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Citation: The Journal of Chemical Physics **41**, 2992 (1964); doi: 10.1063/1.1725664
View online: http://dx.doi.org/10.1063/1.1725664
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/41/10?ver=pdfcov
Published by the AIP Publishing

Inserting (A2.11) into (A2.6) and taking the zeroth-order approximation for the destruction operator,

$$\langle k_1 | -\lambda\delta L^{1j}[1/(L_0-i\epsilon)] | k_1+l, -l_j\rangle^{(1)} \equiv \langle 0 | -\lambda\delta L^{1j}[1/(L_0-i\epsilon)] | l, -l_j\rangle$$
$$= \langle 0 | \lambda\tilde{D}^{\{1\}}(0) | l, -l_j\rangle, \tag{A2.12}$$

we get, finally,

$$\lambda^2 I_{k_1}{}^{\{2\}} = i\beta\sum_j \int dp_j \sum_l \langle 0 | \lambda\tilde{D}^{\{1\}}(0) | l, -l_j\rangle \lambda[(\hat{J}_K{}^{\mu\nu}+\hat{J}_V{}^{\mu\nu})\rho^{eq}]^{\{1\}}{}_{l,-l_j}(\nabla^\mu u_\nu)_{k_1}, \tag{A2.13}$$

which is precisely the second-order term of (4.15).

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 41, NUMBER 10 15 NOVEMBER 1964

Isotropic Shifts of Some Ionic Complexes of Cobalt(II) and Nickel(II): Evidence for Ion Pairing*

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(Received 15 July 1964)

Isotropic proton resonance shifts have been observed for the ionic complexes, $[\mathrm{Bu_4N}][(\phi_3\mathrm{P})\mathrm{CoI_3}]$ and $[\mathrm{Bu_4N}][(\phi_3\mathrm{P})\mathrm{NiI_3}]$. In addition to the phenyl (ϕ) proton shifts for the complex anions, isotropic shifts were observed for the cation protons as well. These shifts for the tetra-*n*-butylammonium cations are interpreted as arising solely from a pseudocontact interaction with the metal in the complex anion through partial ion pairing in the deuterochloroform solutions. From the magnitudes of the shifts for the butyl protons, an estimate is made for the relative extent of *g*-tensor anisotropies for the two anionic complexes. The observed shifts for the phenyl protons are interpreted as arising from both contact and pseudocontact interactions. Based on the postulate that the unpaired spin will distribute itself in a like manner in a given ligand whether attached to cobalt or nickel, and using the estimate of the relative anisotropies of the two metals, the phenyl proton shifts are separated into their respective contact and pseudocontact contributions. The resulting unpaired spin densities on the phenyl rings compare well with those reported for the related bis(triphenylphosphine) complexes.

INTRODUCTION

A CONSIDERABLE amount of useful knowledge about electronic structure, magnetic properties, and sometimes thermodynamic properties of ligands and complexes can be derived from the studies of the isotropic shifts in the nuclear magnetic resonance spectra of paramagnetic transition metal complexes.[1–7] The conditions[8,9] for the observation of the spectrum of a paramagnetic complex are that $1/T_1 \gg A$ or $1/T_{1e} \gg A$, or both, where T_1 and T_{1e} are the electronic spin-lattice relaxation time and characteristic electronic exchange time, respectively, and A is the hyperfine interaction constant.

These isotropic shifts, defined as the difference in resonance positions for a proton in the paramagnetic complex and in the diamagnetic ligand such that an upfield shift is considered a positive shift, can arise from two distinct interactions, one relating to the electronic structure of the complex, the other interaction resulting from magnetic dipole interactions which are essentially independent of the electronic structure of the ligands. The former interaction, known as the Fermi[10] contact interaction, results from the presence of unpaired spin at the resonating nucleus, while the latter interaction results from the dipole interaction between the nuclear moment and the electron spin magnetization of a paramagnetic metal with

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* This research has been supported by grants from the National Institutes of Health and the Petroleum Research Fund of the American Chemical Society, and by the Directorate of Chemical Sciences, U.S. Air Force Office of Scientific Research Grant No. AF-AFOSR-242-63.

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[1] D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, Mol. Phys. **5**, 407 (1962); J. Chem. Phys. **37**, 347 (1962); *ibid.* **39**, 3513 (1963); D. R. Eaton, W. D. Phillips, and D. J. Caldwell, J. Am. Chem. Soc. **85**, 397 (1963).

[2] R. H. Holm, A. Chakravorty, and G. O. Dudek, J. Am. Chem. Soc. **85**, 821 (1963); **86**, 379 (1964).

[3] J. A. Happe and R. L. Ward, J. Chem. Phys. **38**, 1211 (1963).

[4] W. D. Horrocks, Jr., R. C. Taylor, and G. N. LaMar, J. Am. Chem. Soc. **86**, 3031 (1964).

