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## Isotropic Nuclear Magnetic Resonance Shifts in Ion-Paired Systems. A Study of Some Unsymmetrically Substituted Quaternary Ammonium Salts<sup>1</sup>

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Proton magnetic resonance spectra of several unsymmetrically substituted quaternary ammonium cations ion paired to the paramagnetic tetrabromocobaltate(II) and -nickelate(II) anions have been studied in dichloromethane solution. It is found that a Fermi contact shift is present in complexes of both metals. The isotropic nmr shifts in the cobalt complexes are shown to be predominantly contact while the shifts in the nickel complexes are shown to contain comparable contributions from both the contact and dipolar mechanisms. A method for factoring the isotropic shift is developed. The estimated dipolar shifts in the nickel complexes are discussed in terms of the cation's average structure in the ion aggregate.

The use of proton magnetic resonance spectroscopy in the study of ion aggregate structure in solution is by now well established.<sup>2-8</sup> The method usually employed is to examine the proton nmr spectrum of a salt consisting of a diamagnetic cation and a paramagnetic anion in a solvent of low dielectric constant. The presence of unpaired electron spins on the anion is sensed by the cation protons in the ion aggregate and results in an isotropic nmr shift,  $\Delta\nu_{iso}$ . This shift is the sum of two components, the Fermi contact shift,<sup>9</sup>  $\Delta\nu_t$ , and the dipolar or "pseudocontact" shift,<sup>10</sup>  $\Delta\nu_{dip}$ . Thus for a given proton,  $i$

$$(\Delta\nu_{iso})_i = (\Delta\nu_t)_i + (\Delta\nu_{dip})_i \quad (1)$$

where

$$(\Delta\nu_t)_i = -\frac{A_i\nu\chi^M}{Ng_N\beta_N} \quad (2)$$

and

$$(\Delta\nu_{dip})_i = -\nu G(R_i, \theta_i) D(\chi_{\parallel}, \chi_{\perp}) \quad (3)$$

Here,  $\chi^M$ ,  $\chi_{\parallel}$ , and  $\chi_{\perp}$  are the average, parallel, and perpendicular components of the magnetic susceptibility tensor, referred to the principal axis of symmetry on the anion.  $A_i$  is the Fermi hyperfine coupling constant for the  $i$ th proton and is a measure of the amount of unpaired electron spin density transferred to the 1s orbital of the resonant proton.  $\nu$  is the spectrometer frequency (Hz). The term  $D(\chi_{\parallel}, \chi_{\perp})$  in eq 3 is a function of the parallel and perpendicular magnetic susceptibilities, the exact form of which depends on the relative magnitudes of the electron spin relaxation time, the susceptibility anisotropy, and the molecular correlation time. This term always has the property that for cubic symmetry ( $\chi_{\parallel} = \chi_{\perp}$ )  $D(\chi_{\parallel}, \chi_{\perp}) = 0$ .

The term  $G(R_i, \theta_i)$  is known as the geometric factor and is a function of the angle,  $\theta_i$ , made by the  $i$ th proton with the principal magnetic susceptibility axis

of the anion, and of the distance,  $R_i$ , between this proton and the unpaired electron. For the case of an axially symmetric anion (such as  $(C_6H_5)_3PCoI_3^-$ ) we have

$$G(R_i, \theta_i) = (3 \cos^2 \theta_i - 1)R_i^{-3} \quad (4)$$

It is from an analysis of this term, averaged over the possible variations of proton position during motion within the ion aggregate, that structural information is obtained.

Unfortunately, the structural information from the isotropic shift is not always unambiguous, due to the presence of a Fermi contact term.<sup>11,12</sup> Thus, interpretations of ion-pair structure by early workers who assumed that this term was not present are thrown into some doubt. We have developed in a previous paper<sup>13</sup> an approximate method for factoring the isotropic shift in these systems which leads to a moderate degree of consistency in the structural results.

Most of the work in this area to date has centered on the structures of the symmetrical tetraalkylammonium ions in ion aggregates. On the other hand, few structural investigations on cations where the substituents on the central nitrogen atom vary in size and shape have been carried out. In this respect, only two studies are of note. The cation  $((C_6H_5)_3P(C_4H_9))^+$  has been studied in association with the triphenylphosphinetrihalometalate(II) anions in deuteriochloroform.<sup>14</sup> In addition, several biquaternary ammonium cations based on 2,2'-bipyridyl and 4,4'-bipyridyl have been studied in association with the hexacyanoferrate(III) cation in water.<sup>15</sup>

We have chosen to study ion association between five  $N,N$ -dimethyl- $N$ -benzyl- $N$ -alkylammonium cations and the tetrabromocobaltate(II) and -nickelate(II) anions. These are as shown in I-V.

This type of cation has several advantages over the usually studied symmetrical cations. Of the four distinguishable protons on the tetrabutylammonium ion, only two are sufficiently well resolved to be studied unambiguously. Each of the cations in this series, on the other hand, contains seven well-resolved protons. As

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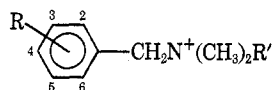
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(12) D. G. Brown and R. S. Drago, *J. Amer. Chem. Soc.*, **92**, 1871 (1970).

(13) I. M. Walker, L. Rosenthal, and M. S. Qureshi, *Inorg. Chem.*, **10**, 2463 (1971).

(14) R. H. Fischer and W. D. Horrocks, Jr., *ibid.*, **7**, 2659 (1968).

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	R	R'	Abbreviation
I	4-CH <sub>3</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	4-BDBu
II	2,4,6-CH <sub>3</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	2,4,6-BDBu
III	2,4,6-CH <sub>3</sub>	<i>n</i> -C <sub>8</sub> H <sub>17</sub>	2,4,6-BDO
IV	3,5-CH <sub>3</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	3,5-BDBu
V	3,5-CH <sub>3</sub>	<i>n</i> -C <sub>8</sub> H <sub>17</sub>	3,5-BDO

a result, we may now begin to address ourselves to the question of how the orientation of the cation in the ion aggregate is influenced by changes in the size of the substituent on the central nitrogen atom.

### Experimental Section

**Reagents.**—*N,N*-Dimethyl-*N*-octylamine was purchased from K & K Laboratories and used without further purification. All other materials were reagent grade. Dichloromethane was dried for at least 48 hr over Type 3A molecular sieves before use, as were all other solvents used in this work.

**Preparation of Substituted Benzyl Halides.**—3,5-Dimethylbenzyl bromide was prepared by the bromination of 1,3,5-trimethylbenzene (mesitylene), according to the method of Herr, Enkoji, and Dailey.<sup>16</sup> 4-Methylbenzyl bromide was prepared by the same method, starting with *p*-xylene. 2,4,6-Trimethylbenzyl bromide was prepared as follows. Mesitylene (120 g, 1.0 mol) was placed in a round-bottom flask, 108 ml (1.3 mol) of 36% aqueous formaldehyde solution and 200 ml of 48% HBr were then added, and the mixture was stirred vigorously for 1.5 hr at 60–70°. The mixture was then permitted to stir a further 15 hr at room temperature. The two layers were separated and the aqueous layer was extracted five times with ether. The organic layer and ether extracts were combined and washed two times with water. The solution was then dried over anhydrous magnesium sulfate for several hours, the ether removed under suction, and the remaining liquid vacuum distilled. The fraction distilling between 80 and 175° (20 mm) was redistilled at 10 mm. The fraction distilling between 140 and 165° was collected. The proton nmr spectrum confirmed the nature of the product.

