$$V(acac)_3 + e^- \rightarrow V(acac)_3^-$$

$$V(acac)_3^- + Hacac \rightarrow V(acac)_3 + Hacac^-$$

The final products are $V(acac)_3^-$ and reduced ligand, as observed in our work.

The apparent reduction of $VO(acac)_2$ at -1.55 V cannot be explained from the present data. The complexity of the V^V solution precludes a clear interpretation of the $V^V + e^- \rightarrow VO(acac)_2$ process. Thus, current work involves attempts to synthesize and study several V^V species directly. New data from these studies should help clarify the nature of the V^V species and its reactions.

Conclusions

A comparison of the oxidation–reduction behavior of analogous vanadium(III) compounds in aprotic solvents shows a distinct similarity. $V(acac)_3$, VQ_3 ($Q^- = 8$ hydroxyquinoline anion), and $V(dtc)_3$ ($dtc^- = $ diethyldithiocarbamate anion) each exhibit reversible one-electron reductions between -1.0 and -1.5 V. These compounds also show oxidations between $+0.25$ and $+1.0$ V. The oxidations of $V(acac)_3$ and VQ_3 are reversible only on the cyclic voltammetry time frame, while the reversibility of $V(dtc)_3$ depends on concentration. Only $V(acac)_3$ undergoes a further oxidation to vanadium(V).

The vanadium(IV) species show few similarities to one another. Although $VO(dtc)_2$ and $VO(acac)_2$ are irreversibly reduced, no distinct reduction wave for VOQ_2 is observed. Only $VO(acac)_2$ shows a reversible oxidation ($+0.81$ V). VOQ_2 is oxidized at a similar potential ($+0.775$ V), but the process is irreversible. No oxidation of $VO(dtc)_2$ is observed.

It is clear that the type of bonding atoms and the ring size (metal to bidentate ligand) are not of great significance for $V^{III}L_3$ (L = bidentate ligand) compounds. In contrast, these factors appear to strongly influence the electrochemistry of $V^{IV}OL_2$ complexes. Comparisons of V^V complexes should be possible with data from our next study.

Registry No. $V(acac)_3$, 13476-99-8; $VO(acac)_2$, 3153-26-2.

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Conformational Equilibria in Pyridine Adducts of Fluorinated Metal Acetylacetonates

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We have used NMR spectroscopy to study $Ni(HFAA)_2$ and $Co(HFAA)_2$ (HFAA = hexafluoroacetylacetonate) in the presence of varying pyridine concentrations over a range of temperatures. Complexes with both 1 mol (1:1 complexes) and 2 mol (1:2 complexes) of pyridine coordinated to the metal atom were observed. In the case of the cobalt complex both cis and trans isomers of the 1:1 and 1:2 complexes were detected. At room temperatures the various isomers are in rapid equilibrium, and the ^{19}F NMR lines are exchange averaged. At lower temperatures the rate of exchange is slowed, and well-resolved NMR spectra are observed from all of the possible isomers. In acetone solutions the cis isomer is favored over the trans isomer in both the 1:1 and 1:2 complexes. The NMR shift of the signal from the nickel complex is mainly due to the Fermi contact interaction while the shifts of lines from the various cobalt complexes are due to both the electron–fluorine dipolar interaction and the Fermi contact interaction.

Introduction

The isotropic NMR shifts observed from cobalt complexes in solution may receive contributions from both Fermi contact and dipolar interactions.[1] The dipolar shifts arise because of anisotropy in the magnetic susceptibility which is not averaged by molecular reorientation. The equations describing the Fermi contact $(\Delta\nu/\nu_0)_F$ and dipolar $(\Delta\nu/\nu_0)_D$ contributions to the total isotropic shift may be written as eq 1. In this

$$(\Delta\nu/\nu_0)_F = -A\left(\frac{\gamma_e}{\gamma_N}\right)\frac{g\beta S(S+1)}{3kT}$$

$$(\Delta\nu/\nu_0)_D = -\frac{1}{3N}\left[\chi_z - \frac{\chi_x}{2} - \frac{\chi_y}{2}\right]G(\theta,r) - \frac{1}{2N}[\chi_x - \chi_y]G'(\theta,\Omega,r)$$

$$G(\theta,r) = \langle(3\cos^2\theta - 1)/r^3\rangle_{av}$$

$$G'(\theta,\Omega,r) = \langle(\sin^2\theta\cos 2\Omega)/r^3\rangle_{av} \qquad (1)$$

