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Methyl Proton NMR Shifts of Coordinated Methanol in a Series of Co(CH₃OH)₅X²⁺ Compounds

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The isotropic contact NMR shifts of the coordinated *cis* and *trans* methanol methyl proton resonances of a series of Co(CH₃OH)₅X²⁺ complexes were measured, where the ligand X was pyridine, β- and α-picoline, DMF, DMSO, acetonitrile, and water. The question of how to separate the observed shifts into their respective Fermi contact and dipolar (pseudocontact) contributions was examined in detail with the result that a new procedure for carrying out the separation was proposed. The dipolar shifts for these complexes were found to vary widely, with the aceto-nitrile complex exhibiting the largest dipolar shift. For the DMSO and water complexes the sign of the dipolar shift was reversed relative to the others. Qualita-tively this sign reversal may be related to the difference in ligand field strengths of methanol and X relative to the spin orbit soupling constant for cobalt (II). It was also concluded that the Fermi contact shift varied between complexes.

INTRODUCTION

Isotropic NMR shifts of paramagnetic transition metal complexes have received rather widespread attention in the past decade. In the cases where the complex is magnetically anisotropic the observed isotropic shift v_i^0 for the ith type nucleus in the complex, is the sum of the Fermi contact v_i^F and dipolar (pseudocontact) v_i^P shift con-tributions, i.e.,

$$v_i^0 = v_i^F + v_i^P. \tag{1}$$

Within a given complex the sign and magnitude of v_i^P is a function of the nucleus's distance from the paramagnetic metal atom and its orientation to the molecule's magnetic axis. This relationship is expressed as follows:

$$v_i^P = -D\langle(3\cos^2\chi_i - 1)/r_i^3\rangle_i, \tag{2}$$

where χ_i is the instantaneous angle made with the molecular magnetic axis by the dis-placement vector from the paramagnetic center to the ith nucleus, and r_i is the length of this displacement vector. The shift is thus written as the product of a geometric factor and D, which gives the dipole field of the metal. The brackets represent averaging over internal vibrations and rotations of the enclosed expression; v_i^P has been averaged over all molecular orientations. A factor of v_0 (v_0 = unshifted resonance frequency = 100 MHz in our work) is often taken out explicitly from D.

In order to gain information about the electronic structure and spin delocalization mechanisms in paramagnetic metal complexes it is necessary to separate the isotropic shift into its Fermi contact and dipolar contributions. There have been a number of

procedures devised to accomplish this. Happe and Ward (*1*) proposed a method based on the assumptions that at least one observed isotropic contact shift in the molecule resulted solely from the dipolar shift contribution and that the required geometric factors were known. Horrocks and coworkers have proposed the *ratio technique* based on the comparison of shifts in analogous Ni^{2+} and Co^{2+} complexes (*2*) since Ni^{2+} should give negligible pseudocontact shifts. Horrocks has also used single crystal anisotropic magnetic susceptibility data to calculate v_i^p for the solution NMR (*3*). Most recently, proton and C^{13} NMR measurements on the same complex were utilized in carrying out the separation (*4*). Some of these techniques are reviewed and discussed by Eaton and Zaw (*5*).

LaMar (*6*) earlier discussed the separation of contact and pseudocontact shifts for some bis-acetylacetonate complexes of Co(II). He assumed that the contact contributions were independent of the other substituents, based on evidence from Ni(II) compounds. The geometric factors were taken from X-ray data, which, aside from introducing an uncertainty of 25 % into the ratio of the two pseudocontact shifts considered, does not take into account changes in configuration on solution, nor the effect of internal rotations. Furthermore, his complexes were not really axially symmetric. These uncertainties made it impossible to obtain reliable values for the contact and pseudocontact contributions. LaMar (*6*) also discusses previous work (*7*) in which *g*-values taken from ESR studies were used to separate contact and pseudocontact contributions.

The aforementioned techniques have been applied to systems subject to at least one of the following complicating factors: (i) The geometric factor was not known. (ii) The observed NMR resonances were rapid exchange averages between two or more nonequivalent magnetic environments. (iii) The position of the resonance of the non-coordinated ligand could have been shifted from the diamagnetic resonance position due to exchange (*8*) with the second coordination sphere of the magnetically anisotropic complex. (iv) The magnitude and possibly even the sign of the magnetic anisotropy of a molecule can be a very sensitive function of the crystal field environment. Since the environment of a molecule in solution may be quite different than in a crystal the use of single crystal magnetic anisotropy data may *not necessarily* be applicable to the calculation of NMR shifts in solution (*9*).