**Preparation of *N,N*-Dimethyl-*N*-benzyl-*N*-butylammonium Salts.**—*N,N*-Dimethyl-*N*-butylamine was prepared from butylamine by the method of Clarke, Gillespie, and Weisshaus.<sup>17</sup>

The quaternary ammonium bromide salts were prepared by treating an acetone solution of *N,N*-dimethyl-*N*-butylamine with equimolar amounts of the substituted benzyl bromide, followed by refluxing for 12 hr. After removal of the acetone, ether was added. Upon scratching, white crystals of the desired salt deposited in nearly quantitative yield. The salts were recrystallized from methylene chloride solution by slowly adding ether and ethyl acetate until precipitation occurred.

The *N,N*-dimethyl-*N*-octyl-*N*-benzylammonium salts were prepared similarly, starting with *N,N*-dimethyl-*N*-octylamine, and were recrystallized by adding ether to a methylene chloride solution of the crude salt.

**Preparation of the Tetrabromometalate(II) Complexes. Tetrabromozincate Complexes.**—Anhydrous ZnBr<sub>2</sub> was dissolved in dry acetone with gentle warming. The stoichiometric amount of quaternary ammonium bromide was added and the solution was warmed further for 15 min. The solution was filtered hot and the filtrate, upon cooling, deposited white crystals. These were collected under nitrogen, washed with ether, and recrystallized from methylene chloride and ethyl acetate. The complexes were dried *in vacuo* over refluxing 1-butanol for 48 hr. *Anal.* Calcd for [3,5-BDO]<sub>2</sub>ZnBr<sub>4</sub>: C, 48.66; H, 7.31. Found: C, 48.45; H, 7.08. Calcd for [2,4,6-BDO]<sub>2</sub>ZnBr<sub>4</sub>: Zn, 6.77; Br, 33.09. Found: Zn, 6.70; Br, 33.25. Calcd for [3,5-BDBu]<sub>2</sub>ZnBr<sub>4</sub>: Zn, 7.92; Br, 38.71. Found: Zn, 7.84; Br, 38.90. Calcd for [4-BDBu]<sub>2</sub>ZnBr<sub>4</sub>: Zn, 8.19; Br, 40.07. Found: Zn, 7.97; Br, 40.35. Calcd for [2,4,6-BDBu]<sub>2</sub>ZnBr<sub>4</sub>: Zn, 7.66; Br, 37.44. Found: Zn, 7.65; Br, 37.69.

**Tetrabromocobaltate Complexes.**—These complexes were prepared in similar fashion, starting with cobalt bromide hexahydrate. This was first dehydrated by refluxing with 15 ml of triethyl orthoformate for 0.5 hr in acetone. The complex was precipitated by adding ethyl acetate and ether to the solution. In a number of instances, a blue oil formed; this was induced to crystallize by decantation of the solvent, followed by addition of anhydrous ethyl ether and cooling to 0° for 36 hr. All complexes were recrystallized as above. *Anal.* Calcd for [3,5-BDO]<sub>2</sub>-CoBr<sub>4</sub>: C, 48.99; H, 7.36. Found: C, 48.65; H, 7.29. Calcd for [4-BDBu]<sub>2</sub>CoBr<sub>4</sub>: C, 42.50; H, 6.11; Br, 40.39. Found: C, 42.32; H, 6.00; Br, 40.51. Calcd for [3,5-BDBu]<sub>2</sub>-CoBr<sub>4</sub>: C, 44.03; H, 6.40; Br, 39.01. Found: C, 43.87; H, 6.30; Br, 38.76. Calcd for [2,4,6-BDO]<sub>2</sub>CoBr<sub>4</sub>: C, 50.06; H, 7.56; Br, 33.31. Found: C, 50.27; H, 7.62; Br, 33.06. Calcd for [2,4,6-BDBu]<sub>2</sub>CoBr<sub>4</sub>: Br, 37.72. Found: Br, 37.96.

**Tetrabromonickelate Complexes.**—The preparative details are similar to the above. The complexes appear as blue oils after treatment of the acetone solution with ether and ethyl acetate. The oils are induced to crystallize by heating with triethyl orthoformate until blue crystals appear. Special precautions were taken against exposure of these crystals to moisture. *Anal.* Calcd for [3,5-BDO]<sub>2</sub>NiBr<sub>4</sub>: C, 49.01; H, 7.36. Found: C, 48.72; H, 7.66. Calcd for [2,4,6-BDO]<sub>2</sub>NiBr<sub>4</sub>: Br, 33.32. Found: Br, 33.54. Calcd for [4-BDBu]<sub>2</sub>NiBr<sub>4</sub>: C, 42.51; H, 6.11; Br, 40.40. Found: C, 42.78; H, 6.26; Br, 40.50. Calcd for [3,5-BDBu]<sub>2</sub>NiBr<sub>4</sub>: Br, 39.02. Found: Br, 38.89. Calcd for [2,4,6-BDBu]<sub>2</sub>NiBr<sub>4</sub>: C, 45.36; H, 6.66; Br, 37.73. Found: C, 45.58; H, 6.72; Br, 37.61.

**Magnetic resonance spectra** were obtained in dichloromethane on the Varian A-60 and HA-100 magnetic resonance spectrometers at ambient temperature, using TMS as internal reference. Conductivities were recorded at 22° on the Wayne-Kerr B221A universal conductance bridge. C and H analyses were performed by Galbraith Laboratories, Knoxville, Tenn., while zinc and halide were determined by standard procedures in this laboratory.

### Results

The tetrahalocobaltate(II) and -nickelate(II) anions have received careful attention from a variety of authors, and their nature in both solid and solution is well understood. Visible spectra obtained for our complexes in both mull and dichloromethane solution are in agreement with those assigned to the CoBr<sub>4</sub><sup>2-</sup> ion by Cotton, *et al.*,<sup>18</sup> and for the NiBr<sub>4</sub><sup>2-</sup> ion by Goodgame, *et al.*,<sup>19</sup> and therefore need no further discussion.

Conductivity data may be found in Table I from

TABLE I  
MOLAR CONDUCTANCE DATA IN NITROBENZENE

Compound	—AM, ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup> —	
	<i>c</i> = 1 × 10 <sup>-3</sup> M	<i>c</i> = 6 × 10 <sup>-5</sup> M
[2,4,6-BDO]Br	26.0	
[3,5-BDBu]Br	31.5	
[4-BDBu] <sub>2</sub> CoBr <sub>4</sub>	45.2	94.1
[4-BDBu] <sub>2</sub> NiBr <sub>4</sub>	47.3	91.2
[4-BDBu] <sub>2</sub> ZnBr <sub>4</sub>	46.6	82.4
[3,5-BDBu] <sub>2</sub> CoBr <sub>4</sub>	42.0	
[3,5-BDBu] <sub>2</sub> NiBr <sub>4</sub>	42.1	
[3,5-BDBu] <sub>2</sub> ZnBr <sub>4</sub>	41.4	
[2,4,6-BDO] <sub>2</sub> CoBr <sub>4</sub>	47.8	74.3
[2,4,6-BDO] <sub>2</sub> NiBr <sub>4</sub>	43.1	
[2,4,6-BDO] <sub>2</sub> ZnBr <sub>4</sub>	41.3	

which it can be readily seen that all molar conductance values fall in the range expected for 2:1 electrolytes in nitrobenzene solution.<sup>20</sup>

It is found that the CoBr<sub>4</sub><sup>2-</sup> and ZnBr<sub>4</sub><sup>2-</sup> complexes are stable indefinitely in dichloromethane, while the NiBr<sub>4</sub><sup>2-</sup> complex, on the other hand, tends to de-

(16) R. R. Herr, T. Enkoji, and J. P. Dailey, *J. Amer. Chem. Soc.*, **79**, 4229 (1957).

