Figure 6. Total energy variation for the model $(PH_3)_3Co(\eta^2\text{-SCNH})$ on opening the three P–Co–P angles from 90°.

fragment and that of the whole complex as shown by the plotting of the total energy of the $(PH_3)_3Co(\eta^2\text{-SCNPh})$ model as a function of the P–Co–P angles in Figure 6. A minimum is calculated at angles of approximately 103° not too far from the experimental values. It was previously pointed out for $L_3Ni(\eta^3\text{-cyclopropenium})$ complexes,[17] and holds for the present complexes as well, that the gain of the total energy corresponds to a weakening of the linkage between the interacting fragments. Here, there is about a 20% decrease of the overlap between P_3Co and SCNH fragments on opening the P–Co–P angles from 90 to 104°. One of the reasons for this is that the e_g orbitals of Figure 5, while are both lowered in energy, become less hybridized and in general overlap less with the heteroallenic orbitals. Also the energy gap argument predicts a lower interaction of type **2**. Perhaps significantly the Co–S distance is slightly longer in **4** than in **1** on account of the same $\pi_\perp^*$ argument that justified the difference between the Ni–S distances in **3** and in **2**. However, in the presence of d^9 metals the $\pi_\perp^*$ orbital is only half-populated and the effect less marked.

Conclusions and Extensions. The comparative study of complexes **1–4** has clarified some aspects of the bonding of heteroallenes toward d^9 or d^{10} L_3M fragments. The structural details confirm the computational results that the HOMO is a metal-centered orbital having $\pi_\perp$ character with a some mixing in antibonding fashion, of a $\pi_\perp$ orbital of CS_2 centered at the sulfur atoms. The LUMO (MO 2A, see Figure 5) is also a $\pi_\perp$ orbital centered on the CS_2 molecule and has C–S antibonding character; moreover, this orbital is largely developed at the carbon atom.

The knowledge of the frontier orbitals is very important in interpreting the chemical reactivity of complexed heteroallenes.

The often invoked similarity[18] between carbene and η^2-heteroallene mononuclear complexes, with respect to nucleophilic attack, may depend on the fact that both types of complexes have LUMOs centered at the α-carbon atom.[19] In the case of CS_2 complexes a nucleophilic attack may sometime lead to the rupture of a C–S bond due to the $CS_2 \pi_\perp^*$ nature of the LUMO.[20] Electrophilic attack usually takes place to β atoms in both species, and we know that the MO 1S (Figure 5) is largely a lone pair developed at the uncoordinated sulfur.[4]

Finally, we note the radical nature of compound **1**: one electron in a largely metallic orbital. It is reasonable that its chemical reactivity, which is in many respect unique, is of the radical type. In this context the reactions of **1** toward O_2, S_8, and Se^{21} can be viewed as following a pathway where the requirement is the splitting of these reactants into radicals.

The study of the specific chemical reactivity, of the L_3M-$(\eta^2\text{-}CS_2)$ complexes mainly developed in this laboratory, is under way.

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Octahedral-Tetrahedral Geometry Changes for Zinc(II) in the Presence of Chloride Ions

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Ultrasonic absorption measurements have been carried out at 25 °C on 0.400 M zinc chloride solutions in aqueous DMF and methanol. An octahedral to tetrahedral geometry change occurs above a water mole fraction of 0.5 in both systems, and the solvation shell consists of water in both solvent systems. A similar change had been previously observed in aqueous Me_2SO. In aqueous methanol even at low water mole fractions where the solvation shell consists of both water and methanol, this geometry change is detected in the presence of any water.

