

- (23) T. Kobayashi, F. Kurokawa, T. Ashida, N. Uyeda, and E. Suito, *Chem. Commun.*, 1631 (1971).
- (24) (a) G. Englesma, A. Yamamoto, E. Markham, and M. Calvin, *J. Phys. Chem.*, **66**, 2517 (1962); (b) A. Yamamoto, L. K. Philips, and M. Calvin, *Inorg. Chem.*, **7**, 847 (1968).
- (25) L. H. Vogt, Jr., A. Zalkin, and D. H. Templeton, *Inorg. Chem.*, **6**, 1725 (1967).
- (26) P. Madura and W. R. Scheidt, to be submitted for publication.
- (27) A. A. Saylor and J. L. Hoard, to be submitted for publication.
- (28) E. B. Fleischer, C. K. Miller, and L. E. Webb, *J. Am. Chem. Soc.*, **86**, 2342 (1964).
- (29) T. A. Hamor, W. S. Caughey, and J. L. Hoard, *J. Am. Chem. Soc.*, **87**, 2305 (1965).
- (30) J. F. Kirner and W. R. Scheidt, *Inorg. Chem.*, **14**, 2081 (1975).
- (31) D. Rogers and R. S. Osburn, *Chem. Commun.*, 840 (1971).
- (32) D. M. Collins, W. R. Scheidt, and J. L. Hoard, *J. Am. Chem. Soc.*, **94**, 6689 (1972); D. L. Cullen and E. F. Meyer, Jr., *Acta Crystallogr., Sect. B*, **29**, 2507 (1973).
- (33) Strictly speaking, this difference in hole size is only appropriate for quasi-S₄ ruffled metalloporphyrins and planar metallophthalocyanines; the difference in hole size may be increased by 0.020–0.030 Å for a planar metalloporphyrin derivative.

Contribution No. 3519 from the Department of Chemistry,
University of California, Los Angeles, California 90024

Preferential Solvation of the Thallous Ion and its Relationship to the Thallium-205 Nuclear Magnetic Resonance Chemical Shift

JAMES J. DECHTER and JEFFREY I. ZINK*

Received October 24, 1975

AIC50773Q

The solvent dependence of the ²⁰⁵Tl(I) NMR chemical shift is found to correlate linearly with the solvent's relative solvating ability toward Tl⁺. The relative solvating ability is quantitatively measured using the mole fraction dependence of the chemical shift and analyzed by a solvent-exchange equilibrium constant theory. The analysis provides a method of obtaining chemical shifts in solvents that do not dissolve thalloses salts. The correlation of solvating ability with the chemical shift is explained by a model utilizing simple symmetry considerations of MO theory. The relative solvating ability determined by Tl NMR is compared to several current thermodynamic models of Lewis acid–base interactions.

Introduction

Investigations of the solvent dependence of the chemical shift of the monovalent ions lithium, sodium, and thallium have usually included an attempt to characterize the chemical shift either by a physical property of the solvent such as pK_a¹ or by empirical solvent parameters such as Gutmann's donor numbers^{2–5} or Kosower's Z parameter.⁶ Although the general features of the chemical shifts can often be explained by one of the many simplified forms of the Ramsey equation,^{7–11} the details of the solvent dependence of the chemical shift are not well understood. In this paper, the solvent-dependent chemical shift for Tl⁺ is shown to be linearly related to the relative solvating ability toward Tl⁺ of the various solvents. This relation can be understood in terms of the amount of p character produced in the ground state by Tl⁺–solvent interactions.

Previous quantifications of preferential solvation have used the isosolvation number^{12,13} as a measure of solvating ability. More recently, Covington et al.^{14–17} have proposed an expression for the equilibrium constant for a solvent-exchange process. It will be shown (vide infra) that these two measures of relative solvating ability are directly related to each other. Both methods have been applied to the study of the mole fraction dependence of the ²³Na⁺ chemical shift.^{12,13} ²⁰⁵Tl⁺, with greater sensitivity relative to protons than ²³Na⁺, with a much greater solvent-dependent chemical shift range, and with an intense uv absorption band, should be a more convenient probe for studying solvation processes.

The solubility of thalloses salts in many types of solvents such as ethers, ketones, and esters is not sufficient to allow the determination of the chemical shift in these solvents. An important consequence of the Covington et al. expression is that Tl⁺ chemical shifts can be determined for solvents in which thalloses salts have very low solubilities (vide infra). The shifts are determined by using successive approximations in fitting the experimental data to an equilibrium constant.