[5] W. D. Horrocks, Jr., and G. N. LaMar, J. Am. Chem. Soc. **85**, 3512 (1963).

[6] "NMR Contact Shifts in NiII Complexes: Evidence for *dπ–dπ* Bonding Between Nickel and Phosphorus," Contrib. 893 from Central Research Dept., E. I. DuPont & Co.

[7] G. N. LaMar, W. D. Horrocks, Jr., and L. C. Allen, "Isotropic Proton Resonance Shifts of Some Bis(d_3p) Complexes of CoII and Ni(II) Dihalides," J. Chem. Phys. (to be published).

[8] H. M. McConnell and D. B. Chesnut, J. Chem. Phys. **28**, 107 (1958).

[9] R. E. Robertson, in *Determination of Organic Structures by Physical Methods*, edited by F. C. Nachod and W. D. Phillips (Academic Press Inc., New York, 1962), Vol. 2, Chap. 10.

[10] E. Fermi, Z. Physik **60**, 320 (1930).

an anisotropic g tensor, and is known[8,9] as the pseudocontact interaction.

Unfortunately, the observed isotropic shifts for paramagnetic complexes in solutions are usually a result of both contact and pseudocontact shifts.[11] Unless the g tensor of the complex is known, or it can be assumed to be isotropic due to cubic symmetry, it is very difficult to quantitatively estimate the relative importance of contact and pseudocontact shifts.

Several systems, such as the aminotroponeimineate[1] and the salicylaldime[1,2] chelates of Ni II, have been studied where the observed shifts can be attributed to the contact interaction since the ligand field of the metal is nearly tetrahedral. Happe and Ward[3] found it necessary to postulate a pseudocontact interaction for the pyridine adducts of cobalt(II) acetylacetonates to make their spectra consistent with the adducts of the analogous nickel chelate. Similar conclusions were drawn by Horrock *et al.*[4] on the triarylphosphine and isonitrile adducts of the same metal chelates. They[3,4] were able to estimate the relative importance of the contact and pseudocontact shifts, but were unable to obtain absolute values for their shifts due to rapid exchange between free and coordinated ligand.

A study of the tetrahedral bis(triarylphosphine complexes of nickel[6,7] and cobalt[5,7] dihalides has shown that the spectra of the nickel complexes can be interpreted as arising only from a contact interaction with unpaired spin in the π orbitals of the ligand, while the analogous cobalt complexes displayed spectra which resulted from a significant pseudocontact interaction in addition to the contact interaction. The quantitative separation of the observed shifts into the contact and pseudocontact contributions was performed on the basis that the unpaired spin would be expected to distribute itself in the same way in a given ligand whether attached to cobalt or nickel. Thus the difference in distribution of the observed shifts for the various protons between the complexes of the two metals was interpreted as arising from pseudocontact shifts in the cobalt complexes. For these complexes[7] it was concluded that the cobalt had an anisotropic g tensor, while the nickel appeared to possess an essentially isotropic g tensor.

The (tetrabutylammonium) (triphenylphosphine) tri-iodides of cobalt(II) and nickel(II), prepared and characterized by Cotton *et al.*,[12,13] are known to be ionic, and from their magnetic susceptibility studies, it was concluded that cobalt has an $S=\frac{3}{2}$ ground state while nickel has an $S=1$ ground state. These complexes are similar to the bis-(triarylphosphine) complexes of the cobalt and nickel dihalides,[7,12] except for the replacement of a triarylphosphine by another halogen resulting in C_{3v} distortions of the tetrahedral field.

The g tensors of these complexes are thus characterized by axial symmetry, the two principal g values being $g_{\|}$ along the C_3 axis and $g_{\perp}$ in the plane perpendicular to the C_3 axis, where the C_3 axis passes through the metal–P bond.

The contact shifts for these complexes follow the simple Curie law, and are given by[8,14]

$$\left(\frac{\Delta H}{H}\right)_i=-A_i\left(\frac{\gamma_e}{\gamma_{\mathrm{H}}}\right)\frac{g\beta S(S+1)}{3kT}, \tag{1}$$

where ΔH is the isotropic shift, A_i the hyperfine interaction constant, γ_e and γ_{H} the magnetrogyric ratios of the electron and proton, respectively, β the Bohr magneton, g the spectroscopic splitting factor, S the total spin quantum number, and the other symbols have the usual significance. For unpaired spin in the π orbital of the ligand, the McConnell equation for several spins can be applied,[9,15]

$$A_i=Q\rho_i/2S, \tag{2}$$

where ρ_i is the spin density of the ith aromatic carbon and Q is a proportionality constant.

The equation for the pseudocontact shift for complexes with axially symmetric g tensors has been derived by McConnell and Robertson,[11] the equation for the dissolved complex being

$$\left(\frac{\Delta H}{H}\right)_i=-\epsilon(g_{\|}+2g_{\perp})\left[\frac{(g_{\|}-g_{\perp})(3\cos^2\chi_i-1)}{R_i^3}\right], \tag{3}$$

where $\epsilon=|\beta|^2S(S+1)/27kT$, χ_i is the angle between the radius vector to the proton of interest and the C_3 axis, and R_i is the length of this radius vector.