This paper presents an analysis of the isotropic shifts of the methyl proton resonances of the coordinated methanol in $Co(CH_3OH)_5X^{2+}$ complexes where X is a neutral monodentate ligand. Proposed in this work is a method of separating the isotropic shifts of the coordinated methanol methyl proton resonances of $Co(CH_3OH)_5X^{2+}$ complexes into their respective dipolar and Fermi contact shift contributions. This information will be of great utility in future work when it will be used to generate information of more direct chemical interest.

The methyl proton spectra of $Co(CH_3OH)_5OH_2^{2+}$ and $Co(CH_3OH)_5Cl^+$ have been reported by Luz and Meiboom (*10, 11*). Horrocks and Hutchison (*12*) have interpreted these spectra in terms of dipolar shifts and have proposed a method of separating the Fermi contact and dipolar shifts. Their technique in separating the shifts will be examined more closely, and a somewhat different procedure for carrying out the separation will be proposed. The relatively high accuracy of the data reported here in comparison to the early measurements permits a more detailed examination of the assumptions made in separating the dipolar and Fermi contact shifts in these complexes.

EXPERIMENTAL

All samples were prepared by adding the appropriate volume or weight of pure ligand to an anhydrous methanol solution of cobalt perchlorate. The procedures for removing water from the sample and standardizing the $Co(ClO_4)_2$ solution have been described in previous publications (13, 14). All samples were prepared under a nitrogen atmosphere, and each sample was 0.133 M in Co^{2+}. The ligand concentrations (pyridine, α- and β-picoline, DMSO, H_2O, DMF, and acetonitrile) varied in the range of 0.05 to 0.15 M. The shifts were found to be independent of the concentration of ligand.

The proton magnetic resonance measurements were made at 100 MHz using a Jeolco 4H-100 instrument. All shifts were made using the superposition of sideband technique. Temperature was maintained to $\pm 0.2°C$.

DATA AND RESULTS

Table 1 summarizes the observed isotropic contact shifts of the methyl proton resonances of the coordinated methanol in $Co(CH_3OH)_5X^{2+}$ complexes, where X is methanol, pyridine, α-picoline, β-picoline, acetonitrile, dimethylformamide, dimethyl

TABLE 1

NMR Shift Data for the Coordinated Methanol Methyl Proton Resonances in $Co(CH_3OH)_6^{2+}$ and $Co(CH_3OH)_5X^{2+}$ Complexes[a]

Ligand X	v_{cis}^0 (Hz)	v_{trans}^0 (Hz)	$Co(CH_3OH)_6^{2+}$ v_{Co}^0	$R_{Calc.}$[b] See Eq. [3]	$v_{Calc.}^F$ See Eq. [4]	$v_{cis}^F - v_{Co}^F$	$D(sec^{-1} Å^3)$
CH₃CN	−13210	+4220	−7780	−2.21	−7400	+380	−40.01 × 10⁴
Pyridine	−9780	−3020	−7750	−2.33	−7530	+220	−15.52 × 10⁴
β-Picoline	−9590	−3020	−7750	−2.57	−7400	+350	−15.08 × 10⁴
α-Picoline	−9210	−3620	−7750	−2.83	−7350	+400	−12.83 × 10⁴
Water	−6760	−9910	−7740	−2.21	−7810	−70	7.23 × 10⁴
DMSO	−7100	−10075	−7750	−3.57	−8090	−340	6.83 × 10⁴
DMF	−8790	−6970	−7750	−0.75	−8180	−430	−4.18 × 10⁴

[a] Negative sign indicates a downfield shift relative to the bulk methanol resonance and a plus sign signifies an upfield shift.

[b] R is calculated assuming the cis and trans dipolar shifts may be obtained by subtracting v_{Co}^0 from the total cis and trans shifts, i.e., that the Fermi contribution is always the same.

sulfoxide, and water. All shifts were measured at −51°C and are given relative to the bulk (uncoordinated) methanol methyl resonance. Each sample consisted of an equilibrium mixture of $Co(CH_3OH)_5X^{2+}$ and $Co(CH_3OH)_6^{2+}$. Two PMR resonances of the coordinated methanol methyl resonances were observed for the $Co(CH_3OH)_5X^{2+}$ complexes. One resonance was assigned to the methanol on the C_4 axis (trans) and the other to the four methanols in the plane perpendicular to the C_4 axis (cis). A third methyl resonance corresponding to the $Co(CH_3OH)_6^{2+}$ complex was also observed. Hereafter, symbols referring to the respective resonances will be denoted with the subscripts trans, cis, and Co. Methods for assigning the resonances have been described

previously (*10, 11, 13, 14*). Entries in Table 1 are arranged in order of decreasing frequency separation between the *cis* and *trans* resonances.