In this paper quantitative values for the relative solvating ability with respect to Tl⁺ of a wide variety of solvents are presented. These values are compared with current empirical thermodynamic models which have been proposed as general measures of solvent–solute interaction. The chemical shift of

solvated Tl⁺ is shown to be linearly related to the relative solvating ability of the solvent. Finally, a model is presented which describes the solvent-dependent chemical shifts using symmetry considerations of MO theory and explains the latter correlation.

Experimental Section

TlClO₄ and TlF were commercially obtained and were recrystallized from deionized water and dried under vacuum over P₂O₅. TlBF₄ was prepared by neutralizing a solution of fluoroboric acid with Tl₂CO₃, recrystallizing the product twice from deionized water and drying under vacuum over P₂O₅.

Organic solvents were generally prepared by refluxing over BaO or CaH₂ and then distilled under reduced pressure just prior to use. DMF was refluxed over MgSO₄ and distilled.

Instrumental Work. Spectra were obtained using an HR 60 modified with an external field/frequency proton lock. The lock signal was cyclohexane contained in a capillary displaced along the z axis from the sample coils. The lock channel frequency of 55.5 MHz was produced by a crystal and was modulated by a VFO. Maximum lock stability was obtained when the lock channel modulation was 1600 Hz. The observation channel frequency of approximately 32.0 MHz was produced by a frequency synthesizer and could be varied by over 100 kHz to cover the full Tl⁺ solvent-dependent chemical shift range. It is modulated by a second VFO; for Tl⁺ the observation channel modulation frequency is 3000 Hz.

Fifteen-millimeter o.d. NMR tubes were spun by means of a precision spinner. Chemical shifts are reported in ppm from the infinite dilution resonance of Tl⁺ in water.¹¹ Downfield shifts are positive. No bulk susceptibility corrections are made since these are estimated to be within the experimental error of the shifts.

The resonance line widths were found to vary nearly linearly with chemical shift from about 5 Hz in pyrrole to almost 60 Hz in *n*-butylamine. Because of this variation in line width, the lowest concentration of Tl⁺ that could be maintained from solvent to solvent and yet still allow detection of the resonance in the solvents that produce large line widths was 0.20 M.

Fitting Procedure. Equilibrium constants were calculated using the expression derived by Covington et al.¹⁴ shown in eq 1. The various

$$K^{1/n} = \left(\frac{\delta}{\delta_p - \delta} \right) \left(\frac{1 - \chi_p}{\chi_p} \right) \quad (1)$$

quantities except *n* which will be discussed later are illustrated in Figure 1 for the mole fraction dependence of the Tl chemical shift in the

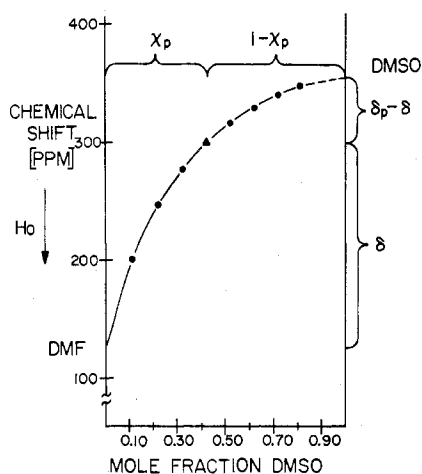


Figure 1. Mole fraction dependence of the chemical shift for a DMF-DMSO mixture illustrating the calculation of $K^{1/n}$ at the point denoted by Δ .

mixed-solvent system of DMF and DMSO.

The fitting procedure fits the experimental data to eq 1 by successive approximations. The experimental values of the chemical shift are plotted as a function of the mole fraction such as in Figure 1. The values of the initial (pure reference solvent) and final (pure competing solvent) shifts used by the fitting procedure are usually five to ten increments from the values estimated from plots such as Figure 1. Using these values and the experimental mole fractions and chemical shifts, the procedure calculates $K^{1/n}$ for each experimental point, finds the average $K^{1/n}$, and then calculates a chemical shift for each experimental mole fraction based on this average. The total variance between the experimental and calculated shifts including the difference between the current adjusted value of the reference solvent shift and the experimental value is calculated. The procedure then increases by increments the competing solvent shift until the total variance is minimized. Then the reference solvent shift is stepped by one increment and the competing solvent shift is adjusted again until the minimum total variance for the current adjusted value of the reference solvent shift is obtained. This last step is repeated until the best values of the reference and competing solvent shifts are found based upon the total variance between calculated and experimental shifts. Local minima are avoided by repeating the procedure with a different size increment of adjustment and by allowing the program to adjust the initial and final shifts to high field rather than to low field. $K^{1/n}$ is generally calculated on the basis of a fit to eight experimental points.

