where μ_i is defined as follows.

$$\mu_i = \frac{\alpha q}{r^2 + 2.37\alpha/r}$$

By substituting $q = 2$, $\alpha = 6.45 \times 10^{-24}$ cm^3,[43] and $r = 3.526$ Å, we obtain $U_p = 123.5$ kcal/mol. Hence $U - 2U_c - U_p = -298$ kcal/mol.

---

(43) J. A. A. Ketelaar, "Chemical Constitution," 2nd ed, Elsevier Publishing Co., Amsterdam, 1958, p 91.

Fermi Contact Shifts in Ion Pairing Systems

Dennis G. Brown[1] **and Russell S. Drago**

Contribution from the W. A. Noyes Laboratory, University of Illinois,
Urbana, Illinois 61801. *Received June 4, 1969*

Abstract: ^{14}N isotropic resonance shifts have been observed for a tetrabutylammonium cation ion paired to several paramagnetic anionic transition metal complexes. The observed shifts substantiate a Fermi contact interaction between the unpaired electrons of the anion and the cation. This requires that there be some type of weak covalent interaction between the cation and anion in the ion pair. Possible mechanisms by which unpaired spin could be delocalized onto the cation are discussed.

There have been several reports over the past few years dealing with proton isotropic resonance shifts in paramagnetic ion pairing systems.[2-9] Most of the systems which have been studied involve the ion pairing of a tetraalkylammonium cation with some anionic paramagnetic transition metal complex. The observed isotropic resonance shifts for protons on the diamagnetic cations have been interpreted as arising solely from a "pseudocontact" shift; that is, from a direct dipolar coupling between the magnetic moment of the unpaired electrons on the metal and the magnetic moment of the nucleus with which one is concerned. The reason for this is that the alternative mechanism contributing to the isotropic resonance shift, the Fermi contact interaction, would require some kind of covalent bonding between the cation and the anion. The assumption that this latter mechanism is completely negligible seems quite reasonable at first glance; however, we shall present evidence below which, in fact, demonstrates that some unpaired spin density is actually transferred to the cation.

Equation 1 is a general form which describes the

$$(\Delta\nu/\nu_0)_i = -\frac{\beta^2 S(S+1)}{45kT}\, f(g)\left(\frac{3\cos^2\theta_i - 1}{R_i^3}\right) \qquad (1)$$

"pseudocontact shift.[10] $\Delta\nu = \nu_{\text{paramagnetic}} - \nu_{\text{diamagnetic}}$ is the resonance shift for the ith nucleus in the paramagnetic complex referenced to an analogous diamagnetic complex. ν_0 is the rf frequency at which the experiment is carried out. S is the total spin quantum number. R_i is the length of the vector from the metal atom to the ith nucleus and θ_i is the angle between this vector and the principal axis of the paramagnetic molecule or ion. f(g) is some function of the components of the **g** tensor. In the cases with which we will be concerned, *i.e.*, for an axial system and for $\tau_c \gg T_1$ where τ_c and T_1 are the molecular correlation and electron spin relaxation times, respectively, $f(g) = (3g_{\parallel} + 4g_{\perp})(g_{\parallel} - g_{\perp})$.[10b] The important thing to notice in eq 1 is that the pseudocontact shift depends on the anisotropy of the g tensor and on a geometric factor, $(3\cos^2\theta_i - 1)/R_i^3$. In order for the anisotropy in g to be nonzero, the paramagnetic metal atom must be in an environment of noncubic symmetry. Sometimes this results from the geometry of the complex and sometimes it can arise from the ion pairing itself even though the metal ion might otherwise be expected to be in a cubic environment.[9] It can also be seen in eq 1 that as one goes from one nucleus to another in a particular complex or even if the nucleus varies from ^{1}H to ^{13}C to ^{14}N the only term which varies is the geometric factor. This point will be relevant to the results given below.