All resonances were shifted downfield, except for the *trans* resonance of the acetonitrile complex, which was observed upfield from the bulk methanol methyl resonance. At total ligand concentrations greater than 0.1 *M* bis and higher complexes were observed for all ligands except DMF, acetonitrile, and DMSO.

An additional set of proton NMR spectra was recorded using samples containing 0.18 *M* nickel perchlorate and varying concentrations of acetonitrile, pyridine, and water ranging from 0.0 to 0.5 *M*. The temperature was maintained at $-51°C$. No indication of new coordinated methanol methyl proton resonances or shifts of the existing methanol methyl resonance were observed in any of the samples. Paramagnetic shifted resonances of coordinated ligand protons were observed, and the observed shifts were in good agreement with available published shift data for the respective nickel(II) coordinated ligands (*15*). The insensitivity of proton shifts to the nature of other coordinated ligands has been observed previously (*6*). From these experiments it was concluded that the coordinated methanol methyl proton shifts were essentially the same in both $Ni(CH_3OH)_6^{2+}$ and $Ni(CH_3OH)_5X^{2+}$. This implies that the Fermi contact shift of the coordinated methanol methyl resonance is the same in the substituted complexes as in the fully solvated species. A similar result for nickel(II)–methanol complexes has been reported by Luz and Meiboom (*16*). Hunt (*17*) in his review on water exchange rates, also noted that metal complexation had little effect on the ^{17}O hyperfine coupling constant of water.

SEPARATION OF THE DIPOLAR AND FERMI CONTACT SHIFTS

The following simple relationship between the dipolar shifts of the *cis*, v_{cis}^D, and *trans*, v_{trans}^D, *coordinated* methanol methyl resonances of $Co(CH_3OH)_5X^{2+}$ complexes forms the basis for determining the dipolar field parameter D of Eq. [2]:

$$R = v_{trans}^D/v_{cis}^D = -2,$$ [3]

where R is the ratio of shifts. As can be seen from [2], R is simply the ratio of the geometric factors for the *cis* and *trans* methyl resonances. Proof of [3] can be demonstrated by direct evaluation of the geometric factors using the expression given in Appendix A, i.e., Eqs. [A1 and A2], but the relation is more general. It can be shown that the same relationship will be obtained as long as the metal to oxygen bonds for the *cis* and *trans* methanols lie along the Cartesian coordinate axes, the structural parameters for the two types of methanols are the same, and the rotational motions (not necessarily free rotations) of the methanols about their respective Cartesian axes are equivalent (*18*). Horrocks and Hutchison have pointed out this relationship before (*12*) using different geometric factors in its derivation. Using Eqs. [A1] and [A2] the geometric factors for the *cis* and *trans* methyl resonances were calculated to be $-0.01452 Å^{-3}$ and $0.02905 Å^{-3}$, respectively. The following parameters were used in the calculation—bond lengths: Co–O, 2.12 Å; O–C, 1.375 Å; C–H, 1.0 Å; bond angles: Co–O–C, 125.5°; and O–C–H, 109.7°.

The relationship expressed in Eq. [3] is dependent on the structural parameters of the *cis* and *trans* methanols being equal. Some feeling for how sensitive R is to differences in the structural parameters for the two methanols can be obtained from the following

calculations. Varying just the Co–O bond length of the *trans* methanol to the extent of ± 0.1 Å caused R to vary by only $\pm 5\%$ (1.95 to 2.05). A similar calculation where only the Co–O–C bond angle was varied caused a variation in R of about 1% per degree change. From this we conclude that R will not differ from -2 by more than $\pm 5\%$.

Based on the assumptions (1) that Eq. [3] is valid and (2) that the Fermi contact shifts of the *cis* and *trans* methyl resonances are equal, the dipolar shifts v_{cis}^{D} and v_{trans}^{D} can be calculated from the observed shifts. From the second assumption, $v_{trans}^{0} - v_{cis}^{0} = v_{trans}^{D} - v_{cis}^{D}$, and, using Eq. [3], one obtains the following relationship:

$$\tfrac{1}{3}(v_{trans}^{0} - v_{cis}^{0}) = -v_{cis}^{D} = \tfrac{1}{2}v_{trans}^{D}. \qquad [14]$$

Then D can be calculated from Eq. [2] using either v_{trans}^{D} or v_{cis}^{D} and the appropriate geometric factor calculated from Eq. [A1] and Eq. [A2]. The Fermi contact shifts, v_{cis}^{F} and v_{trans}^{F}, can be calculated from their respective observed and dipolar shifts using Eq. [1]. The calculated values of v_{cis}^{D}, v_{trans}^{D}, v_{cis}^{F} (or v_{trans}^{F}) and D are listed in Table 1 for a series of $Co(CH_3OH)_5X^{2+}$ complexes.

