

(py)MnTPP (Mn-Cl = 2.467 Å; Mn-N_{py} = 2.44 Å) as compared to the ClMnTPP (Mn-Cl = 2.363 Å). Further in Cl(py)MnTPP the manganese is displaced by only 0.12 Å from the center of the mean porphyrin plane as against 0.27 Å in the ClMnTPP, implying a stronger equatorial interaction in the former. Both these factors are expected to produce larger ZFS in the pyridine adduct as compared to the ClMnTPP.

Conclusion

The measurement of magnetic anisotropy in the liquid-nitrogen temperature range has been found to be useful in deducing accurately the sign and magnitude of the zero-field splitting parameter in manganese(III) porphyrins. If this measurement is done down to liquid-helium temperatures, a more accurate and reliable value could be deduced. On the other hand the temperature dependence of $\bar{\mu}$ even down to 4

K is unable to decide uniquely the sign of D . There appears to be not much variation in D either with the change in axial ligand or with the substitution on the porphyrin ring in ClMnTPP, Cl(py)MnTPP, and ClMnDPME. It is however interesting that the ZFS in the isoelectronic high-spin deoxyhemoglobin is rather higher and opposite in sign ($D \approx 5 \text{ cm}^{-1}$), indicating the difference in the nature of the bonding in the two cases.

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Contribution from the Kitami Institute of Technology,
Kitami 090, Japan

Proton Nuclear Magnetic Resonance Study of Ion Hydration in Acetone. 2

K. MIURA and H. FUKUI*

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Ab initio calculation of the shielding change of the water proton due to a point charge has been performed and compared with the experimental shifts of the ion-water associations in acetone reported in our previous paper. From the theoretical and experimental shielding changes, it was concluded that (a) anion-water associations do not occur in acetone solvent and (b) the theoretical calculation leads to a shielding change of -1.6 to -3.9 ppm, which is in qualitative agreement with the experimental results.

Introduction

Water proton nuclear magnetic resonance (¹H NMR) chemical shifts produced by diamagnetic salts in aqueous solution have been used to study the effects of electrolytes on the structure of water and the nature of water-solvent interaction.¹ According to Shoolery and Alder,² the chemical shift produced by ions in aqueous solution is the sum of at least two factors: (i) polarization of water molecules and (ii) structure breaking of the water hydrogen-bonded network, by ions. If we want to investigate the mechanism of the shielding change due to the hydration of ions, it is desirable to separate the above two contributions. In paper 1³ of this series, we showed that the structure-breaking effect is negligible in the solution of low water content in acetone solvent.

A water molecule in acetone seems to form the hydrogen bond of water hydrogen to acetone oxygen. This hydrogen bonding will obstruct water-water and water-anion associations. Therefore, we can observe the shielding change owing to water-cation bonding only. Moreover, it is possible to observe a favorable 1:1 water-cation complex formation at low water concentrations in acetone solvent. The 1:1 complex formation allows us to analyze the chemical shift changes as a function of added ion concentration and obtain the polarization shift and equilibrium constant. However, the detailed relationship between proton magnetic shielding and the geometrical configuration of the hydrated ion system is not completely understood. This places some uncertainty on conclusions resulting from the use of proton NMR spectroscopy for probing ion-water interactions. Our purpose in this study is

to perform an ab initio calculation of the shielding change of the water proton due to a point charge and compare it with the experimental results in paper 1.

In the Calculations, a brief explanation of the method used and its results are given. In the Discussion, a brief survey of experimental results in paper 1 is stated and compared with the ab initio estimates.

Calculations

A. Theory. According to the Ramsey theory of chemical shielding,⁴ the components of the shielding tensor are given by eq 1 where $\sigma_{\alpha\beta}^d$ are components of the diamagnetic term

$$\sigma_{\alpha\beta} = \sigma_{\alpha\beta}^d + \sigma_{\alpha\beta}^p \quad (1)$$

given by eq 2, where \vec{r}_O denotes the vector between the gauge

$$\sigma_{\alpha\beta}^d = 26.626 \times 10^{-6} \sum_{\mu\nu} P_{\mu\nu} \langle \mu | (\vec{r}_O \cdot \vec{r}_N \delta_{\alpha\beta} - r_{O\alpha} r_{N\beta}) r_N^{-3} | \nu \rangle \quad (2)$$

origin and electron and \vec{r}_N is the vector between nucleus N and electron. r_O and r_N are expressed here in atomic units. Components of the paramagnetic shielding tensor, $\sigma_{\alpha\beta}^p$, are given by eq 3, in atomic units, where $\vec{l}_O = \vec{r}_O \times \vec{\nabla}$ and $\vec{l}_N =$

