formation of a sterically uncrowded Hg–C σ bond. Naturally, the π configuration is less favored than that in the product $Cr–NC–Hg^{4+}$, so that further rearrangement of **3** should be facile. It should, of course, be noted that the mechanisms invoked for all the processes considered here necessarily proceed *without* the complete cleavage of a chromium–cyanide bond, because under the acidic conditions considered re-formation of a bond to chromium is prohibited thermodynamically. Of course, one cannot rule out the intervention of intermediates such as a solvent-separated ion pair in preference to the π-bonded possibilities.

Acknowledgment.—The author is grateful to Professors K. Schug, R. G. Linck, and A. Haim for making their results available prior to publication.

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Fermi Contact and Dipolar Nuclear Magnetic Resonance Shifts in Paramagnetic Ion-Paired Systems. Studies on Some Anionic Lanthanide Complexes

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Received March 3, 1971

The observation of ^{14}N contact shifts in ion-paired systems requires that the nature of the geometrical models used to describe the ion-pairing process be reevaluated. The relative contribution of both Fermi contact and dipolar shifts to the total isotropic shift is discussed for a new series of anionic lanthanide complexes and for the previously studied tetrahalometalate(II) complexes.

The chemical shifts which result from delocalization of very small fractions of an unpaired electron from a paramagnetic metal ion onto a ligand or from through-space dipolar coupling between electron and nucleus have begun to shed light on the nature of relatively weak interactions in solution.[1–6] In particular nmr studies of solutions containing ion pairs having one paramagnetic ion, usually the anion, have given rise to information on ion-pair geometries in solution.

The total isotropic resonance shift in the nmr due to the presence of unpaired electrons can be expressed as the sum of two parts, the Fermi contact shift, $\Delta\nu_f$, and the dipolar shift, $\Delta\nu_{dip}$, thus[1]

$$(\Delta\nu)_i = (\Delta\nu_f)_i + (\Delta\nu_{dip})_i \tag{1}$$

where

$$(\Delta\nu_f)_i = \frac{A_i\chi_M}{Ng_N\beta_N} \tag{2}$$

and

$$(\Delta\nu_{dip})_i = \frac{|\beta|^2\nu S(S+1)}{45kT}F(g)\left[\frac{3\cos^2\chi_i - 1}{R_i^3}\right] \tag{3}$$

Here, A_i is the electron–nuclear hyperfine coupling constant, χ_M is the paramagnetic susceptibility of the complex, and $F(g)$ is a function of $g_{||}$ and $g_\perp$, the parallel and perpendicular components of the g tensor of the paramagnetic complex. The exact form of $F(g)$ depends critically on the relative magnitudes of the electron Zeeman anisotropy energy, the electronic relaxation time, and the molecular tumbling correlation time.[1]

The term at the far right of eq 3 is the so-called "geometric factor" (GF) and contains the structural information we desire. χ_i is the angle made by the ith proton with the principal magnetic axis of the complex (the axis of $g_{||}$). R_i is the distance between proton and electron, the latter assumed to be located on the center of the metal complex. The other symbols have their usual meanings.[2] In the absence of a specific knowledge of the g tensors for a paramagnetic complex or of the relaxation times involved, geometrical information is usually obtained by noting that, for two distinguishable protons

$$(\Delta\nu_i)_{dip}/(\Delta\nu_j)_{dip} = (GF)_i/(GF)_j \tag{4}$$

The principal interest to most of the workers in this area has been in the behavior of the symmetrical tetra-n-alkylammonium cations in solution. Larsen and Wahl[4] studied D_2O solutions of $[(CH_3)_4N]_3Fe(CN)_6$ and of $K_3Fe(CN)_6$ containing R_4NBr ($R = CH_3$, C_2H_5, n-C_3H_8, n-C_4H_9). The interionic distance, which can be defined as the distance between the metal and the central nitrogen atom of the cation, A, was estimated at 8–9 Å; further studies on the system $R_4N^+Cr(CN)_6^{3-}$ using line broadening techniques[6] estimated A as 11 Å. The interionic distances so derived are found to be independent of the alkyl chain length.

Studies on the system $(C_4H_9)_4N^+(C_6H_5)_3PCoI_3^-$ by La Mar[1,2] yielded A values of 3.8 Å in chloroform, while similar results were obtained in the system $(C_4H_9)_4NCo(acac)_3$ studied by Horrocks, *et al.*,[3] in chloroform and carbon tetrachloride.