Larson and Wahl[2] have examined the proton isotropic resonance shifts of tetraalkylammonium cations in aqueous solutions containing paramagnetic Fe(CN)$_6^{3-}$ anions. The observed upfield shifts were considered to be due to a pseudocontact mechanism and the results were used to draw conclusions about the extent of ion pairing in the systems studied. LaMar[4,5] has investigated the proton nmr of the tetrabutylammonium cation in the paramagnetic complexes [Bu$_4$N][(Ph$_3$P)MI$_3$] where M = Co(II) and Ni(II). Once again the shifts were interpreted as arising solely from a pseudocontact interaction with the unpaired electrons on the metal. In this work a geometry for the ion pair ([Bu$_4$N][(Ph$_3$P)MI$_3$]) was determined using the observed shifts for the H$_1$ and H$_2$ protons[11] in the butyl chains and the calculated geometric factors for these protons.

---

(1) National Science Foundation Predoctoral Fellow, abstracted in part from Ph.D. thesis of Dennis G. Brown.

(2) D. W. Larsen and A. C. Wahl, *Inorg. Chem.*, **4**, 1281 (1965).

(3) D. W. Larsen, *ibid.*, **5**, 1109 (1966).

(4) G. N. LaMar, *J. Chem. Phys.*, **41**, 2992 (1964).

(5) G. N. LaMar, *ibid.*, **43**, 235 (1965).

(6) W. D. Horrocks, Jr., R. H. Fischer, J. R. Hutchinson, and G. N. LaMar, *J. Amer. Chem. Soc.*, **88**, 2436 (1966).

(7) G. N. LaMar, R. H. Fischer, and W. D. Horrocks, Jr., *Inorg. Chem.*, **6**, 1798 (1967).

(8) J. C. Fanning and R. S. Drago, *J. Amer. Chem. Soc.*, **90**, 3987 (1968).

(9) I. M. Walker and R. S. Drago, *ibid.*, **90**, 6951 (1968).

(10) (a) H. M. McConnell and R. E. Robertson, *J. Chem. Phys.*, **29**, 1361 (1958); (b) G. D. LaMar, *ibid.*, **43**, 1085 (1965); (c) J. P. Jesson, *ibid.*, **47**, 579 (1967).

(11) The numbering system for the butyl chain will be that used in ref 4, 5, and 9 and is as follows: N(C$_1$-C$_2$-C$_3$-C$_4$)$_4^+$.

In order to calculate the geometric factors a simple model of the molecular motion must be used in order to average the protons over the motion. It was assumed that the tumbling motion of the cation with respect to the anion was isotropic and that there was free rotation about the C–N and the C–C bonds. From this model, the isotropic shifts, and the geometric factors for H_1 and H_2, an ion pairing distance of 3.8 ± 0.2 Å was calculated. Horrocks,[6] *et al.*, carried out a very similar investigation on the tetrabutylammonium tris(acetylacetonato)cobalt(II) and -nickel(II) complexes, $[Bu_4N][M(acac)_3]$, and calculated a short ion pairing distance of 3.6–3.7 Å. Walker and Drago[9] have recently observed isotropic resonance shifts in the butyl proton resonances of tetrabutylammonium tetrahalometalates (II). One might expect these complexes to be effectively cubic in solution and, as a result, might not expect a pseudocontact interaction since $(g_{\parallel} - g_{\perp})$ must be nonzero to observe a pseudocontact shift. However, in these solutions the ion pairing induces an anisotropy in the g tensor and isotropic shifts in the butyl protons are observed. There was some evidence in this study that perhaps not all of the isotropic shift observed was due to the pseudocontact interaction. In all of the complexes studied it is a requirement that $|\Delta\nu_{H_1}| > |\Delta\nu_{H_2}| > |\Delta\nu_{H_3}| > |\Delta\nu_{H_4}|$ ($\Delta\nu_{H_i}$ is the observed isotropic shift for the ith proton) if the isotropic shift is due solely to a pseudocontact mechanism. This is because the geometric factor, $3\cos^2\theta_i - 1/R_i^3$ in eq 1, decreases in the order $H_1 > H_2 > H_3 > H_4$. However, the NiX_4^{2-} complexes studied by Walker and Drago exhibited somewhat different behavior; in general for those complexes it was observed that $|\Delta\nu_{H_2\text{ and }3}| \gtrless |\Delta\nu_{H_1}| > |\Delta\nu_{H_4}|$. This is clearly impossible if only a pseudocontact mechanism is operative and they were forced to postulate a weak contact interaction between the paramagnetic anion and the cation in the ion pair. The behavior exhibited by these complexes was one factor which led us to look into this situation further. Another factor which caused us to look at these systems more closely was a very short note by Burkert, *et al.*,[12] which reported the observation of a downfield ^{14}N shift in $[Bu_4N][(Ph_3P)CoI_3]$. This is opposite from what one would expect based on the direction of the proton isotropic shifts in this complex. However, there were no experimental details or even numerical data given in this article and because of the difficulty with referencing the nitrogen shifts in these kinds of systems we felt that this unexpected result was suspect. In fact, because of the questionable interpretation of the nature of the pseudocontact mechanism demonstrated in this note, it would have been quite easy to disregard the qualitative observations reported. In fact, one article[13] completely rejects the interpretation of Burkert, *et al.*