EXPERIMENTAL

The proton magnetic resonance spectra were recorded on a Varian DP-60 spectrometer, using deuterochloroform as the solvent and the proton peak of added chloroform as internal calibrant. Frequency calibrations were performed by the usual sideband techniques. All spectra were obtained at 25°. The proton spectra of each of the complexes were also obtained upon addition of increasing amounts of tetrabutylammonium iodide.

The triphenylphosphine and tetrabutylammonium iodide were purchased from Eastman Chemical Company, and were used without further purification. The NiI_2 and CoI_2 were obtained from the Amend Drug Company and K & K Laboratories, respectively. The only purification employed was the filtering of the boiling alcoholic solutions.

$[Bu_4N][(\phi_3P)CoI_3]$ was prepared according to Cotton *et al.*,[12] mp 141.5°; they reported 141°.

Analysis calculated for $C_{34}H_{51}CoI_3NP$: C, 43.23%; H, 5.43%. Found: C, 43.16%; H, 5.47%.

$[Bu_4N][(\phi_3P)NiI_3]$ was prepared according to Cotton, Faut, and Goodgame,[3] though it was found necessary to add several drops of water to the butanol

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[11] H. M. McConnell and R. E. Robertson, J. Chem. Phys. **29**, 1361 (1958).

[12] F. A. Cotton, O. D. Faut, D. M. L. Goodgame, and R. H. Holm, J. Am. Chem. Soc. **83**, 1780 (1961).

[13] F. A. Cotton, O. D. Faut, and D. M. L. Goodgame, J. Am. Chem. Soc. **83**, 344 (1961).

[14] H. M. McConnell and C. H. Holm, J. Chem. Phys. **27**, 314 (1957).

[15] H. M. McConnell, J. Chem. Phys. **24**, 632, 764 (1956); Proc. Natl. Acad. Sci. (U.S.) **43**, 741 (1957).

Table I. Observed isotropic shifts for $[Bu_4N][(\phi_3P)\,MI_3]$.[a]

M	Phenyl protons					Butyl protons			
	o-H	*m*-H	*p*-H	*p/o*	*m/o*	C_1	C_2	C_3	C_4
Co	515	−449	670	1.30	−0.87	360	(180)[b]	(100)	(30)
Ni	342	−677	748	2.19	−1.98	−161	(−100)	−(80)	(−30)

[a] Shifts in cycles per second at 60 Mc/sec; $CDCl_3$ solutions at 25°.

[b] Shifts in brackets only approximate, since positions in Bu_4NI are uncertain.

before the NiI_2 dissolved completely, mp 132.5°; they reported 132.5°.

Analysis calculated for $C_{34}H_{51}NiI_3NP$: C, 43.25%; H, 5.44%. Analysis found: C, 43.49%; H, 5.42%.

RESULTS

The observed spectra of the two complexes are illustrated in Fig. 1. The measured isotropic shifts for the phenyl protons are listed in Table I. In addition to the expected shifts for the phenyl protons, there were also observed isotropic shifts for the protons in the butyl group in the tetra-(*n*-butyl)ammonium cation. The shifts for these four types of protons, numbered as in the diagram below, are also listed in Table I:

$$[N^+(\overset{1}{C}H_2-\overset{2}{C}H_2-\overset{3}{C}H_2-\overset{4}{C}H_3)_4].$$

The effect on the proton resonance spectra of the butyl protons upon addition of tetra-(*n*-butyl)ammonium iodide, $[Bu_4N][I]$, is illustrated in Figs. 2 and 3 for the cobalt and nickel complexes, respectively.

DISCUSSION

The observed peaks for the phenyl protons were assigned on the basis of intensities and by comparison with the proton spectra[6,7] of the related bis(triphenylphosphine) dihalides of cobalt and nickel. Only the spectrum of the nickel complex displayed spin–spin splittings, the multiplet structure being identical to that observed[7] for the bis(triphenylphosphine) complex of NiI_2. The *ortho* proton spin is again relaxed sufficiently fast by the nickel ion so as not to produce splitting of the *meta* proton resonance peak. The *ortho* proton resonances of the cobalt complex cannot be directly observed due to overlap by the peaks from the butyl protons in Bu_4N^+. The *ortho* proton peak can, however, be resolved upon addition of $[Bu_4N][I]$ (*vide infra*).