(17) H. T. Clarke, H. B. Gillespie, and S. Z. Weisshaus, *ibid.*, **55**, 4571 (1933).

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(20) D. J. Phillips and S. Y. Tyree, Jr., *ibid.*, **83**, 1806 (1961).

TABLE II  
 PROTON CHEMICAL SHIFTS<sup>a</sup> FOR THE QUATERNARY AMMONIUM SALTS IN DIAMAGNETIC ENVIRONMENTS

Cation	Anion	Ortho	Meta	Para	CH <sub>2</sub> - (benzyl)	N-CH <sub>3</sub>	α-CH <sub>2</sub>	CH <sub>3</sub> - (terminal)
[4-BDBu]	Br	454.2	434.6	142.3	299.5	194.8	214.1	58.8
	ZnBr <sub>4</sub>	451.6	432.9	139.9	277.9	188.2	203.5	58.5
[3,5-BDBu]	Br	434.7	139.6	426.6	294.6	196.5	216.0	59.1
	ZnBr <sub>4</sub>	433.8	139.7	426.0	273.6	190.2	204.0	59.5
[2,4,6-BDBu]	Br	151.3	419.0	137.3	296.8	190.9	235.7	60.0
	ZnBr <sub>4</sub>	146.7	419.3	137.0	282.7	185.8	214.3	59.1
[2,4,6-BDO]	Br	152.2	418.8	137.2	299.2	192.0	236.4	52.4
	ZnBr <sub>4</sub>	147.3	418.2	137.2	284.2	187.9	212.1	52.6
[3,5-BDO]	Br	433.1	139.9	427.0	289.5	194.8	209.0	52.8
	ZnBr <sub>4</sub>	432.0	139.9	425.0	274.0	191.6	200.7	52.1

<sup>a</sup> Shifts are in Hz from TMS at 60 MHz. The concentration of bromide salt is 0.25 *M* in each case, while the concentration of tetrabromozincate(II) is 0.125 *M*. The data are presumed accurate to ±0.5 Hz.

compose on short standing in solution with deposition of the pale yellow, anhydrous NiBr<sub>2</sub>. The decomposition is readily suppressed by addition of small amounts of free quaternary ammonium bromide.

**Nmr Spectra of the Diamagnetic Compounds.**—The chemical shifts of the diamagnetic quaternary ammonium bromide and tetrabromozincate(II) salts in H<sub>2</sub>CCl<sub>2</sub> are to be found in Table II. Due to the small size of the ring proton chemical shift differences in the unsubstituted benzyl group, it was considered advantageous to eliminate the resulting complex spectrum by substituting methyl groups in appropriate places around the ring. We were not able to resolve the very small ring methyl-ring proton couplings in any of the cases studied.

As expected, the 4-methylbenzyl group exhibits an AB quartet,  $J_{23} = 8$  Hz, while the 3,5-dimethylbenzyl group exhibits two peaks in the phenyl region in a 2:1 intensity ratio ( $J_{24} \approx 0$ ). The ortho proton is downfield with respect to the para, presumably due to the electron-withdrawing effect of the quaternary nitrogen atom. The 2,4,6-trimethylbenzyl group exhibits two resonances in the methyl region, and a single sharp line in the phenyl region, as expected.

Spectra at 60 MHz fail to give a clear resolution of the α-CH<sub>2</sub>(alkyl) and N-CH<sub>3</sub> protons, due to their very similar chemical shift values. In addition, as was observed with the tetrabutylammonium ion, the β and γ chain protons are not resolved, but occur as one overlapping multiplet. At 100 MHz, on the other hand, the β resonance occurs as a broad septet, while the γ resonance occurs as a sharp septet. At this frequency, the α-CH<sub>2</sub>(alkyl) and N-CH<sub>3</sub> resonances are also well resolved.

Table II also reveals an interesting dependence of chemical shift of the cation α-type protons on the nature of the anion. The resonances in the free bromide are uniformly to lower field of those in the tetrabromozincate complex. The benzyl CH<sub>2</sub> protons are the most affected, the relative shift being as much as 0.33 ppm while that of the α-chain and N-CH<sub>3</sub> protons is about 0.17 ppm. We may tentatively ascribe these shifts to local electric field effects resulting from the ion-pairing process or alternatively to hydrogen-bonding effects involving the N<sup>+</sup>-C-H...Br<sup>-</sup> unit. The N-CH<sub>3</sub> resonance in the tributylmethylammonium cation similarly reveals a strong dependence of chemical shift on both anion and solvent.<sup>21,22</sup>

(21) R. P. Taylor and I. D. Kuntz, Jr., *J. Amer. Chem. Soc.*, **91**, 4006 (1969).

(22) R. P. Taylor and I. D. Kuntz, Jr., *ibid.*, **92**, 4813 (1970).

**Spectra of the Paramagnetic Salts.**—It is generally observed that ion-association equilibria are very rapid on the nmr time scale.<sup>5,8,13</sup> Thus the fast-exchange equation (eq 5) holds for cations exchanging between

$$\Delta\nu_{\text{obsd}} - \Delta\nu_{\text{dia}} = f_{\text{para}}(\Delta\nu_{\text{para}} - \Delta\nu_{\text{dia}}) = f_{\text{para}}(\Delta\nu_{\text{iso}}) \quad (5)$$

diamagnetic (dia) and paramagnetic (para) sites. It is thus possible to obtain the shift of the complex in a paramagnetic environment ( $\Delta\nu_{\text{para}}$ ) relative to TMS, by studying mixtures of paramagnetic and diamagnetic complex. A plot of observed shift ( $\Delta\nu_{\text{obsd}}$ ), relative to TMS, *vs.* mole fraction of the paramagnetic components ( $f_{\text{para}}$ ) on extrapolation to  $f_{\text{para}} = 1$  yields  $\Delta\nu_{\text{para}}$  and, as a result,  $\Delta\nu_{\text{iso}}$ , the isotropic shift.

The extrapolation method is particularly useful in the study of the tetrabutylammonium ion in paramagnetic environments,<sup>5</sup> where the resonances broaden and overlap badly, such that the shifts in the fully paramagnetic solution cannot be identified with certainty. In the present instance, since free bromide must be present to prevent the nickel complex from decomposing, the method is essential for obtaining meaningful results. Since we need to compare data from analogous cobalt and nickel complexes, it is necessary to measure the resonance shifts under conditions as similar as possible. The following technique was therefore adopted.