Results

The solvation equilibrium constants have been calculated for the solvents shown in Table I relative to DMF and to pyridine. The values of the quantity $(1/n) \log K$ are shown in Table I because the logarithm of $K^{1/n}$ is related to the free energy of solvation relative to that of the reference solvent. The chemical shifts of TlClO_4 in the solvents are also listed. None of the solvents listed below pyrrole in the table will dissolve TlClO_4 to sufficient concentration for its resonance to be observed. Therefore, for solvents below pyrrole in Table I, the reported shift is the best fit value obtained from the fitting procedure (vide infra), while for solvents above and including pyrrole, the shift is the experimental value of the extrapolated zero anion concentration chemical shift. The relationship between the solvation values for the two reference solvents is shown in the plot of $(1/n) \log K_{\text{DMF}}$ vs. $(1/n) \log K_{\text{py}}$ in Figure 2. The correlation between the two sets of values is 0.956.

The independence of the equilibrium constant from anion effects for the anions perchlorate, fluoroborate, and nitrate was investigated for *n*-butylamine as the competing solvent and DMF as the reference solvent. The $(1/n) \log K_{\text{DMF}}$ values for these salts shown in Table II are the same within experimental error. Although the equilibrium constant is independent of these anions, the chemical shift is sensitive to

Table I. Experimental Values of Relative Solvating Ability and the Tl^+ Chemical Shift for Selected Solvents

| Solvent | No. | $(1/n) \log K_{\text{DMF}}^a$ | $(1/n) \log K_{\text{py}}^a$ | Chem shift ^b |
|----------------------------------|-----|-------------------------------|------------------------------|-------------------------|
| Pyrrolidine | 1 | 1.127 | 0.898 | 1757 ^e |
| <i>n</i> -Butylamine | 2 | 1.048 | | 1896 ^e |
| Hexamethylphosphoramide | 3 | 0.987 | 0.334 | 443 ^e |
| Diethylamine | 4 | 0.788 | | 794 |
| Dimethyl sulfoxide | 5 | 0.560 | 0.279 | 369 ^e |
| Pyridine | 6 | 0.161 | 0.000 | 664 ^e |
| Dimethylformamide | 7 | 0.000 | -0.114 | 124 ^f |
| Pyrrole | 8 | -0.175 | | -506 |
| Dimethoxyethane ^c | 9 | -0.215 | | -170 ^d |
| Tributyl phosphate ^c | 10 | -0.431 | -0.108 | -20 ^d |
| Methanol ^c | 11 | -0.470 | | 35 ^d |
| Dioxane ^c | 12 | -0.496 | | -130 ^d |
| Tetrahydrofuran ^c | 13 | -0.686 | -0.458 | -80 ^d |
| Methyl acetate ^c | 14 | -0.686 | | -130 ^d |
| Acetone ^c | 15 | -0.967 | -0.717 | -240 ^d |
| Propylene carbonate ^c | 16 | -1.252 | | -470 ^d |

^a Error ± 0.02 . ^b Error ± 1 ppm except as indicated. ^c Solvent will not dissolve TlClO_4 . ^d Shift obtained from fitting procedure; estimated error ± 20 ppm. ^e Reference 10. ^f The chemical shifts reported for DMF and formamide in ref 21 are in error; the correct value for DMF is listed above; the correct value for formamide is listed in ref 11 and is 96 ppm.

Table II. Independence of the Relative Solvating Ability from Anion Effects

| Anion | DMF shift | <i>n</i> -Butylamine shift | $(1/n) \log K_{\text{DMF}}$ |
|------------------|------------------|----------------------------|-----------------------------|
| ClO_4^- | 124 | 1896 | 1.048 |
| BF_4^- | 120 | 1958 | 1.037 |
| NO_3^- | 124 ^a | 1708 | 1.037 |

^a TlNO_3 is insoluble in DMF.