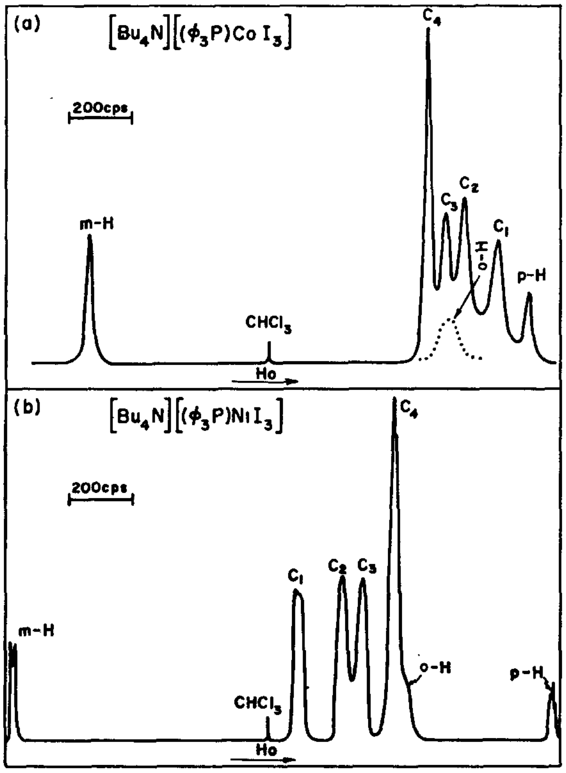

Fig. 1. The PMR spectra of (a) $[Bu_4N][(\phi_3P)CoI_3]$, and (b) $[Bu_4N][(\phi_3P)NiI_3]$ in $CDCl_3$ at 25°.

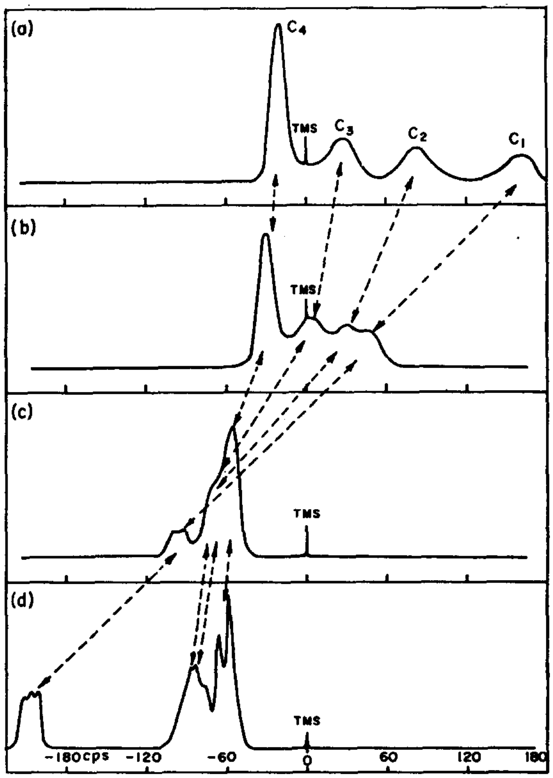

Fig. 2. Spectra of butyl protons in $[Bu_4N][(\phi_3P)CoI_3]$; (a) pure complex, (b) slight excess $[Bu_4N][I]$, (c) moderate excess $[Bu_4N][I]$, (d) pure $[Bu_4N][I]$.

Due to the observed alternation of shifts and the similarity between the spectra of the phenyl protons of these complexes and the related bis-(triphenylphosphine) complexes,[6,7] it was concluded that the isotropic shifts were primarily the result of contact interaction with unpaired spin in the π orbital of the ligand.[1,15] Any contact interaction with unpaired spin in the σ system of the ligand seems unlikely, since σ spin densities would result[3] in downfield shifts for all protons, the size of the shift attenuating rapidly with increase in the number of bonds from the metal ion, while for these complexes the *ortho* proton peak is almost as far upfield as the *para* proton resonance.

It was noted, however, that the observed shifts seemed to indicate a large difference in distribution of the unpaired spin in the phenyl ring of the two complexes. The distribution of unpaired spin should depend only[7] on the π molecular orbital, so that the same unpaired spin distribution would be expected whether the ligand is attached to cobalt or nickel. Should the metal atom exert any perturbation on the π orbital of the ligand, the effect should be small and be approximately the same for cobalt and nickel.

This difference in distribution can be characterized by the ratios of isotropic shifts for the protons on the phenyl ring.[7] The (*para*-H/*ortho*-H) and (*meta*-H/*ortho*-H) ratios of shifts are given in Table I. The discrepancies in ratios between the two complexes are as great as 120%. These differences in ratios of isotropic shifts have also been observed for the bis-(triarylphosphine) complexes of the cobalt and nickel dihalides, where they were satisfactorily interpreted by postulating a pseudocontact interaction in the cobalt complexes. It thus appears that a pseudocontact interaction may also be significant in the complexes of interest.