Introduction

Zinc ions have been known to be important in biological systems for approximately 100 years, but only over the last 30 years have zinc-containing systems been increasingly studied.[2] Because zinc(II) is transparent to normal optical spectroscopic radiation, information about the mechanism and geometry at the metal site is normally obtained by indirect techniques such as kinetics or by substitution of the zinc by

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other colored metal ions.[3] For example, studies on carbonic anhydrase have involved zinc substitution by metal ions such as Co(II), Cu(II), V(IV), Ni(II), and Mn(II), with different geometries and coordination numbers reported.[3] Since metal ion substitution does not guarantee that the results are identical for both metal ions, care must be exercised before interpreting these results. In recent years a number of techniques have been applied to zinc systems in order to determine the geometries and coordination numbers of the zinc ions in solution, with attention being paid to simple inorganic zinc salts that can be utilized as model systems.
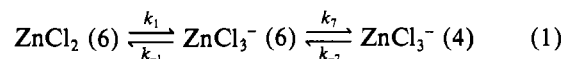
The stability constants of zinc chloride salts have been determined in water,[4] in dimethyl sulfoxide (Me_2SO),[5,6] in aqueous Me_2SO,[7] and in methanol.[8] In a potentiometric study at $I = 0.5$ M in water and aqueous Me_2SO, the major zinc-containing species are hydrated Zn(II), $ZnCl_2$, and $ZnCl_3^-$.[7] In the presence of high concentrations of zinc chloride, in excess of 1 M, $ZnCl_4^{2-}$ has been detected by a variety of techniques. In water the equilibrium constant for the addition of two chlorides to $ZnCl_2$ to form $ZnCl_4^{2-}$ has been measured to be 0.040 M^{-2}.[9] In 99% Me_2SO (less than 1% water), β_2, the overall potentiometric stability constant for the formation of the 1:2 complex is 1.45×10^6, K_3 is 398, and K_4 is undetected in 0.01 M $ZnCl_2$ solutions at 0.5 ionic strength.[7] As water is added to the Me_2SO solutions, the equilibrium constants for each of the successive steps decrease. In methanol and with use of ion-selective electrodes, the stepwise thermodynamic stability constants are $K_1 = 7.76 \times 10^3$, $K_2 = 1.74 \times 10^4$, $K_3 = 400$, and $K_4 = 26$.[8] In all of the solvent systems the $ZnCl_2$ complex is most stable, with a decrease observed for both the 1:1 and the 1:3 complexes. In methanol the 1:1 complex is stable enough to be detected, unlike the Me_2SO results.

Irish has utilized Raman measurements to detect an octahedral $ZnCl_4(H_2O)_2^{2-}$ species[10] and Quicksall and Spiro obtained a tetrahedral $ZnCl_4^{2-}$ species by spectral measurements on 2.88 M $ZnCl_2$ solutions in 9.35 M HCl.[11] The existence of two different geometries for the tetrakis complex under different reaction conditions suggests that the possible existence of an equilibrium both geometric forms of the complex can occur under intermediate reaction conditions.

Maciel and co-workers have utilized FT-NMR techniques using ^{67}Zn (natural abundance of 4.1%, spin $^5/_2$) to study the chloride binding to zinc at an ionic strength of 4.5.[12] They measured chemical shifts for 0.25 and 1.0 M $ZnCl_2$ in 12 M HCl and for 2.0 M $ZnCl_2$ in water, assuming all zinc species containing from zero to four chlorides were present in the solutions. The calculated differences in chemical shifts between the various zinc species were ascribed to differences in the coordination geometry and coordination numbers. Li and Popov have investigated zinc chlorides and oxysalts in water and organic solvents.[13] In organic solvents, they determined that the ^{67}Zn resonances were too broad to characterize the zinc halide systems, consistent with earlier measurements.[14] Li and Popov interpreted their Zn shift data in methanol or DMF to indicate that either organic solvent molecule has a

lower solvating ability for the zinc ion than does water.[13]