Solutions containing a mixture of tetraalkylammonium tetrabromometalate(II) and tetraalkylammonium bromide in dichloromethane having the same total cation concentration (0.25 *M*) were prepared. Since each mole of paramagnetic complex provides 2 mol of cation,  $f_{\text{para}}$  becomes

$$f_{\text{para}} = \frac{2C_{\text{MBr}_4}}{2C_{\text{MBr}_4} + C_{\text{Br}}} \quad (6)$$

where  $C_{\text{MBr}_4}$  and  $C_{\text{Br}}$  are the molar concentrations of paramagnetic complex and bromide, respectively. In the present case,  $f_{\text{para}}$  represents the fraction of cations associated with the paramagnetic anion at any given time. All the resulting plots of  $\Delta\nu_{\text{obsd}}$  *vs.*  $f_{\text{para}}$  are linear, as is illustrated by Figure 1.

We have found in previous studies<sup>5,13</sup> that ion association is virtually complete at the cation concentrations chosen for this work. Thus all the cations must be distributed between either the bromide or tetrabromometalate anions. The linearity of our plots suggests therefore that this distribution is not affected by changes in the relative concentration of either anion.

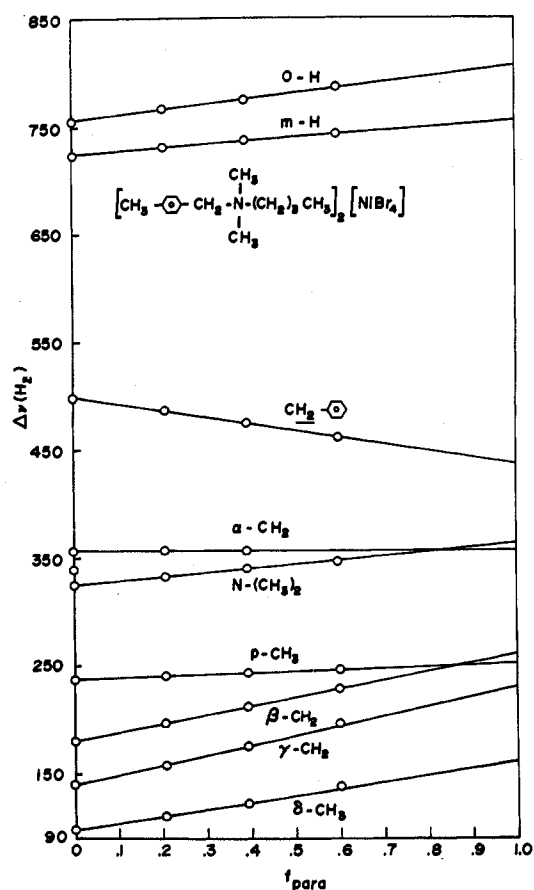


Figure 1.—A plot of observed chemical shift (Hz from TMS at 100 MHz) vs.  $f_{para}$ , the mole fraction of cations associated with the paramagnetic  $NiBr_4^{2-}$  ion.

The resulting isotropic shifts ( $\Delta\nu_{iso}$ ) for the cobalt and nickel complexes are collected in Table III.

### Discussion

**The Isotropic Shift.**—It is readily seen that the cobalt ion pairs exhibit uniformly upfield shifts relative to the diamagnetic  $ZnBr_4^{2-}$  complex while most protons in the nickel complexes give downfield shifts. This behavior is similar to that previously observed in the tetrabutylammonium salts.<sup>5</sup>

The exceptions are the benzyl  $CH_2$  protons and the  $\alpha$ - $CH_2$ (alkyl) protons, which shift upfield. This anomalous shift-direction reversal has already been noted at the  $\alpha$ - $CH_2$  protons in the  $[(C_4H_9)_4N]_2NiI_4$  complex.<sup>5</sup> The conclusion previously reached was that there is a dominant upfield Fermi contact interaction at the  $\alpha$  position and it appears that this effect is especially marked at the benzyl  $CH_2$  protons.

The behavior of the cobalt vs. nickel complexes becomes markedly different when we examine the ring proton shifts, as well as those of the alkyl chain protons. If there were no contact interaction present at any of the protons on the cation and since we expect that the structures of the ion pairs are the same for cobalt and nickel, then we would expect from eq 3 that

$$\frac{(\Delta\nu_{iso})_{i,Co}}{(\Delta\nu_{iso})_{i,Ni}} = \frac{D_{Co}}{D_{Ni}} \quad (7)$$

*i.e.*, the ratios of the isotropic shifts at any given proton would be constant and the same for any other proton chosen. The reason, simply, is that the averaging of the geometric factor is expected to be the same for two very similarly shaped and charged ion pairs. It is patently obvious, on examining the isotropic shift data

TABLE III  
ISOTROPIC NMR SHIFTS FOR THE QUATERNARY AMMONIUM CATIONS

Cation	Anion	Ortho <sup>b</sup>	Meta <sup>b</sup>	Para <sup>b</sup>	Isotropic shift <sup>a</sup>			
					$CH_2$ (benzyl)	$N-CH_3$	$\alpha-CH_2$	$CH_3$ (terminal)
[4-BDBu]	$CoBr_4$	1.66	0.00	(0.00)	3.29	2.48	2.77	0.00
	$NiBr_4$	-0.55	-0.34	(-0.16)	+0.24	-0.48	-0.18	-0.67
[3,5-BDBu]	$CoBr_4$	1.13	(0.00)	0.00	2.93	2.52	2.85	0.00
	$NiBr_4$	-0.37	(-0.27)	-0.24	+0.23	-0.40	0.04	-0.62
[2,4,6-BDBu]	$CoBr_4$	(0.90)	0.17	(0.00)	2.67	2.48	2.84	0.00
	$NiBr_4$	(-0.52)	-0.210	(-0.14)	-0.21	-0.56	-0.21	-0.74
[3,5-BDO]	$CoBr_4$	1.21	(0.00)	0.00	3.10	2.67	2.68	0.00
	$NiBr_4$	-0.39	(-0.23)	-0.18	+0.07	-0.48	<sup>c</sup>	-0.09
[2,4,6-BDO]	$CoBr_4$	(0.93)	0.20	(0.00)	2.66	2.46	2.83	0.00
	$NiBr_4$	(-0.50)	-0.21	(-0.12)	-0.22	-0.54	0.00	-0.11

<sup>a</sup> All shifts are in ppm relative to the resonance frequency of the corresponding proton in the diamagnetic  $ZnBr_4^{2-}$  complex. The data were obtained by the extrapolation procedure outlined in the text. A positive sign indicates an upfield shift. <sup>b</sup> Numbers in parentheses correspond to ring methyl proton shifts. <sup>c</sup> Masked by  $N-CH_3$  protons.

Further, comparison of the  $\Delta\nu_{para}$  values obtained by this method with those obtained from a study in which  $ZnBr_4^{2-}$  was used as the diluent with  $CoBr_4^{2-}$  reveals that the isotropic shifts are identical within experimental error.

The range of mole fractions from which usable data can be obtained is larger in the case of nickel ( $f_{para} = 0-0.8$ ) than in the case of cobalt ( $f_{para} = 0-0.4$ ), the reason in the latter case being that the lines are strongly broadened due to the longer electron relaxation time in tetrahedral cobalt(II).