These ion-pairing distances were estimated on the reasonable assumption that the tetraalkylammonium cation contains no orbitals through which covalent bonding between anion and cation can take place. Since the Fermi contact shift requires some form of covalency between metal and ligand, the earlier workers

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[1] G. N. La Mar, *J. Chem. Phys.*, **41**, 2992 (1964); J. P. Jesson, *ibid.*, **47**, 579 (1967); R. J. Kurland and B. R. McGarvey, *J. Magn. Resonance*, **2**, 286 (1970).

[2] G. N. La Mar, *J. Chem. Phys.*, **43**, 235 (1965).

[3] W. D. Horrocks, Jr., R. H. Fischer, J. R. Hutchison, and G. N. La Mar, *J. Amer. Chem. Soc.*, **88**, 2436 (1966).

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

[5] I. M. Walker and R. S. Drago, *J. Amer. Chem. Soc.*, **90**, 6951 (1968).

[6] D. W. Larsen, *Inorg. Chem.*, **5**, 1109 (1966).

have assumed that the resonance shifts arise solely from the dipolar, or "pseudocontact," interaction, to the complete exclusion of the Fermi contact[4] interaction. Since only one average signal for each type of proton is observed, the cation is obviously in motion due either to fast chemical exchange between free and ion-paired environments[4] or simply to some form of tumbling within the ion-paired complex.[2] In either case, since the resonating protons are not firmly attached to ligands of the first coordination sphere, it is necessary to average the geometric factor over the angles and distances which we expect a cation to encounter while associated with the anion. We will critically examine several of the averaging procedures and models used by previous workers at an appropriate place in this paper.

The interpretation of the ion-pairing shifts has been complicated by recent studies on the cation ^{14}N resonances,[7,8] which have shown conclusively that unpaired spin density from the anion reaches the cation. This renders the original assumptions about the purely dipolar nature of the shifts untenable.

In order to obtain geometrical information from the isotropic shift studies, it will therefore be necessary to separate the contact portion of the shift from the dipolar portion. We will show how this can be done with reasonable consistency for a series of anionic lanthanide complexes, which have the advantage of being quite similar chemically, thus reducing some of the uncertainties associated with comparing data for a series of complexes of different metals.

Experimental Section

Reagents.—Rare earth oxides of 99.9% purity were supplied by American Potash and Chemical Co., Chicago, Ill., and were converted to the hydrated chlorides. All other materials were of reagent grade.

Preparation of Complexes $[(C_4H_9)_4N]_3LnCl_6$.—Tetrabutylammonium iodide (5.55 g, 0.015 mol) was stirred with an excess of freshly precipitated silver chloride in dry ethanol for 24 hr under gentle reflux in the dark. After cooling to room temperature, the mixture was allowed to stand for several hours, followed by removal of the AgI precipitate by filtration. The solvent was removed from the resulting $(C_4H_9)_4NCl$ on a rotary evaporator. The resulting solid was taken up in 50 ml of acetone, and ~0.004 mol of hydrous rare earth chloride was added, along with 20 ml of either dimethoxypropane or triethyl orthoformate and ~0.05 ml of concentrated HCl, to repress hydrolysis. After 6–8 hr reflux, the solvent was reduced to approximately 20 ml and ethyl acetate was added slowly. The complexes precipitated in 60% yield. They are somewhat moisture sensitive; the solvent was thus removed by filtration under nitrogen. The complexes were recrystallized from concentrated dichloromethane solution by dropwise addition of ethyl acetate. The solids were washed with ethyl acetate, and the complexes dried *in vacuo* over P_2O_5 for 24 hr at 77°.

The compounds are very soluble in dichloromethane and chloroform, although the chloroform solutions have a marked tendency to precipitate the metal chloride on standing. Stable solutions are also formed in nitrobenzene and acetonitrile.