Experimental Section

Preparation of Complexes. The tetrabutylammonium triphenylphosphine triiodometalates(II), $[(n\text{-}C_4H_9)_4N][(C_6H_5)_3PMI_3]$, M = Zn, Ni, Co, were prepared by the method of Rettig.[14] The tetrabutylammonium tetrahalometalates were prepared by methods previously outlined by Walker.[9]

Nuclear Magnetic Resonance Spectra. In all cases the solvent used was Mallinckrodt spectrophotometric grade dichloromethane. The concentration of the solutions was about 0.3 *M* in complex. All measurements were made at room temperature. The nmr equipment used was a Varian DP-60 spectrometer operating in the wide line mode with a Varian Model 4210A variable frequency rf unit and Model V4230B probe. All measurements were made at a rf frequency of 4.334300 ± 0.000010 Mc/sec.

Because of the potential problems associated with referencing the spectra when using this equipment, attention will now be given to this question. Initially attempts were made to reference the spectra using an external reference in a concentric capillary tube. It is necessary to have as a reference a sample giving a very sharp signal. Several potential reference samples which satisfy this requirement (*e.g.*, NO_3^- ion) have resonance positions quite some distance from that of the tetrabutylammonium cation. As a result, in order to record the reference and sample on the same spectrum, it is necessary to compress the field sweep scale enough so that small changes in the position of the sample cannot be measured. On the other hand, if one attempts to use a reference material occurring at a resonance position very close to that of the sample (*e.g.*, aqueous $(CH_3)_4NCl$), the two peaks often overlap somewhat and, once again, it is difficult to accurately measure changes in the resonance position of the sample. Due to these difficulties the following procedure was employed and found to be quite satisfactory. The field sweep was expanded so that a small magnetic field change could be scanned. If a spectrum is then run on a diamagnetic zinc complex (*e.g.*, $[(C_4H_9)_4N]_2ZnCl_4$), one can reset the field sweep, rerun the spectrum, and observe no significant change in the resonance position of the complex due to instability of the instrument. In addition, any other sample of a tetrabutylammonium zinc complex will give a resonance at the same position. However, when one uses a paramagnetic anion, the same procedure can be carried out and the resonance position is shifted measurably. It will be shown below that these shifts cannot be attributed to differences in the bulk susceptibilities of the reference and sample. In order to obtain a reasonably accurate measurement of the paramagnetic shift the following procedure was carried out for each paramagnetic sample. Several spectra were run on an analogous zinc compound to determine a reference position. The paramagnetic sample was then run, and finally the diamagnetic reference was run again to ensure that the magnetic field had remained constant for all of the measurements. The shifts reported are the differences between the resonance position of the paramagnetic sample and the resonance position of the reference. It was found that repeated measurements on the same sample gave quite reproducible results and it appears that this procedure gives fairly reliable data.

