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The Proton Magnetic Resonance Spectra of Pentaammine Complexes of Cobalt(III), Rhodium(III), and Iridium(III)

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Received December 1, 1969

The proton magnetic resonance spectra of some pentaammine complexes of cobalt(III), rhodium(III), and iridium(III) in concentrated sulfuric acid have been studied. Only one nonsolvent peak was detected for the rhodium and iridium pentaammines, whereas the cobalt pentaammines showed two peaks with an intensity ratio of 4:1. Proton exchange with the solvent was eliminated as an explanation for the missing peak in the rhodium and iridium cases by comparing the observed signal intensity with that expected for a complex not undergoing exchange. *Intra*molecular proton exchange was excluded as the explanation for the missing rhodium and iridium peaks by comparison of the temperature dependence of the widths of the peaks observed for various cobalt–, rhodium–, and iridium–ammine complexes. The loss of the 4:1 pattern in the rhodium and iridium pentaammines, the trends in shifts observed for $Co(NH_3)_5X^{n+}$ as a function of X, and the additivity of effects observed for the cobalt complexes can be explained by considering the relative magnitudes of the "diamagnetic" and "paramagnetic" shielding in these complexes.

Introduction

Proton magnetic resonance (pmr) spectroscopy is a useful technique for studying the reactions of metal–ammine complexes. It has been used to measure the rate of hydrogen–deuterium exchange between ligands and various solvent molecules[1,2] and to follow solvolytic reactions of cobalt(III) ammines in sulfuric acid.[3] The technique has been used to study the aquation of the nitropentaamminecobalt(III) ion[4] and the base hydrolysis of *trans*-$Co(NH_3)_4(^{15}NH_3)X^{2+}$ ions.[5]

Proton magnetic resonance has been used to identify geometrical isomers of metal complexes[6–8] and to study the rates of conformational changes in ethylenediaminecobalt rings.[9] The spectra of cobalt(III)–ammine complexes show separate resonances for geometrically different ammine groups.[1,8] In pentaammine complexes the *trans* ammine signals generally appear upfield of the cobalt hexaammine signal, whereas the *cis* ammine signals appear downfield. The chemical shift of an ammine proton in these complexes can be estimated as the sum of five terms characteristic of the other five ligands and their geometric positions. Similar geometric effects have been observed in the pmr spectra of bis(ethylenediammine)cobalt(III) complexes.[10]

To gain a better understanding of ammine proton chemical shifts in metal complexes, pmr studies were initiated for a series of rhodium(III) and iridium(III) pentaammines. Chemical shifts and line width–temperature data for these complexes are reported and interpreted in this paper.

Experimental Section

Preparation of Complexes.—A standard procedure[11] was used for the synthesis of $[Rh(NH_3)_5Cl]Cl_2$. *Anal.* Calcd for $[Rh(NH_3)_5Cl]Cl_2$: N, 23.79; H, 5.14; Cl, 36.13. Found: N, 23.96; H, 4.90; Cl, 36.06.

A sample of $[Rh(NH_3)_6](NO_3)_3$ was prepared by a modification of Jörgensen's recipe.[12] A solution of 1.09 g of $[Rh(NH_3)_5]Cl_2$ in 20 ml of concentrated aqueous ammonia was sealed in a thick-walled glass tube of 340-ml volume. The tube was held for 2 days at 100° in an oil bath; the yellow solution became colorless, and a white solid formed. The tube was opened; the mixture was added to water to dissolve the solids, and the solution was boiled to eliminate excess ammonia. Addition of concentrated nitric acid gave a white precipitate which was then recrystallized from a minimum of water, washed with ethanol and diethyl ether, and air dried (1.13 g, 87% yield). *Anal.* Calcd for $[Rh(NH_3)_6](NO_3)_3$: N, 32.23; H, 4.64. Found: N, 32.48; H, 4.83.

A sample of $[Rh(NH_3)_5]Br_3$ was prepared[13] by heating $[Rh(NH_3)_5H_2O]Br_3$[14] at 110° for 3 hr. *Anal.* Calcd for $[Rh(NH_3)_5Br]Br_2$: N, 16.37; H, 3.53; Br, 56.04. Found: N, 16.32; H, 3.70; Br, 56.42. The complexes *trans*-$[Rh(NH_3)_4Cl_2]Cl$ and *trans*-$[Rh(en)_2Cl_2]NO_3$ were prepared by standard synthetic procedures[15] and identified by their visible and ultraviolet absorption spectra.

