for this supposition is the observation that exchange contributions to both the cis and trans relaxation rates are identical. If one postulates mechanisms requiring cis and trans effects and internal rearrangements to explain the relaxation data, it would be necessary to postulate very specific relationships between the processes to account for the equality of $(1/T_2)_{ex}$. It is felt that the existence of such relationships is improbable.

The rate constant and activation parameters summarized in Table I are based on the above mechanism. Included in Table I and in Figure 3 are the data for the line widths and methanol exchange rate of $Co(CH_3OH)_6{}^{2+}$. These data indicate that $NCS^-$ exchanges very slowly compared to the methanol exchange rate of $Co(CH_3OH)_5NCS^+$. If this were not the case, appreciable line broadening for the $Co(CH_3OH)_6{}^{2+}$ resonance would have been observed, and one would be forced to consider the exchange of $NCS^-$ as providing an additional relaxation mechanism for the $Co(CH_3OH)_5NCS^+$ resonances.

## Discussion

The simplest mechanistic interpretation of the coordinated methanol relaxation data appears to require that exchange occurs exclusively between the bulk and bound environments, and that no appreciable rearrangement in either the activated complex or an intermediate occurs. These results are markedly different from those previously reported for similar systems. Earlier studies of methanol exchange of $Co(CH_3OH)_5OH_2{}^{2+}$ [3] and $Co(CH_3OH)_5Cl^+$ [5] indicate that the mean lifetime of a methanol molecule in the

trans site is 0.59 times that for the cis. To account for this difference in relaxation rates one must postulate a mechanism implying either a cis effect, a trans effect, internal rearrangement, or some combination of these processes. The results for the $NCS^-$ system indicate that neither internal rearrangement nor kinetic cis or trans effects are operative. Thus, there is retention of configuration on exchange, whereas for the $H_2O$ and $Cl^-$ systems this is unclear.

It is a well documented fact, especially for $Ni^{2+}$, that substitution into the first coordination sphere by some nonsolvent ligand enhances the rate of exchange of the remaining coordinated solvent molecules. This was observed in the present work, as well as previously reported for cobalt(II) complexes in methanol.[3,5] The reasons for the rate increase, however, are not clear.

One could speculate on the role total charge plays in determining the solvent exchange rates and point out differences between water and methanol exchange rates for analogous complexes. But, in fact, there has as yet been an insufficient number and variety of systems studied to provide a basis to judge the generality of such conclusions. A systematic investigation of the methanol exchange rates of a wide variety of cobalt(II) complexes is presently underway in this laboratory in an attempt to assemble sufficient information to draw correlations between exchange rates and various possible factors influencing them.

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# Unusual Solvent Effect on the Paramagnetic Proton Chemical Shift of a Cobalt(II) Complex

By TIM W. McGAUGHY and B. M. FUNG*

The proton nmr of hydrotris(1,2,4-triazol-1-yl)boratocobalt(II) was studied in solutions of varying $D_2O$–$D_2SO_4$ content. In dilute acid solutions ($D_2O/D_2SO_4 > 150$), there are three sets of proton peaks for the protons in the ligand. One set is due to the dissociated ligand. The second set is due to the normal paramagnetic complex. The third set, which has smaller paramagnetic shifts, is due to a species in which water replaces one (or more) triazole unit in the ligands. The positions of the paramagnetic peaks change significantly with an increase in acid content; this phenomenon is explained by a change in the geometry of the complexes. In concentrated acid solutions ($D_2O/D_2SO_4 < 1.2$), the two sets of paramagnetic signals merge into one set of three peaks, indicating fast chemical exchange. The change of chemical shifts with solvent composition in this range is dominated by the shift in equilibrium between the two species.

## Introduction

Nuclear magnetic resonance (nmr) studies on the second coordination sphere of transition metal complexes have been reported in several experiments.[1-7]

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(1) B. M. Fung, *J. Amer. Chem. Soc.*, **89**, 5788 (1967).
(2) B. M. Fung and I. H. Wang, *Inorg. Chem.*, **8**, 1867 (1969).
(3) J. L. Sudmeier and G. L. Blackmer, *J. Amer. Chem. Soc.*, **92**, 5238 (1970).
(4) L. R. Froebe and B. E. Douglas, *Inorg. Chem.*, **9**, 1513 (1970).
(5) D. R. Eaton, *Can. J. Chem.*, **47**, 2645 (1969).