Results

For reference, Table I gives the previously observed proton isotropic resonance shifts which have been observed for the systems with which we are concerned. All of the numbers reported are referenced to an analogous diamagnetic zinc complex so that the shifts can be attributed predominantly to the paramagnetism of the complexes.

Table I

Complex	Proton resonance shifts, ppm[a]			
	H_1	H_2	H_3	H_4
$[(n\text{-}C_4H_9)_4N][(C_6H_5)_3PCoI_3]$	6.00	3.00	1.66	0.50
$[(n\text{-}C_4H_9)_4N][(C_6H_5)_3PNiI_3]$	−2.68	−1.50	−1.25	−0.50
$[(n\text{-}C_4H_9)_2N]_2[CoCl_4]$	2.08	0.63[b]		0.07
$[(n\text{-}C_4H_9)_4N]_2[CoBr_4]$	2.45	0.93		0.20
$[(n\text{-}C_4H_9)_4N]_2[CoI_4]$	2.33	0.93		0.07
$[(n\text{-}C_4H_9)_4N]_2[NiCl_4]$	−0.97	−0.95		−0.63
$[(n\text{-}C_4H_9)_4N]_2[NiBr_4]$	−0.55	−0.72		−0.53
$[(n\text{-}C_4H_9)_4N]_2[NiI_4]$	0.28	−0.27		−0.22
$[(n\text{-}C_4H_9)_4N]_2[Co(SCN)_4]$	0	0		0

[a] Shifts are referenced to a diamagnetic zinc complex. [b] For all the tetrahalometalates only one peak can be resolved for the H_2 and H_3 protons. The numbers reported are the center of this broad peak.

---

[12] P. K. Burkert, H. P. Fritz, W. Gretner, H. J. Keller, and K. E. Schwarzhans, *Inorg. Nucl. Chem. Lett.*, **4**, 237 (1968).

[13] R. H. Fischer and W. D. Horrocks, Jr., *Inorg. Chem.*, **7**, 2659 (1968).

[14] M. F. Rettig and R. S. Drago, *J. Amer. Chem. Soc.*, **88**, 2966 (1966).

Table II

Complex	Bulk susceptibility shift, ppm	Predicted[b] ^{14}N dipolar shift, ppm	Observed ^{14}N chemical shift, ppm[a]	Total downfield shift, ppm
$[(n\text{-}C_4H_9)_4N][(C_6H_5)_3PCoI_3]$	5.4	5.9	−9	−20
$[(n\text{-}C_4H_9)_4N][(C_6H_5)_3PNiI_3]$	3.1	−2.8	−10	−10
$[(n\text{-}C_4H_9)_4N]_2[CoCl_4]$	5.8	1.7	+1	−6
$[(n\text{-}C_4H_9)_4N]_2[CoBr_4]$	6.1	2.1	−5	−13
$[(n\text{-}C_4H_9)_4N]_2[CoI_4]$	6.2	2.1	−12	−20
$[(n\text{-}C_4H_9)_4N]_2[NiCl_4]$	3.8	−1.3	−6	−8
$[(n\text{-}C_4H_9)_4N]_2[NiBr_4]$	3.8	−.9	−7	−10
$[(n\text{-}C_4H_9)_4N]_2[NiI_4]$	3.4	−.1	−12	−15
$[(n\text{-}C_4H_9)_4N]_2[Co(SCN)_4]$	5.3	0	−1	−6
$[(n\text{-}C_4H_9)_4N]_2[MnBr_4]$	9.1		−5	−14

[a] All numbers are referenced to an analogous zinc(II) complex. [b] Calculated from the geometric factors and the data in Table I incorrectly assuming the proton shifts are dipolar in nature.

