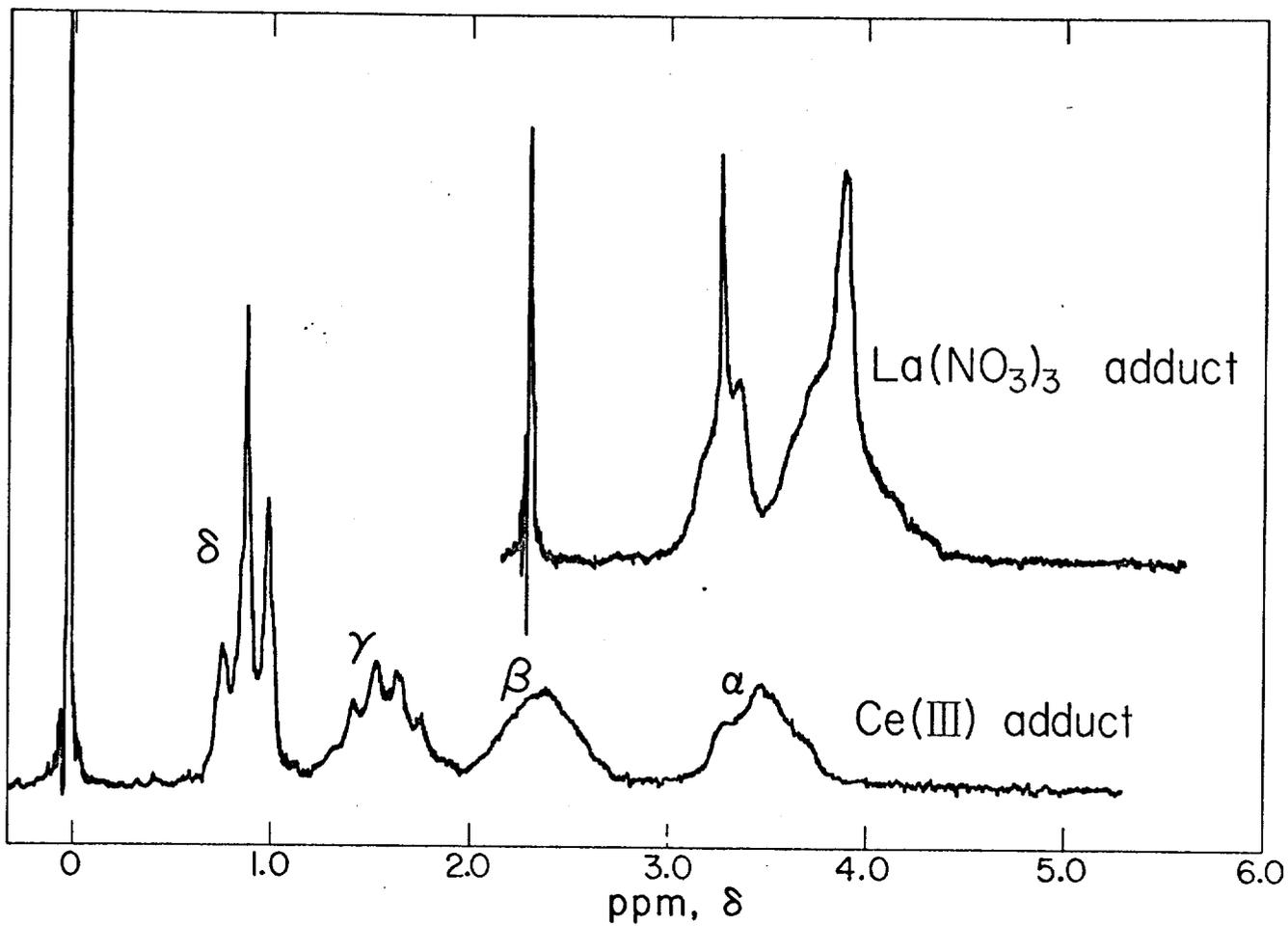


FIG. 3 PMR SPECTRA OF LANTHANUM NITRATE AND CERIUM NITRATE ADDUCTS OF TBP

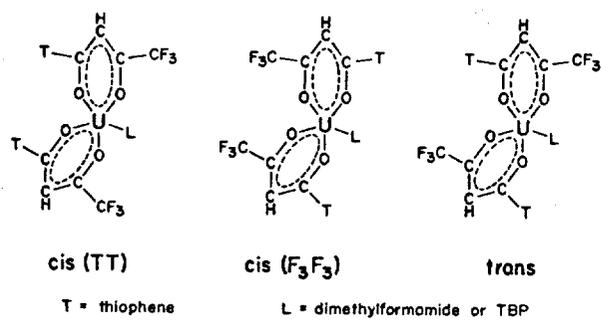


FIG. 4 $UO_2(TTA)_2 \cdot L$ ISOMERS

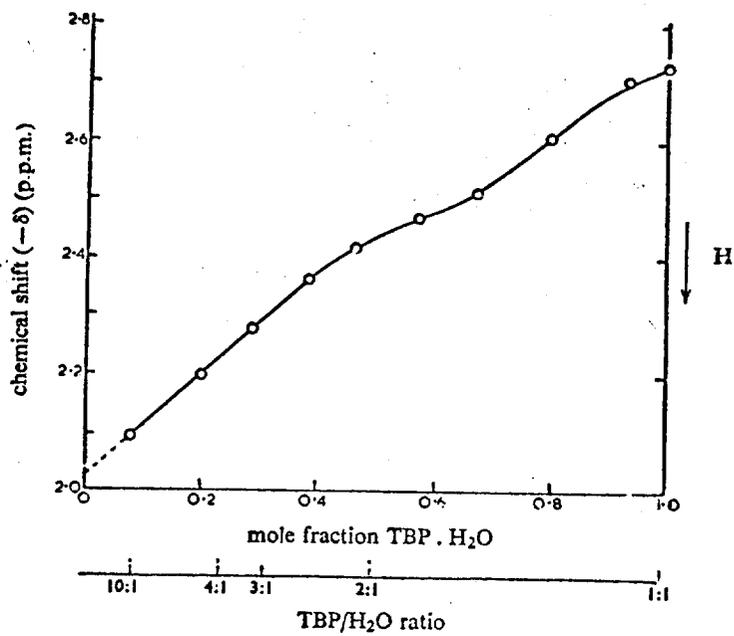


FIG. 5 CHEMICAL SHIFT δ OF THE RESONANCE SIGNAL OF H_2O PROTONS IN TBP + $\text{TBP} \cdot \text{H}_2\text{O}$ MIXTURES (FROM REFERENCE 44)