Anal. Calcd for $C_{48}H_{108}N_3LaCl_6$: C, 53.43; H, 10.09; Cl, 19.71. Found: C, 53.22; H, 10.32; Cl, 19.75. Calcd for $C_{48}H_{108}N_3CeCl_6$: Cl, 19.69. Found: Cl, 19.50. Calcd for $C_{48}H_{108}N_3PrCl_6$: C, 53.33; H, 10.07; Cl, 19.67. Found: C, 53.22; H, 10.44; Cl, 19.99. Calcd for $C_{48}H_{108}N_3NdCl_6$: C, 53.16; H, 10.03; Cl, 19.62; Nd, 13.30. Found: C, 52.84; H, 10.24; Cl, 19.70; Nd, 13.17. Calcd for $C_{48}H_{108}N_3SmCl_6$: C, 52.86; H, 9.98; Cl, 19.50; Sm, 13.78. Found: C, 53.04; H, 10.38; Cl, 19.57; Sm, 13.80. Calcd for $C_{48}H_{108}N_3ErCl_6$: C, 52.06; H, 9.83; Cl, 19.21; Er, 15.11. Found: C, 51.71; H, 10.00; Cl, 19.38; Er, 15.05. Calcd for $C_{48}H_{108}N_3TmCl_6$: C, 51.98; H, 9.81; Cl, 19.18; Tm, 14.99. Found: C, 51.74; H, 9.73; Cl, 19.42; Tm, 14.97. Calcd for $C_{48}H_{108}N_3YbCl_6$: C, 51.79; H, 9.78; Cl, 19.11; Yb, 15.54. Found: C, 51.15; H, 9.78; Cl, 19.26; Yb, 15.76.

Magnetic resonance spectra for the rare earth complexes were recorded on a Varian A-60 nmr spectrometer, at 28°, and on a Varian HR-220 spectrometer, at 22–23°.

Molar conductivities were recorded on a Wayne–Kerr universal bridge, B221A. C and H analyses were performed by Galbraith Microanalytical Laboratories, Knoxville, Tenn. Metal was determined by ignition to the oxide, while chloride was determined potentiometrically by titration with Ag^+ ion.

Results

General Information.—In recent years, a number of anionic complexes of the trivalent lanthanides with the general formula M_3LnX_6, where X is a uninegative anion and Ln is a lanthanide, have been prepared and characterized.[9–12] The best known and characterized are the $LnCl_6^{3-}$ and $Ln(SCN)_6^{3-}$ complexes for which visible spectra for the $f^n \rightarrow f^n$ transitions,[9–11] molar conductivities, and infrared spectra[9] have been reported.

The molar conductance values (Λ_M) for the series $[(C_4H_9)_4N]_3LnCl_6$ in nitrobenzene may be found in Table I. As can be seen by comparison with data reported for the representative $Er(SCN)_6^{3-}$ complex,[9] agreement is excellent. Since the latter series have been shown not to dissociate appreciably in nitrobenzene or acetonitrile, it is safe to assume that our data also indicate 3:1 electrolyte behavior.

TABLE I

MOLAR CONDUCTANCE VALUES FOR THE COMPLEXES $[(C_4H_9)_4N]_3LnCl_6$ IN NITROBENZENE

Anion	Concn $\times 10^3$, *M*	Λ_M,[b] ohm^{-1} cm^2 mol^{-1}	Anion	Concn $\times 10^3$, *M*	Λ_M,[b] ohm^{-1} cm^2 mol^{-1}
$CeCl_6^{3-}$	0.267	81.6	$ErCl_6^{3-}$	0.912	73.8
	0.0534	96.2		0.0547	99.5
$PrCl_6^{3-}$	1.128	74.8	$TmCl_6^{3-}$	1.118	73.9
	0.0677	106		0.0671	103
$NdCl_6^{3-}$	1.064	73.5	$YbCl_6^{3-}$	1.008	75.1
	0.0638	107		0.0605	101
			$Er(NCS)_6^{3-}$	1	72.1[a]

[a] Data taken from ref 9. [b] All values recorded at 23 ± 1°.

Spectra in the visible region are consistent with those previously assigned for the complexes $[(C_6H_5)_3PH]_3$-$LnCl_6$, studied by Ryan and Jørgensen,[10] and will be the subject of a future communication.