expression A is the Fermi contact coupling constant, the χ's are the principal components of the magnetic susceptibility,

and r is the electron–nucleus separation, while θ and Ω determine the angles between the electron-nucleus vector and the components of the susceptibility. The dipolar term is seen to depend on the magnitude of the magnetic anisotropy, the separation of the nucleus from the metal, and the relative geometry of a given nucleus with respect to the magnetic axes. The Fermi contact term depends on the mechanism for spin delocalization from the metal into a given ligand and the spin distribution in the ligand. Octahedral cobalt(II) complexes have a T_1 ground state which is split into A and E states in the presence of tetragonal distortion. The A state is the ground state and is separated from the E state by the tetragonal distortion energy. In the case of 1:1 complexes of $Co(HFFA)_2$ with pyridine one predicts a tetragonally distorted complex with changes in the components of the magnetic susceptibility. The various cis and trans isomers which are possible may also have different symmetries with different values for the components of the susceptibilities. These changes in symmetries and susceptibilities will produce variations in the dipolar shifts.

Proton and ^{13}C NMR have been used to investigate a number of base adducts of acetylacetonate (AA) complexes. Happe and Ward[2] studied pyridine adducts of cobalt(II) and nickel(II) AA complexes and attempted to separate the relative

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contributions of the dipolar and Fermi contact terms for the pyridine protons assuming geometric factors[3] for an axially symmetric trans 2:1 complex. A ^{13}C NMR study has been conducted[4] and the carbon shifts of nuclei in the pyridine ring have been analyzed on the assumption that the dipolar contribution was small. Studies of the effect of the coordinated base on the shifts of signals from the metyl and methylene protons in $Ni(AA)_2$ and $Co(AA)_2$ have been conducted.[5] A study of changes in shifts in mixed-ligand complexes has also been carried out.[6] Crystal structures of both $Ni(AA)_2(py)_2$[7] and $Co(AA)_2(py)_2$[8] have been determined. In an elegant study conducted to separate the dipolar and Fermi contact contributions to the isotropic shifts, Horrocks[9] has measured the principal components of the magnetic susceptibility of a single crystal of *trans*-$Co(AA)_2(py)_2$ and used these data along with crystal structure data to calculate the shifts. This study showed that the trans isomer does not have axial symmetry and that both the dipolar and Fermi contact shifts are negative. It assumed that the solution NMR spectra could be analyzed in terms of only the trans 1:2 complex.

We have conducted ^{19}F NMR experiments of $Ni(HFAA)_2$ and $Co(HFAA)_2$ with varying mole percentages of pyridine to determine if one can observe NMR signals from species other than the trans 1:2 complex. In principle, one should be able to observe signals from five distinct species if they are present in solution and the NMR shift differences are greater than the line widths. These species include free $M(HFAA)_2$ with weakly associated solvents, cis and trans 1:1 complexes, and cis and trans 1:2 complexes. NMR signals from all of these species are observed at low temperatures where interconversion of the various complexes is slow on the NMR time scale. At higher temperature, the complexes are found to be in rapid equilibrium and the lines are exchange averaged.

Experimental Section

$Co(HFAA)_2$ and $Ni(HFAA)_2$ were purchased from Pierce Chemical Co. and recrystallized from chloroform before use. The NMR spectra were taken with a pulsed-Fourier transform spectrometer which has previously been described.[10] The magnet of this spectrometer has an inhomogeneity of about 120 Hz which defined the minimum line width which could be observed. The ^{19}F spectra were taken at 94 MHz with acetone as the solvent over the temperature interval from 297 to 192 K. The temperature was monitored with a copper–constantan thermocouple. A small amount of hexafluorobenzene was added to the samples and used as an internal reference for the shifts. The shifts reported are referenced to $Zn(HFAA)_2$.