We have developed a method of applying ultrasonic absorption measurements to metal salts in aqueous organic solvents that can yield information about coordination number changes,[15,16] as well as the more common complexation kinetics. An early ultrasonic relaxation study of aqueous $ZnCl_2$ solutions in water indicated that only one relaxation is present.[17] Since the investigators expected multiple relaxations in the zinc chloride system with solvated zinc and mono, bis, tris, and tetrakis complexes postulated, they attributed the relaxation to nonchemical effects.[17] Tamura also obtained only a single relaxation for the zinc chloride system, but he attributed this relaxation to equilibrium reactions involving the addition of a third chloride to $ZnCl_2$ to form $ZnCl_3^-$, coupled to coordination number changes from 6 to 5 to 4.[18] We have modified the Tamura mechanism to exclude $ZnCl_4^{2-}$, which is absent below 1.0 M:[19]

$$ZnCl_2 \ (6) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ZnCl_3^- \ (6) \underset{k_{-7}}{\overset{k_7}{\rightleftharpoons}} ZnCl_3^- \ (4) \qquad (1)$$

The subscripts on the rate constants are those from Tamura's paper, the numbers in parentheses are the coordination numbers, and the coordination number 5 species, predicted to be present only in vanishingly small concentration, is excluded. Evidence for the octahedral–tetrahedral geometry change in aqueous Me_2SO is found in the large maximum reported for the excess absorption maxima (μ_{max}) in 0.400 M $ZnCl_2$ solutions between water mole fractions (X_w) of 0.5 and 1.[19] The same concentration of zinc nitrate solution did not have this maximum, and for this salt, no coordination number change has been postulated.[19] The kinetics of chloride complexation in Me_2SO were determined in the region of low X_w (0.039) and high X_w (0.904), with both complex formation rate constants being within experimental error of each other. Since the low X_w result is ouside the region of any structural change and the high X_w result is within the region of the structural change, this geometry change neither is influenced by the kinetics nor can be detected by kinetic measurements.

The ultrasonic experiments in one solvent system cannot determine the environment surrounding the zinc ion in the solvent region where the geometry change takes place. For example, the bound solvent may be composed of water, Me_2SO, or a combination of the two solvent molecules. Also, the bound solvent may be different for the octahedral and the tetrahedral species. Therefore, this investigation of zinc chloride complexation in aqueous DMF and aqueous methanol was initiated. Since DMF and Me_2SO are of similar molecular size, if only steric effects are important, the results should be very similar in both solvent systems. If the metal ion solvation shell is composed solely of water molecules, then we might expect the same excess absorption in the three solvent systems, with only small deviations due to the expected small differences in the association constants in the aqueous region for the three solvent systems.

Experimental Section

Materials. Reagent grade $ZnCl_2$ (Fisher Scientific) was used without further purification. The salt was dried, and all stock solutions were made by weight and volume. The concentration of Zn(II) was determined by cation exchange by passing a weighed portion of the zinc stock solution through a Dowex 50W-XB cation-exchange column and titrating the resulting acid solution with standardized base. The

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Table III. Calculated Relaxation Results for 0.400 M ZnCl$_2$ Solutions at 25 °C