The solvent-induced changes in the proton chemical shifts of the ligands in several cobalt(III) complexes illustrate the formation of the second coordination sphere through hydrogen bonding.[1,2] Complex formation between the tris(ethylenediamine)cobalt(III) ion and the phosphate ion decouples the $^{59}Co$–$^1H$ spin-spin coupling because of more effective $^{59}Co$ quadrupole relaxation.[3,4] The formation of outer-sphere complexes

(6) L. S. Frankel, *J. Phys. Chem.*, **73**, 3897 (1969).
(7) L. S. Frankel, C. H. Langford, and T. R. Stengle, *ibid.*, **74**, 1376 (1970).

between paramagnetic complexes and solvents also affects the proton chemical shifts[5] and the proton line widths[6,7] of the solvent molecules. For paramagnetic complexes with short electronic relaxation times, the nuclear resonance of the ligands may give relatively narrow lines with large paramagnetic shifts.[8,9] If there are specific interactions between the complex and the solvent or counterions, the change in the nmr spectrum of the ligand may be more pronounced than that for diamagnetic complexes. We now wish to report the solvent effect on the proton nmr of a cobalt(II) complex in $D_2O-D_2SO_4$ solutions.

Polypyrazolylborates are an interesting class of ligands and form paramagnetic complexes with a number of transition metals.[10] Eaton found that Co(II) complexes of polypyrazolylborates cause changes in the proton chemical shifts of aniline and pyridine due to pseudocontact interaction.[5] However, the ligand resonance is not affected[11] because the interaction between the complex and the organic bases is very weak. In this paper we wish to report the effect of solvent on the proton chemical shift of hydrotris(1,2,4-triazol-1-yl)-boratocobalt(II) (abbreviated as $Co[HB(tri)_3]_2$) and

$$HB \underset{}{\overset{}{-}} \left( N \underset{N}{\overset{N}{\diagup}} \right)_3 \downarrow \quad Co/2$$
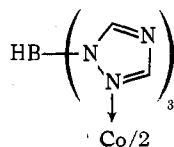
discuss the results in terms of the first and second coordination spheres of the complex.

## Experimental Section

$Co[HB(tri)_3]_2$ and the corresponding nickel(II) and zinc(II) complexes were prepared as described by Trofimenko.[12] The composition of the cobalt complex was checked by elemental analysis. *Anal.* Calcd for $C_{12}H_{14}B_2CoN_{18}$: C, 29.36; H, 2.87; N, 51.35. Found: C, 29.32; H, 2.81; N, 51.17.

Proton nmr spectra were taken on a Varian HA-100 spectrometer. Tetramethylammonium chloride (TMAC) was used as an internal standard in aqueous solutions and in sulfuric acid. All chemical shifts are recorded relative to the methyl resonance of sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) by taking the TMAC peak at −3.13 ppm. In organic solvents tetramethylsilane (TMS) was used as an internal standard.

Magnetic susceptibility data on the solid were obtained by the Gouy method. The magnetic susceptibility of the solutions was determined by the nmr method.[13]

Optical spectra were recorded on a Cary 17 spectrometer.

## Results

$Co[HB(tri)_3]_2$ is soluble in dilute sulfuric acid solutions and concentrated sulfuric acid solutions, but is insoluble in the solvent range of $D_2O/D_2SO_4$ mole ratio of 1.2–9.

In the dilute region, when the $D_2O/D_2SO_4$ mole ratio is larger than 150, there are six rather broad peaks in the paramagnetic region for the three different types of protons, plus two peaks for the ring protons in the diamagnetic region. The B–H proton resonance in the diamagnetic region was not observed. The peaks broaden as the concentration of the sulfuric acid in-

(8) D. R. Eaton and W. D. Phillips, *Advan. Magn. Resonance*, **1**, 103 (1965).

(9) E. de Boer and H. van Willigen, *Progr. Nucl. Magn. Resonance Spectrosc.*, **2**, 111 (1967).

(10) S. Trofimenko, *Accounts Chem. Res.*, **4**, 17 (1971).

(11) This was not reported in ref 5. It will be discussed in the text.

(12) S. Trofimenko, *J. Amer. Chem. Soc.*, **89**, 3170 (1967).

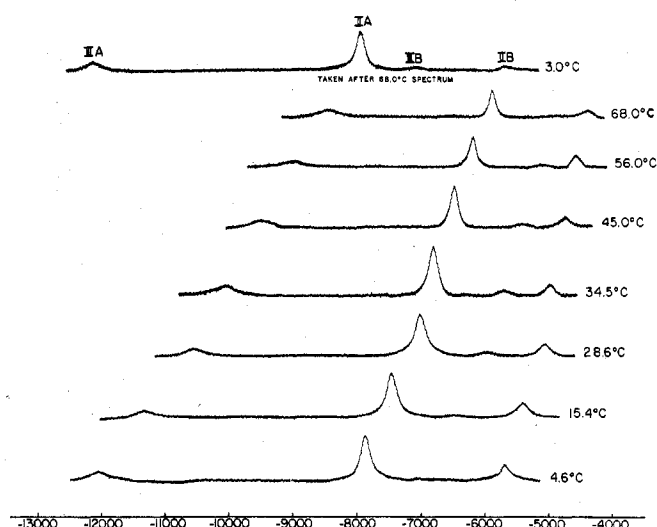(13) D. R. Evans, *J. Chem. Soc.*, 2003 (1959).