Results and Discussion

The metal complexes can exist with the solvent acetone weakly associated to open coordination sites,[11] with a single pyridine coordinated (1:1 complexes) or with two pyridine molecules coordinated (1:2 complexes). The 1:1 and 1:2 complexes can exist as either cis or trans isomers. Consideration of the geometry of the possible isomers indicates that the four trifluoromethyl groups in the cis 1:1 complex should be magnetically nonequivalent while all of these groups should be equivalent in the trans 1:1 complex. Figure 1 shows a schematic structural representation of the various complexes
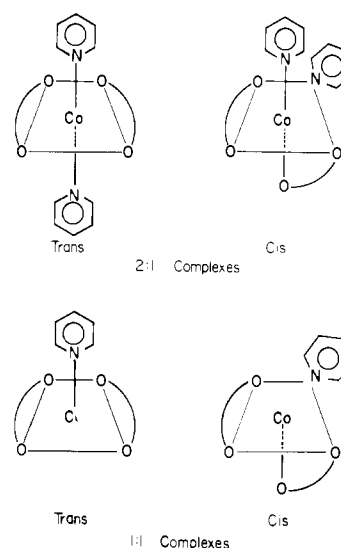

Figure 1. Schematic structural representation of cis and trans complexes. The 1:1 complexes are shown to be five-coordinate but may have solvent in the sixth coordination site.
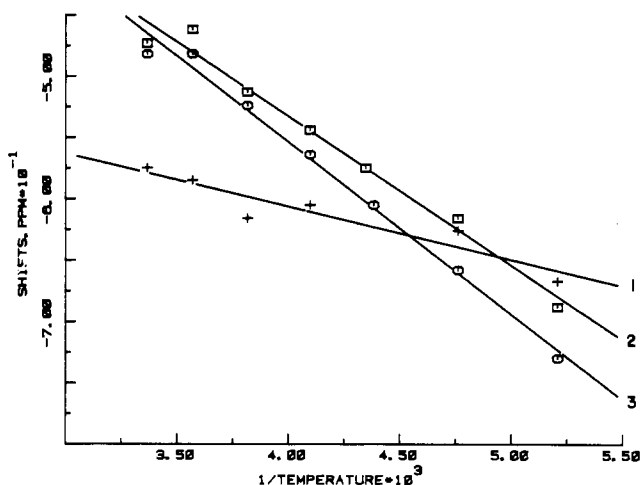

Figure 2. Plots of shift vs. the reciprocal of temperature for (1) $Co(HFAA)_2$ in acetone, (2) $Ni(HFAA)_2$ in acetone, and (3) $Ni(HFAA)_2(py)_2$ in acetone.

which are possible. The cis 1:2 complex should have two sets of nonequivalent trifluoromethyl groups while all of these groups should be magnetically equivalent in the trans 1:2 complex. The free complex with weakly associated acetone ligands should also have equivalent trifluoromethyl groups if the geometry of the metal complex is unperturbed by solvent association.

Both $Co(HFAA)_2$ and $Ni(HFAA)_2$ showed single ^{19}F resonances with acetone as the solvent at room temperature. The line from the nickel complex shifted linearly with the reciprocal of temperature in the temperature interval between 297 and 192 K (Figure 2). The line from $Co(HFAA)_2$ also shifted linearly with the reciprocal of temperature, but two smaller satellite lines were observed at temperatures below about 244 K.

Complexes of this type are known to associate into clusters[12] although the complexes with fluorinated ligands have less of a tendency to associate than the protonated analogues.[13] Apparently at very low temperatures $Co(HFAA)_2$ is partially

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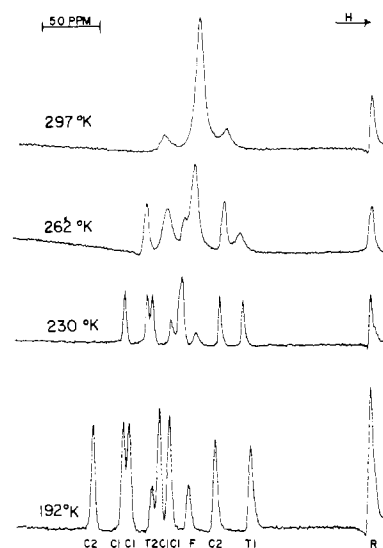(13) D. A. Buckingham, R. C. Gorges, and J. T. Henry, *Aust. J. Chem.*, **20**, 281 (1967).