Finally, the  $\Delta\nu_{obsd}$  values for the tetrabromozincate complexes are subtracted from  $\Delta\nu_{para}$  obtained from the extrapolation procedure to yield  $\Delta\nu_{iso}$  (eq 5).

in Table III, that this condition simply does not hold.

The breakdown of eq 7 indicates that we must consider the possibility that a significant contact interaction exists at a majority of the protons, and therefore that the observed isotropic shift must be factored into its components (eq 1). Although, as will become apparent, there is no exact way to perform this operation, it is still possible to obtain a rough estimate of the two contributions at each proton and from this to formulate some conclusions about the cation's structure in the ion aggregate.

First, let us examine the factors expected to contribute to the isotropic shift in tetrahedral cobalt and nickel complexes, after which we will examine the iso-

tropic shifts at the individual groups in some detail.

**Origins of the Dipolar Shift.**—Several studies have appeared recently dealing with the problem of estimating the magnitude of the dipolar shifts in pseudotetrahedral cobalt and nickel complexes.<sup>23–25</sup> Tetrahedral nickel(II), since it possesses a  $^3T_1$  ground state, possesses considerable orbital angular momentum, which, on applying a low-symmetry crystalline field, gives rise to appreciable anisotropy in the magnetic susceptibility. Of particular interest to our work are the single-crystal susceptibility results of Gerloch and Slade<sup>23</sup> for  $[(C_2H_5)_4N]_2NiCl_4$ , which indicate that the anion is axially symmetric, with  $\Delta\chi = \chi_{\parallel} - \chi_{\perp} = -1000 \times 10^{-6}$  cgsu. The magnetic anisotropy is presumably due to crystal packing, which in this case causes the tetrahedron to become elongated. McGarvey<sup>24</sup> has recently completed a theoretical analysis of nmr shifts in pseudotetrahedral nickel systems and concluded that very small distortions from regular tetrahedral symmetry can result in very large dipolar shifts, a fact which has apparently not been well understood in the past.

Anisotropy in the susceptibility can arise due to ion pairing even for ions that are formally regularly tetrahedral. The mechanism has already been discussed.<sup>5</sup> Briefly, a noncubic crystalline field can arise due either to the presence of the cationic positive charges in the vicinity of the anion or to actual squashing of the ligand polyhedron of the anion by the cation, caused by the mutual electrostatic attraction between the two. In any case, while we do not necessarily expect the anisotropy in solution to be the same as that in the crystal, we do expect it to reveal axial symmetry.<sup>13</sup>

Magnetic anisotropy is also known to occur in pseudotetrahedral cobalt(II) complexes, particularly ones in which the distortion is imposed by an unsymmetrically substituted coordination polyhedron.<sup>25</sup> For the present case, however, due to the fact that the ground state is orbitally nondegenerate, we expect that the anisotropy will be considerably smaller than that for the nickel complex. Therefore, while we cannot rule out completely the possibility that a dipolar shift is present in the cobalt complexes, we believe that its neglect will not seriously affect the interpretation of our results. In this regard, it should be pointed out that the data of La Mar<sup>26</sup> and Wayland and Drago<sup>27</sup> for a series of pseudotetrahedral pyridine complexes of cobalt have been analyzed successfully on the presumption that the dipolar shift is negligible. We now turn to the analysis of the shifts at the individual protons.

**Ring Proton Shifts.**—Contact shift studies of ring protons situated on benzyl groups are available.<sup>23</sup> Data obtained for the hexakis(benzylamine)nickel(II) tetrafluoroborate complex indicate that the dominant delocalization mechanism is of the  $\pi$  type at the phenyl ring protons. This is believed to originate by transfer of spin density from the  $\sigma$  system to the ring  $\pi$  system via a  $\pi$ -type linear combination of methylene hydrogen

1s orbitals.<sup>29</sup> The reversal of sign of the isotropic shift at the 4 position upon replacement of the proton by a methyl group is a classic test for  $\pi$ -spin density and vindicates this argument.

The shift behavior of the ring protons in the ion-pair benzyl groups shows several differences from the case of benzylamine. Taking the  $CoBr_4^{2-}$  complexes first, let us concentrate on the groups attached to the 4 position. The resonance lines are not appreciably broadened, so that the isotropic shift can be determined with exceptional accuracy ( $\pm 1$  Hz). Examination of Table III shows that all shifts at this position are zero. There are of course two ways in which this situation can come about: first, there is neither contact nor dipolar shift at this position; and second, the absence of a shift is caused by the cancelation of two opposing effects. Thus, replacement of 4-H by 4-CH<sub>3</sub> would change the sign of the contact contribution if the spin density at this position originated in the  $\pi$  system. If there was a cancelation in the C-H case, methyl substitution would result in a shift. Table III reveals that this is not the case, indicating that the spin density distributes itself quite differently in the present case than in benzylamine.

The absence of a para shift is consistent with a dominant  $\sigma$ -type delocalization mechanism in the ring which would also be expected from the observed attenuation of shift with increasing distance from the central nitrogen atom ( $\Delta\nu_o > \Delta\nu_m > \Delta\nu_p$ ).

**Alkyl Chain Protons.**—There are several previous reports of isotropic shifts in alkyl chains.<sup>30,31</sup> Of particular interest to this study are the shifts in the hexakis(propylamine)nickel(II) cation.<sup>31</sup> It is observed that the spin density attenuates very rapidly down the chain ( $\Delta\nu_{\alpha}/\Delta\nu_{\gamma} = 100$ ), leading us to believe that the unpaired spin density at the terminal methyl group in a similar butyl derivative should be zero. One may safely neglect the dipolar shift in octahedral nickel complexes, due to the magnetically isotropic ground state ( $^3A_2$ ), and the absence of low-lying excited states.

It is readily seen from Table III that the terminal methyl proton shifts in the cobalt complexes are all identically zero. This result suggests that the small shifts previously seen in the tetrabutylammonium ion at the terminal methyl position may be in error, presumably due to the lower resolving power of the 60-MHz instrument used.<sup>5</sup> The  $\beta$  and  $\gamma$  protons show attenuation consistent with a  $\sigma$ -delocalization mechanism (Figure 1). In the case of nickel, large downfield proton shifts occur at the  $\delta$  position in the butyl-substituted cations. On replacing a butyl by an octyl chain, the downfield shift attenuates by a factor of 5, consistent with a larger distance from the paramagnetic anion, hence a smaller value of  $G(R_i, \theta_i)$  (Table III). The observations of sizable  $\delta$ -proton shifts are consistent with our previous observations<sup>5</sup> on the tetrabutylammonium cation ion paired to  $NiCl_4^{2-}$  and  $NiBr_4^{2-}$ .

**Interpretation of the Shifts.**—It is possible, using the preceding data, coupled with our expectations based on the magnetic behavior of these complexes, to adopt some guidelines for the interpretation of the

(23) M. Gerloch and R. C. Slade, *J. Chem. Soc. A*, 1022 (1969).

(24) B. R. McGarvey, *J. Amer. Chem. Soc.*, **94**, 1103 (1972).

(25) W. D. Horrocks, Jr., and E. S. Greenberg, *Inorg. Chem.*, **10**, 2190 (1971).