Figure 1.—Proton nmr spectra (100 MHz) of $Co[HB(tri)_3]_2$ in a solution of $D_2O/D_2SO_4$ mole ratio = 500. The spectra show the 5-H (II) and B–H (III) signals at different temperatures: A, $Co[HB(tri)_3]_2$; B, $Co[HB(tri)_3]_2(D_2O)_n$, as discussed in the text.
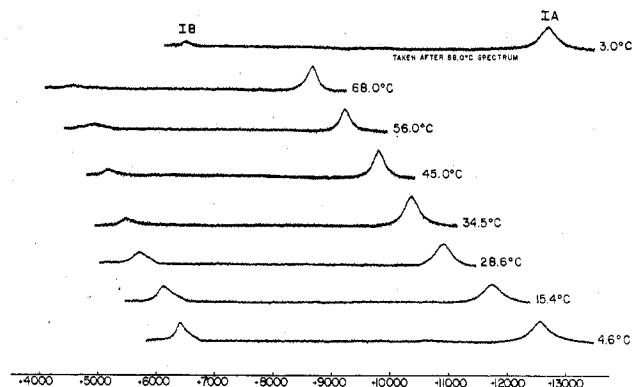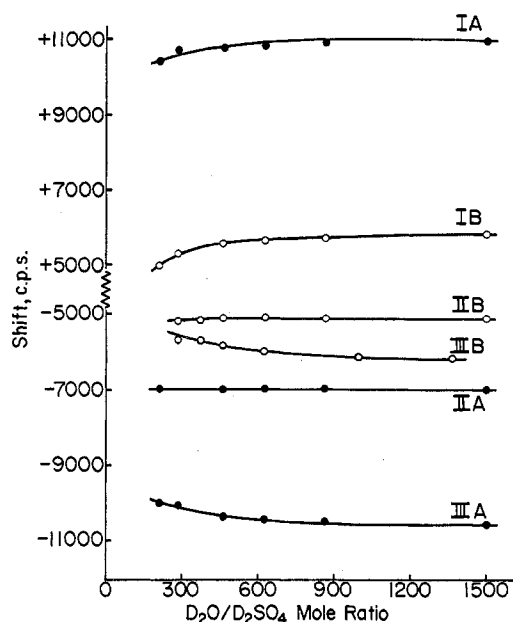


Figure 2.—Proton nmr spectra (100 MHz) of $Co[HB(tri)_3]_2$ in a solution of $D_2O/D_2SO_4$ mole ratio = 500. The spectra show the 3-H (I) signal at different temperatures: A, $Co[HB(tri)_3]_2$; B, $Co[HB(tri)_3]_2(D_2O)_n$, as discussed in the text.

creases, and the paramagnetic peaks become too broad to be observed when the $D_2O/D_2SO_4$ mole ratio is smaller than 150.

The paramagnetic regions of typical proton nmr spectra of $Co[HB(tri)_3]_2$ in a dilute $D_2O-D_2SO_4$ solution at different temperatures are shown in Figures 1 and 2. Of the six paramagnetic peaks, three are in the same regions as those for the complex dissolved in $CDCl_3$ (−112.9, −71.1, and +118.5 ppm, respectively). In analogy to $Co[HB(pz)_3]_2$ (pz = pyrazole),[10] the three peaks can be assigned to the B–H, 5-H, and 3-H of the complex, and are labeled IIIA, IIA, and IA, respectively. The three other paramagnetic peaks are due to the three different types of protons for another paramagnetic complex, as discussed below. They are labeled IIIB, IIB, and IB, respectively. The two peaks in the diamagnetic region are of the same intensity, and their chemical shifts are −8.73 and −9.46 ppm. They are assigned to the dissociated ligand, because $K[HB(tri)_3]$ in dilute $D_2SO_4$ also shows two peaks in the same positions, but the BH proton is also too broad to be observed.

The chemical shifts of the six paramagnetic peaks are temperature dependent (Figures 1 and 2). They de-