Differences in bulk susceptibility between a paramagnetic sample and a similar diamagnetic sample can cause differences in the resonance positions of the two samples or in the resonance positions of a reference molecule dissolved in each solution. This phenomenon has been taken advantage of in determining magnetic moments of paramagnetic molecules.[15] In this experiment, diamagnetic and paramagnetic samples are placed in concentric tubes and the resonance position of a neutral molecule in each solution is determined. Two resonance positions will be observed, one for the diamagnetic sample and one for the paramagnetic sample. The difference in the resonance positions can be related to the susceptibility of the paramagnetic sample. The relation governing the difference in resonance positions and the molar susceptibility is

$$\chi_M' = \frac{3\Delta f M}{2\pi f m} + \chi_D$$

Here χ_M' is the molar susceptibility of the complex, Δf is the difference in resonance frequency of the two internal standards, measured in cps, f is the probe frequency, and m is the number of grams of complex per milliliter of solution. χ_D is a diamagnetic correction to the molar susceptibility. It is observed that the resonance position of the paramagnetic sample always occurs at *higher frequency*.[15] It is possible to use this relationship to calculate a correction in the resonance position of the samples at which we have looked from a knowledge of the magnetic moment of each paramagnetic complex. For example, a reference molecule in a 0.3 *M* solution of $[(C_4H_9)_4N]_2CoCl_4$ ($\mu_{eff} = 4.8$) would be expected to show a resonance position 5.8 ppm upfield from that of the same molecule in a solution of an analogous diamagnetic zinc complex assuming only bulk susceptibility differences determine the resonance position. These corrections have been calculated for 0.3 *M* solutions of each of the complexes investigated.

The first column of Table II gives the shift to higher field expected in going from a diamagnetic to paramagnetic sample based only on the bulk susceptibility differences in the samples. There is another effect which will determine the shift in the resonance position of the nitrogen atom in going from a diamagnetic to paramagnetic complex. This is a dipolar coupling of the magnetic moment of the unpaired electron to the magnetic moment of the nucleus. A number can be calculated for this effect from the data given in Table I. The way in which this number is calculated will be described below. The second column of Table II gives the contribution to the ^{14}N shift due to the dipolar interaction. The third column of Table II gives the observed ^{14}N isotropic resonance shifts once again referenced to the analogous diamagnetic zinc complexes. The numbers reported are the average of several measurements. However, because of the fact that we were forced to operate the instrument in the wide line mode, a large error limit should be associated with these numbers. For example, when a paramagnetic sample is run at different concentrations, there should be some change in the resonance position because of differences in bulk susceptibility. However, when a sample was run at concentrations different enough so that one might expect a shift of about 2 ppm due to susceptibility differences, the instrument did not consistently detect this. As a result, we feel the accuracy of these numbers is probably no better than 2 ppm. It should be pointed out, however, that the trends observed in going from Cl^- to Br^- to I^- as a ligand were always reproducible, and we are quite confident that the general trends shown in Table II are significant. The magnitudes of the downfield shifts observed are considerably outside the range of experimental error. It would be desirable to perform this experiment using ^{15}N nmr to improve the accuracy.

The last column in Table II gives the discrepancy between the observed shift and that which would have been observed if the ^{14}N shift were solely dipolar in origin; *i.e.*, column 4 is column 3 − (1 + 2). The numbers in column 4 are our estimates of the downfield shift due to unpaired spin density on the cation.