X_w	$10^{17}A_{III}$, Np cm^{-1} s^2	f_{III}, MHz	$10^4\mu_{III}$, Np	$10^{17}A_{12}$, Np cm^{-1} s^2	f_{12}, MHz	$10^4\mu_{12}$, Np	$10^{17}B$,[a] Np cm^{-1} s^2	v, m s^{-1}
				Aqueous DMF				
0.0684	259.6 ± 77.8	5.76 ± 1.12	11.0 ± 5.4	6.5 ± 0.9	168.6 ± 40.8	8.1 ± 3.1	26.07	1467.6
0.193	396.8 ± 99.3	6.30 ± 1.07	18.7 ± 7.8	10.2 ± 1.5	222.0 ± 81.2	16.9 ± 8.7	23.31	1493.0
0.350	145.6 ± 8.1	11.58 ± 0.71	13.0 ± 1.5	9.7 ± 1.1	228.2 ± 61.1	17.1 ± 6.4	22.97	1536.5
0.500	212.9 ± 17.3	9.22 ± 0.58	15.6 ± 2.3				32.84 ± 0.44	1590.0
0.650	1098.1 ± 95.9	6.49 ± 0.37	58.8 ± 8.5				34.20 ± 0.84	1649.5
0.715	3641.9 ± 317.3	4.62 ± 0.23	140.5 ± 19.4				34.39 ± 0.80	1669.6
0.810	4212.3 ± 213.4	7.60 ± 0.27	268.4 ± 23.1				31.41 ± 2.76	1677.5
0.870	9933.7 ± 580.5	5.72 ± 0.21	471.6 ± 44.9				30.13 ± 3.68	1658.3
0.890	9072.5 ± 687.2	6.32 ± 0.31	471.5 ± 59.1				33.22 ± 5.77	1645.8
0.910	5233.8 ± 215.0	9.86 ± 0.36	420.5 ± 32.5				19.81 ± 9.82	1629.6
0.940	7152.5 ± 189.4	8.27 ± 0.17	472.6 ± 22.5				40.28 ± 5.27	1597.4
0.97	3310.4 ± 130.1	13.06 ± 0.52	336.1 ± 26.5				21.02 ± 9.30	1554.3
				Aqueous Methanol				
0.0047	580.8 ± 122.2	5.79 ± 0.98	18.6 ± 7.1	14.2 ± 7.1	121.4 ± 92.5	9.5 ± 12.0	30.43	1105.8
0.0477	2848. ± 1600	2.83 ± 0.89	45.6 ± 40.0				43.67 ± 3.70	1131.9
0.197	4704. ± 1149	2.71 ± 0.37	77.5 ± 29.5				47.95 ± 2.27	1213.8
0.351	8515. ± 1807	2.85 ± 0.34	158.1 ± 52.4				44.28 ± 4.33	1303.8
0.487	9388.5 ± 456.2	3.76 ± 0.13	245.9 ± 20.4				40.35 ± 8.45	1393.3
0.591	11354. ± 558	4.21 ± 0.13	350.3 ± 28.0				46.51 ± 5.12	1464.3
0.685	14486. ± 665	4.47 ± 0.13	492.2 ± 37.1				40.93 ± 7.51	1520.5
0.727	13996. ± 930	4.87 ± 0.20	524.6 ± 56.1				43.66 ± 5.58	1540.6
0.763	13024. ± 722	5.28 ± 0.20	534.3 ± 50.1				46.43 ± 13.76	1554.5
0.843	12048. ± 549	5.75 ± 0.19	543.6 ± 42.7				54.04 ± 13.89	1568.9
0.873	11504. ± 619	5.85 ± 0.23	527.5 ± 49.2				66.86 ± 17.05	1566.9
0.901	9381.1 ± 240.6	6.49 ± 0.13	475.1 ± 21.6				58.23 ± 8.78	1560.8
0.953	7147.8 ± 652.8	7.64 ± 0.60	419.7 ± 71.2				63.75 ± 38.36	1536.4
0.973	5980.8 ± 400.3	8.27 ± 0.41	376.5 ± 44.1				44.09 ± 7.54	1522.2
0.991	5121.0 ± 293.7	8.62 ± 0.39	332.5 ± 34.1				42.48 ± 7.20	1506.5
1.000	2799.8 ± 66.3	11.54 ± 0.32	241.9 ± 12.5				45.23 ± 9.07	1499.7

[a] When errors are reported, the data could only be fit by a single-relaxation procedure.

water content in the low-water mole fraction solutions was determined by Karl Fischer titrations using a Metrohm Karl Fischer automatic titrator with a calibrated electronic buret. All test solutions in the ultrasonic studies were 0.400 M in ZnCl$_2$.