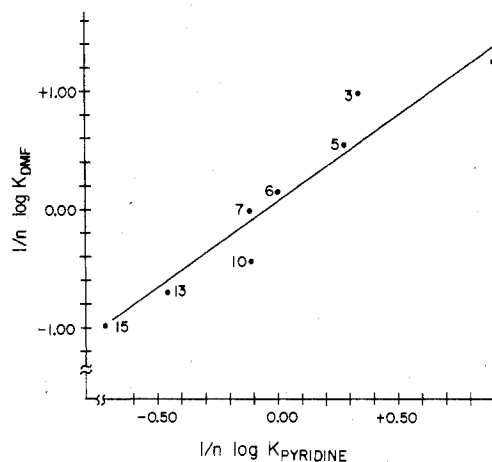


Figure 2. Plot of solvating ability relative to DMF vs. solvating ability relative to pyridine. Competing solvents are identified by numbers according to Table I. Correlation factor is 0.956.

the anion. In *n*-butylamine, for example, the shift varies by 250 ppm from the fluoroborate to the nitrate salt. Since it is expected that $K^{1/n}$ should include ion-pairing equilibria, the invariance in $K^{1/n}$ for these anions indicates that none of them appreciably perturbs the ion-pairing equilibrium constant. The change in chemical shift reflects the change in the intrinsic shift produced by each anion.

In order to determine the reliability of the shifts and $(1/n) \log K$ values for competing solvents which will not dissolve thallous salts, solvent systems in which all the data points can be obtained are truncated to model the former systems. Truncation to mole fractions of 0.75 affects the value of $K^{1/n}$ by about 10% and the fitted value of the competing solvent

Table III. Empirical Descriptions of Relative Solvating Ability^a

| Ref solvent | α_{E_T} | $\bar{\alpha}_{E_T}$ | β_{DN} | $\bar{\beta}_{DN}$ | β_{E_B} | $\bar{\beta}_{E_B}$ | β_{C_B} | $\bar{\beta}_{C_B}$ | R |
|-------------|----------------|----------------------|---------------|--------------------|---------------|---------------------|---------------|---------------------|-------|
| DMF | 0.038 ± 0.029 | 41 | 0.096 ± 0.010 | 59 | 3.08 ± 0.66 | 60 | 0.22 ± 0.19 | 40 | 0.990 |
| | | | 0.094 ± 0.010 | 100 | | | | | 0.981 |
| Pyridine | 0.029 ± 0.03 | 35 | 0.048 ± 0.011 | 65 | 2.53 ± 0.47 | 100 | 0.19 ± 0.15 | 35 | 0.971 |
| | | | 0.050 ± 0.010 | 100 | | | | | 0.952 |
| | | | 1.80 ± 0.53 | 65 | 0.957 | | | | |
| | | | 1.32 ± 0.39 | 100 | 0.941 | | | | |
| | | | | | | | | | 0.940 |
| | | | | | | | | | 0.890 |

^a The competing solvents used are HMPA, DMSO, DMF, THF, and acetone.

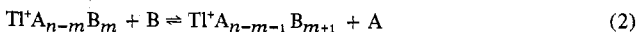
shift by about 10 ppm. When a similar truncation of data is performed for competing solvents which will not dissolve thallos salts and for which data are normally obtainable up to mole fractions of about 0.9, the same slight variance of $K^{1/n}$ and the chemical shift is observed.

For systems in which the competing solvent will dissolve thallos salts, the average deviation between the fitted reference solvent shifts and the experimental values is about 4 ppm while that for the competing solvents is about 17 ppm. For systems in which the competing solvent will not dissolve thallos salts, the average deviation between the fitted and experimental reference solvent shifts is again about 4 ppm. Thus, comparison of the truncation behavior of the two types of systems and the average deviations of fitted and experimental shifts for the reference solvents in the two types of systems leads to an estimated error of ±20 ppm for the fitted shifts in competing solvents which will not dissolve thallos salts.

Discussion

A. Solvation as Measured by $(1/n) \log K$. The solvation equilibrium constants were calculated by the fitting procedure described above (see Experimental Section). The procedure uses eq 1 which does not directly give K , but rather $K^{1/n}$, where n is the solvation number of the Tl^+ ion.