$$\sigma_{\alpha\beta}^p = 53.251 \times 10^{-6} \sum_{\substack{i, \text{occ} \\ j, \text{unocc}}} (\epsilon_j - \epsilon_i - J_{ij} + 2K_{ij})^{-1} \times \\ \sum_{\mu\nu\lambda\sigma} C_{\mu}^* C_{\nu} C_{\lambda}^* C_{\sigma} \langle \mu | r_N^{-3} l_{N\alpha} | \nu \rangle \langle \lambda | l_{O\beta} | \sigma \rangle + \\ \langle \mu | l_{O\alpha} | \nu \rangle \langle \lambda | r_N^{-3} l_{N\beta} | \sigma \rangle \quad (3)$$

$\vec{r}_N \times \vec{\nabla}$. Other notations conform to those in the formula by Barfield and Grant.⁵ Integrals of the following types occur in eq 2 and 3: (i) $\langle \mu | r_N^{-3} x_{O\alpha} y_{N\beta} | \nu \rangle$; (ii) $\langle \mu | x_O (\partial/\partial y_O) | \nu \rangle$; (iii)

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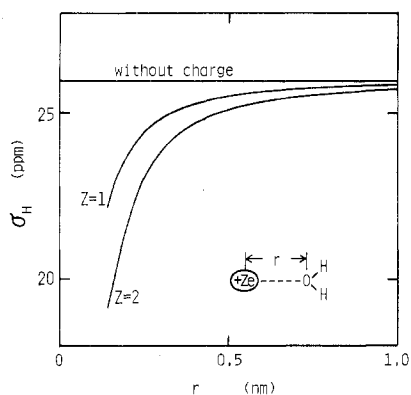


Figure 1. Variation of the isotropic proton shielding constant in H_2O with the oxygen-positive point charge separation, r .

$\langle \mu | r_N^{-3} x_N (\partial / \partial y_N) | \nu \rangle$. Integral ii is quite easy to calculate. The other types of integrals (i, iii) result in the evaluation of a $\langle \mu | r_N^{-3} x_N | \nu \rangle$ type integral. An integral of this type can be reduced to such field integrals as in eq 4 where (X_N , Y_N , Z_N)

$$\langle \mu | r_N^{-3} x_N | \nu \rangle = \frac{\partial}{\partial X_N} \langle \mu | r_N^{-1} | \nu \rangle \quad (4)$$

is the coordinate of nucleus N. Owing to the properties of Gaussian functions, the computation of the field integral requires no particular difficulty.

In a few attempts⁶⁻⁸ to rationalize the shielding change in a static electric field, ab initio methods have been employed quite recently by some authors with success. This paper is essentially aimed at investigating the ab initio predictions of the water proton shielding change due to an ionic field by using a point-charge model. The most difficult problem is always to get a reasonable compromise between the quality of a basis set and its size (computation time). In this calculation, we used Pople's 4-31G basis⁹ and were able to get a reasonable result.

In the computation of magnetic properties, further complications arise because of the gauge dependence of calculated values, which is due to the finite extension of the basis set, and some special choice of the gauge of the vector potential is commonly made in order to get accurate paramagnetic susceptibility and shielding. In this calculation, the nucleus of the oxygen atom was selected as the gauge origin in order to minimize the paramagnetic term.

B. Results. The calculated isotropic shielding changes of the water proton due to a point charge are shown in Figures 1 and 2, corresponding to positive and negative charges, respectively. The position of the point charge is drawn in each figure. The positive charge was set on the dipolar axis of the water molecule and the negative one on the hydrogen-oxygen bond axis.¹⁰ An experimental geometry¹¹ was used as the geometrical configuration of the H_2O molecule.

Discussion

Both Figures 1 and 2 indicate that the calculated isotropic shielding constant of the water proton shows a marked decrease with the decreasing distance, r , between a point charge and a water molecule. An analysis of the theoretical results showed that the downfield proton shift due to ion hydration arises (a) from a decrease of the electronic charge on the hydrogen by an ionic field σ^d effect and (b) from a deshielding effect of

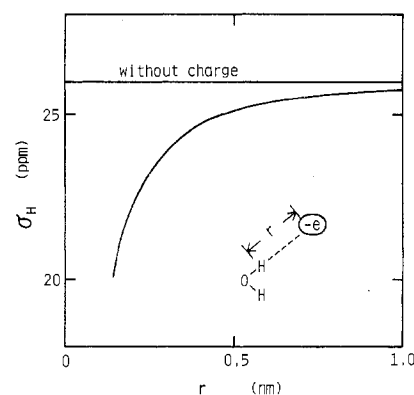


Figure 2. Variation of the isotropic proton shielding constant in H_2O with the proton-negative point charge separation, r .