Figure 3.—Plot of proton chemical shift of Co[HB(tri)₃]₂ *vs.* D₂O/D₂SO₄ mole ratio (dilute region): ●, A, Co[HB(tri)₃]₂ complex; O, B, Co[HB(tri)₃]₂(D₂O)₂ complex; I, 3-H; II, 5-H; III, B–H.
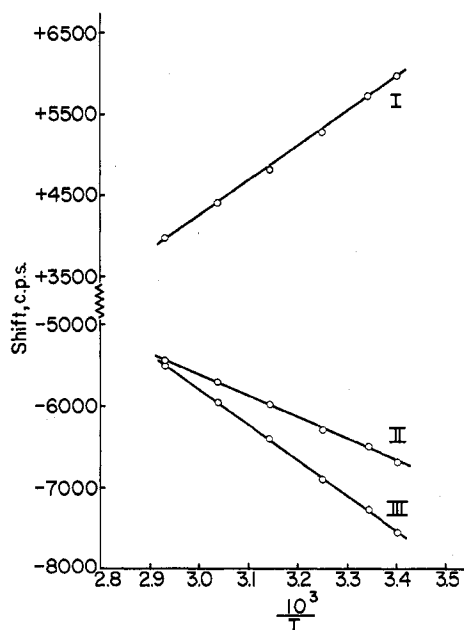


Figure 4.—Plot of proton chemical shifts of Co[HB(tri)₃]₂ in concentrated D₂SO₄ *vs.* the reciprocal of temperature: I, 3-H; II, 5-H; III, B–H.

pend on $1/T$ linearly, obeying the Curie law. As the temperature was raised, the intensity was diminished. The change in the chemical shift was reversible when the temperature was brought back to 3° after being raised to 68°. The line widths decrease slightly with temperature (Figures 1 and 2), but the changes are not large enough to be measured accurately by the side-band technique that was used to record the spectra.

A most interesting observation is that the chemical shifts for four of the six paramagnetic peaks are strongly dependent upon the solvent composition, especially in the less dilute acid region (Figure 3). The cause of this dependence will be discussed in the next section.
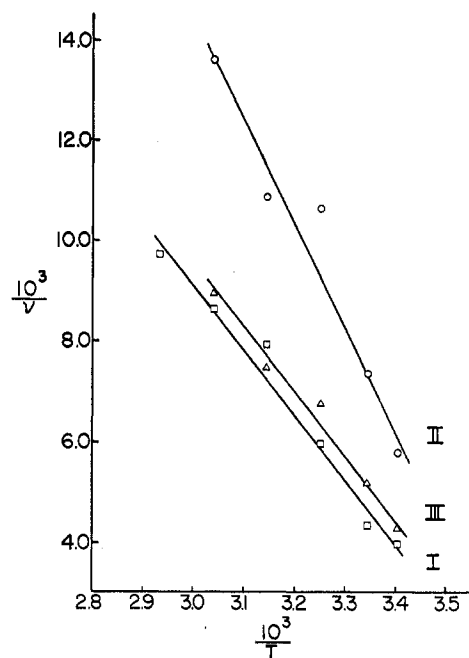


Figure 5.—Plot of reciprocal peak widths $(1/\nu)$ *vs.* $1/T$ for Co[HB(tri)₃]₂ in concentrated D₂SO₄: □, I, 3-H; O, II, 5-H; △, III, B–H.

In the concentrated sulfuric acid solutions (D₂O/D₂SO₄ mole ratio ≤1.2) the proton nmr of Co[HB-(tri)₃]₂ has only three peaks in the paramagnetic region and, in all cases except one, one peak in the diamagnetic region. The single peak in the diamagnetic region can be assigned to triazole, which is produced by the decomposition of the ligand in strong acid. It has the same chemical shift (−9.20 ppm) as free triazole in concentrated sulfuric acid, and its intensity builds up over time at the expense of the paramagnetic peaks. In one case, D₂O/D₂SO₄ = 1.20, three peaks were observed in the diamagnetic region. One peak was assigned to triazole and the other two were ascribed to the dissociated but not decomposed ligand, all on the basis of their positions. This demonstrates that part of the complex first dissociates into free solvated Co(II) ion and free ligands, and the ligand further decomposes in concentrated sulfuric acid.

The chemical shifts for the three paramagnetic peaks of Co[HB(tri)₃]₂ in concentrated sulfuric acid solutions show the normal Curie dependence (Figure 4), and their widths decrease regularly with an increase in temperature (Figure 5). The most interesting facts are that the values of the shifts are between those for the two sets of paramagnetic peaks in the dilute acid region and that their dependence on the solvent composition (Figure 6) is opposite to that in the dilute acid region Co[HB(tri)₃]₂ also shows three peaks in trifluoroacetic acid (TFA): 5-H, −60.2; 3-H, +45.4; and B–H, −74.5 ppm. When dimethyl sulfoxide (DMSO) was added, the absolute values of the shifts decreased, showing a similar dependence on acid concentration as in concentrated sulfuric acid solutions. On the contrary, Co[HB(pz)₃]₂, which is insoluble in aqueous solutions but soluble in TFA–DMSO solutions, shows no solvent dependence for the paramagnetic proton chemical shifts, which have values similar to those of CDCl₃ solutions.
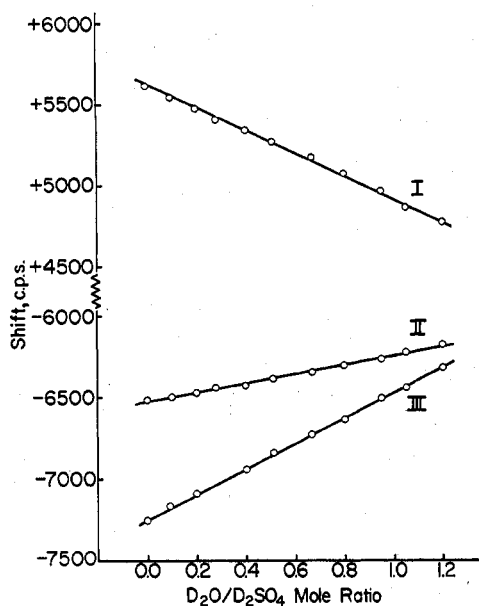
Figure 6.—Plot of chemical shift of Co[HB(tri)₃]₂ *vs.* D₂O/D₂SO₄ mole ratio (concentrated region): I, 3-H; II, 5-H; III, B–H.