Ultrasonic Equipment and Data Analysis. The ultrasonic absorption equipment and techniques are similar to those described previously.[20] For a chemical system containing one or more relaxation, the experimental sound absorption α/f^2, as a function of frequency, f, is given by

$$\alpha/f^2 = B + \sum A_i/(1 + (f/f_i)^2) \quad (2)$$

where B is the solvent absorption in the absence of chemical relaxation, A_i is the relaxation amplitude, and f_i is the relaxation frequency for each independent step. An alternate method of presenting the data is to utilize the excess absorption, μ, which is the difference in sound absorption between the test solution and the solvent, given by

$$\mu = (\alpha/f^2 - B)fc \quad (3)$$

where c is the solution sound velocity in methanol[21] or DMF.[22] For each independent relaxation, the maximum in the excess absorption curve, μ_{max}, is given by

$$\mu_{max} = A_if_ic/2 \quad (4)$$

At constant salt concentrations in solutions in which the enthalpy of complexation is small, μ_{max} is also proportional to the square of the reaction volume change. Hence, ultrasonic relaxations on constant-concentration salt solutions as a function of solvent composition act as a means to monitor reaction volume changes. If complexation is coupled to a geometry or coordination number change, this will show up as an unusual increase in μ_{max} as a function of solvent composition.

The calculations of the relaxation parameters as either a single or a double relaxation are made by using a nonlinear regression program on either an Apple II+ or IIe computer. If the calculated B value

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is significantly greater than that for the solvent in the absence of salt, it is assumed that more than one relaxation is present and the double-relaxation calculation is made.

Results

An excess absorption is present in all of the zinc chloride solutions. The experimental data are presented in the supplementary material. Figure 1 is a graph of the excess absorption for the zinc chloride solutions at water mole fractions of 0.35 and 0.87 for both solvent systems. Several observations are in order. First, as the water content increases, the μ increases in both solvent systems. Second, as water is added to the organic solvent, a change from double-relaxation to single-relaxation behavior occurs. In DMF the change is complete above X_w of 0.5, whereas in aqueous methanol it occurs at very low water mole fractions. However, in the methanol solutions, the sound absorption does not clearly decrease to the solvent background. This can be caused either by the salt changing the effective solvent background due to ion–solvent interactions or by the existence of a second high-frequency relaxation having such a small amplitude compared to the first that the computer program cannot accurately calculate the high-frequency relaxation. This difference between the two salts is clear at X_w of 0.35, where the shape and the amplitudes of the two curves are different, partially reflecting the difference between a single- and a double-relaxation system. The amplitude differences between the two solvent systems will be discussed later. At X_w of 0.87, only a small difference is observed between the two solvent systems.

The calculated relaxation parameters for both solvent systems are summarized in Table III. When the results are calculated on the basis of the assumption of a single-relaxation fit, the solvent background is reported with the calculated errors. The deviations reported in the table are those directly from the calculation. When the relaxation frequency is significantly below the lower frequency limit, the numbers should represent the precision of the calculation, and the accuracy
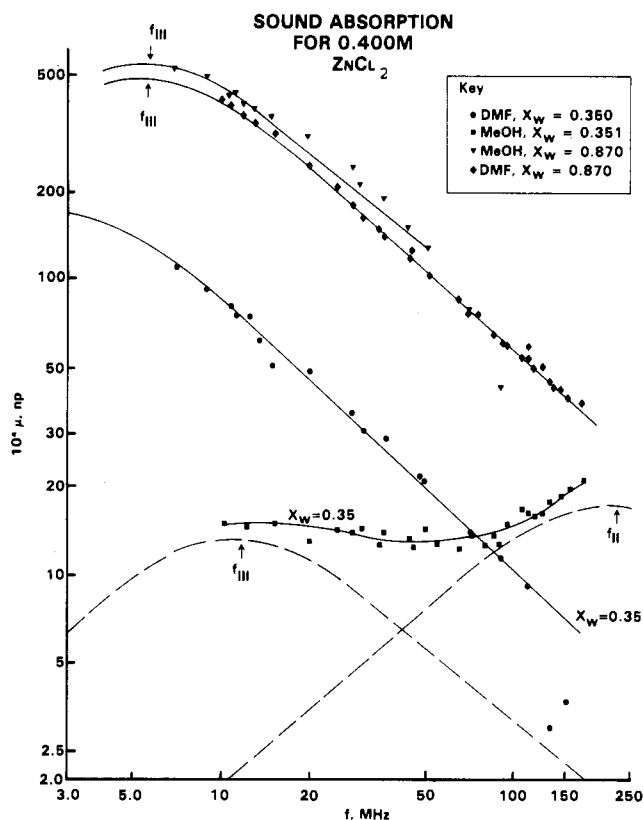
Figure 1. Excess absorption for 0.400 M $ZnCl_2$ in aqueous methanol and aqueous DMF at two water compositions.