Solutions of $M(NH_3)_5HSO_4^{2+}$ in H_2SO_4 and of $M(NH_3)_5(SO_3Cl)^{2+}$ in HSO_3Cl were prepared by treating the appropriate chloropentaammine chloride with concentrated H_2SO_4 and HSO_3Cl, respectively (M = Co, Rh, or Ir). The reactions were easily followed by pmr.

The complex $[Ir(NH_3)_5Cl]Cl_2$ was prepared by a modification of Palmaer's method.[16] An aqueous ammonia solution of $K_3(IrCl_6)\cdot 3H_2O$ was heated in a sealed tube at 100° for 10 hr. The tube was cooled and opened; excess ammonia was evaporated from the solution, and the product was precipitated by acidification with 12 *M* HCl. The precipitate was washed with alcohol and ether and then oven dried (80% yield). *Anal.* Calcd for $[Ir(NH_3)_5Cl]Cl_2$: Ir, 50.0; N, 18.25; H, 3.94; Cl, 27.76. Found: Ir, 50.1; N, 18.16; H, 4.07; Cl, 27.82.

Samples of $[Ir(NH_3)_5H_2O](ClO_4)_3$[16] and $[Ir(NH_3)_5NCS]$-

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(1) P. Clifton and L. Pratt, *Proc. Chem. Soc.*, 339 (1963).

(2) D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *J. Am. Chem. Soc.*, **90**, 6028 (1968), and references therein.

(3) W. L. Jolly, A. D. Harris, and T. S. Briggs, *Inorg. Chem.*, **4**, 1064 (1965).

(4) A. D. Harris, R. Stewart, D. Hendrickson, and W. L. Jolly, *ibid.*, **6**, 1052 (1967).

(5) D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, *J. Am. Chem. Soc.*, **89**, 5129 (1967).

(6) R. C. Fay and T. S. Piper, *Inorg. Chem.*, **3**, 348 (1964), and references therein.

(7) A. Chakravorty and R. H. Holm, *ibid.*, **3**, 1521 (1964).

(8) J. I. Legg and D. W. Cooke, *ibid.*, **4**, 1577 (1965).

(9) B. M. Fung, *J. Am. Chem. Soc.*, **89**, 5788 (1967), and references therein.

(10) J. R. Lantzke and D. W. Watts, *Australian J. Chem.*, **20**, 35 (1967).

(11) S. N. Anderson and F. Basolo, *Inorg. Syn.*, **7**, 216 (1963).

(12) S. M. Jörgensen, *J. Prakt. Chem.*, **44**, 49 (1891).

(13) S. M. Jörgensen, *ibid.*, **27**, 453, 462 (1883).

(14) S. M. Jörgensen, *ibid.*, **34**, 399 (1886).

(15) S. N. Anderson and F. Basolo, *Inorg. Syn.*, **7**, 217, 218 (1963).

(16) W. Palmaer, *Z. Anorg. Allgem. Chem.*, **10**, 320 (1895).

$(ClO_4)_2$[17] were prepared by published syntheses and characterized by ultraviolet spectrophotometry.[17] The complex $[Ru(NH_3)_5N_2](BF_4)_2$ was kindly provided by Dr. D. F. Harrison of Stanford University, and $[Co(NH_3)_5CN]SO_4$[18] and $[Co(NH_3)_5NCS](NCS)_2$[19] were prepared by published methods.

Proton Resonance Measurements.—Most measurements were made with a Varian A-60 spectrometer using solutions in either concentrated H_2SO_4 or HSO_3Cl. Temperature studies were made using a Varian N-6040 unit; 15 min of equilibration time was allowed at each temperature setting. All chemical shifts were measured relative to external TMS.

Results and Discussion

Chemical Shifts.—Proton chemical shifts were determined for a series of rhodium(III)- and iridium(III)-ammine complexes dissolved in concentrated sulfuric acid. The results are given in Table I together with chemical shift values (some previously determined and some newly determined) for the analogous cobalt(III) complexes. The rhodium and iridium pentaammines show only one pmr peak, whereas most of the cobalt pentaammines show two peaks with an intensity ratio of 4:1. The cobalt ammine resonances (the weighted averages of the *cis* and *trans* values) appear upfield of the corresponding rhodium ammine resonances, and the iridium resonances appear correspondingly downfield.