Ni[HB(tri)₃]₂ shows only one unresolved peak similar to Ni[HB(pz)₃]₂.[14] The peak appeared at −40.0 ppm in concentrated sulfuric acid and −40.8 ppm in TFA–DMSO solutions. However, unlike the Co(II) complex, the paramagnetic peak showed no dependence on the acid concentration in the acidic solvents. In dilute sulfuric acid solutions the paramagnetic peak broadened beyond detection, and only two diamagnetic peaks due to the dissociated ligand were observed.

The proton nmr spectrum for the diamagnetic zinc complex, Zn[HB(tri)₃], shows two peaks at −9.59 and −9.16 ppm in concentrated sulfuric acid. In a D₂O–D₂SO₄ solution of mole ratio equal to 12 the proton peaks were found at −9.67 and −8.87 ppm. As the acidity decreased the peaks moved upfield until in D₂O they appeared at −8.56 and −7.91 ppm, respectively. Again, the BH proton was not observed.

The magnetic susceptibility of Co[HB(tri)₃]₂ was determined to be 4.8 BM by the Gouy method and 4.95 ± 0.05 BM by the nmr method of Evans.[13] These values are quite different from the value reported for Co[HB(pz)₃]₂ of 5.40 BM.[14] Therefore, several determinations of the susceptibility of Co[HB(pz)₃]₂ by the nmr technique were carried out. Solutions were run in both CHCl₃ and CH₂Cl₂. The average value obtained was 5.11 ± 0.05 BM which again is substantially different from the previously reported value. The susceptibility of Co[HB(tri)₃]₂ in dilute D₂SO₄ and concentrated D₂SO₄ solutions was also measured. It was determined equal to 4.84 BM in the concentrated region and about 5.05 BM in the dilute region. Because of the different species which exist in these solutions (see below) it is difficult to elaborate on the significance of these numbers.

A thorough optical study was also performed on the complex. In concentrated H₂SO₄ the visible spectra showed two broad peaks just after mixing. One was centered around 508 mμ (ε 6.5) and the other at 468

mμ (ε 8.5). Over the course of several days the peak at 508 mμ moved to 540 mμ while increasing somewhat in intensity (ε 10.5). The peak at 468 mμ, after 1 hr, had moved to 488 mμ and remained there over the time scale of the experiment. It also took on the appearance of a shoulder. Other solutions in the concentrated regions showed similar trends. Some comparison might be drawn to the CoCl₂·6H₂O–concentrated H₂SO₄ system. It showed initially two peaks, one at 546 mμ and a shoulder at 485 mμ. Therefore, the movement of one peak in the concentrated H₂SO₄ solutions is most likely due to the gradual decomposition of the complex. In the dilute region the visible spectra show again two peaks, one around 510 mμ (ε 5) and a shoulder at 470 mμ. Unlike the concentrated region these peaks do not change over several days. The cobalt complex was also run in CH₂Cl₂. This solution showed a peak at 457 mμ and a very weak shoulder at about 515 mμ. This is very close to the results of Jesson, Trofimenko, and Eaton for the pyrazole analog.[14]

## Discussion

The most notable feature of the proton nmr spectra of Co[HB(tri)₃]₂ is the strong dependence of the chemical shifts on the solvent composition in both aqueous and nonaqueous solutions, whereas the peaks of Co[HB(pz)₃]₂ have no solvent dependence. Since the major structural difference between pyrazole and triazole is the substitution of the CH fragment in the 4 position by a nitrogen, the probable explanation for the solvent dependence certainly lies in the existence of some solvent–triazole interaction *via* the 4 nitrogen. In other words, the change in the paramagnetic shifts of Co[HB(tri)₃]₂ with acid concentration is most likely a consequence of the second coordination sphere formed between the complex and the acidic part of the solvent *via* hydrogen bonding. In principle, Ni[HB(tri)₃]₂ should have similar interaction with the solvent. However, no dependence of the proton chemical shift on the acid content was observed. In order to understand this, two important differences between the cobalt and the nickel complexes must be noted. First, the paramagnetic shifts in Ni[HB(pz)₃]₂ and Ni[HB(tri)₃]₂ are due to contact interaction, whereas the shifts in the corresponding Co(II) complexes are mainly due to pseudocontact interaction.[10,14,15] Second, octahedral Ni(II) complexes are usually more stable than octahedral Co(II) complexes by several orders of magnitude.[16]