Discussion

All of the previous proton nmr work done on these types of systems has assumed that the interaction between a nucleus in the diamagnetic cation and the unpaired electrons in the anion is by a purely pseudocontact mechanism. As will be shown in the following discussion our results demonstrate that this is not completely true, but that there is a small contact interaction between the anion and cation. From eq 1 it can be seen that the only term which varies for the pseudocontact shift as one goes from one point in a molecule to another is the geometric factor. Let us assume that the isotropic proton shifts observed in these systems are due entirely to a pseudocontact interaction. If this

---

(15) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

were true, one could, by knowing the geometric factor and the shift at one position, calculate the shifts to be observed at every other position from a knowledge of the geometric factors for those positions. The expected pseudocontact shifts for the nitrogen have been calculated in this manner as described below. However, it is of interest to first make some predictions about the shifts at various nuclei from knowing only qualitatively the relative magnitudes of the geometric factors. Considering the protons on the alkyl chain of the cation, it can be shown that the geometric factor G_i for the ith proton varies as $G_1 > G_2 > G_3 > G_4$.[5] Therefore, the magnitude of the pseudocontact shift should vary in the same manner, *i.e.*, $|\Delta\nu_{H_1}| > |\Delta\nu_{H_2}| > |\Delta\nu_{H_3}| > |\Delta\nu_{H_4}|$. This is in general the behavior which has been observed as can be seen from Table I. If one then considers the position of the nitrogen atom in the tetraalkylammonium cation, it will be on the principal axis of the anion and the geometric factor at this position will be a maximum. Therefore, one would expect the pseudocontact shift at the nitrogen to be of the same sign as, and larger than, the shift at the H_1 proton; $|\Delta\nu(N)|/\nu_0(N) \geq |\Delta\nu_{H_1}|/\nu_0(H)$. As can be seen from a comparison of Tables I and II this is not observed. Thus the isotropic ^{14}N shifts we have measured cannot be explained using the purely pseudocontact shift model that has been used in explaining the previous proton work.

The preceding qualitative discussion can be put in more quantitative terms because we know the geometric factors and observed shifts at protons H_1 and H_2. The average geometric factors for protons H_1 and H_2 have been calculated[5] as a function of the ion pairing distance, r. The averaging procedure for the tumbling of the cation is also described. To get an idea of the approximate magnitude of the isotropic shift one would expect at the nitrogen, we have calculated this number using the same model that has been used to explain the proton results. We have chosen an ion pairing distance of 3.8 Å, but this arbitrary choice is not critical to the conclusions to be drawn. The values of the geometric factors for the H_1 and H_2 protons are about 0.031 and 0.022 Å^{-3}, respectively. For this distance the geometric factor for the nitrogen atom is 0.0365 Å^{-3}. Using these geometric factors and the proton isotropic shifts, one can calculate the expected isotropic shift at the nitrogen from either the H_1 shift or the H_2 shift. When these are compared they often do not agree too well due to the simplified model being used and to the choice of ion pairing distance. The second column of Table II shows the average of these two numbers for various complexes. So to summarize, the numbers shown in Table II are the isotropic shifts to be expected at the nitrogen atom based on the assumptions that the averaging procedures used are correct and that the shift is due entirely to a pseudocontact interaction. These numbers are to be contrasted with those shown in the third column of Table II which report the measured ^{14}N isotropic resonance shifts. The sum of columns 1 and 2 in Table II give the shifts to be expected if only bulk susceptibility and dipolar interaction are effective. However, in all cases, the observed resonance position comes downfield from where it would be expected. The magnitude of this downfield shift is given in the fourth column of Table II. The only way in which this behavior can be explained is to postulate a direct contact interaction between the anion and cation in which a small amount of unpaired spin density is transmitted to the tetrabutylammonium ion.

There is precedence for a Fermi contact contribution to the shift in an ion pairing system. Alei[16] has observed isotropic shifts for ^{17}O in the system $Cr(H_2O)_6^{+3}$, H_2O, ClO_4^-. The isotropic shifts reported there were for uncoordinated H_2O and ClO_4^-. They were attributed to a direct contact interaction in which labile H_2O and ClO_4^- received a small amount of unpaired spin density when they were in the "second coordination sphere" of the $Cr(H_2O)_6^{+3}$ complex.