TABLE I

PROTON CHEMICAL SHIFTS OF SOME AMMINE COMPLEXES IN CONCENTRATED SULFURIC ACID

Complex	Chem shift *vs.* external TMS, ppm		
	Co(III)	Rh(III)	Ir(III)
$M(NH_3)_6^{3+}$	-3.59^a	-3.82	
$M(NH_3)_5HSO_4^{2+}$	-4.24 *cis*^{a}	-4.13	-4.80
	-2.75 *trans*		
$M(NH_3)_5H_2O^{3+}$	-4.16 *cis*^{a}		-4.68
	-2.92 *trans*		
$M(NH_3)_5Cl^{2+}$	-3.76 *cis*^{a}	-3.78	-4.55
	-3.10 *trans*		
$M(NH_3)_5Br^{2+}$	-3.65 *cis*^{a}	-3.80	
	-3.17 *trans*		
$M(NH_3)_5NO_2^{2+}$	-3.59^a		
$M(NH_3)_5NCS^{2+}$	-3.99 *cis*		-4.58
	-3.54 *trans*		
$M(NH_3)_5CN^{2+}$	-3.38 *cis*		
	-4.27 *trans*		
trans-$M(NH_3)_4Cl_2^+$	-3.93^a	-3.85	
	-5.22 (NH_2)	-4.60 (NH_2)	
trans-$M(en)_2Cl_2^+$	-3.65 (CH_2)	-3.18 (CH_2)	

[a] See ref 3.

Spectra of the $Ru(NH_3)_5N_2^{2+}$ ion in formamide and in 66 wt % H_2SO_4 consist of a 1:4 pattern; in 66 wt % H_2SO_4 the two peaks appear at δ -2.87 (*cis* ammine protons) and δ -3.58 (*trans* ammine protons) *vs.* external TMS. By rapid manipulation it was possible to observe a similar 1:4 pattern in concentrated H_2SO_4 (δ -2.62 and -3.29). It was possible to recover the nitrogen compound from both solvents; the compound was identified by the characteristic N–N stretching band in the ir spectrum.[20]

Solvolytic Reactions.—Solutions of either $[Rh(NH_3)_5Cl]Cl_2$ or $[Rh(NH_3)_5Br]Br_2$ in concentrated H_2SO_4 gave spectra with single resonances (excluding the solvent peak). When these solutions were kept for a few days, a second peak appeared downfield of the initial peak. This new peak appeared at the same field (δ -4.13 *vs.* external TMS) for both solutions and was assumed to be the resonance for $Rh(NH_3)_5HSO_4^{2+}$ in analogy with the cobalt complexes.[3] The reaction of the $Co(NH_3)_5Cl^{2+}$ ion in concentrated H_2SO_4 to form the bisulfatopentaammine complex has been found to have a half-time of 4 hr at room temperature when dry air was bubbled through the solution.[3] In the case of the rhodium complex the solvolysis is so slow that it required 1 day of flushing with dry air at 70° to complete the formation of the bisulfato complex. The chloropentaammineiridium complex required even higher temperatures and a longer time to effect completion of the reaction.

Studies of the pmr spectra of both *trans*-$[Rh(NH_3)_4Cl_2]Cl$ and *trans*-$[Rh(en)_2Cl_2]Cl$ in concentrated H_2SO_4 as a function of time indicated that solvolytic reactions occurred. In the case of the ethylenediammine complex the reaction was probably

trans-$Rh(en)_2Cl_2^+ + H_2SO_4 \rightarrow$ *trans*-$Rh(en)_2Cl(HSO_4)^+ + HCl$

A second NH_2 peak appeared at δ -4.89, and the CH_2 peak at δ -3.18 remained unchanged. Identification of the initial complex observed in the pmr was achieved by visible absorption spectroscopy, but this was not possible for the solvolytic product. The solvolysis appears to be acid catalyzed; the rate more than doubles by changing the concentration of H_2SO_4 from 85 to 95%. In the case of the *trans*-$Rh(NH_3)_4Cl_2^+$ ion in concentrated H_2SO_4 two solvolytic products were indicated by pmr. The spectrum soon showed a second peak at δ -4.10 and eventually a third peak at δ -4.53.