Magnetic Resonance Spectra. Isotropic Shifts in Dichloromethane.—The 60-MHz nmr spectrum of tetrabutylammonium ion in diamagnetic environments is well known.[4–6] The spectrum consists of three groups of lines, strongly perturbed by second-order effects. In the $LnCl_6^{3-}$ complex the α resonance occurs 200 Hz (τ 6.67) downfield from TMS, while the central chain (β, γ) protons resonate around 95 Hz (τ 8.42) as a diffuse unsymmetrical group of lines. The terminal methyl (δ) resonance is strongly perturbed by the β,γ protons and appears as a collapsed triplet centering on 60 Hz. Comparison of the lanthanum complex with H_2CCl_2 solutions of the diamagnetic $ZnBr_4^{2-}$ complex previously studied[5] indicates that only the α protons

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

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

(9) J. L. Burmeister, S. D. Patterson, and E. A. Deardorff, *Inorg. Chim. Acta*, **3**, 105 (1969).

(10) J. L. Ryan and C. K. Jørgensen, *J. Phys. Chem.*, **70**, 2845 (1966).

(11) J. L. Ryan, *Inorg. Chem.*, **8**, 2053 (1969).

(12) L. Morss, M. Siegal, L. Stenger, and N. Edelstein, *ibid.*, **9**, 1771 (1970).

show a detectable nmr shift; protons α to nitrogen in quaternary ammonium salts are known to be sensitive to environmental effects.[13]

While resolution of the β,γ protons in the diamagnetic spectrum is still incomplete, even at 100 MHz, the spectrum at 220 MHz shows two bands: a poorly resolved sextet at τ 8.36 and a sharper sextet at τ 8.54, which we assign, respectively, to the β and γ protons (see Figure 1). As might be expected, the δ protons at this frequency are a first-order triplet.

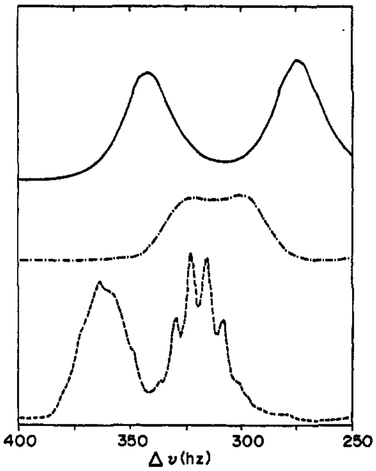

Figure 1.—The 220-MHz spectrum of the β and γ chain protons in the complexes $[(C_4H_9)_4N]_3LnCl_6$: – – –, Ln = Sm; ·–·–·–·, Ln = Nd; ——, Ln = Er, diluted with $SmCl_6^{3-}$ (n_{Er} = 0.211).

Due to the short 4f-electron relaxation times,[14] associated with rare earth ions at higher temperatures, the broadening of the nmr lines is, in most cases, sufficiently small that resolution is not impeded. Only in the case of erbium(III) are the line broadenings sufficient to mask the details of the β, γ, and δ methyl shifts. The erbium spectra were therefore recorded indirectly using a technique found successful in the study of the CoX_4^{2-} complexes.[5] Solutions of a given total molarity (0.2 *M*) were prepared from $[(C_4H_9)_4N]_3LaCl_6$ and $[(C_4H_9)_4N]_3ErCl_6$, and the shift relative to pure La complex was recorded for each solution. The shift data were plotted as a function of mole fraction of erbium, n_{Er}, and the straight-line fit which was obtained was extrapolated to n_{Er} = 1, from which the total isotropic shift of the erbium complex was obtained.

The corresponding $SmCl_6^{3-}$ complex, which is only very slightly paramagnetic, can be used as a diamagnetic diluent with equal success, as the resonances are neither greatly shifted nor broadened. This complex has the advantage of being far less susceptible than that of lanthanum(III) to deposition of metal halide on standing. The isotropic shift data in H_2CCl_2 at 60 MHz are to be found in Table II. Data were also obtained at 220 MHz for some of the paramagnetic complexes in order to resolve some of the ambiguities noted in the 60-MHz spectra; these are to be found in Table III.

The cerium(III) (f^1), praseodymium(III) (f^2), neodymium(III) (f^3), and samarium(III) (f^5) complexes in dichloromethane reveal a shift pattern similar to that observed in the CoX_4^{2-} complexes previously studied.[4] The proton shifts are uniformly upfield, with attenuation of shift proceeding from the α to the δ protons. The spectra of $PrCl_6^{3-}$, $CeCl_6^{3-}$, and $NdCl_6^{3-}$ at 60 MHz reveal that the broad β,γ multiplet collapses. We attribute this behavior to an upfield shift of ~10 Hz for the β resonance. This is borne out well by comparsion with the 220-MHz spectrum (Figure 1 and Table III) of the $NdCl_6^{3-}$ complex. For the $SmCl_6^{3-}$ complex, the β,γ shifts are detectable only at 220 MHz and are uniformly upfield.