Table I. Experimental Proton Shielding Changes, Δ_C , by Substrate-Anion Bonding

salt	Δ_C , ppm	
	H_2O in $(\text{CH}_3)_2\text{CO}$	CHCl_3 in CCl_4
$(n\text{-C}_4\text{H}_9)_4\text{NCl}$	-0.75	-2.92
$(n\text{-C}_4\text{H}_9)_4\text{NBr}$	-0.48	-2.51
$(n\text{-C}_4\text{H}_9)_4\text{NI}$	-0.06	-2.30

Table II. Anion Dependences of Δ_C of Lithium, Calcium, Zinc, and Cadmium Salts in Acetone

cation	anion	Δ_C , ppm	cation	anion	Δ_C , ppm
Li^+	ClO_4^-	-1.85	Zn^{2+}	SCN^-	-5.23
Li^+	NO_3^-	-1.92	Zn^{2+}	Cl^-	-4.42
Li^+	SCN^-	-1.87	Zn^{2+}	Br^-	-4.75
Li^+	Br^-	-1.86	Cd^{2+}	NO_3^-	-3.78
Li^+	I^-	-1.88	Cd^{2+}	I^-	-3.43
Ca^{2+}	ClO_4^-	-2.33			
Ca^{2+}	NO_3^-	-2.22			
Ca^{2+}	SCN^-	-2.34			

the paramagnetic contribution induced by an ion-water bonding σ^p effect. The former contribution (a) is particularly important to cation hydration, in which the latter one (b) is only responsible for approximately 20% of the total calculated shielding change. On the other hand, the contribution (b) is not so small to anion hydration. In this case the (b)-type contribution represents approximately 35% of the total change.

Table I shows the experimental proton shielding changes, Δ_C , owing to the water-anion bondings in acetone³ and the chloroform-anion ones in carbon tetrachloride.¹² Observed shielding results for the latter system indicate the deshielding of 2-3 ppm, which is in reasonable agreement with the theoretical result in Figure 2. On the other hand, the former system represents negligibly small shifts. This result corresponds well with the expectation from the water-acetone hydrogen bonding as stated in the Introduction.

The further verification of the assumption that the water-acetone hydrogen bonding will obstruct water-anion bonding was obtained from the experiment of the anion dependence of the water proton Δ_C in acetone containing the salt of the same cation. The results are listed in Table II. The shielding changes in Table II show little variation with the anion. This fact indicates clearly that the above assumption is correct.

From the data presented in Tables I and II, we conclude that the shielding change, Δ_C , of a metal salt in acetone is primarily determined by the metal ion and the anion has a negligible effect on it. In order to investigate the cation shifts, we have performed a theoretical calculation of the shielding

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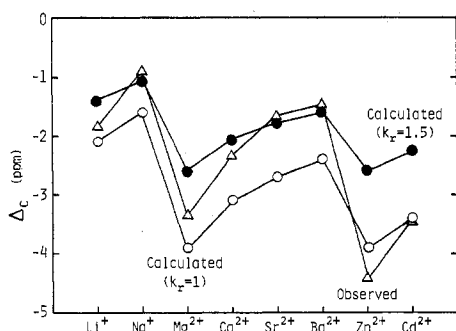


Figure 3. Graphic display of the observed and calculated ΔC depending on the cations.

changes due to cations by using the result in Figure 1. The theoretical and experimental shifts are shown in Figure 3. The used cation-oxygen distances are the values of the X-ray diffraction studies by Lawrence and Kruh.¹⁰ Figure 3 shows that the theoretical shifts are larger than the experimental ones, except those of the zinc and cadmium ions. In a study of this type, we should be gratified with a qualitative agreement with the available experimental data. There are at least three probable sources of error. First, a point-charge model is too crude an approximation to cation-water association. We should include atomic orbitals of the ion. Second, there are errors due to use of the 4-31G basis set (without gauge factors) in the magnetic calculations. Although the 4-31G magnetic shielding values are considerably more accurate than those calculated by using a minimal set,¹³ it does not allow an estimate of the value of σ_H which would correspond to the Hartree-Fock limit.¹⁴ However, gauge dependences of σ_H will be canceled in the calculation of the shielding change, ΔC . Finally, there are errors due to the counterion effect and the dielectric constant of the solvent. Our calculation neglected the fields originating from counterions and dipolar solvent