Exchange with the Solvent.—The absence of a 4:1 pattern in the spectra of the rhodium and iridium pentaammines could be explained by a rapid exchange of the *trans* ammine hydrogens with the solvent and a consequent merging of the smaller *trans* peak with the large solvent peak. Such an explanation implies an increased *trans* ammine proton–solvent exchange rate on going from a cobalt complex to either a rhodium or an iridium complex. Such a trend seems unlikely, for Palmer and Basolo[21] have found that for proton exchange with the solvent, the ratio of rates for $Co(NH_3)_6^{3+}$, $Rh(NH_3)_6^{3+}$, and $Ir(NH_3)_6^{3+}$ is approximately 100:15:1, respectively. Nevertheless, to test this hypothesis, the integrated intensity of the signal of $Rh(NH_3)_5Br^{2+}$ was compared with that calculated assuming that the signal was due to all 15 protons. By using the signal of a known concentration of NH_4^+ as an internal calibration standard, the observed signal intensity was found to agree within 2% of the calculated value.

Intramolecular Proton Exchange.—Another conceivable explanation for the loss of the second peak for the rhodium and iridium pentaammines is rapid intra-

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(17) H.-H. Schmidtke, *Inorg. Chem.*, **5**, 1682 (1966).

(18) H. Siebert, *Z. Anorg. Allgem. Chem.*, **327**, 63 (1964).

(19) A. Werner, *ibid.*, **22**, 91 (1900).

(20) A. D. Allen, F. Bottomley, R. O. Harris, V. P. Reinsalu, and C. V. Senoff, *J. Am. Chem. Soc.*, **89**, 5595 (1967).

(21) J. W. Palmer and F. Basolo, *J. Inorg. Nucl. Chem.*, **15**, 279 (1960).

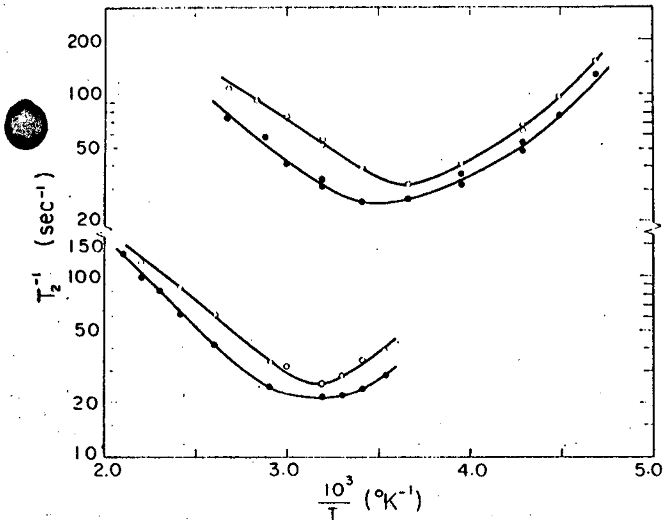

Figure 1.—The temperature dependence of log (T_2^{-1}) for solutions of $Co(NH_3)_6^{3+}$ and $Rh(NH_3)_6^{3+}$ in HSO_3Cl (upper curves) and concentrated H_2SO_4 (lower curves). The symbols ● and O refer to $Rh(NH_3)_6^{3+}$ and $Co(NH_3)_6^{3+}$, respectively.

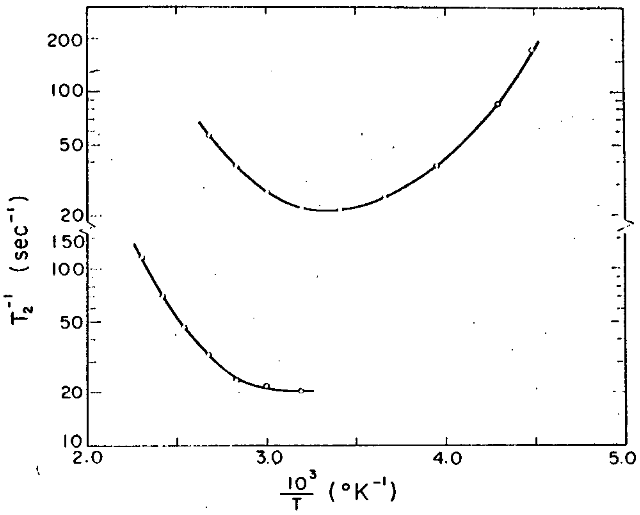

Figure 2.—The temperature dependence of log (T_2^{-1}) for an HSO_3Cl solution (upper curve) of $Co(NH_3)_5SO_3Cl^{2+}$ and for a concentrated H_2SO_4 solution (lower curve) of $Co(NH_3)_5HSO_4^{2+}$.