Solutions of the corresponding "hole-analog" complexes of ytterbium(III) (f^{13}), thulium(III) (f^{12}), and erbium(III) (f^{11}) reveal an entirely different distribution of isotropic shifts. Particularly noticeable are the large δ-proton shifts, which are virtually absent for the early members of the series. In addition the shift order is erratic. Thus we find, for example, downfield α,β-proton shifts in the $TmCl_6^{3-}$ and $YbCl_6^{3-}$ complexes but upfield γ,δ-proton shifts. In the erbium complex, the magnitude of the δ-proton shift actually exceeds that of the β-proton shift (Table III). The γ-proton shift is the largest of all; in fact the γ and δ protons overlap

TABLE II

PROTON RESONANCE DATA FOR THE COMPLEXES $[(C_4H_9)_4N]_3LnCl_6$ AT 60 MHz IN DICHLOROMETHANE

Anion	Concn, *M*	$\Delta\nu\alpha^a$	$\Delta\nu\beta^a$		$\Delta\nu\gamma^a$	$\Delta\nu\delta^a$
$LaCl_6^{3-}$	0.17	200		(95)		60
$CeCl_6^{3-}$	0.20	190		(87)		60
$PrCl_6^{3-}$	0.22	173		(85)		59
	0.16	170		(90)		61
	0.11	168		(85)		59
	0.08	171		(88)		60
	0.05	175		(90)		61
	0.02	180		(91)		61
$NdCl_6^{3-}$	0.24	174		(84)		57
	0.12	173		(84)		57
$SmCl_6^{3-}$	0.22	197		(94)		59
$ErCl_6^{3-}$	0.20	170	52		(12)	(12)
$TmCl_6^{3-}$	0.16	269	110		70	47
$YbCl_6^{3-}$	0.14	245	116		75^b	50
	0.08	240	110		72^b	50
	0.04	223	102		75	53
	0.02	212	91		75	54

[a] Shifts are downfield, in Hz, referred to internal TMS. Numbers in parentheses correspond to strongly overlapping (unresolved) resonances. All spectra were recorded at 28 ± 2° and may be considered accurate to within ±3 Hz, with the exception of erbium (±10 Hz). [b] Shoulder on δ resonance.

TABLE III

220-MHz CATION PROTON RESONANCE DATA FOR DICHLOROMETHANE SOLUTIONS OF $[(C_4H_9)_4N^+]_3LnCl_6^{3-}$ (Ln = TRIVALENT LANTHANIDE ION)

Anion	n_{Er}^b	$\Delta\nu_\beta^a$	$\Delta\nu_\gamma^a$	$\Delta\nu_\delta^a$
$LaCl_6^{3-}$	...	362	321	220
$NdCl_6^{3-}$	...	320 (42)	300 (21)	211 (9)
$SmCl_6^{3-}$	...	362 (0)	319 (2)	217 (3)
$ErCl_6^{3-}$	0.094	350 (12)	295 (26)	204 (16)
	0.151	344 (18)	282 (39)	195 (25)
	0.211	337 (25)	269 (52)	186 (34)
	1^c	253 (109)	74 (247)	72 (148)

[a] All shifts are downfield relative to TMS, in Hz. Numbers in parentheses are upfield shifts in Hz relative to the diamagnetic lanthanum(III) complex. All solutions are 0.2 *M* in total complex. [b] n_{Er} represents the mole fraction of erbium complex in the solution. The samarium(III) complex was used as diluent. [c] Calculated from the slope of a plot of resonance shift *vs.* mole fraction of erbium complex.

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

(14) K. D. Bowers and J. Owen, *Rept. Progr. Phys.*, **18**, 304 (1955).

nearly exactly in both the 60- and 220-MHz nmr spectra of the undiluted erbium salt.

We have examined the effect of dilution on the magnitude of the shifts in detail for two representative complexes of this series. $PrCl_6^{3-}$ and $YbCl_6^{3-}$. Table II reveals that there is no detectable variation in shift with concentration in the range 0.14–0.2 *M*, within experimental error. This leads us to believe that the structure of the ion aggregate is reasonably constant on a time average within this concentration range and that we are therefore justified in comparing data for different metals within this range. At lower concentrations (0.1–0.02 *M*) the resonances shift back toward their diamagnetic values, which is, of course, a natural consequence of the dissociation of the ion aggregates into free ions. The dilution effect is most noticeable for the α proton, since this, in general, shows the largest isotropic shift.