There are three important assumptions involved in Covington's derivation of eq 1. First, the solvation number, n is assumed to be the same for both solvents and constant throughout the exchange process. The validity of this assumption will be discussed below. Second, the equilibrium constants for the n individual solvent-exchange processes, e.g.



are assumed to be statistically related to the overall K , i.e., $K_m = [(n-m+1)/m](K_1K_2 \dots K_n)^{1/n}$. Third, the shift of all intermediately solvated species is assumed to be proportional (for the above example) to the amount of solvent B in the solvation sphere, i.e., $\delta(Tl^+A_{n-m}B_m) = (m/n)\delta(Tl^+B_n)$. Covington has dealt further with the first two assumptions in succeeding papers.^{16,17} We have found that the third assumption is invalid when the competing solvents are HMPA or water. For these two solvents the shift reaches a maximum and then decreases before a mole fraction of 1.00 is reached. For HMPA, the maximum is sufficiently close to the shift extreme that a reasonable fit to an equilibrium constant is still achieved.

Prior to the formalization of Covington et al. for the exchange process, preferential solvation was often measured by the isosolvation number (ISN), i.e., the mole fraction at which $\delta = \delta_p/2$. It is possible to calculate $K^{1/n}$ directly from such data by rearranging eq 1 as shown in eq 3. For the Tl^+

$$K^{1/n} = (ISN)^{-1} - 1.0 \quad (3)$$

solvation, the values of $K^{1/n}$ calculated from eq 3 agree within 2% with the values listed in Table I. A generalized fitting procedure using eq 1 is more useful because it allows solvation equilibrium constants to be calculated for competing solvents

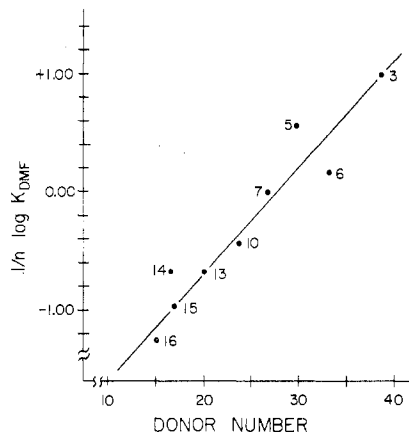


Figure 3. Correlation of solvating ability relative to DMF with Gutmann's donor numbers. Competing solvents are identified by number according to Table I. Correlation factor is 0.958.

which will not dissolve thallos salts.

Empirical Descriptions of Relative Solvating Ability. Table III contains the results of comparing $(1/n) \log K$ with three empirical descriptions of solvating ability that have been proposed as general measures of solute-solvent interaction: the Krygowski-Fawcett description,¹⁸ Gutmann's donor numbers,¹⁹ and Drago's E and C numbers.²⁰ For this comparison, only the solvents which are common to all of the studies are used: HMPA, DMSO, DMF, THF, and acetone.

The Krygowski-Fawcett acid-base description of solvent effects uses Gutmann's donor numbers, DN, as a measure of Lewis basicity and the Dimroth-Reichardt parameter,¹⁸ E_T , as a measure of Lewis acidity. Q in this case is $(1/n) \log K$.

$$Q = Q_0 + \alpha(E_T) + \beta(DN) \quad (4)$$

A multiple regression analysis of Q , E_T , and DN is performed. When this model is used, a good correlation is obtained as is shown in rows 1 and 5 of Table III. α_{E_T} and β_{DN} are the regression coefficients for E_T and DN, respectively. $\bar{\alpha}_{E_T}$ and $\bar{\beta}_{DN}$ may be regarded as the percentage contribution from solvent acidity and basicity, respectively, to the observed solvent effect.¹⁷

When donor numbers alone are used to describe $(1/n) \log K$, a smaller value of R is obtained as shown in rows 2 and 6 of Table III. The value of β_{DN} does not change significantly. A plot of $(1/n) \log K_{DMF}$ vs. DN for all solvents for which both quantities are known is shown in Figure 3.

Basicity can also be measured in terms of E_B and C_B numbers. E_B contains predominantly electrostatic effects and C_B contains predominantly covalent effects.²⁰ When $(1/n) \log K$ is compared with the E and C model, the quantities in rows 3 and 7 of Table III are obtained. Clearly R is not as great for solvation described in terms of E_B and C_B as it is for solvation described in terms of donor numbers alone. Rows 4 and 8 show the results of an attempt to describe solvation by E_B alone. Five solvents do not provide sufficient data for a test of the solvation model of E_B , C_B , and E_T , but of the

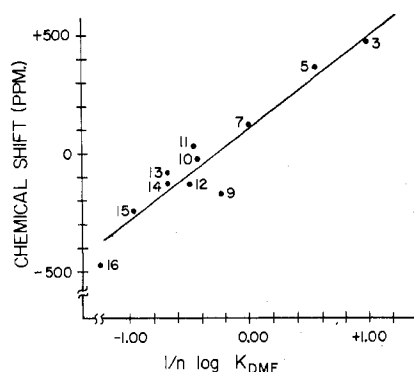


Figure 4. Plot of chemical shift vs. solvating ability relative to DMF for solvents which coordinate via an oxygen atom. Solvents are numbered as shown in Table I. Correlation factor is 0.945.