It remains to discuss the mechanism by which unpaired spin density can be transfered to the diamagnetic cation through a direct contact interaction. The equation for the Fermi contact shift is shown below.

$$(\Delta\nu/\nu_0)_i = -\frac{Ag_{av}\beta_e S(S+1)}{g_N\beta_N 3kT} \tag{2}$$

$\Delta\nu$ is the shift in cps, ν_0 is the probe frequency in cps, g_{av} is the average g value for the complex being considered, and g_N is the nuclear g value. A, the electron–nuclear hyperfine coupling constant in ergs, is defined by the equation

$$A = \frac{8\pi}{6S} g_{av}\beta_e g_N \beta_N |\Psi(0)|^2 \tag{3}$$

where $\Psi(0)$ is the value of the wave function containing the unpaired spin evaluated at the nucleus being considered. The term $|\Psi(0)|^2$ is the measure of unpaired spin density residing at a particular nucleus. We are interested in explaining how this spin density gets into the cation (or alternatively we want to know what the wave function Ψ looks like). There are a number of possibilities. Unpaired spin density resides on the halide ligands in question in all of the paramagnetic complexes considered. It is possible that the relatively diffuse orbitals of these halogen ligands could overlap with an s orbital of the N atom in the tetrabutylammonium cation. This would impart a small amount of unpaired spin to the nitrogen which could be left by the nucleus. To rephrase this in terms of a molecular orbital description, one would say that the molecular orbital containing unpaired spin density which has large coefficients from the iodine ligands also has nonnegligible coefficients from atoms on the cation. In particular there is a small coefficient from the nitrogen 2s orbital.

It is also possible that spin could be transferred from the halide to the cation in a somewhat different manner. If one builds molecular models of a tetrabutylammonium ion and arranges the alkyl chains so that the anion and cation could approach each other as closely as possible, he finds that the H_1 protons are pointed directly at the complex. Because of this, it is possible that these protons are forced to "hydrogen bond" to the halides just because of the close approach of the cation and anion. Then unpaired spin might enter the σ framework of the cation through this interaction. Since the sequence of shifts $|\Delta\nu_{H_1}| > |\Delta\nu_{H_2}| > |\Delta\nu_{H_3}| > |\Delta\nu_{H_4}|$ based on a pseudocontact interaction is not observed in some cases, this mechanism must be of importance to the proton shifts. In the NiX_4^{2-} complexes the H_1 protons are apparently shifted upfield from where one would expect the resonance to come. Similar behavior has been observed for the proton of chloroform when

---

[16] M. Alei, Jr., *Inorg. Chem.*, 3, 44 (1964).

it hydrogen bonds to a paramagnetic triphenylphosphine triiodometalate(II).[14] However, it is questionable whether this type of interaction could transmit enough unpaired spin density to the nitrogen atom to give the size of contact shift observed. The third way in which unpaired spin could be transferred to the cation is through direct overlap of the metal orbitals containing unpaired spin with a nitrogen s orbital. This, of course, depends critically on the ion pairing distance. In the ^{17}O work on $Cr(H_2O)_6(ClO_4)_3$ mentioned previously,[16] it was assumed that the downfield ^{17}O shift for ClO_4^- and H_2O in the second coordination sphere was due to σ overlap of oxygen sp hybrid orbitals of H_2O or ClO_4^- with the Cr(III) t_{2g} orbitals. For our system it appears that this means of transferring spin to the cation is unlikely. If one calculates the value of a nickel 3d orbital at a distance 3.8 Å from the nickel and squares this number, the result is on the order of 10^{-8} au^{-3}. This is too small to contribute significantly to $|\Psi(0)|^2$ in eq 3. From eq 2 one would expect a value on the order of 1 au^{-3} for $|\Psi(0)|^2$ for a 1-ppm resonance shift. In addition, if spin were transferred directly to the cation by the metal 3d oribitals one might expect more spin to be transferred for a chloro complex than for an iodo complex because the cation could approach the metal more closely in the chloro complex. However, for both NiX_4^{2-} and CoX_4^{2-} anions the magnitude of the observed downfield shifts vary with X as $MCl_4^{2-} < MBr_4^{2-} < MI_4^{2-}$. This seems to be rather convincing experimental evidence that a nitrogen s orbital does not receive much spin from direct overlap with metal orbital, so that in all likelihood spin is transmitted to the cation through the halogen ligands of the complex. The halide orbitals containing unpaired spin must donate spin directly into a nitrogen s orbital giving the observed spin density at the nitrogen nucleus. The alternative proposed to this, that spin enters the σ framework of the cation through the H_1 proton, would not transfer enough spin to the nitrogen to give the isotropic shifts observed. However, it cannot be disputed that the H_1 proton is interacting with the halide ligands as evidenced by the results seen for the NiX_4^{2-} complexes. In fact it is quite likely that in all cases the H_1 resonance occurs at higher field than might be expected from only pseudocontact interaction.