Table I. Slopes and Intercepts of Least-Squares Fits of Plots of Shifts vs. the Reciprocal of Temperature

compd	slope, ppm K^{-1}	intercept, ppm
Ni(HFAA)$_2$(acetone)	-1.21×10^4	-4.8
Ni(HFAA)$_2$(py)$_2$	-1.40×10^4	0.7
cis-Co(HFAA)$_2$(py)	-2.49×10^4	7.3
cis-Co(HFAA)$_2$(py)	-2.33×10^4	3.6
cis-Co(HFAA)$_2$(py)	-1.46×10^4	-15.4
cis-Co(HFAA)$_2$(py)	-1.46×10^4	-7.45
trans-Co(HFAA)$_2$(py)	7.11×10^3	-51
cis-Co(HFAA)$_2$(py)$_2$	-3.23×10^4	20
cis-Co(HFAA)$_2$(py)$_2$	-5.20×10^3	17
trans-Co(HFAA)$_2$(py)$_2$	-1.95×10^4	4
free Co(HFAA)$_2$	-7.5×10^3	-27
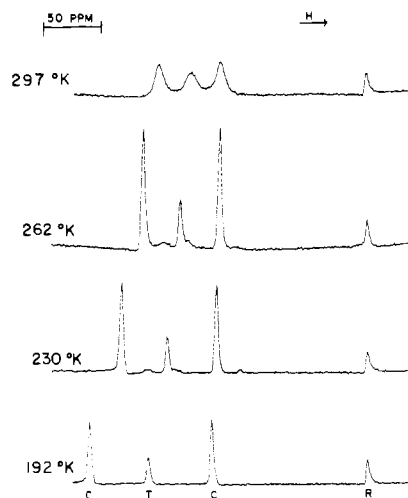
Figure 3. NMR spectra of Co(HFAA)$_2$(py)$_2$ as a function of temperature in acetone. C's are the lines from cis complex, T is the line from trans complex, and R is the line from the hexafluorobenzene reference.

Figure 4. NMR spectra of Co(HFAA)$_2$ with 1 mole equiv of pyridine in acetone as a function of temperature. C1's are the lines from the cis 1:1 complex, T1 is the line from the trans 1:1 complex, F is the line from the free complex, C2's are the lines from the cis 1:2 complex, T2 is the line from the trans 1:2 complex, and R is the line from the hexafluorobenzene reference.

associated and the satellite lines are from clusters of this complex. When 2 mole equiv of pyridine is added to an acetone solution of Ni(HFAA)$_2$, one still observes a single NMR line over the temperature range studied (Figure 2). There is a small shift between the signal from the pyridine complex and that from the free complex. The slopes and intercepts from the temperature dependence plots are given in Table I. The shifts from the nickel complexes are mainly due to the Fermi contact interaction, and if different geometric isomers are present, the difference in the dipolar interaction for various isomers is not large enough to allow one to resolve separate lines. The small change in shift between the nickel complex and the pyridine-substituted complex is expected because of changes in occupancy of the coordination sphere of the complex.[5]

When 2 mole equiv of pyridine is added to an acetone solution of Co(HFAA)$_2$, one observes three broad overlapped lines at room temperature (Figure 3). As the temperature is lowered, the lines sharpen and shift with respect to one another and with respect to the reference signal. Two of the signals are of equal intensity and are assigned to the two types of nonequivalent trifluoromethyl groups predicted for the cis isomer of Co(HFAA)$_2$(py)$_2$. The third signal is assigned to the equivalent trifluoromethyl groups in the trans 1:2 complex. Only signals from the 1:2 complex are observed, indicating a large equilibrium constant for formation of this complex. At higher temperatures (ca. 297 K) interconversion of the cis and trans isomers is relatively rapid on the NMR time scale, and the lines are broadened and overlapped. As the temperature is lowered, the interconversion process becomes slower while the shifts between the lines become large, and well-re-

solved spectra are observed. The cis isomer of the 1:2 complex is favored over the trans isomer in acetone solution which is in contrast to the formation of only the trans isomer in crystalline solids of Co(AA)$_2$(py)$_2$ and the assumption of only trans isomer for the analysis of previously reported NMR spectra.[9] One can measure the equilibrium constant between the cis and trans isomers by determining the relative areas of the NMR signals. For the process trans 1:2 $\rightleftarrows$ cis 1:2, the equilibrium constant is 4.8 ± 0.2 and independent of temperature within experimental error. The temperature independence of this equilibrium indicates that the enthalpy difference between the two isomers is close to zero and that the cis isomer is favored over the trans isomer because of entropy differences. Our measurements indicate that the cis isomer is favored by 3.1 ± 0.1 eu over the trans isomer.