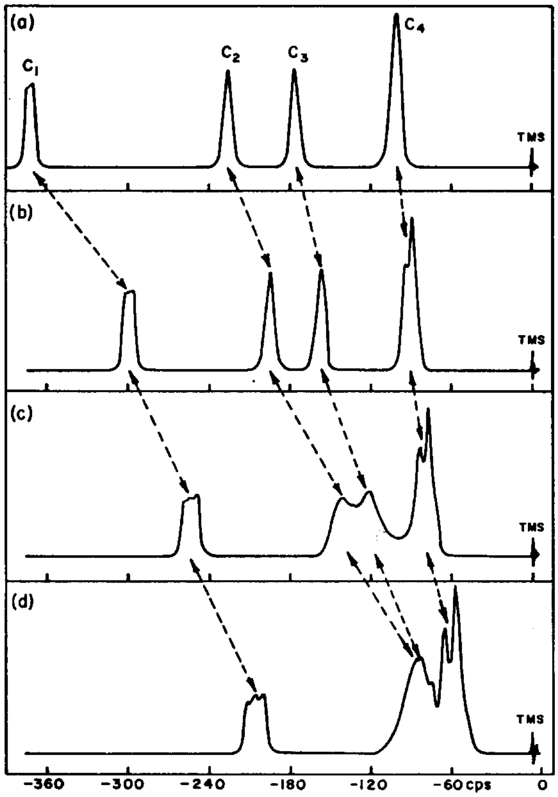

FIG. 3. Spectra of butyl protons in $[\mathrm{Bu_4N}][(\phi_3\mathrm{P})\mathrm{NiI_3}]$; (a) pure complex, (b) slight excess $[\mathrm{Bu_4N}][\mathrm{I}]$, (c) moderate excess $[\mathrm{Bu_4N}][\mathrm{I}]$, (d) pure $[\mathrm{Bu_4N}][\mathrm{I}]$.

Butyl Proton Shifts

As was indicated above, the resonance positions of the butyl protons in $[\mathrm{Bu_4N}]^+$ were also shifted, but the peaks for the cobalt complex were shifted upfield, while those of the nickel complex were shifted downfield from their positions in diamagnetic $[\mathrm{Bu_4N}][\mathrm{I}]$. (See Fig. 1.) These complexes are known[12,13] to be ionic, and any form of a covalent bond between $[\mathrm{Bu_4N}]^+$ and $[(\phi_3\mathrm{P})\mathrm{MI_3}]^-$ is highly unlikely because the cation is completely saturated, all the electrons and orbitals of C, H, and N having been utilized for σ bonding within the $[\mathrm{Bu_4N}]^+$ cation. A contact interaction with the butyl protons therefore seems very unlikely. These shifts of the butyl protons can thus have but one origin, that being the pseudocontact interaction.[11]

These complexes, though ionic, would be expected to travel around as ion pairs[16,17] in a medium with as poor solvating properties as $\mathrm{CDCl_3}$. The $[\mathrm{Bu_4N}]^+$ cation thus could also experience the dipolar field exerted by the anisotropic g tensor of the complex anion. For the complexes of interest, it is quite simple to picture the most probable relative orientation of the two ions in solution, since that orientation allowing for closest approach of charge centers with minimum steric hindrance would seem most likely. This position of the $[\mathrm{Bu_4N}]^+$ cation relative to $[(\phi_3\mathrm{P})\mathrm{MI_3}]^-$ would be along the C_3 axis of the anion, and on the opposite side of the metal atom from the phosphine ligand. Any other position would involve steric effects from the much more bulky triphenylphosphine ligand, which sweeps out a very large solid angle on rotation about the metal–phosphorus bond. The fact that only one resonance appears per set of equivalent butyl protons indicaties that the $[\mathrm{Bu_4N}]^+$ cation is tumbling rapidly, though its center of mass remains approximately at a fixed distance relative to the complex anion.

Addition of excess $[\mathrm{Bu_4N}]^+$ cations from $[\mathrm{Bu_4N}][\mathrm{I}]$ should decrease the observed shifts if the rate of exchange of $[\mathrm{Bu_4N}]^+$ ion paired to the paramagnetic anion and that ion paired to the diamagnetic iodide is sufficiently rapid, until in the limit of a large excess of $[\mathrm{Bu_4N}][\mathrm{I}]$, the proton resonances should approach their positions in diamagnetic $[\mathrm{Bu_4N}][\mathrm{I}]$.

This procedure was followed, and the spectra of the butyl protons for the cobalt and nickel complexes are shown in Figs. 2 and 3, respectively. For each figure,

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[16] C. W. Davies, *Ion Association* (Butterworths Scientific Publications, Ltd., London, 1962).

[17] R. M. Fuoss and F. Accascina, *Electrolytic Conductance* (Interscience Publishers, Inc., New York, 1959), Chap. 16.

(a) represents the spectrum of the butyl protons in the pure complex, (b) and (c) correspond to the spectra after increasing amounts of [Bu$_4$N][I] have been added, and (d) in both cases is the spectrum of pure [Bu$_4$N][I].

