Diamagnetic *cis*-$(Co(Meen)_2CO_3)_2CO_3$ has been prepared by the reaction of aquated $(Co(Meen)_2Cl_2)_2CoCl_4$ with Ag_2CO_3 and isolated by the evaporation of the aqueous solution resulting, after filtration to remove AgCl and $CoCO_3$. Reaction of methanolic HCl with the carbonate produces a purple solution which slowly changes to green on standing overnight.

Although it appears that *cis*-$Co(Meen)_2Cl_2^+$ has been prepared in solution, as evidenced by the purple color, it has not been isolated free from both *trans*-$Co(Meen)_2Cl_2^+$ and *cis*-$Co(Meen)_2CO_3^+$. A half-time of about 8 hr at room temperature (about 23°), estimated by visible spectrophotometry, for the *cis–trans* isomerization of $Co(Meen)_2Cl_2^+$ in methanol is comparable with the time for the same type of isomerization of $Co(en)_2Cl_2^+$ or $Co(pn)_2Cl_2^+$, as reported by Brasted and Hirayama.[18]

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CONTRIBUTION FROM THE CHEMISTRY DIVISION,
ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS 60439

Contact Shifts of Acetonitrile Solutions of Cupric Chloride and Titanium Trichloride

BY C. C. HINCKLEY[1]

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In solutions of solvated paramagnetic metal ions in which there is a chemical exchange of coordinated solvent molecules and bulk solvent, nuclear magnetic resonance absorptions of the solvent protons are shifted from the magnetic field values observed for the pure solvent.[2,3] Contact interactions between the ligand and metal ion in the solvation complexes are the principal contributors to the resonance shift for solutions of first-row transition metal ions.[4] When chemical exchange is rapid and the resonance absorptions of complexed and bulk protons are averaged, the observed shift, $\Delta\omega$, is related to the hyperfine coupling constant, A, in the paramagnetic molecule by

$$\frac{\Delta\omega}{\omega} = -\frac{\gamma_e}{\gamma_N}\frac{g\beta S(S+1)}{6kTS}CA \qquad (1)$$

where ω is the resonance frequency, C is the concentration of complexed ligand protons, g is the g factor of the metal complex, and the remaining symbols have the usual significance. The temperature dependence is $1/T$ in this case. If the resonances of complexed and bulk protons are not completely averaged, *i.e.*, if chemical exchange is slow,[5] the temperature dependence is not straightforward, but, in general, the resonance will shift toward the average as the temperature is increased. In either case, a positive hyperfine constant results in a downfield shift of the nmr absorption relative to the pure solvent, and a negative constant yields an upfield shift. Both the sign and magnitude of the shifts depend upon the detailed mechanism of spin density transfer in the paramagnetic molecule. It is the transfer of positive or negative spin density to a nucleus that results in a positive or negative hyperfine coupling with that nucleus.[6] The transfer process may be considered in two parts: first, the transfer of unpaired spin density from metal to ligand, and, second, the distribution of unpaired spin throughout the ligand molecules. Eaton, Phillips, and co-workers[7,8] and others[9,10] have shown that the free-radical formalism developed by McConnell[11] and others[12] may be successfully applied to the second factor. This note is concerned with the first, specifically, the comparison of hyperfine coupling constants in acetonitrile–metal complexes in which the initial metal–ligand spin density transfer involves σ- or π-antibonding electrons.

Proton magnetic resonance contact shifts were measured as a function of temperature for copper(II) chloride and titanium(III) chloride solutions in acetonitrile. Both metal ions have single unpaired electrons, but in complexes of copper(II), a d^9 ion, unpaired spin transfer should be predominantly through σ-antibonding orbitals. Spin transfer in complexes of titanium(III), a d^1 ion, should be predominantly through π-antibonding orbitals. Acetonitrile coordinates through the nitrile group for which both σ and π bonding may be expected.

Experimental Section

Materials and Solutions.—Acetonitrile purified by the method of O'Donnell, Ayres, and Mann[13] was used throughout. The cupric chloride solution (0.02 *M*) was prepared by adding acetonitrile to a weighed amount of the anhydrous salt in a volumetric flask. The titanium trichloride solution (0.01 *M*) was prepared under a nitrogen atmosphere with previously degassed solvent. The concentration of the titanium in solution was checked by adding 1-ml aliquots to ceric nitrate solution and back titrating with ferrous ammonium sulfate.

Nmr Measurements.—Proton magnetic resonance spectra were obtained with a Varian A-60 nmr spectrometer. Temperatures were controlled to ±1° by a Varian variable-temperature unit. A minimum of six spectra were taken at each

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[1] Department of Chemistry, Southern Illinois University, Carbondale, Ill. 62901

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temperature, and the shifts were averaged. Chemical shifts were measured by the usual side-band technique. Hexamethyldisilane was used as an internal standard. Reported contact shifts (Figure 1) are differences between the measured chemical shifts of the solutions and pure acetonitrile.