When 1 mole equiv of pyridine is added to an acetone solution of Co(HFAA)$_2$, one observes one relatively broad NMR signal with two broad weak satellite lines at room temperature. As the temperature is lowered, the lines sharpen and shift until nine different signals are observed (Figure 4). These nine lines include signals at the positions of the lines previously assigned to the 1:2 complex and a signal from free Co-(HFAA)$_2$. The additional five lines arise from 1:1 complexes. Four of these lines have the same intensity and are assigned to the four nonequivalent trifluoromethyl groups of the cis 1:1 complex. The remaining line is assigned to the trans 1:1 complex. It was impossible to measure the relative areas of the signals from the 1:1 cis and trans isomers over the entire temperature range because of overlap of the signals, but in the interval from 230 to 192 K the total intensity of signals from the cis isomer was about 5 times larger than that from the trans isomer. The equilibrium between isomers for the 1:1 complex appears to be similar to that for the 1:2 complex with the cis isomer favored over the trans isomer. At higher temperatures the cis and trans isomers of both the 1:1 and 1:2 complexes interconvert rapidly on the NMR time scale and averaged signals are observed. Broad satellite lines from the cis 1:2 complex are observed at room temperature while all of the other signals are averaged into a single line. The interconversion process slows, and the shifts increase at lower temperature to produce the well-resolved nine-line spectrum observed at 192 K.
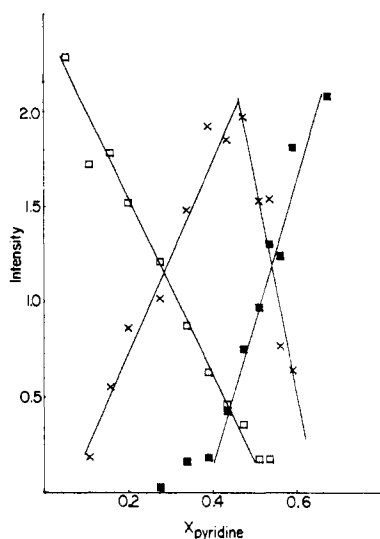
Figure 5. Plot of signal intensity vs. pyridine mole fraction. □ is the free complex, × is the 1:1 complex, and ■ is the 1:2 complex.

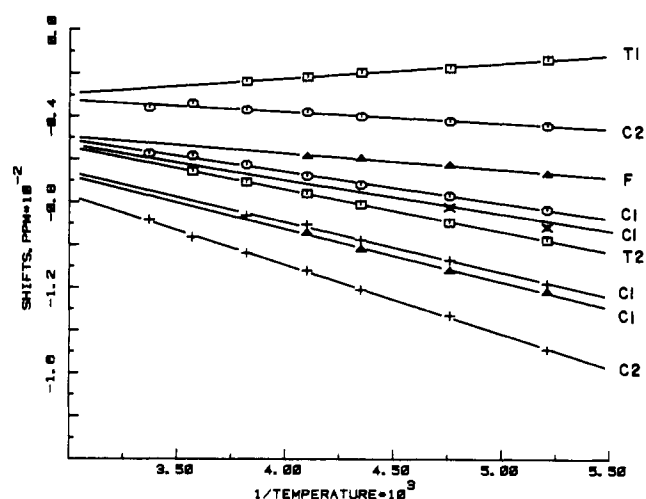**Figure 6.** Plot of shifts of NMR lines from Co(HFAA)₂ with 1 mole equiv of pyridine in acetone as a function of the reciprocal of temperature. C1's are the lines from the cis 1:1 complex, T1 is the line from the trans 1:1 complex, F is the line from the free complex, C2's are the lines from the cis 1:2 complex, and T2 is the line from the trans 1:2 complex.

A titration of $Co(HFAA)_2$ with pyridine was carried out at 189 K to substantiate the assignment of the NMR signals and to obtain information about the formation constants of the complexes. At low concentrations of pyridine NMR signals were observed from only the free complex and the 1:1 complex. As the pyridine concentration was raised, the signal from the free complex decreased while the intensity of the signal from the 1:1 complex increased. At a pyridine mole fraction of about 0.3, signals from the 1:2 complex appeared in the spectrum. Above a pyridine mole fraction of about 0.5 the signal from the free complex was lost in the base line. The signals from the 1:1 complexes decreased until they were lost while the signals from the 1:2 complexes increased and finally were the only lines observed in the spectrum. A plot of signal intensity from the various complexes vs. mole fraction of pyridine is given in Figure 5. These data indicate stepwise equilibria for formation of the 1:1 and 1:2 complexes (eq 2 and 3). The data were not precise enough to accurately

$$Co(HFAA)_2 + py \rightleftharpoons Co(HFAA)_2py \qquad (2)$$

$$Co(HFAA)_2py + py \rightleftharpoons Co(HFAA)_2(py)_2 \qquad (3)$$
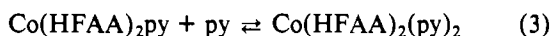
measure equilibrium constants but indicate that both formation constants are large.