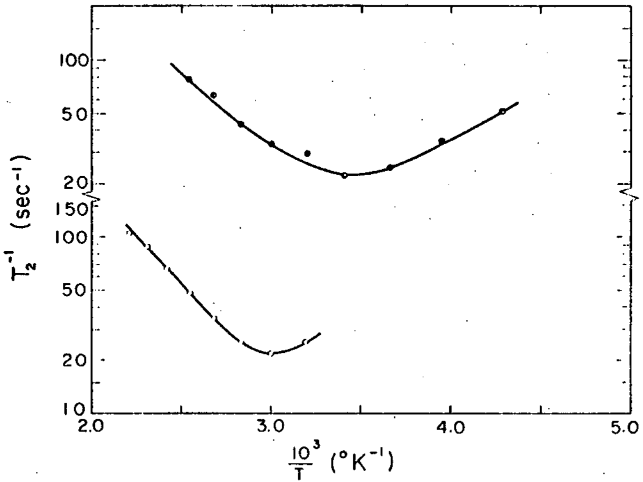

Figure 3.—The temperature dependence of log (T_2^{-1}) for an HSO_3Cl solution (upper curve) of $Rh(NH_3)_5SO_3Cl^{2+}$ and for a concentrated H_2SO_4 solution (lower curve) of $Ir(NH_3)_5HSO_4^{2+}$.

molecular exchange of the protons between the *cis* and *trans* sites. We tested this hypothesis by studying the temperature dependence of the line width of pmr peaks for various ammine complexes. The line width of a metal ammine pmr peak is affected by various processes: nuclear dipole–dipole interactions, nitrogen quadrupole interaction, and chemical exchange.[22] By comparing the temperature dependences of the line widths of cobalt complexes with those of the analogous rhodium and iridium complexes, we can determine whether the same processes are involved. In the case of the cobalt(III) pentaammines the observed 4:1 pattern is proof that rapid proton exchange does not occur. Thus a comparison of the temperature dependence of the line widths should show whether proton exchange occurs in the rhodium and iridium complexes. We have already shown for these complexes that there is no significant proton exchange with the solvent, so this study should determine whether intramolecular exchange occurs.

The temperature dependence of the line width is shown in Figure 1 for both $Co(NH_5)_6^{3+}$ and $Rh(NH_3)_6^{3+}$ in concentrated H_2SO_4 and HSO_3Cl. For each solvent the plot of log T_2^{-1} *vs.* $1/T$ shows two limiting regions. (T_2^{-1} is the reciprocal of the effective spin–spin relaxation time, given by half the width of a peak at half-height, in radians per second.) In the low-temperature region the peak width decreases as the temperature increases. This is the behavior expected when the line width is principally controlled by dipolar relaxation.[22] In the high-temperature region the peak width increases with increasing temperature. This behavior is expected when only a single peak is observed for a proton bonded to a nitrogen atom because of quadrupolar relaxation and a rapidly flipping nitrogen spin.[22,23] (The increased molecular tumbling at higher temperatures uncouples the nitrogen quadrupole moment from the electric field gradient and causes a reduced transition probability within the nitrogen spin system. In principle, at high enough temperatures a triplet should be seen.[23]) The similarity of the peak width *vs.* $1/T$ curves for the $Co(NH_3)_6^{3+}$ and $Rh(NH_3)_6^{3+}$ ions indicates that the same relaxation processes and interruptive mechanisms are operative. In the case of the bisulfato- and chlorosulfatopentaammines of cobalt, rhodium, and iridium the same types of curves have been found (see Figures 2 and 3). We conclude that the unsplit signals of the rhodium and iridium pentaammines are not due to intramolecular proton exchange. If such exchange occurred rapidly enough to give only one peak, raising the temperature would not cause broadening but, because of increased proton exchange, would cause a narrowing of the peak.