Epr Measurements.—Electron paramagnetic resonance spectra of the $CuCl_2$ solutions were obtained with a Varian 4502 epr spectrometer. Resonances were observed at room temperature and below. The average g value is 2.1570. No epr spectrum was observed for the $TiCl_3$ solutions.

Results and Discussion

Observed contact shifts for $CuCl_2$ solutions in acetonitrile are upfield (Figure 1) indicating a negative hyperfine coupling constant and thus a negative spin density at the proton nuclei. Negative coupling constants are also observed for solutions of nickel(II) and cobalt(II) perchlorate in acetonitrile.[14,15] The initial transfer of spin density from metal to ligand is positive.[16] A spin-transfer mechanism to explain the negative spin density observed in the nickel and cobalt complexes was proposed by Matwiyoff and Hooker[14] and is applied here to the copper solution data. The first of three steps is the transfer of positive spin density from metal to ligand through a σ bond to the acetonitrile nitrogen. Spin is then transferred to the nitrile carbon by σ–π configuration interaction with an accompanying change in sign. The final step is a transfer by hyperconjugation[17] of this negative spin density to the methyl protons.

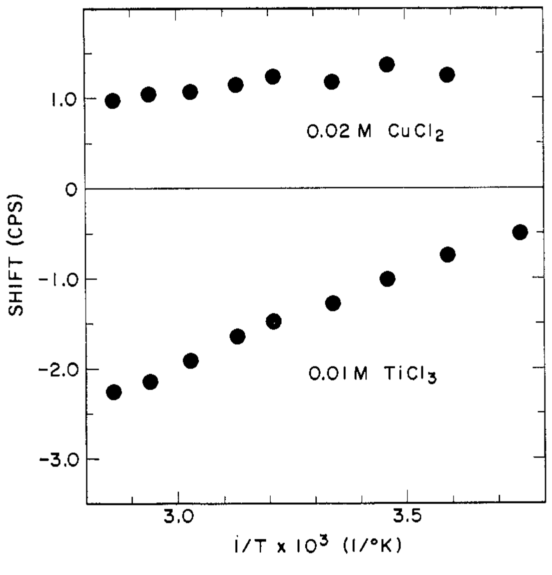

Figure 1.—Proton contact shifts of 0.02 *M* $CuCl_2$ and 0.01 *M* $TiCl_3$ solutions in acetonitrile plotted as a function of reciprocal temperature.

In complexes of octahedral symmetry, the unpaired electron of Ti(III) will be in a T_{2g} orbital suitable for π bonding with ligands.[18] Substituted complexes will have lower symmetry than O_h, but the unpaired electron will still be in a π molecular orbital. Transfer of unpaired spin from the titanium ion to the ligand molecules will be principally through the π system. Thus, initial transfer of spin density from Ti(III) to complexed acetonitrile molecules will place positive spin at the nitrile carbon. Transfer by hyperconjugation places positive spin at the proton nuclei. This π-transfer process is also important in cobalt(II)–acetonitrile complexes.[14]

Measured contact shifts for a solution of $TiCl_3$ in acetonitrile are plotted in Figure 1 as a function of temperature. Downfield shifts indicate a positive spin density at the proton nuclei.

Comparison of the data from the copper and titanium solutions may be made on two levels. First, the signs of the hyperfine coupling constants are clearly different, indicating that the constants are dependent upon the specific metal to ligand spin density transfer process. Second, the magnitudes of the shifts suggest that the spin transfer process in the titanium complex is more effective.

The hyperfine coupling constant of the copper complex may be estimated by the use of eq 1. Manahan and Iwamoto[19] studied copper(II) chloride complexes in acetonitrile and obtained the formation constants for the various chloro-substituted complexes. Their results require that the average species in solution is the dichloro complex. No $Cu(NCCH_3)_4^{2+}$ is expected. The hyperfine coupling constant calculated on the basis of two exchanging acetonitrile molecules per complex is −550 cps.

Acetonitrile solutions of $TiCl_3$ have not been previously studied, and the complexes in solution are not known. The temperature dependence of the measured contact shifts for the $TiCl_3$ solution does not follow eq 1. The magnitude of the shift increases as temperature increases. Kluiber and Horrocks[20] have observed similar temperature dependence in measured shifts of picoline N-oxide coordinated with bis(1,1,1-trifluoro-2,4-pentanedionato)copper(II) which were attributed to temperature-dependent equilibria. A likely possibility for the titanium solutions studied here is slow chemical exchange. In this instance the resonance absorptions of solvent and complexed acetonitrile are separate. As the temperature increases, chemical exchange becomes more rapid and the solvent resonance shifts downfield toward the average of the two absorptions.

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