In following the resonance going from (a) to (d) in Figs. 2 and 3, the assignment of peaks could easily be made. The values for the shifts could not be ascertained with accuracy for any but the protons on C_1, next to the nitrogen, since the positions of the other peaks in the diamagnetic [Bu$_4$][I] are not exactly known, due to the complexity of the spectrum caused by spin–spin splitting. The accurate shifts for C_1 and the approximate shifts for the other protons are listed in Table I. That the two types of [Bu$_4$N]$^+$ ions gave an averaged spectrum indicates that the two species must be exchanging at a rate in excess of 10^3 sec^{-1}, since the largest difference in shifts between the two species is about 360 cps. Also, the *ortho* proton resonance peak in the cobalt complex, which was obscured in the spectrum of the pure complex by overlap from the butyl proton peaks, could readily be observed in the presence of an excess of [Bu$_4$N][I], where the butyl peaks, due to the exchange averaging, are shifted downfield. The excess of [Bu$_4$N][I] did not in any way affect the positions of the phenyl proton peaks.

From Table I, it is obvious that for both metal complexes, the protons on C_1, next to the N atom, are shifted farthest from their position in diamagnetic [Bu$_4$N][I], as a matter of fact, the shifts become increasingly smaller the farther the butyl protons are situated from the central N atom, with the methyl peaks being shifted an almost insignificant amount. This, at first, may seem inconsistent with a $1/R^3$ behavior of the pseudocontact shift,[11] which seems to predict shifts in the opposite order of that observed. Even when averaged over the free rotations about the N atom, $\langle 1/R^3 \rangle$ will still be largest for C_4 protons and smallest for C_1 protons. It turns out, however, that the angular part of the geometric factor in Eq. (3), $(3\cos^2\chi_i - 1)$, is more important than the radial part in determining the magnitudes of the shifts. For the C_1 protons, though $1/R^3$ is smallest, the angle χ subtended by these protons upon free rotation about the N atom is such that $(3\cos^2\chi_i - 1)$ is always positive and quite large. As the distance between the butyl protons and the N atom increases, χ subtends a larger angle, making $(3\cos^2\chi_i - 1)$ negative for large χ, which cause the average value of the geometric factor to decrease, until for the methyl protons, the geometric factor averages to nearly zero. Fortunately, the resonance position of the C_1 protons in diamagnetic [Bu$_4$N]$^+$ is known, giving accurate values for the observed shifts for these protons. Since the distribution of isotropic shifts observed for the butyl protons follows the pattern prescribed by the geometric factors in the equation for pseudocontact shifts, it appears that the origin of these shifts is indeed a pseudocontact interaction resulting from ion pairing or ion association in solution.

The pseudocontact shifts for the butyl protons will be governed by the same equation, Eq. (3), which governs the pseudocontact shifts of the phenyl protons. The fact that the butyl protons are shifted in opposite directions for the cobalt and nickel complexes indicates that the term $(g_{\parallel} - g_{\perp})$, for the cobalt and nickel complex, will differ in sign. Since the geometric factor $(3\cos^2\chi - 1)/R^3$ for the C_1 butyl protons is positive, we have $g_{\perp} > g_{\parallel}$ for the cobalt complex and $g_{\parallel} > g_{\perp}$ for the nickel complex. It is thus evident that the g tensors of both cobalt and nickel are anisotropic, so that pseudocontact interaction could contribute significantly to the observed isotropic shifts of the phenyl protons for both complexes.

Phenyl Proton Shifts

In order to separate the observed isotropic shifts for the phenyl protons into contact and pseudocontact contributions,[7] the geometric factors, $\langle (3\cos^2\chi_i - 1)/R_i^3 \rangle_{\text{Av}}$, which relate the pseudocontact shifts for the three types of phenyl protons must be evaluated, and a method must be devised to obtain information about the relative extent of pseudocontact interaction for the cobalt and nickel complex anions.

For these complexes, $(3\cos^2\chi_i - 1)/R_i^3$ depends on the internal rotation of the phenyl group about the C–P bond. The geometric factor for each proton was thus calculated, averaging over the internal rotation, using the bond distances[18] C–C = 1.40, C–H = 1.08 and C–P = 1.90 Å. The metal–P distances are not exactly known for these complexes, but a value of 2.32 Å, approximately the sum of the covalent radii, seems reasonable.[7,19] It was assumed that this distance is identical in the nickel and cobalt complex. The calculated ratios[7] for the geometric factors for the three types of protons, *ortho*, *meta*, and *para* are 1.000:0.225:0.432, respectively, with the *ortho* proton resonance shift normalized to unity.

The pseudocontact shifts experienced by the various protons are proportional to their geometric factors,[3,4,7] so that the ratios, $[(3\cos^2\chi_i - 1)/R_i^3]:[(3\cos^2\chi_j - 1/R_j^3]$, etc., relate the pseudocontact shifts for the various protons. These geometric factors were also calculated for a range of metal–P distances, and it was discovered that the ratios varied slightly with the choice of this distance. Though the variation of ratios of geometric factors is small in the region of the metal–P = 2.3 Å, the magnitudes of the geometric factors varied quite sharply with the metal–P bond length (*vide infra*).