Intramolecular Ammonia Exchange.—Another possible explanation of the loss of the second peak for the rhodium and iridium pentaammines is rapid intramolecular exchange of the NH_3 groups. However such intramolecular NH_3 group exchange seems unlikely

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[22] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959. We will not consider the chemical anisotropy broadening, for it is probably small.

[23] J. D. Roberts, *J. Am. Chem. Soc.*, **78**, 4495 (1956).

in view of the known isolation of *cis* and *trans* isomers of some rhodium- and iridium-tetraammine complexes, and the temperature dependence of the line widths, reported above, can be construed as evidence against intramolecular NH_3 exchange under certain conditions. If the exchange of an ammonia from a *cis* to the *trans* position in a pentaammine resulted in appreciably different shielding for the nitrogen atom, rapid exchange would increase the transition probability in the nitrogen spin system. Increasing the temperature would then tend to decrease the width of the peak for the proton attached to this nitrogen atom. In fact we have observed the opposite: increasing the temperature increases the width of the ammine proton peaks of the rhodium and iridium complexes.

Discussion

Any interpretation of the pmr spectra of cobalt(III), rhodium(III), and iridium(III) pentaammines must explain the loss of the 4:1 pattern in the latter two cases. The observed variation of chemical shift with X and the additivity of the chemical shifts[3] for $Co(NH_3)_5X^{n+}$ complexes should be explained.

Proton exchange with the solvent has been shown not to occur in the rhodium and iridium pentaammines. The observed temperature dependence of the pmr line width for rhodium and iridium pentaammines excludes the possibility of intramolecular proton exchange as an explanation for the loss of the 4:1 pmr pattern. Intramolecular NH_3 group exchange seems improbable. We are led to the conclusion that the degeneracy of chemical shifts observed in these complexes is a manifestation of the electronic structure of the complexes.

It is well known that the effective magnetic field felt by a nucleus in a molecule which is in an external magnetic field is a function of electron densities in the various parts of the molecule. Using second-order perturbation theory, Ramsey obtained a two-term expression for the "shielding constant" σ.[24] For a molecule rapidly tumbling in a solution, the shielding constant is given by

$$\sigma = \mathrm{av}_\lambda \sigma_\lambda = \frac{e^2}{3Mc^2}\left\langle 0 \left| \sum_k \frac{1}{r_k} \right| 0 \right\rangle - 2\mathrm{av}_\lambda \sum_n \left(\frac{1}{E_n - E_0}\right)\left\langle 0 \left| \sum_k \frac{m_{zk}{}^2}{r_k{}^3} \right| n_\lambda \right\rangle$$

Here σ is an average over all orientations of some value σ_λ obtained for one particular orientation of the nuclear magnetic dipole μ and the static magnetic field H. The sums are over the k electrons in the molecule and the molecular excited-state wave functions $\langle n|$. The operator $m_{zk}{}^\circ$ is the usual angular momentum operator

$$m_{zk}{}^\circ = \frac{-eh}{2Mci}\left(x_k \frac{\partial}{\partial y_k} - y_k \frac{\partial}{\partial x_k}\right)$$

When considering the shielding constant for a particular nucleus, all operators have their origin at that nucleus. The first term in the shielding constant expression corresponds to the diamagnetic circulation of the electrons about the nucleus. This ground-state term (*i.e.*, $\langle 0|$) represents the shielding of the nucleus by the nearby electron density; it would be sensitive to inductive effects of neighboring atoms as they influence the electron density about the nucleus of interest.