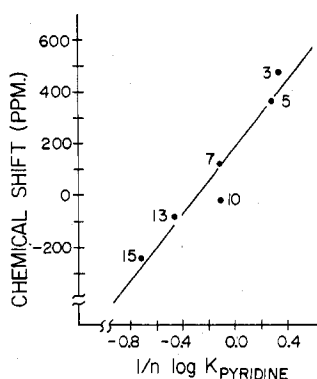


Figure 5. Plot of chemical shift vs. solvating ability relative to pyridine for solvents which coordinate via an oxygen atom. Solvents are numbered as shown in Table I. Correlation factor is 0.968.

general models tested, the one which most adequately describes the results in Table I is the Krygowski-Fawcett model.

As was previously mentioned, the value of n in the solvation equilibrium constant $K^{1/n}$ is assumed to remain constant throughout the solvent-exchange process. The validity of this assumption is reinforced by the observation that the average deviation between the experimental mole fraction dependence of the shift and that calculated by the fitting procedure is small. If n were changing, significantly poorer fits would be obtained. For example, when pyrrole is the competing solvent, an appreciably better fit is obtained by assuming that the solvation number of Tl^+ in pyrrole is $n/2$. The solvation value is then $(2/n) \log K$ which can be converted to $(1/n) \log K$ for comparison with other solvents. The value of n has not been determined for Tl^+ , but with the exception of pyrrole it appears to be constant in the solvents studied.

B. Correlation of $(1/n) \log K$ with Shift. Previously we pointed out that Tl^+ was preferentially solvated by solvents giving rise to resonances at lower fields.²¹ The data in Table I allow a quantitative examination of this trend. The $(1/n) \log K$ values correlate quite well with the chemical shift. Figure 4 shows a plot of chemical shift vs. $(1/n) \log K_{DMF}$ for the solvents coordinating via an oxygen atom. Figure 5 shows a similar plot with $(1/n) \log K_{py}$ for the same category of solvents. The good experimental correlation is somewhat surprising in view of the fact that correlations between thermodynamic properties and spectroscopic properties are not always found. For example, in transition metal systems, bond strengths do not correlate with spectroscopic $10Dq$ values. It appears that both shifts and $(1/n) \log K$ reflect the thermodynamic base strength of the solvent (vide infra).

When the donor atom is changed, the slope of the shift vs. $(1/n) \log K$ plot changes but a linear relationship is retained. Figure 6 shows a plot of shift vs. $(1/n) \log K_{DMF}$ for a series

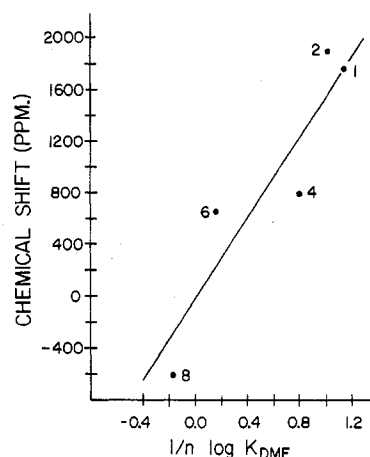


Figure 6. Plot of chemical shift vs. solvating ability relative to DMF for solvents which coordinate via a nitrogen atom. Solvents are numbered as shown in Table I. Correlation factor is 0.934.

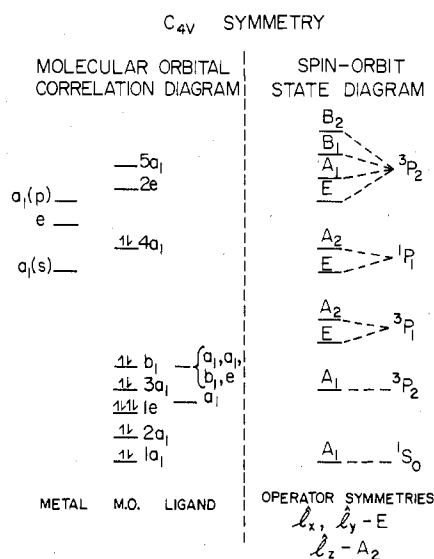


Figure 7. Left side: molecular orbital correlation diagram for a solvated $Tl^+ClO_4^-$ ion pair with C_{4v} symmetry. Right side: the spin-orbit state diagram for a Tl^+ ion with C_{4v} symmetry and correlation of the levels to free-ion states.

of solvents which coordinate via a nitrogen atom.