In dilute sulfuric acid solutions, there are three sets of peaks for each type of proton in Co[HB(tri)₃]₂. For the 3 and 5 hydrogens of Co[HB(tri)₃]₂ the intensity ratio of the diamagnetic peaks to the sum of the four paramagnetic peaks varied from 3.0 to 0.6 as the D₂O/D₂SO₄ mole ratio increased from 374 to 1370. We propose that there are slow (on the nmr time scale) equilibria between ligands that are coordinated to two different paramagnetic species and free ligands. Because the 4 nitrogen can form hydrogen bonding with a proton donor, an increase in the acidity favors the solvent–complex interaction and the dissociation of the complex. An increase in temperature would also favor

(14) J. P. Jesson, S. Trofimenko, and D. R. Eaton, *J. Amer. Chem. Soc.*, **89**, 3148 (1967).

(15) J. P. Jesson, *J. Chem. Phys.*, **47**, 582 (1967).

(16) K. B. Yatsinirskii and V. P. Vasil'ev, "Instability Constants of Complex Compounds," Consultants Bureau, New York, N. Y., 1960.

the dissociation of the complex to form more free ligands. In order to test the existence of the equilibria, we have examined the intensity change of the two diamagnetic peaks with temperature. For a solution of $D_2O/D_2SO_4 = 500$, the ratio of the diamagnetic peaks to the TMAC (internal standard) peak varied from 3.3 at 4.6° to 4.3 at 68°, indicating an increase in the dissociated ligands at higher temperatures. Then, the temperature was dropped to 4.6° and the intensity ratio also dropped back to 3.3–3.4, demonstrating that the equilibrium is reversible. The positions of the paramagnetic peaks undergo large shifts with temperature, obeying the Curie law. The change in the chemical shifts is also reversible (Figures 1 and 2).

The six paramagnetic peaks of $Co[HB(tri)_3]_2$ in dilute sulfuric acid solutions can be divided into two sets. One set, labeled A in Figures 1–3, have chemical shifts similar to those in $CDCl_3$ and can be attributed to the fully chelated complex. The peaks can be assigned as: IA, 3-H; IIA, 5-H; and IIIA, B–H, in analogy to $Co[HB(pz)_3]_2$.[12,14] The other set of peaks which are labeled IB, IIB, and IIIB in Figures 1–3 have smaller paramagnetic shifts. They must be due to another paramagnetic species. This species probably has the form of $Co[HB(tri)_3]_2(D_2O)_n$, with one or more coordination sites occupied by $D_2O$. The $D_2O$ and the triazole rings in the first coordination sphere must exchange positions rapidly, because all the triazole rings in this complex are indistinguishable. A complete displacement of one ligand by $D_2O$ to form $Co[HB(tri)_3]_2$-$(D_2O)_3$ is also possible but less likely, as we will discuss later. The IIIB signal can be assigned to the B–H proton on intensity basis. The IB and IIB signals have opposite signs and can be most reasonably assigned to the 3-H and 5-H protons, respectively, in analogy to the fully chelated species A. For both species, the 5-H proton chemical shifts are independent of the solvent composition, while the 3-H and the B–H shifts become "less paramagnetic" as the acidity of the solvent increases (Figure 3). The changes for the two species are almost parallel. These facts can be explained by a change in the geometry of the complexes caused by formation of the second coordination sphere. As the 4-N of triazole forms a hydrogen bond with a proton donor, the charge density of the triazole ring decreases and the ligand has a tendency to leave the first coordination sphere. This hypothesis is substantiated by the facts that when the acidity increases, the proton chemical shifts of the diamagnetic zinc complex move slightly downfield and the free-ligand intensity of the cobalt(II) complex increases, as described in the previous section. Since the pseudocontact shift for a paramagnetic species having tetragonal symmetry is[8,9]