is somewhat less. It should be noted that the calculated high-frequency relaxation errors even at the lowest X_w are large and can be interpreted to suggest that only a single relaxation is present in aqueous methanol. The relaxation parameters are reported in terms of a multistep complexation process, where the subscript 12 corresponds to outer-sphere complexes and III to inner sphere complexes, consistent with the earlier study in Me_2SO.[19] The Me_2SO results were obtained at different solvent compositions, and the results are therefore not available under the same water mole fractions.

Information about the kinetics of zinc complexation is obtained from an analysis of the variation of the relaxation frequencies as a function of solvent composition, shown in Table III. Although there is usually a small difference in f_{III} depending upon whether the results are calculated as a single- or double-relaxation system, this difference is much smaller than the variation in the calculated f_{III} as a function of X_w. The variation in μ_{III} with X_w is utilized to predict if a coordination number change occurs as a function of solvent composition, and these data are shown in Figure 2.

A measure of the data reproducibility can be obtained by comparing the ultrasonic relaxation results on 0.400 M $ZnCl_2$ at 25 °C in water from this study with similar measurements made from a different stock solution and with older ultrasonic absorption equipment, a different temperature bath, and a different experimenter several years ago. The earlier results for 0.400 M $ZnCl_2$ in water at 25 °C are[19] $A_{III} = (2626 \pm 86) \times 10^{-17}$ np cm⁻¹ s², $f_{III} = 11.74 \pm 0.43$ MHz, $\mu_{III} = (230.7 \pm 16.0) \times 10^{-4}$ np, and $B = (41.8 \pm 10.8) \times 10^{-17}$ np cm⁻¹ s². Except for the relaxation amplitude, these results are all within experimental effor of the values reported in Table III, and the difference in relaxation amplitude is less than 1% between the results.

Discussion

In water, the single relaxation observed is attributed to the formation of inner-sphere complexes for reaction 1.[18,19] Under
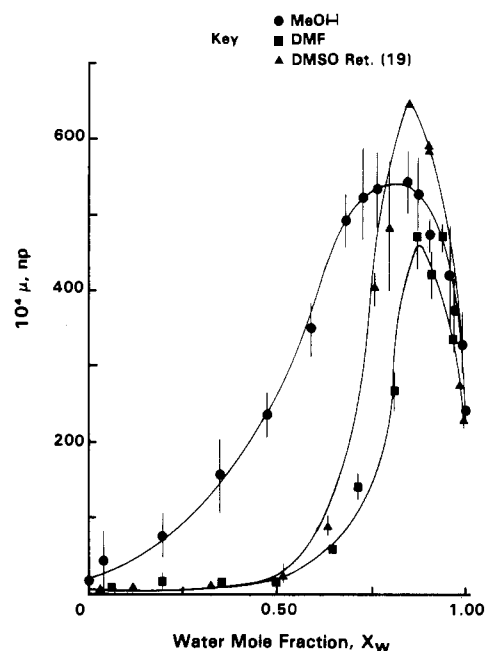

Figure 2. Excess absorption maxima for 0.400 M $ZnCl_2$ in aqueous organic solvents.

the reaction conditions where outer-sphere complexes become stable, the major reaction under investigation is

$$ZnCl_2S_x + Cl^- \xrightleftharpoons{\text{step 12}} ZnCl_2S_yCl^- \xrightleftharpoons{\text{step III}} ZnCl_3^-S_z \quad (5)$$

