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Detailed Solvation Shell Geometry of Cupric Ion in Ethanol Determined by Electron-Spin-Echo Modulation Analysis

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Abstract: The analysis of electron-spin-echo modulation patterns for Cu^{2+} in variously deuterated ethanol glasses shows that Cu^{2+} is solvated by six approximately equivalent ethanol molecules with their molecular dipoles oriented toward Cu^{2+}. A distance of >0.03 nm between in-plane and out-of-plane molecules should be distinguishable in this analysis, so a single shell analysis is a good approximation. From specific deuteration studies the average orientation of a first solvation shell ethanol molecule with respect to Cu^{2+} is deduced. The distance from Cu^{2+} to the ethanol oxygen is 0.21 nm, that to the hydroxyl proton is 0.26 nm, those to the methylene protons are 0.35 and 0.41 nm, and those to the methyl protons are 0.38, 0.49, and 0.49 nm. The HOC plane is perpendicular to the OCC plane in ethanol, giving a molecular conformation intermediate to the trans and gauche forms.

Few methods exist for studying the detailed solvation geometry of species in solution or frozen solutions. However, such information is critical for understanding the chemistry of solvated species. By analyzing electron-spin-echo modulation patterns to measure very weak hyperfine interactions, it has recently been shown that the solvation structures of *paramagnetic* species in frozen solutions or glasses can be elucidated. Perhaps the most important application has been to the structure of solvated electrons,[1-6] but the solvation of anions,[7] cations,[8-10] and atoms[11,12] has also been reported. The analysis gives the number of first solvation shell molecules, the distance from the paramagnetic species to magnetic nuclei in the molecules, and the isotropic hyperfine coupling to these nuclei. By using selective isotopic substitution, the distances to different groups in the solvent molecules can be deduced, thus determining the solvent molecule orientation. Thus, electron-spin-echo modulation analysis gives detailed information on solvation geometries which have not been obtained by other methods.

In a previous paper we have determined the solvation structure for Cu^{2+} in methanol and acetone.[10] In both solvents the Cu^{2+} is solvated by six approximately equivalent molecules, with their molecular dipoles oriented toward Cu^{2+}. Although the geometries were determined in rapidly frozen solutions, the solvation structures also seem compatible with expected average liquid-phase structures.

In this paper we deduce the detailed solvation structure of Cu^{2+} in ethanol where it is possible to determine more detail about the molecular orientation and conformation of the first solvation shell ethanol molecules than was the case for methanol molecules.

Experimental Section

The deuterated ethanols used were CH_3CH_2OD and CD_3CH_2OH from Stohler Isotope Chemicals and CH_3CD_2OH from Dr. Yu. D. Tsvetkov. Solutions of 2×10^{-3}-mol/dm^3 $CuCl_2$ in these solvents were prepared and sealed in 3-mm O.D. Suprasil quartz tubes. Twofold lower concentrations gave similar results with reduced echo intensity.

Electron-spin-echo signals were obtained on a home-built pulsed spectrometer that has been described.[12] The microwave pulse width was 30 ns, and typical pulse powers used were 100 W. All experiments were carried out at 4.2 K with a microwave frequency of 9.15 GHz and the magnetic field on the $g_\perp$ line of Cu^{2+} which gave the maximum echo intensity.

Two- and three-pulse electron-spin-echo methods were used for obtaining the modulation patterns from D nuclei.[13] In the two-pulse method, the time between the first and second pulses, τ, was varied, and the echo signals observed at τ after the second pulse were recorded as a function of τ. In the three-pulse method, the time between the first and second pulses, τ, was fixed at 0.26 μs, and the echo signals observed at τ after the third pulse were recorded as a function of T, the time between the second and third pulses. The main advantage of using the three-pulse method is that the modulation extends over a longer time scale than the two-pulse modulation, because the lifetime of the three-pulse echo signal is limited by the electron spin-lattice relaxation time whereas the two-pulse echo lifetime is limited by the phase memory time.