To obtain a relation between the extent of pseudocontact interaction in the cobalt and nickel complex, the butyl proton resonances were studied, since their shifts should arise solely from a pseudocontact interaction. The magnitudes of the butyl proton shifts can

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[18] *Tables of Interatomic Distances and Configurations in Molecules and Ions*, edited by L. E. Sutton (Burlington House, London, 1958).

[19] G. Garton, D. E. Henn, H. M. Powell, and L. M. Venanzi, J. Chem. Soc. **1963**, 3625.

Table II. Separation into contact and pseudocontact shifts.[a]

	Pseudocontact shifts			Contact shifts			Corrected ratios	
M	*o*-H	*m*-H	*p*-H	*o*-H	*m*-H	*p*-H	*p/o*	*m/o*
Co	195	44	85	320	−493	585	1.83	−1.54
Ni	−87	−19	−39	429	−658	787	1.83	−1.53

[a] Shifts in cycles per second at 60 Mc/sec.

be influenced by a number of effects, however, among which are the geometric factor, the g-tensor anisotropy, the average g value, and the extent of ion pairing with the complex anion in solution.

The average g values for the two metal ions are essentially identical.[12,13,20] Since Co II and Ni II have the same charge, about the same radii, and are bonded to identical ligands, it should be a good approximation that the average distance between ion pairs is the same for both metal complexes, so that their geometric factors should also be equal. Also, since the spectra were all obtained at the same temperature, and since the sizes and charges of the two paramagnetic anions are the same, it will be assumed that the extent of ion pairing in $CDCl_3$ solution will be identical for both complexes.

Thus the observed ratio of the pseudocontact shifts for the C_1 protons of $[Bu_4N]^+$ in the nickel and cobalt complexes should give the ratio of the magnitudes of the dipolar fields exerted by the g tensors of the two metal complexes. Since all other terms in Eq. (3) are either known or assumed to be the same for both the cobalt and nickel complexes, this ratio for the C_1 proton shifts will yield the value of $(g_{\parallel}-g_{\perp})_{Ni}/(g_{\parallel}-g_{\perp})_{Co}$, which we now know to be negative. It we let the pseudocontact shift at the *ortho* proton for the cobalt complex be X_0, the pseudocontact shift at the same position in the nickel complex will be $(-161/369)X_0=-0.445X_0$. The value of the pseudocontact shifts at the *meta* and *para* protons for both complexes can be obtained from the ratios of their calculated geometric factors. The contact shifts for the two complexes could be expressed as follows:

	cobalt	*nickel*
ortho-H	$515-X_0$	$342+0.445X_0$
meta-H	$-449-0.225X_0$	$-667+0.100X_0$
para-H	$670-0.432X_0$	$748+0.192X_0$.

Since the ratio of the contact shifts for two protons is expected to be the same for the two complexes,[7] a least-squares fit was performed which yielded that value of X_0 which reproduced the ratios for the contact shifts of the cobalt and nickel complexes as closely as possible. In Table II are given the calculated contact and pseudocontact contributions to the observed shifts and the resulting ratios of contact shifts. The discrepancy between ratios is now less than 1%. This high precision may be a little misleading, however, since a choice of 2.30 Å for the M–P distance gave geometric factors which resulted in a fit with a 3% discrepancy, though the values of the calculated shifts for the best fit varied less than 2%. This is still a very satisfactory fit. This indicates that for these complex anions, the g tensors of both cobalt and nickel are anisotropic, with the degree of anisotropy being approximately twice as great in the cobalt as in the nickel complex. The fact that the nickel complex displays definite evidence for significant pseudocontact shifts is of some interest, since for the related bis (triarylphosphine) complexes of cobalt and nickel,[7] it appeared that the nickel possessed an isotropic g tensor while the cobalt was anisotropic. This suggests the possibility that the g tensor for the bis(triarylphosphine) complexes of nickel also may actually be anisotropic, but that the pseudocontact shifts are negligible due to cancellation of terms[7] in the equation for the pseudocontact shifts.

Calculation of $(g_{\parallel}-g_{\perp})$

In the equation for the pseudocontact shift, Eq. (3), $(\Delta H/H)$ has been obtained by the methods just outlined, $\beta=0.9273\times10^{-20}$ Bohr magnetons, $k=1.38\times10^{-1}$ erg/°K, $S=\frac{3}{2}$ for Co II and 1 for Ni II, and T is 298°K. The term $(g_{\parallel}+2g_{\perp})$ can be estimated[20] for both complexes from magnetic susceptibility measurements,[12,13] and the geometric factors were calculated as indicated above, so that at least in principle, the sign and magnitude of $(g_{\parallel}-g_{\perp})$ for each complex could be calculated from Eq. (3). From the knowledge of $(g_{\parallel}-g_{\perp})$ and $(g_{\parallel}+2g_{\perp})$, $g_{\parallel}$ and $g_{\perp}$ could then be easily obtained.