The high-frequency relaxation is identified with step 12, which actually involves two individual steps of the Eigen multistep complexation mechanism.[23,24] In a diffusion-controlled process the third chloride ion forms a solvent-separated outer-sphere complex with the bis species. This is followed by loss of bound solvent on the anion to form a second solvent-separated outer-sphere ion pair. In step III, solvent is lost from the inner sphere of the cation, followed by rapid bond formation between the chloride and the bis complex to form the inner-sphere tris complex. In transition-metal ions for the formation of the 1:1 complex, the slow step in the process is usually the loss of solvent from the metal ion coordination shell. In aqueous Me_2SO at both high and low water mole fractions, the slow step in the formation of the tris complex was predicted to be the rate of solvent exchange, and the measured complexation rate constant was within experimental error of the Zn(II)–water solvent-exchange rate.[19] The similarity in f_{III} for $ZnCl_2$ as a function of X_w suggests that the same mechanism holds in aqueous methanol, DMF, and Me_2SO. In aqueous Me_2SO, the kinetics of chloride complexation were independent of concentration and the same result is expected in aqueous methanol and DMF. Under the same reaction conditions, zinc nitrate has both a concentration-dependent complexation rate and relaxation frequencies significantly higher than those observed for the corresponding chloride.

The amplitude of μ_{III} in the region of low water mole fractions in all three solvent systems is very low. There are several possible explanations for this effect, some of which can be eliminated. Since μ_{III} is proportional to the concentration of ion pairs, one explanation is that the association constants are small at low X_w. This neither is the expected behavior nor is true. In methanol, β_2 equals 1.35×10^8,[8] whereas in Me_2SO β_2 is 1.45×10^6.[7] K_3 in both solvents is virtually identical, being 400 in methanol[8] and 398 in Me_2SO.[7] In water, where the sound absorption is very high, the overall association

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constant for the addition of three chlorides (β_3) is approximately unity.[4] Not only is this difference in association constants very large, but also the experimental sound absorption appears to be opposite in behavior to that expected on the basis of the magnitude of the association constants. Further confirmation that the effect is independent of the magnitude of the equilibrium constants comes from an analysis of the corresponding zinc nitrate data. The association constant for zinc nitrate was too low to be detected by our potentiometric technique in Me_2SO,[19] but the sound absorption in Me_2SO was greater than for the same concentration of chloride salt. A better explanation comes from examining reaction 5 in anhydrous media. This reaction adds a chloride ion to a neutral complex to form a charged monovalent anion. Although the association constant for this process is of the order of 400 in methanol and Me_2SO, it is at least a factor of 400 less than that observed for the formation of the neutral species. We believe that the resulting complex may be stable only because the ion–solvent interactions are similar for both the chloride and the resulting tris complex, so that the effective volume change on going from reactants to products becomes very small. Thus, if this is the case, the excess absorption, which is proportional to the square of the reaction volume change, would be extremely small in anhydrous solvents, as is observed in all three systems. Therefore, in the absence of any structural change for zinc chloride solutions, the ultrasonic absorption is of low amplitude.