The analysis of electron-spin-echo modulation including cases where g anisotropy occurs has been described in detail.[3,8,9,13] A ratio analysis procedure was used to separate the decay and modulation functions.[3] The parameters determined are the number of equivalent nuclei, n, at distance r from the unpaired electron with an isotropic coupling of a_{iso}. For a direct comparison of the simulated and experimental data, the normalized modulation is multiplied by a power series decay function

$$g(\tau) = \exp(A_0 + A_1\tau + A_2\tau^2 + A_2\tau^2 + A_3\tau^3) \qquad (1)$$

for two-pulse modulation and with $\tau = T$ for three-pulse modulation. The A_i coefficients are determined by a least-squared method.

Results

The lifetimes of the two-pulse echo signals from Cu^{2+} in ethanol glass not only depend on the position of deuteration but also on the physical nature of the glass. Generally the order of the lifetime is $CD_3CH_2OH > CH_3CH_2OD > CH_3CD_2OH$. However, even when the same solvent is used, the lifetime in a cracked glassy matrix is much shorter than that in a crack-free glass. The liquid solutions were directly immersed into liquid He because this procedure was most effective for preparing crack-free samples.

There was no indication of Cl modulation on the Cu^{2+} echo signals. Thus the Cl^- counterion does not seem to be in the first solvation shell of Cu^{2+}.

Figures 1 and 2 show the experimental two-pulse echo modulation for CH_3CH_2OD and CD_3CH_2OH, respectively. The spectral simulations therein will be discussed below. In CH_3CD_2OH the two-pulse echo signals decayed in less than 1 μs which

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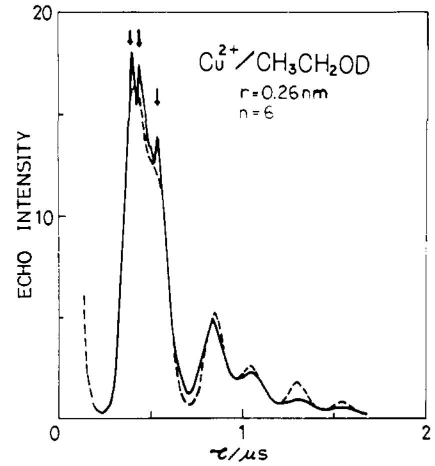

Figure 1. Comparison of the experimental (—) and calculated (---) two-pulse deuteron modulation for Cu^{2+} in CH_3CH_2OD. The parameters used for calculation are $r = 0.26$ nm, $a = -0.1$ MHz, $n = 6$, and $g(\tau) = \exp(3.7 - 2 \times 10^6\tau)$. Arrows indicate the proton modulation.

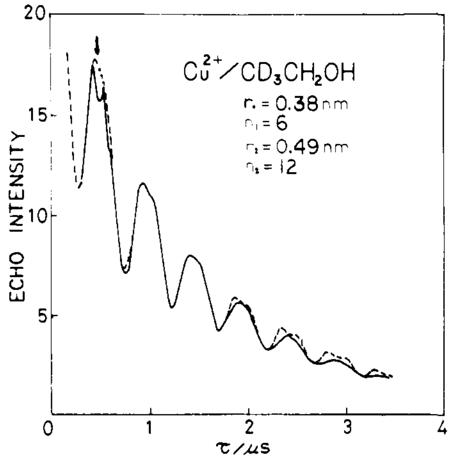

Figure 2. Comparison of the experimental (—) and calculated (---) two-pulse deuteron modulation for Cu^{2+} in CD_3CH_2OH. The parameters for the calculations are $r_1 = 0.38$ nm, $n_1 = 6$, $r_2 = 0.49$ nm, $n_2 = 12$, $a_1 = a_2 = 0$, and $g(\tau) = \exp(3.34 - 1.15 \times 10^6\tau + 0.25 \times 10^6\tau^2 - 0.037 \times 10^6\tau^3)$. Arrows indicate the proton modulation.

is too fast for quantitative analysis of the modulation pattern. The longer lived three-pulse echo signal shown in Figure 3 was therefore analyzed.

The experimental modulation patterns were analyzed under the assumptions that the first solvation shell ethanols are equivalently coordinated to Cu^{2+}, the geometry of the ethanols is the same as in the gas phase, and the Cu^{2+} is in the HOC plane of ethanol which is the same plane as the molecular dipole.