$$\Delta H = -D(3 \cos^2 \theta - 1)/r^3$$

which depends upon the distance $r$ between the metal ion and the nucleus in resonance and the angle $\theta$ between $r$ and the tetragonal axis, an alteration in geometry would affect $\Delta H$ (species B may not have tetragonal symmetry, but $\Delta H$ also depends upon the geometry of the complex). The complex–solvent interaction may also affect the spin densities on the protons and cause changes in the contact shifts. The change in the spin densities for the 3-H and 5-H would be of the same sign and much larger than that for the B–H.
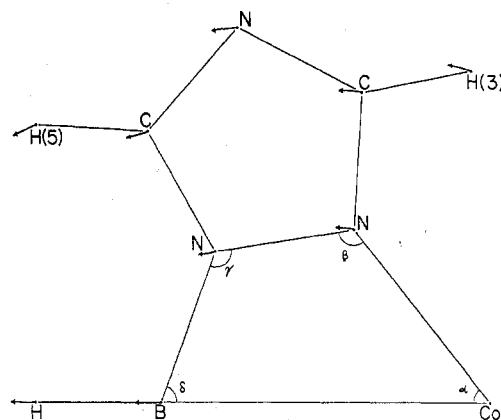


Figure 7.—Diagram showing the geometry changes induced in $Co[HB(tri)_3]_2$ by changes in the solvent acidity. The arrows denote the path the ligand would follow from its undisturbed equilibrium position. The change indicated by the arrows corresponds to a change in the chemical shifts of up to 20 ppm in the 3-H and B–H proton positions and 0 ppm in the 5-H proton position. The observed changes in chemical shifts were less than 10 ppm.

This was not observed. Moreover, the proton chemical shifts in $Ni[HB(tri)_3]_2$, which are determined by contact interaction only, do not show dependence on the acid concentration in aqueous sulfuric acid solutions. Therefore, we conclude that the change in the spin density during the formation of second coordination sphere is not important in determining the change in the shifts of $Co[HB(tri)_3]_2$.

Jesson was able to estimate the contact and pseudocontact contributions to the chemical shifts of $Co[HB-(pz)_3]_2$.[15] This cannot be done in the case of $Co[HB-(tri)_3]_2$ because information on the $g$ values in various solutions is lacking. However, both complexes have approximately the same proton chemical shifts in chloroform, and it is safe to assume that they behave similarly magnetically in the absence of solvent interaction. This is especially true for the dipolar or pseudocontact contribution, because the BH shifts ($-112.9$ ppm in the triazole complex and $-114.6$ ppm in the pyrazole complex), which have very small scalar or contact contribution, are almost the same for the two compounds. Therefore, the decrease in pseudocontact shifts for $Co[HB(tri)_3]_2$ due to the change in geometry during an increase in the acid concentration can be estimated by using the value of $D$ (in eq 1) determined for the pyrazole complex.[15]

The structure of triazole was determined by X-ray diffraction.[17] We assume that its geometry does not change in the cobalt complex, except that a value of 1.084 Å is used for the C–H distance because the values from typical X-ray works are usually too short. The bond lengths of 2.129 Å for Co–N, 1.554 Å for B–N, and 3.195 Å for Co–B have been determined recently for $Co[HB(pz)_3]_2$[18] and are used for the triazole complex. Although it was determined that cobalt is not coplanar with any of the pyrazole rings in $Co[HB(pz)_3]_2$ in the solid state,[18] for the sake of simplicity in our model we will assume $D_{3d}$ symmetry for $Co[HB(tri)_3]_2$ in solution. This is not an unreasonable assumption and the

(17) D. Goldstein, J. Ladell, and G. Abowitz, *Acta Crystallogr., Sect. B*, **25**, 135 (1969).
(18) M. R. Churchill, K. Gold, and C. E. Maw, Jr., *Inorg. Chem.*, **9**, 1597 (1970).

TABLE I

DEPENDENCE OF BOND ANGLES (DEG) AND BOND DISTANCES (Å) OF Co[HB(tri)₃]₂ ON CHANGES IN PSEUDOCONTACT SHIFTS

| | | Shift, cps (from original pseudocontact shifts[a]) | | | | | | |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| | | No change | 200 | 400 | 600 | 800 | 1200 | 2000 |
| 5-H | Angle[b] | 31.2 | 31.1 | 30.95 | 30.7 | 30.5 | 30.15 | 29.1 |
| | $r^c$ | 5.154 | 5.162 | 5.172 | 5.187 | 5.202 | 5.224 | 5.288 |
| 3-H | Angle[b] | 86.6 | 86.2 | 85.9 | 85.5 | 85.2 | 84.4 | 82.5 |
| | $r^c$ | 3.205 | 3.214 | 3.224 | 3.233 | 3.243 | 3.260 | 3.288 |
| B-H | Angle[b] | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| | $r^c$ | 4.405 | 4.426 | 4.448 | 4.470 | 4.492 | 4.539 | 4.638 |
| N(2) | Angle[d] | 51.5 | 51.4 | 51.1 | 50.8 | 50.5 | 49.9 | 48.5 |
| | $r^c$ | 2.129 | 2.143 | 2.155 | 2.167 | 2.179 | 2.204 | 2.254 |
| Co-N(2)-N(1)($\beta$) | Angle | 119.25 | 118.9 | 119.0 | 119.1 | 119.0 | 119.8 | 120.5 |
| B-N(1)-N(2)($\gamma$) | Angle | 119.25 | 120.2 | 121.0 | 121.5 | 121.7 | 122.9 | 124.2 |
| Co-B-N(1)($\delta$) | Angle | 70.0 | 69.5 | 69.2 | 69.2 | 68.8 | 68.05 | 67.0 |