(26) G. N. La Mar, *ibid.*, **6**, 1939 (1967).

(27) B. B. Wayland and R. S. Drago, *J. Amer. Chem. Soc.*, **88**, 4597 (1966).

(28) R. J. Fitzgerald and R. S. Drago, *ibid.*, **89**, 2879 (1967).

(29) D. H. Levy, *Mol. Phys.*, **10**, 233 (1966).

(30) D. R. Eaton, A. D. Josey, and R. E. Benson, *J. Amer. Chem. Soc.*, **89**, 4040 (1967).

(31) R. J. Fitzgerald and R. S. Drago, *ibid.*, **90**, 2523 (1968).

shifts. First, on the basis of the expected magnetic behavior we believe that we are justified in using the large upfield shifts in the cobalt complexes as a measure of the contact effect.

Second, past experience has shown that the mechanisms of spin density transmission and the resulting delocalization patterns are similar between tetrahedral cobalt and nickel(II) complexes of the same ligand.<sup>2,32</sup> We will give a fuller discussion of this point in a later section. For the moment, it is possible to state with some confidence that there will be an upfield contact contribution to the shifts in the nickel complexes which follows the observed cobalt isotropic shift pattern closely.

Finally, in such cases as the para ring protons and the terminal alkyl chain protons, it seems certain that the downfield shifts observed in the nickel complexes may be ascribed to a predominantly dipolar effect.

The validity of these conclusions will now be tested, using the data for the  $\alpha$ -methylene protons.

**N(CH<sub>3</sub>), CH<sub>2</sub>(benzyl), and  $\alpha$ -CH<sub>2</sub>(alkyl) Protons.**—As an examination of the central columns of Table III shows, the isotropic shifts of the  $\alpha$ -CH<sub>2</sub>(alkyl) protons in the cobalt series do not depend on the substituents on the benzene ring, since they are equal within experimental error for the series (0.15 ppm). A similar conclusion holds for the *N*-CH<sub>3</sub> protons. We may conclude from this that the extent of ion aggregation and the structure of the ion aggregate are not sensitive functions of the substituents on the benzene ring. The shifts of the *N*-CH<sub>3</sub> protons are smaller (2.45 ppm) than those of the  $\alpha$ -CH<sub>2</sub>(alkyl) protons (2.80 ppm) on the average, while the benzyl CH<sub>2</sub> protons are the most strongly shifted of all. These last also reveal the largest apparent scatter; we believe, however, that the exceptionally low values observed in the 2,4,6-BDBu and 2,4,6-BDO cases are outside experimental error, as will presently be seen.

In contrast to the value<sup>5</sup> of  $\Delta\nu_{\alpha} = -0.55$  ppm in [(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>N]<sub>2</sub>NiBr<sub>2</sub> the  $\alpha$ -CH<sub>2</sub>(alkyl) chain protons exhibit considerably smaller downfield shifts in the nickel complexes; in fact, only the *N*-CH<sub>3</sub> shifts are comparable to the tetrabutylammonium case. The benzyl CH<sub>2</sub> isotropic shifts are positive or negative, depending apparently on the placement of the methyl substituents. These apparent anomalies are best explained as follows. The small isotropic shifts at the protons closest to nitrogen in the nickel complexes result because there is a rather delicate balance between the upfield contact and downfield dipolar shifts. Thus, the smaller observed downfield isotropic shift in the  $\alpha$ -CH<sub>2</sub>(alkyl) protons relative to *N*-CH<sub>3</sub> is caused by a larger upfield contact contribution in the former case. This would be expected if the nickel spin-delocalization pattern were similar to the cobalt pattern and vindicates our earlier assumptions. Similarly, one finds upfield benzyl CH<sub>2</sub> isotropic shifts in nickel in just those cations where the corresponding cobalt shifts are largest. A reduced contact interaction at these protons in cobalt, such as occurs in the 2,4,6-BDBu and 2,4,6-BDO salts, similarly shows up as a reduced interaction at the nickel and permits a slight dominance of the dipolar interaction, with the resulting downfield isotropic shift.

**Factoring the Isotropic Shift.**—The problem now becomes one of separating the contact from the dipolar portion of the isotropic shift in the nickel complexes. A central feature of this problem is the model which one chooses to explain the presence of the Fermi contact term. Thus, Burkert, *et al.*,<sup>11</sup> chose an "intimate contact" model where the central nitrogen atom of the cation rehybridizes to give a five-coordinate structure presumably containing a partial nitrogen-halide single bond. Other reasonable structures for an intimate ion pair<sup>13</sup> involve hydrogen bonding between the somewhat acidic protons on the  $\alpha$ -carbon atoms and the coordinated halide ions. The common feature of these models is the involvement of the lone-pair orbitals of the halide ions in bonding with the cation. It follows that the observation of a contact shift on the *i*th proton of the cation may be related to the presence of spin density,  $\rho$ , on the lone pairs of the anion by an equation<sup>2</sup>

$$A_i = \frac{Q_i \rho}{2S} \quad (8)$$

where  $Q_i$  is a proportionality constant, characteristic of the delocalization mechanism on the cation, and  $S$  is the total spin quantum number for the cobalt ( $S = 3/2$ ) or nickel ( $S = 1$ ) complex. We do not know the individual values of  $\rho$  for the cobalt or nickel complexes, but since  $Q_i$  is a property of the cation,<sup>32</sup> we can write, from eq 2

$$\frac{(\Delta\nu_i)_{i,\text{Co}}}{(\Delta\nu_i)_{i,\text{Ni}}} = \frac{2 \rho_{\text{Co}} \chi_{\text{Co}}^{\text{M}}}{3 \rho_{\text{Ni}} \chi_{\text{Ni}}^{\text{M}}} = R \quad (9)$$

All that is needed is an independent estimate of the ratios of the lone-pair spin densities in suitable cobalt- and nickel-halo complexes. One such estimate is provided by the work of Rettig and Drago,<sup>33</sup> who have established by the study of infrared frequency shifts that the complexes [(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>N][MI<sub>3</sub>P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>] (M = Co, Ni) interact with the proton of solvent chloroform via hydrogen bonding. The chloroform resonance was found to shift strongly upfield in both the cobalt and nickel complexes, the shifts being essentially equal for a given weight of added solute. The evidence suggests that between four and five chloroform molecules are associated with each anion. The chloroform proton is believed to lie on the Co-I bond axis in the hydrogen-bonded complex. Since this axis makes a polar angle of 55° with the principal susceptibility axis ( $\chi_{\parallel}$ ), the term in  $G(R_i, \theta_i)$  for this proton should very nearly vanish in axial symmetry (eq 4). Thus the observed chloroform proton shifts should be largely dominated by the Fermi contact interaction.

Since  $Q_i$  in eq 8 is a property of the chloroform molecule, and since the isotropic shift per molecule of HCCl<sub>3</sub> is the same for the cobalt complex as it is for the nickel complex, we obtain  $R = 1$  from eq 9. In order to obtain the ratio of the spin densities ( $\rho_{\text{Co}}/\rho_{\text{Ni}}$ ) in the iodide lone pairs, it is convenient to rewrite eq 9 in terms of the observed magnetic moments.<sup>13</sup> We obtain

$$\frac{(\Delta\nu_i)_{i,\text{Co}}}{(\Delta\nu_i)_{i,\text{Ni}}} = \frac{2 \left( \frac{\rho_{\text{Co}}}{\rho_{\text{Ni}}} \right) [\mu_{\text{eff}}^2]_{\text{Co}}}{3 [\mu_{\text{eff}}^2]_{\text{Ni}}} \quad (10)$$

Using the published room-temperature magnetic mo-

(32) G. N. La Mar, W. D. Horrocks, Jr., and L. C. Allen, *J. Chem. Phys.*, **41**, 2126 (1964).