The best simulation shown in Figure 1 for CH_3CH_2OD corresponds to six equivalent interacting deuterons at a distance of 0.26 nm. This indicates six equivalent ethanol molecules in the first solvation shell. On the basis of single-crystal structures[14] there may be a small distance difference between four molecules coplanar with Cu^{2+} and the other two out-of-plane molecules. We explored two-shell model simulations of this type, but no distinction can be made for distance differences of <0.03 nm when the closest nucleus is 0.26 nm. Thus we designate the six first solvation shell molecules as *approximately* equivalent within this possible dispersion.

The best simulation in Figure 3 for CH_3CD_2OH was then constrained to six first solvation shell molecules. Distances to the two deuterons in each ethanol were then varied as a function of the Cu^{2+}–O distance and the angle between the HOC and OCC planes together with the other assumptions mentioned above. The best fit corresponds to Cu^{2+} to methylene deuteron distances of 0.35 and 0.41 nm with a Cu^{2+}–O distance of 0.21 nm and a 90° angle between the HOC and OCC planes.

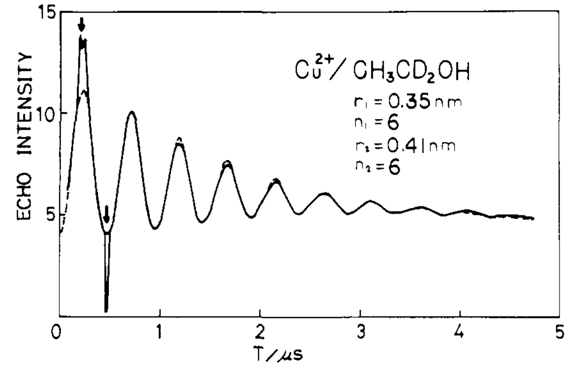

Figure 3. Comparison of the experimental (—) and calculated (---) three-pulse deuteron modulation for Cu^{2+} in CH_3CD_2OH. The parameters used for the calculation are $r_1 = 0.35$ nm, $n_1 = 6$, $r_2 = 0.41$ nm, $n_2 = 6$, $a_1 = a_2 = 0$, and $g(\tau) = \exp(2.46 - 0.075 \times 10^6\tau)$. Arrows indicate the interference effect by the two-pulse echoes.

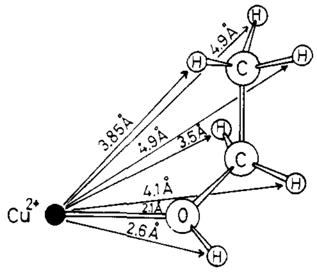

Figure 4. Suggested solvation geometry for a first solvation shell ethanol around Cu^{2+}. The ethanol molecule dipole is oriented toward the cation, and the OCC plane is perpendicular to the HOC plane. The first solvation shell contains six approximately equivalent molecules arranged approximately octahedrally.

This geometry is also consistent with a fixed methyl group orientation such that one Cu^{2+} to methyl deuteron distance is 0.38 nm and the other two Cu^{2+} to methyl deuteron distances are 0.49 nm. The simulation for this geometry is given in Figure 2 for CD_3CH_2OH. If the methyl group is assumed to be rotating and the simulation is averaged over an entire rotation, the result is quite similar to the fixed orientation simulation in Figure 2. Thus, we cannot distinguish whether the methyl group is rotating or not at 4.2 K from our data; we assume that it is not.

A suggested geometry for a single first solvation shell ethanol around Cu^{2+} is illustrated in Figure 4. The Cu^{2+} is in the HOC plane approximately on the bisector of the HOC bond angle which is the molecular dipole direction.[15] The complete solvation shell contains six ethanols oriented thus and arranged approximately octahedrally.

Discussion

It is of interest to compare the solvation structure of Cu^{2+} in ethanol with the results previously obtained for solvation of Cu^{2+} in methanol.[10] In methanol solution the molecular solvation number in the first solvation shell is also found to be six and the average Cu^{2+}–$O(CH_3OH)$ distance is 0.21 nm, the same as found for ethanol. Thus the dominant interactions controlling the solvation structure of Cu^{2+} seem very similar for methanol and ethanol.