All the results depend on the assumption that $v_{cis}^{F} = v_{trans}^{F}$. In support of this, we note that the hyperfine coupling constant for the methanol methyl resonance in nickel(II) complexes appears to be independent of complexation by nonsolvent ligands. NMR shifts of six-coordinate nickel(II) complexes have no appreciable dipolar shift contribution; that is, the observed shifts result from Fermi interactions. For σ-bonded nonsolvent ligands it is reasonable to assume the same insensitivity of the Fermi contact shifts will be found for geometrically nonequivalent methanol molecules in the analogous cobalt(II) complex. Some measure of support for assuming that conclusions based on data for nickel(II) complexes can be used for cobalt(II) complexes comes from the success of the *ratio technique* (2) for separating dipolar and Fermi contact shifts in σ-bond ligands coordinated to cobalt(II). This approach assumes similar bonding in analogous cobalt(II) and nickel(II) complexes. Furthermore, a similar insensitivity of the hyperfine coupling constant for the ^{17}O NMR resonance in water coordinated to cobalt (II)and nickel(II) in a number of complexes has been observed (16). ^{17}O shifts of metal coordinated water are dominated by the Fermi contact mechanism.

It should be noted that the effect of a small difference between contact shifts for the *cis* and *trans* methanol protons is not extremely serious. Two peaks differing by 300 Hertz could be hidden under the single peak of the nickel resonance. The contribution to the left side of Eq. (4) would be 100 cycles. Our calculated values for $|v_{cis}^{D}|$ range from 5810 cycles for CH_3CN down to 610 Hertz for DMF, so that the error would be 2% for CH_3CN and less than 10% for all the cases of Table 1 except for DMF, where it is 16%. In contrast, the assumption that the Fermi shifts are identical for the hexamethanol and pentamethanol complexes would lead to serious errors, as is shown by the fact that (see Table 1), $v_{cis}^{F} - v_{Co}^{F}$ varies from -430 Hertz to $+400$ Hertz.

DISCUSSION

Horrocks and Hutchison (12) have proposed a method of separating the dipolar and Fermi contact shift contributions of the methyl resonances of $Co(CH_3OH)_5X^{2+}$ complexes. They assumed that the Fermi contact shifts of the *cis* and *trans* resonances were

equal and that the magnitude of v^F was equal to the methyl shift of $Co(CH_3OH)_6^{2+}$, v_{Co}^0, which is a result of only the Fermi contact interaction. Values of R calculated from our values of v_{cis}^D and v_{trans}^D, using these assumptions, are listed in Table 1. The range in R values found is far greater than can be explained in terms of variations of geometry. These discrepancies probably arise because v_{Co}^0 is not equal to v_{cis}^F or v_{trans}^F. This approach also lacks consistency in that different values of D will be obtained depending on whether cis or trans shift data are used to compute it. Table 1 also shows the deviations of our calculated Fermi contact shifts from the $Co(CH_3OH)_5X^{2+}$ complexes from those for the hexamethanol complexes. The point is that these relatively small deviations have a drastic effect when ignored in the separation of contact from pseudocontact shifts.

The Fermi contact shift is a function of the hyperfine coupling constant and the average magnetic moment of the complex (19). Since $Co(CH_3OH)_6^{2+}$ is magnetically isotropic while $Co(CH_3OH)_5X^{2+}$ complexes are magnetically anisotropic, the average magnetic moment of these species should in general differ by at least a small amount. Even if the hyperfine coupling constants are the same in each of these complexes, as is the case for analogous nickel(II) complexes, small differences in Fermi contact shifts would be expected due to differences in average magnetic moments. These small differences can be seen in Table 1 where the values of $v_{cis}^F - v_{Co}^0$ are listed. The smallness of this difference, even for complexes with very large dipolar shifts, suggests that $v_{cis}^F - v_{trans}^F$ is even smaller; of course, it is the latter that is ignored in our separation method.