The lines from the cis and trans 1:1 and 1:2 complexes shifted linearly with the reciprocal of temperature (Figure 6). The slopes and intercepts of least-squares fits of these plots are given in Table I. The shifts from the trifluoromethyl groups in the various cobalt and nickel complexes are all negative (low field). The ^{19}F shift observed from Ni-$(HFAA)_2(py)_2$ is about a factor of 15 larger than that reported for the methyl protons of $Ni(AA)_2(py)_2$. Fluorine contact interactions are generally a factor of $2-3^{[14]}$ larger than proton contact interactions with the opposite sign if the π-electron spin distribution is constant. The large shift observed for $Ni(HFAA)_2(py)_2$ indicates a significantly greater delocalization of spin into the ligand in this complex than in the analogous protonated molecule. If the π-electron spin density at the carbonyl carbon in $Ni(HFAA)_2(py)_2$ is negative and the spin density at the methylene carbon is positive, one predicts a positive Fermi contact shift for the methylene proton and a negative Fermi contact shift for the fluorines in the trifluoromethyl groups. The signal from the methylene proton in $Co(HFAA)_2(py)_2$ has a positive shift[6] while the signal from

this proton has a small negative shift in $Co(AA)_2(py)_2$. If the signs of the spin densities are the same in the various cobalt and nickel complexes, the small negative shift observed from the methylene signal in $Co(AA)_2(py)_2$ would be due to a positive Fermi contact shift with a slightly larger negative dipolar shift.

The Fermi contact shift should be almost constant for the cis and trans isomers of the 1:1 and 1:2 complexes of $Co-(HFAA)_2(py)_2$, although the number of pyridines coordinated may make a small difference in the amount of spin delocalization. If the Fermi shifts of the cis and trans isomers are nearly identical, interconversion of the isomers will not affect the shift from this interaction and the observed separation of the NMR lines at a lower temperature would be due to differences in dipolar terms of the different isomers. The shift of the exchange narrowed line which is observed at higher temperatures should be mainly due to the Fermi interaction with a smaller contribution from the dipolar terms if they are not exchange averaged to zero. The relative displacement of signals from nonequivalent trifluoromethyl groups reflects differences in either or both the geometric term $G(\theta,r)$, $G'-(\theta,\Omega,r)$ or the magnetic anisotropy. In principle one should be able to determine geometries of the individual isomers from the dipolar shifts, but one would need independent measurements of the magnetic anisotropy for each type of complex in order to separate the terms. The signals move to both high and low field of the extrapolated shift of the exchange narrowed line, indicating changes in the sign of the geometric terms for trifluoromethyl groups located at different relative angles with respect to the magnetic axes. The nonzero intercepts of the shifts at infinite temperature are probably due to the contribution of partial averaging to the position of the individual lines[15] but may also show differences in the position of the diamagnetic reference peak for the various types of complexes.

The trans 1:1 and 1:2 complexes and the free complex with weakly associated solvent might be thought to have similar geometries with the HFAA ligands forming a plane with axial pyridine or solvent molecules. The difference in shift observed from the trans 1:2 complex and the free complex is probably due to the effect of pyridine substitution on either the Fermi contact term or the magnetic anisotropy. The large difference

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in shifts from the trans 1:2 and the trans 1:1 complexes can be explained by a geometric distortion of the 1:1 complex which has a pyridine molecule at one axial position and a solvent molecule at the other axial position. This type of distortion would change both the geometric terms and the magnetic anisotropy of this complex. The slope of the line (Figure 6) of the trans 1:1 complex is positive while the slopes of the lines from all of the other complexes are negative. The positive slope of this line shows that the contribution of the dipolar interaction to the total shift is positive and the negative shift which is observed is due to the large negative intercept. The positive dipolar shift shows either that the magnetic anisotropy has changed sign (χ_x or $\chi_y > \chi_z$) or that $G(\theta,r)$ has a negative value. This angular term has negative values when $\theta > 54.4°$ and less than $125.6°$. A relatively large distortion in the relative geometry of this complex would be required to produce either a change in the sign of the magnetic anisotropy or a large value of θ.