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

TABLE IV  
 ESTIMATED DIPOLAR SHIFTS IN THE TETRABROMONICKELATE(II) COMPLEXES<sup>a</sup>

Complex	Ortho <sup>b</sup>	Meta <sup>b</sup>	Para <sup>b</sup>	CH <sub>2</sub> (benzyl)	N-CH <sub>3</sub>	α-CH <sub>3</sub>	CH <sub>3</sub> (terminal)
[4-BDBu] <sub>2</sub> NiBr <sub>4</sub>	-2.37	-0.34	(-0.16)	-3.38	-3.20	-3.22	-0.67
[3,5-BDBu] <sub>2</sub> NiBr <sub>4</sub>	-1.61	(-0.27)	-0.24	-2.99	-3.17	-3.09	-0.62
[2,4,6-BDBu] <sub>2</sub> NiBr <sub>4</sub>	(-1.51)	-0.40	(-0.14)	-3.14	-3.28	-3.33	-0.74
[3,5-BDO] <sub>2</sub> NiBr <sub>4</sub>	-1.72	(-0.23)	-0.18	-3.34	-3.41	-3.09	-0.09
[2,4,6-BDO] <sub>2</sub> NiBr <sub>4</sub>	(-1.52)	-0.43	(-0.12)	-3.14	-3.24	-3.11	-0.11

<sup>a</sup> All values are in ppm. The dipolar shift is calculated from eq 1 and the relation  $R = (\Delta\nu_{\text{f}})_{\text{Co}}/(\Delta\nu_{\text{f}})_{\text{Ni}} = 0.91$ . <sup>b</sup> Numbers in parentheses correspond to ring methyl proton shifts.

ments<sup>34,35</sup> for  $[\text{CoI}_3\text{P}(\text{C}_6\text{H}_5)_3]^-$  and  $[\text{NiI}_3\text{P}(\text{C}_6\text{H}_5)_3]^-$  results in  $\rho_{\text{Co}}/\rho_{\text{Ni}} = 0.84$  for the iodide lone pairs.

Values of  $\rho_{\text{Co}}/\rho_{\text{Ni}}$  less than unity are not uncommon in a series of tetrahedral complexes and have been explained in the past as resulting from a slightly greater degree of electron-electron repulsion in the  $t_{2g}$  set on the nickel ion.<sup>2,32</sup>

In particular,  $\rho_{\text{Co}}/\rho_{\text{Ni}}$  values for the phenyl protons in the series  $\text{M}[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{X}_2$  ( $\text{M} = \text{Co}, \text{Ni}; \text{X} = \text{Br}, \text{I}$ ) as well as for the  $[\text{MI}_3\text{P}(\text{C}_6\text{H}_5)_3]^-$  complexes<sup>2</sup> all cluster about the range 0.6–0.65. The isotropic shifts in these complexes were factored into their components without the benefit of magnetic anisotropy studies. The compounds  $\text{M}[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{Cl}_2$  do not suffer from this lack.<sup>23</sup> Using the unambiguous contact shift results for this salt, we obtain  $\rho_{\text{Co}}/\rho_{\text{Ni}} = 1.09$  (ortho), 0.89 (meta), and 0.82 (para), indicating that the delocalization patterns are quite similar in these tetrahedral complexes as was originally claimed.<sup>2,32</sup>

Although we have no data with which to evaluate  $\rho_{\text{Co}}/\rho_{\text{Ni}}$  for the bromide lone pairs, we have every reason to believe that a value close to that for iodide would be realistic.<sup>2</sup> Thus, for the tetrabromometalates using eq 10 and the magnetic moments for  $\text{CoBr}_4^{2-}$  ( $\mu_{\text{eff}} = 4.85$  BM)<sup>36</sup> and for  $\text{NiBr}_4^{2-}$  ( $\mu_{\text{eff}} = 3.80$  BM)<sup>37</sup> and the above value for the ratio of the spin densities in the lone pairs, we obtain  $R = 0.91$ . Finally, assuming the cobalt shifts to be completely Fermi contact, we calculate the nickel contact shifts, and from eq 1, the dipolar contribution at each proton. These estimated dipolar shifts are collected in Table IV.

In our previous treatment of this problem,<sup>13</sup> we arbitrarily assumed that  $\rho_{\text{Co}}/\rho_{\text{Ni}}$  for the lone pairs was identically unity, which results in  $R = 1.08$  for the bromide complexes. In view of the fact that we must allow for the error introduced by our inability to estimate the dipolar contribution to the chloroform isotropic shifts, we believe that a spin density ratio  $\rho_{\text{Co}}/\rho_{\text{Ni}}$  in the range 0.80–1.10 is appropriate to the present series of complexes. We will show that, while variations within this range affect the absolute magnitudes of the dipolar shifts, our conclusions, which involve the relative magnitudes of the shifts, are relatively unaffected by the uncertainty.

### Conclusions

Regrettably, this study has not enabled us to shed much light on the exact means by which unpaired spin density reaches the cation protons. We are therefore

forced to restrict ourselves to conclusions which are independent of these considerations. Our chief concern will be to derive information from the dipolar portion of the shifts, but, nonetheless, the contact portion deserves comment as well. We shall treat the contact effect first.

Of particular note is the large variation in the size of the  $\text{CH}_2$ (benzyl) contact shifts, mentioned earlier. With the exception of the 2,4,6-BDBu and 2,4,6-BDO cations, the contact shifts center around 3.1 ppm, making them the largest observed. We believe the discrepancy of 0.5 ppm is best explained as arising from the presence of methyl groups in the 2,6 positions on the ring. Since the delocalization of spin onto the cation requires intimate contact between anion and cation, it is not difficult to see that bulky groups on the ortho positions will decrease the probability of such interactions taking place. That the decrease is not more substantial may be attributed to the fact that the ring is free to rotate; hence rotamers where the steric effect is minimized are accessible to the attacking anion.

By contrast it is interesting to note that, as one might expect, the substitution of an octyl for a butyl chain has no perceptible effect on the sizes of either the contact or dipolar shifts at the  $\alpha$ -methylene protons, since the steric effect of an  $n$ -alkyl group is approximately independent of its length.

The dipolar shifts on the phenyl ring (Table IV) reveal the expected behavior. Thus the meta and para proton dipolar shifts attenuate when replaced by methyl substituents, although the amount of scatter makes any firmer conclusions unreliable. The ortho dipolar shift in 4-BDBu appears anomalously large and presumably represents a less sterically hindered position, *i.e.*, one in which the anion approaches the ring more closely than in the other cases.