It may be noted that the dipolar shift of the acetonitrile complex is far greater than that of any of the other complexes studied here. To answer the obvious question of "why?", we note that, of all the ligands considered here, only for acetonitrile can a substantial case be made supporting the existence of metal-ligand π-bonding interactions with cobalt(II). These arguments are based on considerations of ligand field parameters (20) and interpretations of Fermi contact NMR shifts (21) of metal-acetonitrile complexes. It is possible that the magnetic anisotropy of the cobalt(II) complex is a sensitive function of π-bonding. The magnetic anisotropy and, therefore, the dipolar shift is principally a function of the properties of the metal-centered d-orbitals, which are of the correct symmetry to interact with the orbitals of the ligand. Calculations by Abragam and Pryce have pointed out that the magnetic anisotropy of cobalt(II) complexes is a sensitive function of metal–ligand interactions (6). Thus we propose that the large dipolar shift of the acetonitrile complex is probably a result of π-type interactions between the metal d-orbitals and the π^*-orbitals of acetonitrile. Admittedly the validity of this supposition needs further substantiation through additional experimentation.

Another interesting feature of the dipolar shifts listed in Table 1 is the occurrence of different signs for the constant D. Similar inversions have been noted before (6a, 7, 11). It is tempting to interpret this by a crystal field model. The replacement of a methanol molecule by a nonsolvent ligand X causes a reduction in symmetry of the cobalt(II) complex from O_h to C_{4v}. Ignoring spin-orbit coupling, the ^4T ground state in O_h symmetry is split to a ^4E and ^4A state in C_{4v} symmetry. The separation of the ^4E and ^4A states is a function of the relative ligand field strengths of methanol and X (22). When the ligand field strengths $10\,Dq$ of methanol and X are sufficiently different to cause the splitting to be greater than that caused by spin orbit coupling (100–$200\ cm^{-1}$), one might

expect the sign of D to correlate with which has a stronger ligand field strength, methanol or X. Some detailed calculations have been begun.

In the past there have been relatively few molecules where the dipolar contribution to the NMR contact shift has been evaluated with high degree of certainty (23). This has been accomplished for the $Co(CH_3OH)_5X^{2+}$ complexes of which only a few of the many complexes possible have been examined in this work. The means of separation of contact from dipolar shift employed in this work require only the spectrum of the cobalt(II) complex, and do not require NMR data on analogous molecules with different metals. With the availability of accurate dipolar shift data on a reasonably extensive series of compounds, it should now become appropriate to consider the theoretical implications of the magnitude and sign of these shifts in relation to metal-ligand bonding.

APPENDIX A

Presented in this appendix are the algebraic expressions for the geometric factors of the *cis* and *trans* methyl protons of methanol in $Co(CH_3OH_5)X^{2+}$ complexes. The necessary averagings, assuming free rotations about the Co–O and O–C bonds, were included in the derivation of these expressions.

$$2\pi\langle(3\cos^2\chi^{-1})/r^3\rangle_{cis} = P(\tfrac{3}{2}C^2 - 3D^2 + \tfrac{9}{2}E^2 + 3A^2 B^{-2}(D^2 - E^2) + 3CEAB^{-1})$$
$$+ Q(3E^2AB^{-2} - 3D^2AB^{-2} - 3CEB^{-1} - 1) \qquad [A1]$$

$$2\pi\langle(3\cos^2\chi^{-1})/r^3\rangle_{trans} = P(3C'^2 + 6C'D'AB^{-1} + 9D'^2 - 6D'^2A^2B^{-2})$$
$$+ Q(6D'^2AB^{-2} - 6C'D'B^{-1} - 1) \qquad [A2]$$

Here,

$$A = \rho_1^2 + \rho_2^2 + \rho_3^2 - 2\rho_1\rho_2\cos\theta_1 + 2\rho_1\rho_3\cos\theta_1\cos\theta_2 - 2\rho_2\rho_3\cos\theta_2$$
$$B = 2\rho_1\rho_3\sin\theta_1\sin\theta_2$$
$$C = \rho_2\sin\theta_1 - \rho_3\cos\theta_2\sin\theta_1$$
$$D = \rho_3\sin\theta_2$$
$$E = -\rho_3\cos\theta_1\sin\theta_2$$
$$C' = -\rho_1 + \rho_2\cos\theta_1 - \rho_3\cos\theta_1\cos\theta_2$$
$$D' = \rho_3\sin\theta_1\sin\theta_2,$$

where the Co–O, O–C and C–H bond lengths are represented by ρ_1, ρ_2, and ρ_3, and the Co–O–C and O–C–H bond angles are represented by θ_1 and θ_2. The remaining quantities,

$$P \equiv \int_0^{2\pi} d\phi(A - B\sin\phi)^{-5/2}$$

$$Q \equiv \int_0^{2\pi} d\phi(A - B\sin\phi)^{-3/2}$$

are easily evaluated in any particular case as convergent power series in $(B/A)^2$.

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