Conclusions

Our variable-temperature ^{19}F NMR investigation of pyridine complexes of Co(HFAA)$_2$ clearly demonstrates that cis and trans isomers of both 1:1 and 1:2 complexes are formed in acetone solutions. The cis isomer is favored over the trans isomer in both the 1:1 and 1:2 complexes. At higher temperatures interconversion of the isomers rapidly averages the dipolar contribution to the shifts and an exchange narrowed line with a shift dominated by the Fermi contact interaction is observed. The pyridine complex of Ni(HFAA)$_2$ exhibits a single ^{19}F NMR line over the accessible temperature range.

The anisotropy of the magnetic susceptibility of nickel complexes is small and the shift which is observed is mainly due to the Fermi contact interaction. If cis and trans isomer are formed by Ni(HFAA)$_2$(py)$_2$, the dipolar shifts are not large enough to allow one to observe individual NMR lines from different species. At lower temperatures interconversion of the various cobalt complexes is slow and large dipolar shifts are observed from the various species. The shifts which are observed can be accounted for by differences in the relative geometry of the trifluoromethyl groups in the complexes. The components of the magnetic susceptibility may also vary in complexes with different structures. Data from earlier studies of Co(AA)$_2$(py)$_2$ have been analyzed by assuming that only the trans isomer is present in solution. If the protonated AA behaves in the same manner as the fluorinated analogue, the NMR spectra which are observed at room temperature are due to a rapidly averaged mixture of cis and trans isomers and the interpretation of the relative contributions of the Fermi contact and dipolar shifts needs to be reconsidered. Our study demonstrates that care must be taken not only in the separation of Fermi and dipolar shifts of paramagnetic metal complexes but also in determining the molecular species present in solution which can contribute to the total shift.

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Crystal Structures of the Picoline *N*-Oxide Complexes M(4-CH₃C₅H₄NO)₆(ClO₄)₂ (M = Cu, Zn) and EPR Spectra of the Pure and Zinc-Doped Copper Complexes

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The hexakis(4-picoline *N*-oxide)copper and -zinc perchlorate complexes crystallize in the monoclinic system, space group $P2_1/c$, with the following unit cell dimensions: for the copper complex $a = 9.523$ (5) Å, $b = 10.707$ (8) Å, $c = 20.512$ (16) Å, and $\beta = 92.47$ (6)°; for the zinc complex, $a = 9.467$ (5) Å, $b = 10.760$ (5) Å, $c = 20.531$ (9) Å, and $\beta = 92.46$ (4)°. The structures were solved with the use of approximately 2400 independent reflections collected for each complex on a single-crystal diffractometer using Mo Kα radiation at ambient temperature. The final, conventional residuals were 0.097 and 0.082 for those reflections with $I > 2\sigma(I)$, these rather high values being the result of the limited sizes of the data sets available for the structure determinations. While the complex cations in the two salts have only $\bar{1}$ symmetry, the coordination polyhedron in the zinc complex comes close to octahedral geometry with an average Zn–O distance of 2.114 Å. The coordination geometry for the copper complex, however, is in accord with the presence of a static Jahn–Teller distortion, the Cu–O distances being 1.965, 2.008, and 2.385 Å. Single-crystal EPR measurements, at both X- and Q-band frequencies, are also indicative of tetragonally elongated geometries for the copper-containing cation, both in the pure complex and in the case when it is doped into the zinc complex. The principal values of the **g** tensor average 2.32, 2.12, and 2.07. In the pure complex, the cations are oriented in approximately a ferrodistortive arrangement, and there is no evidence from the EPR spectra for any appreciable magnetic exchange between the two nonequivalent sites in the monoclinic cell. For the doped system, there is no evidence for the operation of a dynamic Jahn–Teller effect even though the zinc host complex is approximately octahedral.

Introduction and Summary

The hexakis(pyridine *N*-oxide) complexes of copper(II) salts, Cu(C₅H₅NO)₆X₂ (X = ClO₄⁻, BF₄⁻, NO₃⁻), exhibit dynamic and cooperative Jahn–Teller distortions and have been extensively investigated both by ourselves[1,2] and by other workers[3,4] using EPR and diffraction techniques. At very low

temperatures, heat capacity measurements indicate that magnetic ordering occurs.[5] The planar antiferromagnetism observed for the fluoborate salt and the linear antiferromagnetism for the perchlorate salt are in accord respectively

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