molecules. We have assumed the dielectric constant of the vacuum (ϵ_0) for the space intervening between the point charge and the water molecule. This is not necessarily so, but the vacuum value is reasonably considered to be much better than the bulk value of acetone, $20.7\epsilon_0$, in this case by reason of the dielectric saturation effect.¹⁵ The shielding effect of the anions and the polarization of the acetone solvent would attenuate the electrostatic field of the cations and make the calculated ΔC smaller.

Among the above three sources of error, we suspect the dielectric effect is the most important. The effect of a dielectric constant should be discussed briefly. Buckingham¹⁶ showed that the σ^d effect depends on the relative dielectric constant, k_r , inversely, but the σ^p term is proportional to k_r^{-2} . The σ^d term is much larger than the σ^p term on cation hydration. Therefore, we can simply suppose that the total σ change by ion, namely, ΔC , depends on k_r , inversely. We calculated the appropriate k_r value from the observed ΔC 's of alkali and alkaline earth metal ions and obtained 1.5 as the effective value for k_r in acetone solvent. This value is close to $n^2 = 1.85$ in which n is the index of refraction of acetone. The dielectric saturation theory¹⁷ predicts that k_r in infinite strength of the electric field will decrease to n^2 asymptotically, that is the square of the optical refractive index. The calculated ΔC values for $k_r = 1.5$ are also shown in Figure 3.

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Registry No. H₂O, 7732-18-5; Mg²⁺, 22537-22-0; Ca²⁺, 14127-61-8; Sr²⁺, 22537-39-9; Ba²⁺, 22541-12-4; Li⁺, 17341-24-1; Na⁺, 17341-25-2; Zn²⁺, 23713-49-7; Cd²⁺, 22537-48-0.

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Contribution from the Institut für Physikalische Chemie, Montanuniversität, A-8700 Leoben, Austria, and the Department of Inorganic and Structural Chemistry, The University, Leeds LS2 9JT, England

Kinetic Study of the Rapid Complexation of *cis*-Diaquobis(ethylenediamine)cobalt(III) with Tungstate(VI). Substitution at Tungstate(VI)

H. GAMSJÄGER,*^{1a} G. A. K. THOMPSON,^{1a} W. SAGMÜLLER,^{1a} and A. G. SYKES^{1b}

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The complexing of *cis*-Co(en)₂(H₂O)₂³⁺ with WO₄²⁻ has been studied at 25 °C, pH 8.0-9.0 (Tris), and $I = 1.0$ M (NaClO₄). A 1:1 reaction is observed: Co(en)₂(OH)(H₂O)₂²⁺ + WO₄²⁻ \rightleftharpoons Co(en)₂(OH)(WO₄) + H₂O, with $K_C = 1160$ M⁻¹. The kinetics was studied by the stopped-flow method, the rapid complexation corresponding to substitution at W(VI). With [W(VI)] = 0.010-0.100 M, the reaction proceeds to completion, and the [H⁺] dependence is consistent with two paths: Co(en)₂(OH)₂²⁺ + HWO₄⁻ \rightarrow Co(en)₂(OH)(WO₄) + H₂O ($k_1 = 3.22 \times 10^7$ M⁻¹ s⁻¹); Co(en)₂(OH)(H₂O)₂²⁺ + HWO₄⁻ \rightarrow Co(en)₂(OH)(WO₄) + H₂O + H⁺ ($k_2 = 1.03 \times 10^7$ M⁻¹ s⁻¹). The results obtained complement previous data on the exchange of H₂O ($k_a = 0.44$ s⁻¹) and OH⁻ ($k_b = 273$ M⁻¹ s⁻¹) with WO₄²⁻ and give a rate constant of ca. 10^7 M⁻¹ s⁻¹ for substitution at HWO₄⁻.

The oxygen-18 exchange of molybdate and tungstate oxyanions (XO₄²⁻) with water has been studied previously in basic media, pH > 11,² and results can be summarized by (1).

$$k_{\text{obsd}} = k_a + k_b[\text{OH}^-] \quad (1)$$

Under more acidic conditions the exchange properties can be assessed by studying the rapid complexing of the oxyanion with substitution-inert metal complexes. Taylor³ has previously reported studies on the complexing of MoO₄²⁻ with Co-

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