The structure of the first solvation shell ethanols as shown in Figure 4 is neither in the trans nor in the gauche configurations which correspond to stable and metastable gas-phase configurations. To understand this we may consider the electrostatic interactions between Cu^{2+} and the solvating ethanols as well as the repulsive steric interactions between the ethanols. The electrostatic interaction is optimized for ethanol in the trans configuration

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because Cu^{2+} can interact most favorably with the induced dipole of the methyl group as well as with the molecule dipole. However, the repulsive steric interactions between the ethanols are largest for this trans configuration. In the gauche configuration the electrostatic interaction with the induced dipole of the methyl group is less favorable, but the repulsive steric interactions are minimized. Thus a balance between the trans and gauche configurations is expected for the solvating ethanols. Experimentally, the balance is found to be halfway between the gauche and trans configurations with the OCC plane perpendicular to the HOC plane.

Finally, we compare the solvation structures of Cu^{2+} and e_{sol}^- in ethanol.[6] For electrons solvated in ethanol the positive end of the molecular dipole is oriented toward the electron with the angle between the OCC and HOC planes being 30–60°. For Cu^{2+} the negative end of the molecular dipole is oriented toward Cu^{2+}, and the angle between the OCC and HOC planes is 90°. The ethanol solvation geometries for the cation and anion are quite similar except for the direction of the molecular dipole. In both cases the solvation structure seems dominated by a charge–molecular dipole interaction.

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Registry No. Cu^{2+}, 15158-11-9; CH_3CH_2OD, 925-93-9; CD_3CH_2OH, 1759-87-1; CH_3CD_2OH, 1859-09-2; CH_3CH_2OH, 64-17-5.

Photodissociation of Stilbene Radical Cation

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Abstract: The fragmentation of stilbene radical cation has been studied with ion cyclotron resonance (ICR) photodissociation spectroscopy. The trans radical cation appears to be formed by electron impact of either the cis or trans neutral based on a comparison of dissociation cross sections with absorption spectra. Dissociation occurred by loss of H, H_2, or CH_3. The fragmentation via loss of a hydrogen atom or molecule can be explained by photoinitiated trans–cis isomerization and electrocyclic ring closure, processes analogous to those of the neutrals. Reaction pathways are discussed in terms of the Woodward–Hoffmann rules for electrocyclic ring closure in examining the involvement of electronically excited states in ion fragmentation.

Since the advent of mass spectroscopy as an instrumental method for structural characterization, workers have sought to correlate mass spectral fragmentation with photochemical or thermal decomposition of organic compounds.[1-3] By accounting for the effects of available energy range and distribution, electronic states, and charge, some analogies can be found. There is still no master plan which allows one to examine experimentally one mode of decomposition and successfully predict the outcome of another. As an example, we consider the well-studied class of photochemical and mass spectral reactions: those of the stilbenes and other similar 1,2-substituted double-bonded compounds.

The primary photochemistry of stilbene consists of two reactions: cis–trans (trans–cis) isomerization[4,5] and electrocyclic ring closure.[6,7] Photoisomerization occurs efficiently in the gas, liquid, or solid phases. It is of importance in understanding vision,[8] has wide synthetic utility,[9] and is a major focus of processes of commercial interest such as photochromism,[10] photomechanics,[11] and ion transport.[12] However, cis–trans isomerization results in no mass change and is unobservable in conventional mass spectrometers unless one of the isomers can fragment differently from the other.[13] The photocyclization of *cis*-stilbene to form phenanthrene by loss of hydrogen does have a mass spectral analogue.

Johnstone and Ward[14] proposed that the mass spectral fragmentations of stilbene and some other aromatic compounds occur via electrocyclic pathways which involve excited electronic states of the ions. They concluded that, from the types and extent of the observed fragmentations, one could infer the geometry of the electrocyclic product and the initial electronic state of the reactant. Bishop and Fleming[15] found cases that apparently contradict Johnstone and Ward's suggestion and proposed instead that selection of mode and extent of fragmentation were much more complicated, and depended among other things on whether the reactants were open shell radical cations or closed shell cations.

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