C. A Model to Explain the Solvent Dependence of the Chemical Shift. For the heavy metals such as Tl^+ , the chemical shift arises primarily from the paramagnetic term in the Ramsey equation.⁹ This term, σ_p , is due to the mixing of excited-state angular momentum into the ground state. Two conditions are necessary for σ_p to be nonzero: (1) there must be metal p character in the ground state and (2) there must exist excited states possessing angular momenta of the proper symmetry to mix with the ground state via the l operator. The magnitude of the σ_p term will therefore be determined by the amount of metal p character in the ground state and by the energy separation between the ground state and the excited state that is being mixed in.

Orgel⁸ has shown that for ions with $d^{10}s^2$ configurations, noncentrosymmetric distortions could allow the requisite excited-state mixing. The model described here uses simple symmetry considerations of MO theory to show explicitly how the ground state can acquire p-orbital character.

The symmetries of the one-electron MO's of the solvated complex are shown in the correlation diagram on the left side of Figure 7. C_{4v} symmetry represents the Tl^+ interacting with an anion and five solvent molecules. In order to illustrate the model with a concrete example, a coordination number of 6

is assumed. The model does not depend on the coordination number but rather on the inversion symmetry. The five solvent ligand group orbitals consist of two of a_1 symmetry, one b_1 , and one e . The anion contributes an additional a_1 orbital. The metal orbitals are an a_1 (of s character), and an e , and an a_1 (of p character). Of the MO's formed, b_1 is nonbonding and the occupancies are shown in Figure 7. Significant p character from the metal $a_1(p)$ and e AO's can be mixed into the ground state by the metal-ligand interactions. The two unoccupied MO's are also primarily metal p in character.

The solvent dependence of the shift is explained in terms of the variable amount of interaction between the solvent and Tl^+ . Increasing the Tl^+ -solvent interaction increases the coefficient of metal p character in the ground state. Furthermore, an increase in this interaction will decrease the energy separation between the ground and excited states by destabilizing $4a_1$ with respect to $2e$. Both of these effects will increase the magnitude of σ_p . Thus this model predicts increasing deshielding as the Tl^+ -solvent interaction increases as is experimentally observed.

As the difference between the Tl^+ -solvent and Tl^+ -anion interaction decreases, the solvation sphere becomes centrosymmetric and σ_p approaches zero.²² In simple MO language, the difference between the Tl^+ -solvent and Tl^+ -anion interaction arises from the different donor orbital energies and the different Tl^+ -ligand overlap integrals. The more strongly a ligand interacts with the Tl^+ , the higher in energy the donor orbital and/or the greater the overlap integral, thus the greater the mixing of the Tl^+ -ligand orbitals. The difference that is expected between Tl^+ -N ligand and Tl^+ -O ligand overlaps may explain the different slopes that were observed for N solvents and O solvents when the shift is correlated with solvating ability in Figures 4 and 6.

The importance of the coefficient of metal p character in the ground state (relative to that of the energy separation) is illustrated by the absence of any correlation between the energy of the lowest energy uv absorption band of Tl^+ ²³ and the chemical shift. If the shift were governed by the denominator of the Ramsey equation, a linear correlation could be expected.

We found it very interesting to observe that the resonance line width was linearly related to the chemical shift. A plot of the chemical shift vs. the peak width at half-height is a straight line of positive slope with a correlation factor of 0.968. One possible explanation for this behavior, consistent with our model, is that the line width reflects relaxation caused by the anisotropic chemical shift, eq 5.²⁴ As the symmetry of the

$$\frac{1}{T_2} \propto (\sigma_{\parallel} - \sigma_{\perp})^2 \tau_c \quad (5)$$

solvated Tl^+ is lowered corresponding to increased solvent-thallium interaction, the difference between the principal components of the shielding tensor may increase. As a result, the relaxation and the line width should increase with increasing solvent-thallium interactions. Because many other factors can contribute to the changing line width, a varia-

ble-field study (which cannot be carried out on our instrument) is necessary to determine which factor causes the observed linearity.