Most interesting is the apparent equality of the dipolar shifts at the  $\alpha$ -methylene protons. It is readily seen that steric effects of the type found in the cobalt data are absent here, nor is there any correlation between the magnitudes of the dipolar shifts and those of the contact shifts derived from the cobalt data. This conclusion is unaffected by variations in  $R$  within the range of possible  $R$  values ( $R = 1.08$ – $0.90$ ). Allowing for the larger shifts and line broadenings at these protons and the consequent uncertainty in the values, the average shifts are  $-3.17 \pm 0.12$  ppm (benzyl),  $-3.26 \pm 0.07$  ppm ( $N\text{-CH}_3$ ), and  $-3.18 \pm 0.07$  ppm (alkyl), *i.e.*, equal within experimental error ( $R = 0.92$ ). Choosing  $R = 1.08$ , on the other hand, leads to  $-2.73$ ,  $-2.83$ , and  $-2.72$  ppm, respectively, for the average dipolar shifts.

We may think of the dipolar shift as arising from a model in which the tetraalkylammonium cation may be

(34)  $[\mu_{\text{eff}}]_{\text{Co}} = 4.63$  BM: F. A. Cotton, O. D. Faut, D. M. L. Goodgame, and R. H. Holm, *J. Amer. Chem. Soc.*, **83**, 1780 (1961).

(35)  $[\mu_{\text{eff}}]_{\text{Ni}} = 3.46$  BM: F. A. Cotton, O. D. Faut, and D. M. L. Goodgame, *ibid.*, **83**, 344 (1961).

(36) R. Holm and F. A. Cotton, *J. Chem. Phys.*, **32**, 1168 (1960).

(37) F. A. Cotton and D. M. L. Goodgame, *J. Amer. Chem. Soc.*, **82**, 2967 (1960); N. S. Gill and R. H. Nyholm, *J. Chem. Soc.*, 3997 (1959).

attacked by the anion on any of the four faces (or apices) of the tetrahedron centered on the nitrogen atom. Although, by symmetry, we might expect the overall probabilities of attack to be different in the present series, this does not appear to be the case.

The dipolar shift represents a time-average shift, which is a weighted sum over a large number of possible instantaneous structures, not all of which involve intimate contact between anion and cation. For this reason, one might expect that the steric effects which determine very close approach geometries tend to be

suppressed in the dipolar shift by the averaging process. On the other hand, since the contact shift occurs only *via* direct anion-cation bonding, it is expected to reflect the local steric requirements of the ion-pairing process to a greater extent.

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## Raman Spectra of Dimethyltin(IV) and Dimethylthallium(III) in Single Crystals and Solutions. Carbon-Tin and Carbon-Thallium Derived Bond Polarizabilities<sup>1,2</sup>

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Raman spectra have been collected with relatively large single crystals of  $(\text{CH}_3)_2\text{SnF}_2$ , and they are in agreement with previous assignments of the vibrations. Relative values for the components of the derived polarizability tensors for the  $531\text{-cm}^{-1}$  Sn-C symmetric stretching and the  $114\text{-cm}^{-1}$  rotatory lattice modes have been measured. From the data on the Sn-C stretching mode, the ratio of the perpendicular and longitudinal components of the tin-carbon derived bond polarizability,  $\alpha'_p/\alpha'_l$ , was calculated to be 0.227. Limited data also were collected from single crystals of  $(\text{CH}_3)_2\text{TlBr}$ , and the vibrations were assigned. The depolarization ratio computed from the  $(\text{CH}_3)_2\text{SnF}_2$  crystal tensor components,  $\rho = 0.24 \pm 0.01$ , was the same within the experimental error as the value obtained for  $(\text{CH}_3)_2\text{Sn}^{2+}(\text{aq})$  by measurements on aqueous solutions of  $(\text{CH}_3)_2\text{Sn}(\text{ClO}_4)_2$ ,  $\rho = 0.22 \pm 0.02$ , indicating that the electron distribution in the  $(\text{CH}_3)_2\text{Sn}^{\text{IV}}$  moiety is very similar in both cases. The experimental depolarization ratio for  $(\text{CH}_3)_2\text{Tl}^+(\text{aq})$  obtained by measurements on aqueous  $(\text{CH}_3)_2\text{TlClO}_4$  also was  $0.22 \pm 0.02$  indicating that  $\alpha'_p/\alpha'_l$  is the same for tin(IV)-carbon and thallium(III)-carbon bonds in the cations. A comparison of the crystal and solution spectra suggests that the lowest frequency solution mode in each case is better described as a libration than as a skeletal deformation mode.

### Introduction

Raman spectroscopy has proved to be especially useful in the study of the stereochemistry of organometallic compounds because of the high intensity of both the metal-carbon stretching vibrations and the internal vibrations of alkyl groups. In a qualitative sense, the stretching of covalent bonds leads to relatively intense Raman scattering, while highly polar bonds give only weak scattering. Discussions of the relation between Raman intensities, molecular structure, and chemical bonding normally are framed in terms of derived bond polarizabilities,  $(\partial\alpha/\partial r)$ , where  $\alpha$  is the ionic or molecular polarizability and  $r$  is the bond stretching coordinate. Unfortunately, there are very few data available on bond polarizabilities, and consequently it is very difficult to treat Raman intensities in any quantitative way.

The bond polarizabilities are computed from the derived polarizability for a vibration,  $\alpha_j' = (\partial\alpha/\partial Q_j)$  where  $Q_j$  is the normal coordinate. The square of the derived polarizability is proportional to the experimentally observed band intensity. A clear discussion of the polarizability theory is given by Brandmüller

and Moser.<sup>3</sup> The bond polarizabilities most often have been related to bond order using the approximate equation of Long and Plane,<sup>4</sup> and the applications to inorganic systems have been reviewed recently by Spiro.<sup>5</sup>

With unoriented samples, *i.e.*, gases, liquids, and solutions, only the derived polarizability tensor invariants, the quantities which are independent of the relation between molecular and laboratory coordinates,<sup>6</sup> can be determined. This limitation can be removed by the use of an oriented single crystal where each of the derived polarizability tensor components can be examined independently.

In this work, relative values have been measured for the derived polarizability tensor components for the totally symmetric tin-carbon stretching vibrations of  $(\text{CH}_3)_2\text{SnF}_2$  which are equivalent to the values for the tin-carbon derived bond polarizabilities. From these data, the depolarization ratio of  $(\text{CH}_3)_2\text{SnF}_2$  can be computed for comparison with the corresponding vibration of  $(\text{CH}_3)_2\text{Sn}^{2+}$  in aqueous solution and the dimethyltin(IV) moiety in other compounds. The Raman spectrum of a powder sample of  $(\text{CH}_3)_2\text{SnF}_2$

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(2) Taken from a thesis submitted by V. B. R. to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the Ph.D. degree, 1972.

(3) J. Brandmüller and H. Moser, "Einführung in die Ramanspektroskopie," D. Steinkopff, Darmstadt, 1962, Chapter 4.

(4) T. V. Long, II, and R. A. Plane, *J. Chem. Phys.*, **43**, 457 (1965).

(5) T. G. Spiro, *Progr. Inorg. Chem.*, **11**, 1 (1970).

(6) Intensities of unoriented samples have been reviewed by R. E. Hester in "Raman Spectroscopy," Vol. 1, H. A. Szymanski, Ed., Plenum Press, New York, N. Y., 1967, Chapter 4.