It should be pointed out that the preceding discussion about the nature of the direct contact mechanism is of necessity very qualitative because of the fact that factors such as the exact manner in which spin is transferred to the cation. In addition to the fact that spin is transferred to the cation in these complexes, it is likely that multiple ion pairs or even micelle formation also occurs. Because of these two factors the simple method previously reported[5,7] for calculating ion pairing distances should not be expected to be particularly reliable. The very short distances calculated for the triphenylphosphine triiodometalates is probably due to a combination of these two effects.

To summarize, it has been shown that in systems with a tetrabutylammonium cation ion paired to a paramagnetic, ^{14}N isotropic resonance shifts have been observed. The only way in which the shifts can be explained is to postulate a Fermi contact interaction between the unpaired electrons on the anion and the cation. This requires some type of weak covalent interaction between the anion and cation in the ion pair.

Acknowledgment. The authors wish to acknowledge the generous support of the research by the National Science Foundation through Grant GP-5498.

The Effect of Coordinated Ligands on the Rate of Replacement of Bound Water by Ammonia in Nickel(II) Complexes. II

J. Paul Jones, E. J. Billo, and Dale W. Margerum[1]

Contribution from the Department of Chemistry,
Purdue University, Lafayette, Indiana 47907.

Received August 30, 1969

Abstract: As the number of coordinated nitrogens in nickel–polyamine complexes increases, the rate of replacement of the remaining coordinated water increases. Rate constants for the exchange of water by ammonia are larger for nickel–trien than for nickel–dien at 8° by a factor of 5. tren, a branched tetradentate polyamine, gives a more rapid NH_3–H_2O exchange than trien. Six-membered chelate rings in polyamine complexes and alkyl groups on en also increase the rate.

The characteristic rate of replacement[2] of water from the first coordination sphere is affected by the presence of other groups bound to the metal ion. An earlier paper[3] showed that the charge of the complex *per se* is not of much importance in the rate of replacement of water in nickel complexes, but that coordinated nitrogens tend to increase the exchange rate. Thus, the ammonia–water exchange in eq 1 increases as L is

$$[NiL(H_2O)_x]^n + NH_3 \underset{k_{21}}{\overset{k_{12}}{\rightleftarrows}} [NiL(H_2O)_{x-1}(NH_3)]^n + H_2O \quad (1)$$

---

[1] Author to whom correspondence should be addressed.

[2] For a review see (a) M. Eigen and R. G. Wilkins, "Mechanism of Inorganic Reactions," American Chemical Society, Washington, D. C., 1965, pp 55–65; (b) M. Eigen and L. DeMaeyer, "Technique of Organic Chemistry," Vol. VIII, Part II, A. Weissberger, Ed., Interscience Publishers, New York, N. Y., 1963, pp 895–1054.

[3] D. W. Margerum and H. M. Rosen, *J. Amer. Chem. Soc.*, **89**, 1088 (1967).