The second term in the expression for the shielding constant is called the "paramagnetic" term and is due to admixture of excited states $\langle n|$ with the ground state $\langle 0|$ under the influence of the magnetic field. According to Ramsey this might physically correspond in part to the fact that the presence of attracting centers from several different massive nuclei prevents a simple diamagnetic circulation of electrons about any one nucleus. When there is a low-lying excited state (*i.e.*, small $E_n - E_0$) of proper symmetry, the second term can dominate the shielding parameter as it probably does in the case of ^{19}F, ^{14}N, ^{17}O, etc.[25] In these cases local "paramagnetic" shielding is involved. However, even when the "paramagnetism" is induced in a part of the molecule remote to the nucleus of concern, shielding or deshielding of the nucleus can result.[22]

It is our intention to show that a consideration of both the "diamagnetic" and "paramagnetic" terms in the shielding constant expression provides an explanation for the loss of the 4:1 pmr pattern for the rhodium and iridium pentaammines as well as other experimental observations. First we note that *cobalt* chemical shifts measured for various cobalt d^6 complexes have been shown to be dominated by a paramagnetic contribution from the low-lying $^1T_{1g}$ excited state.[26] *This same "paramagnetism" centered at the cobalt nucleus would be expected to influence the shielding for ammine protons in the cobalt pentaammines, but of course the greater electron distance (i.e, greater r_k in the second term) would result in a marked reduction in the shielding influence.* Similarly the large upfield chemical shifts observed for hydridic protons in transition metal hydride complexes have been shown to be partially attributable to the "paramagnetism" induced in the metal atom by the static magnetic field.[27]

Fung[28] has shown that the proton chemical shift for the $Co(NH_3)_6{}^{3+}$ ion *vs.* free NH_3 is reasonable considering the estimated[29] electron density on the protons in this complex. If, as expected, coordination of NH_3 to Rh(III) and Ir(III) results in a greater decrease of electron density around the hydrogen, then a shift to a field even lower than that observed for $Co(NH_3)_6{}^{3+}$ would result. Experimentally this is what is observed (see Table I). Recent results of nitrogen X-ray photoelectron spectroscopy[30] have indicated that the nitrogen atoms in rhodium(III)- and iridium(III)-ammine complexes have a more positive charge than

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(24) N. F. Ramsey, *Phys. Rev.*, **78**, 699 (1950).

(25) For example see A. Saika and C. P. Slichter, *J. Chem. Phys.*, **22**, 26 (1954).

(26) J. S. Griffith and L. E. Orgel, *Trans. Faraday Soc.*, **53**, 601 (1957).

(27) A. D. Buckingham and P. J. Stephens, *J. Chem. Soc.*, 2747 (1964).

(28) B. M. Fung, *J. Phys. Chem.*, **72**, 4708 (1968).

(29) F. A. Cotton and T. E. Haas, *Inorg. Chem.*, **3**, 1004 (1964).

(30) D. N. Hendrickson, J. M. Hollander, and W. L. Jolly, unpublished data.

those in the cobalt(III) ammines. Thus the chemical shifts of the cobalt triad hexammines can probably be understood by considering only the diamagnetic term in the shielding constant expression. However, the disappearance of the 4:1 pmr patterns in the rhodium and iridium pentaammines cannot be explained by considering only this term; the influence of the "paramagnetic" term must be considered.

The "paramagnetic" term in the ammine proton shielding constant expression is approximately proportional to the inverse of the ligand field stabilization energies (the energy difference between the ground $^1A_{1g}$ and excited $^1T_{1g}$ states is measured by $\Delta = 10Dq$) in the three different metal complexes and is also proportional to some magnetic moment integrals that depend on inverse cubes of distances. Thus the "paramagnetism" induced mainly in the metal atom (*i.e.*, Δ refers to the splitting between the t_{2g} and e_g orbitals, which are mainly metal 3d orbitals) will influence the shielding of the ammine protons. In the case of rhodium and iridium complexes, the Δ values (*i.e.*, $E_n - E_0$) are relatively large and the

$$\left\langle 0 \middle| \sum_k \frac{m_k^2}{r_k^3} \middle| n \right\rangle$$

values are small; thus there is very little contribution from the second term to σ for rhodium and iridium ammine protons. The values for the m_k^2/r_k^3 integrals are small because the distance from the proton to the mainly metal t_{2g} electron (*i.e.*, r_k) is large. We believe that the *cis* and *trans* ammine protons in the iridium and rhodium pentaammines are affected only by the diamagnetic term and therefore resonate at the same field position. That is, these protons "feel" the sixth group X only by inductive effects transferred through the metal atom.