The results of this calculation are much less satisfactory, however, than for the separation of the contact and pseudocontact shifts, which is actually not unexpected. Using the value of the geometric factor for the *ortho* proton for an M–P distance of 2.32 Å, the results obtained were $(g_{\parallel}-g_{\perp})=-1.68$ for cobalt and $+1.05$ for nickel. These values are obviously larger than could be expected for these complexes. The fact that the magnitude of the calculated Δg's is unreasonable can be easily rationalized. As was indicated above, though the ratios of geometric factors were not appreciably affected by the exact choice of the M–P distance in the region of 2.3 Å, their magnitudes were found to vary quite sensitively with the choice of this parameter,

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[20] C. J. Ballhausen, *Introduction to Ligand Field Theory* (McGraw-Hill Book Company, Inc., New York, 1962), Chap. 6.

TABLE III. Calculated spin densities.

Complex	*Ortho*	*Meta*	*Para*
$[Bu_4N][(\phi_3P)CoI_3]$	0.00160	−0.00247	0.00293
$[Bu_4N][(\phi_3P)NiI_3]$	0.00262	−0.00402	0.00482

causing a difference of an order of magnitude between 2.25 and 2.38 Å for the metal–P distance. Without accurate values for the metal–P distances, these calculations are not significant. Some x-ray work on these complexes may resolve some of these difficulties.

Unpaired Spin Densities

The unpaired spin densities[1,15] obtained by Eq. (2) from the calculated contact shifts are given in Table III. The magnitudes and distribution of the unpaired spin densities for these complexes are very similar to those reported for the related bis(triarylphosphine) complexes of the cobalt[7] and nickel[6,7] halides, with the nickel complex having approximately 50% more unpaired spin on the ligand than the cobalt complex. This difference in unpaired spin densities can again be explained[7] by the slightly greater interelectronic repulsion on the nickel, due to it possessing one more electron in the antibonding *t* orbitals than cobalt. This results in a small electron shift towards the ligand for the nickel complex.

A more detailed investigation of the phenomena of ion pairing in these complexes is in process and will be reported in the near future.

ACKNOWLEDGMENTS

The hospitality of the Bell Telephone Laboratories, Inc., Murray Hill, New Jersey, is greatefully acknowledged, and I thank E. W. Anderson for obtaining the PMR spectra. I wish to express my thanks and sincere appreciation to Professor L. C. Allen and Professor W. D. Horrocks, Jr., for their help and advice pertaining to this research.

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 41, NUMBER 10 15 NOVEMBER 1964

Mass-Spectrometric Study of Ion–Molecule Reactions in Propane

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(Received 26 June 1964)

Ion–molecule reactions in propane have been studied up to pressure of 0.12 Torr inside the ion source of the mass spectrometer. All but four of the propane ions followed the exponential decay law remarkably well and their total cross sections of disappearance have been determined. The major reactions of these ions lead to the formation of $C_3H_8^+$, $C_3H_7^+$, $C_3H_6^+$, and $C_3H_5^+$ which, with the exception of C_3H_5, show very low reactivity. The ionic current due to purely secondary ions did not exceed few percent of the total ionic current at the highest pressure attained. The kinetics of most of the ion–molecule reactions occurring in propane have been investigated, and the pertinent cross sections have been determined.

INTRODUCTION

ION–molecule reactions occurring in propane have received but little attention. Thus, Field and Lampe[1] in their study of hydride-ion transfer reactions have identified a large number of primary ions in propane reacting to form the propyl ion $C_3H_7^+$:

$$R^+ + C_3H_8 \rightarrow RH + C_3H_7^+,$$

where $R = CH_3$, C_2H_3, C_2H_4, C_2H_5, C_3H_3, and C_3H_5. But apart from giving a value for the "effective" cross section of formation of $C_3H_7^+$ of 66×10^{-16} cm^2 molecule^{-1}, no details of the kinetics of these reactions were presented. More recently, Fuchs[2] has observed few secondary ions in propane at $m/e = 51$, 53, 54, 55, 56, and 57 corresponding to C_4 ions with 3, 5–9 hydrogen atoms respectively. But it seems that the relatively low pressure used inside the ion source of the mass spectrometer (pressure corresponding to 10^{12} molecule cm^{-3} is indicated) has prevented any kinetic study due to the weakness of the secondary ionic current obtained. Pettersson and Lindholm[3] in their study of charge-exchange processes in propane have reported a few ion–molecule reactions mainly of the hydride-transfer and proton-transfer types. Interestingly, they presented some argumentative evidence for the formation of $C_3H_9^+$ although the peak which they observed at $m/e = 45$ was of uncertain origin.

Recently a number of investigations[4–6] have been carried out in this laboratory on ion–molecule reactions

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