In summary, the correlation of the relative solvating ability with the chemical shift reported here can be understood in terms of the varying thallium-solvent interactions varying the p character in the ground state. Because the thermodynamic models of Lewis acid-base interactions which we have examined in this paper correlate with the relative solvating ability, the correlations between the chemical shift and the parameters of these thermodynamic models can also be explained.

Acknowledgment. We gratefully acknowledge the National Science Foundation for support of this work. J.I.Z. gratefully acknowledges a Camille and Henry Dreyfus Teacher-Scholar Award, 1974-1979.

Registry No. Tl^+ , 22537-56-0; pyrrolidine, 123-75-1; *n*-butylamine, 109-73-9; hexamethylphosphoramide, 1608-26-0; diethylamine, 109-89-7; dimethyl sulfoxide, 67-68-5; pyridine, 110-86-1; dimethylformamide, 68-12-2; pyrrole, 109-97-7; dimethoxyethane, 25154-53-4; tributyl phosphate, 102-85-2; methanol, 67-56-1; dioxane, 123-91-1; tetrahydrofuran, 109-99-9; methyl acetate, 79-20-9; acetone, 67-64-1; propylene carbonate, 108-32-7.

References and Notes

- (1) E. G. Bloor and R. G. Kidd, *Can. J. Chem.*, **46**, 3426 (1968).
- (2) R. H. Erlich, E. Roach, and A. I. Popov, *J. Am. Chem. Soc.*, **92**, 4989 (1970).
- (3) R. H. Erlich and A. I. Popov, *J. Am. Chem. Soc.*, **93**, 5620 (1971).
- (4) M. Herlem and A. I. Popov, *J. Am. Chem. Soc.*, **94**, 1431 (1972).
- (5) J. F. Hinton and R. W. Briggs, *J. Magn. Reson.*, **19**, 397 (1975).
- (6) G. E. Maciel, J. K. Hancock, L. F. Lafferty, P. A. Mueller, and W. K. Musker, *Inorg. Chem.*, **5**, 554 (1966).
- (7) R. Freeman, G. R. Murray, and R. E. Richards, *Proc. R. Soc. London, Ser. A*, **242**, 455 (1957).
- (8) L. E. Orgel, *Mol. Phys.*, **1**, 322 (1958).
- (9) W. G. Schneider and A. D. Buckingham, *Discuss. Faraday Soc.*, **34**, 147 (1962).
- (10) S. Hafner and N. H. Nachtrieb, *J. Chem. Phys.*, **40**, 2891 (1964).
- (11) J. J. Dechter and J. I. Zink, *J. Am. Chem. Soc.*, **97**, 2937 (1975).
- (12) R. H. Erlich, M. S. Greenberg, and A. I. Popov, *Spectrochim. Acta, Part A*, **29**, 543 (1973).
- (13) M. S. Greenberg and A. I. Popov, *Spectrochim. Acta, Part A*, **31**, 697 (1975).
- (14) A. K. Covington, T. H. Lilley, K. E. Newman, and G. A. Porthouse, *J. Chem. Soc., Faraday Trans. 1*, 963 (1973).
- (15) A. K. Covington, K. E. Newman, and T. H. Lilley, *J. Chem. Soc., Faraday Trans. 1*, 973 (1973).
- (16) A. K. Covington, I. R. Lantzke, and J. M. Thain, *J. Chem. Soc., Faraday Trans. 1*, 1869 (1974).
- (17) A. K. Covington and J. M. Thain, *J. Chem. Soc., Faraday Trans. 1*, 1879 (1974).
- (18) T. M. Krygowski and W. R. Fawcett, *J. Am. Chem. Soc.*, **97**, 2143 (1975).
- (19) V. Gutmann, "Coordination Chemistry in Non-Aqueous Solutions", Springer-Verlag, New York, N.Y., 1968, Chapter 2.
- (20) R. S. Drago, G. C. Vogel, and T. E. Needham, *J. Am. Chem. Soc.*, **93**, 6014 (1971).
- (21) J. J. Dechter and J. I. Zink, *J. Chem. Soc., Chem. Commun.*, 96 (1974).
- (22) It is unlikely that σ_p will strictly equal zero since vibronic coupling with a vibration of ungerade symmetry could always allow a small amount of mixing to occur.
- (23) J. J. Dechter, Ph.D. Thesis, University of California, Los Angeles, Calif., 1975, Chapter 6.
- (24) T. C. Farrar and E. D. Becker, "Pulse and Fourier Transform NMR", Academic Press, New York, N.Y., 1971, p 60.