On the other hand, the *cis* and *trans* ammine protons in a cobalt pentaammine experience different effective magnetic fields because of differences in the paramagnetic term. In an octahedral d^6 cobalt complex the $^1T_{1g}$ state is mixed with the $^1A_{1g}$ ground state under the influence of a magnetic field. Lowering the symmetry to C_{4v} (as in a pentaammine) splits the $^1T_{1g}$ state to ^1E and $^1A_2$ states. Admixture of these two low-energy mainly metal states with the ground state of the cobalt pentaammines is the main source of the "paramagnetism." Whether or not a *trans* proton resonates at higher field than a *cis* proton in a particular $Co(NH_3)_5X^{n+}$ ion depends on the differences in cobalt susceptibility[31] when the magnetic field is directed parallel or perpendicular to the symmetry axis of the pentaammine.

The paramagnetic contribution to the shielding constant for a proton can be represented as an average $\sigma = {}^1/_3(\sigma_{xx} + \sigma_{yy} + \sigma_{zz})$.[22,27] In the pentaammines the ^1E state contributes to $\sigma_{x'x'}$ and $\sigma_{y'y'}$ whereas the $^1A_2$ state contributes to $\sigma_{z'z'}$ (x', y', z' are given here for local coordinates about the metal where the z' axis is the symmetry axis of the pentaammine). In a series of $Co(NH_3)_5X^{n+}$ complexes, the energy of the ^1E state varies appreciably, whereas that of the $^1A_2$ state does not.[24] If we consider the *trans* ammine protons in $Co(NH_3)_5X^{n+}$, variation of X results in only $\sigma_{x'x'}$ and $\sigma_{y'y'}$ changing. The geometric position of the *trans* ammine proton is such that both $\sigma_{x'x'}$ and $\sigma_{y'y'}$ will shield the proton. Thus the shielding should increase for the *trans* proton as the ligand field strength of X decreases (*i.e.*, as $E(^1E) - E(^1A_1)$ becomes smaller in the paramagnetic term). This is what is observed in Table I.

Consideration of the shielding of the cobalt *cis* ammine protons shows that when X is varied the same trend would not be expected. Here one of the directions perpendicular (*i.e.*, the $\sigma_{x'x'}$ or $\sigma_{y'y'}$ term) to the Co–X axis will be directed along the Co–N bond for a particular *cis* proton. The paramagnetism induced in the metal center when the magnetic field is so oriented produces deshielding at the *cis* ammine proton. If this deshielding outweighs the shielding, a chemical shift trend opposite to that observed for the *trans* protons should result and the *cis* ammine protons would be expected to resonate at lower fields for weaker field X ligands. This is the observed behavior (seee Table I).

Thus we predict that the *trans* protons in $Co(NH_3)_5X$ should resonate at a higher field for weak-field X ligands and that the opposite trend should be possible for the *cis* protons. From Table I we see that these trends are indeed observed if we accept the following order of increasing ligand field strength: $HSO_4^- < H_2O < Cl^- < Br^- < NH_3 \sim NO_2^- < CN^-$, with NCS^- between H_2O and Cl^- in one case and between Br^- and NH_3 in the other. We are not surprised that this series does not exactly match the "spectrochemical series," because in the shielding expression the exponential behavior of the metal radial functions might be expected to vary. Such variation was noted by Buckingham and Stephens in their analysis of metal hydride chemical shifts.[27] The overall result of the *cis* and *trans* trends is that we observe a 4:1 pattern for the weak-field X's and a 1:4 pattern for the strongest field X, namely, CN^-.

The fact that we see a 1:4 pmr pattern for $Ru(NH_3)_5N_2^{2+}$ is not surprising, because Ru(II) would, like Co(III), be expected to have low ligand field stabilization energies relative to Rh(III) and Ir(III).[32]

Finally, the additivity of chemical shielding in the cobalt pentaammines and tetraammines[3] is probably a manifestation of the average environment concept for ligand field splittings. Thus the Δ ($10Dq$) value is an additive function of the six ligands about the metal.

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(31) In ref 28 the difference in shielding between *trans* and *cis* ammine protons was briefly ascribed to magnetic anisotropy in the Co–X bond. Certainly some of the unpaired electron density resultant from admixture of the $^1T_{1g}$ excited state under the influence of the magnetic field will be delocalized onto the X atom; nevertheless, assignment of the exact center for the induced "paramagnetism" is not critical to this discussion.

(32) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press Inc., New York, N. Y., 1962, Chapter 7.

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