[a] Calculated original pseudocontact shifts, based on the geometry under the column marked "no change": 5-H, −5210 cps; 3-H, +17,940 cps; B-H, −13,970 cps. Changes in geometry shown in the other columns were calculated assuming equal shifts of the amount noted at the top of each column (in cps) for the 3-H and B-H and no shift for the 5-H. All shifts are toward the diamagnetic region. [b] Angles noted are the angles defined by H-Co-B. [c] All distances are the length of the vectors joining the central Co and the proton or nitrogen in question. [d] The angle noted is N(2)-Co-B($\alpha$).

subsequent errors would be no larger than errors resulting from other assumptions. Thus, the geometry of the complex can be calculated, and the parameters are listed in Table I in the column under no change. The alterations in geometry of the complex (with a fixed triazole entity and constant bond lengths) corresponding to decreases in pseudocontact shifts for the 3-H and B-H are also listed in Table I. It was observed that the chemical shift of the 5-H (IIA) in Co[HB(tri)₃]₂ does not change and that the shifts of the 3-H (IA) and the B-H (IIIA) change in a similar fashion with an increase of acidity (Figure 3). If this is due solely to changes in pseudocontact interactions, the alteration in the geometry of the complex would be represented by the arrows in Figure 7. It is seen in Figure 7 that the ligand is pulled away from the cobalt ion and twisted slightly as the acidity increases, presumably accompanied by the formation of hydrogen bonding between the 4-N and a proton donor. Calculations for species B are not possible because of the undetermined nature of its structure. However, the changes in chemical shifts with acidity are almost parallel to those for species A (Figure 3), and it is expected that the geometry changes are also similar.

In concentrated sulfuric acid and TFA–DMSO solutions, Co[HB(tri)₃]₂ shows only three paramagnetic peaks. The variations in their shifts with acid concentration (Figure 6) are opposite to those in dilute aqueous sulfuric acid. This effect can be explained if the observed peaks are time-averaged signals of species A and B, and the change in chemical shifts are dominated by a shift in equilibrium. Species B may have the form Co[HB(tri)₃]₂(D₂O)ₙ. Protonated ions and uncharged sulfuric acid are not likely to enter the first coordination sphere because of their acidity; HSO₄⁻ also may not easily occupy a coordination site because of steric hindrance. Then, as the water content decreases in concentrated sulfuric acid, the equilibrium Co[HB(tri)₃]₂ + $n$D₂O = Co[HB(tri)₃]₂(D₂O)ₙ would shift to the left. Since the proton peaks of the fully chelated species A have larger paramagnetic shifts, the peaks of the time-averaged species move to the "more

paramagnetic" side. The alteration in geometry with acidity for both species A and B would cause the shifts to move toward the opposite direction, but the overall effect is dominated by the shift in equilibrium. Since in concentrated sulfuric acid the free ligands decompose into triazole, it is unlikely that the equilibrium between A and B involves a complete dissociation of one ligand. In other words, species B would not have the structure of Co[HB(tri)₃](D₂O)ₙ ($n \geq 3$). The situation in TFA–DMSO solutions is similar only in that DMSO is more sterically hindered for entering the first coordination sphere.

The assertion that the proton peaks of Co[HB(tri)₃]₂ in concentrated sulfuric acid solutions are time-averaged signals is substantiated by two other facts. First, the two sets of paramagnetic peaks in dilute acid broaden with the increase of acidity until too broad to be observed for D₂O/D₂SO₄ < 150, typical for the increase of exchange rate. Second, the peak widths in the concentrated region decrease with an increase of temperature, again typical for the increase of exchange rate, now for time-averaged signals. In order to ascertain that the change in line widths is not a viscosity effect, the line width of the internal standard (TMAC) was checked. It was observed to be constant over the entire temperature range studied. Because of the lack of knowledge about the true $T_2$'s for A and B in concentrated acid in the absence of exchange, it is not possible to calculate the exchange rate.

## Summary

Co[HB(tri)₃]₂ exists in two forms in acidic solvents. One is fully chelated; the other has one or more ligand positions occupied by electron-donating solvent molecules. The 4-N in the triazole unit is capable of forming hydrogen bonding with a proton donor, forming a second coordination sphere. The change in the first and second coordination spheres causes large changes in the paramagnetic proton chemical shifts.