Examination of Figure 2 demonstrates that the behavior of $ZnCl_2$ in aqueous methanol is different from that in aqueous Me_2SO or DMF. In the latter two solvent mixtures, μ_{III} is small below X_w of 0.5 and increases rapidly until approximately X_w of 0.9. In aqueous Me_2SO this abnormal increase in μ_{III} was attributed to an octahedral–tetrahedral equilibrium, which has also been detected in aqueous Me_2SO by other techniques.[5,10,18,19] The similarity in excess absorption at high X_w suggests that the same process occurs in the water-rich region in both DMF and Me_2SO. One possible explanation for the amplitude difference is that the association constants at high X_w vary significantly in the two solvent systems, even though the solvation shell contains only water and chloride ions. An alternate explanation assumes that even at high X_w there is preferential solvation by the organic molecule over water for the bis complex, resulting in the net loss of three organic molecules to form the tetrahedral tris complex. If the inner solvation shell contains DMF or Me_2SO molecules, respectively, then the volume change should be proportional to the partial molar volumes of the organic molecules. In the pure organic solvents, these volumes can be calculated from the molecular weights and the densities alone. The approximate values are 71 mL/mol for Me_2SO, 77 mL/mol for DMF, and 40 mL/mol for methanol. We have measured the partial molar volumes for DMF in the presence of water from 0 to 100% DMF.[25] For X_w between 0.8 and 1, the partial molar volume of DMF decreases from about 74 to 73 mL/mol, a result that is higher than that even of pure Me_2SO. Since μ_{III} is greater in Me_2SO, the experimental observations are opposite to the assumption that there are significant quantities of the organic molecules in the inner coordination or solvation shell. Thus, we conclude that only water is present in the inner solvation shell of the bis and tris complexes above X_w of 0.5.

The association constants for zinc chloride complexation at high X_w were too small to detect by our potentiometric tech-

nique. Although some difference is expected for the association constants due to dielectric constant differences, the dielectric constant in Me_2SO is greater than that in DMF and, hence, we would not predict the larger amplitude in aqueous Me_2SO on the basis of simple dielectric arguments. Thus, although the organic molecules are not present in the inner coordination shell, we believe the amplitude effect is due to interactions between the solvated complexes and the bulk solvents, which are different in the two media.

The methanol results are clearly different from those of the other two solvent systems below X_w of 0.5. Even in the region of low water content, the amplitude of the sound absorption is higher than in the other two systems. The dielectric constants are different in the three anhydrous solvents, being 32.6 in methanol, 36.7 in DMF, and 46.6 in Me_2SO, and as water is added, all three systems increase their dielectric constants. If the effect is simply due to the effect of dielectric constant variations on the association constant, then the excess absorption in aqueous methanol should be higher than in DMF and both should be higher than in Me_2SO. Analysis of Figure 2 demonstrates that, within experimental error, the results are the same for DMF and Me_2SO below X_w of 0.5. Although β_2 is about a factor of 100 greater in methanol than Me_2SO, K_3 is the same in both solvents. In addition, the zinc nitrate results in aqueous Me_2SO demonstrated that even though the chloride had an association constant 10^8 bigger than that of the nitrate, the nitrate μ_{III} was greater. Hence, we believe another explanation is required for the higher amplitude in aqueous methanol. Since both methanol and DMF have been reported to have a lower solvating ability for zinc than does water,[13] it is likely that even at low X_w there is some water present in the inner coordination shell of the zinc ion. Since steric hindrance is responsible for the coordination number change, the chloride ions are closer together in a solvation shell composed of the smaller water and methanol molecules than they are with water and either Me_2SO or DMF. Thus, chloride–chloride repulsions become more significant at lower water mole fractions in aqueous methanol, thereby triggering the geometry change at lower water mole fractions. Figure 2 suggests that the octahedral to tetrahedral coordination change occurs throughout the aqueous methanol solvent range and may actually exist even in anhydrous methanol, a feature absent in both Me_2SO and DMF.

In summary, our ultrasonic absorption results on $ZnCl_2$ in aqueous organic solvents have demonstrated the ability of the ultrasonic relaxation technique to detect geometry changes in zinc systems. Possible future applications of these techniques will be to apply them to studies of zinc-containing enzymes in the presence of physiological concentrations of chloride in order to determine whether a geometry change occurs at the zinc site during the enzyme action.

Registry No. Zn^{2+}, 23713-49-7; Cl^-, 16887-00-6; DMF, 68-12-2; MeOH, 67-56-1; $ZnCl_2$, 7646-85-7.

Supplementary Material Available: Tables I and II of ultrasonic relaxation data (2 pages). Ordering information is given on any current masthead page.

(25) Cervantes, R. A.; Silber, H. B., unpublished results.