Isotropic Shifts in $DCCl_3$.—The accumulation of a complete set of data for these compounds in chloroform is hampered by the tendency of the complexes to decompose, particularly in the less concentrated solutions (<0.2 *M*). This tendency is most pronounced with the lighter (and larger) lanthanide ions, which presumably coordinate the halide ion more weakly. The available shift data are to be found in Table IV.

TABLE IV

PROTON RESONANCE DATA FOR THE COMPLEXES $[(C_4H_9)_4N]_3LnCl_6$ AT 60 MHz IN $DCCl_3$

Anion	Concn, *M*	$\Delta\nu_\alpha$[a]	$\Delta\nu_\beta$[a]		$\Delta\nu_\gamma$[a]	$\Delta\nu_\delta$[a]
$LaCl_6^{3-}$	0.2	203		(95)[e]		60
$CeCl_6^{3-}$	0.2	191		(91)[e]		58
$ErCl_6^{3-}$	0.2[b]	295	103		*c*	(35)[d]
$TmCl_6^{3-}$	0.18	382	120		85	55
$YbCl_6^{3-}$	0.18	259	162		101	60

[a] All shifts in Hz, downfield with respect to internal TMS. [b] Shifts were measured by dilution with $LaCl_6^{3-}$. [c] Resonance cannot be located with certainty. [d] Estimated error ±15 Hz. All other shifts reported are accurate to within ±5 Hz. [e] β,γ protons not resolved at 60 MHz.

The shift patterns at 60 MHz roughly parallel those observed in dichloromethane, with two notable additional features. The α-resonance shifts for the thulium and ytterbium compounds are larger than in dichloromethane and further downfield, while the δ-resonance shifts are smaller. As in dichloromethane, the erbium spectra were determined by the mole fraction technique, but due to the overlapping of several multiplets in the δ region, the γ,δ-proton resonances are uncertain. The α protons, which shifted slightly upfield in dichloromethane, are shifted strongly downfield in chloroform. As will be seen, many of these differences in behavior between the two solvents can be attributed to the differing contributions of the Fermi contact and dipolar terms to the isotropic shift. We will now proceed to a discussion of the theoretical aspects of the problem, after which we will return to the analysis of the data.

Discussion

Theoretical Models Describing Cation Motion.—Two fundamentally different models for the time-average behavior of the cation in an ion pair have been described.[2,4] The "isotropic tumbling model" of La Mar[2] considers the cation sitting at a fixed interionic distance *A*, tumbling freely about the central nitrogen atom (Figure 2). It was assumed here that the cation center is located on the principal magnetic axis ($g_{||}$) of an axially symmetric anion. Using these assumptions, La Mar calculated a rotationally averaged geometric factor for the α protons of a tetraalkylammonium ion

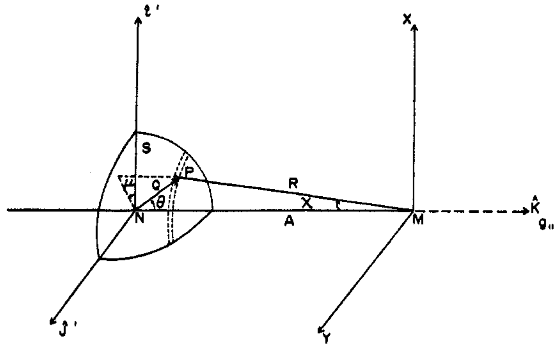

Figure 2.—The "isotropic tumbling model" of La Mar.[2] The proton may occupy any position on a sphere of radius *Q* (one octant shown). The center of the sphere is located on the principal magnetic axis at a distance *A* from the central metal of the anion.

$$\left\langle \frac{3\cos^2\chi - 1}{R^3} \right\rangle_{\text{av}} = \frac{2}{A^3}\left[\frac{A^2 - 1.25Q^2}{A^2 - Q^2}\right] \tag{5}$$

where $Q = 2.11$ Å represents the distance between the α proton and the central nitrogen atom. The β-chain protons form a spherical shell centered on the cation nitrogen, the shell thickness (*Q*) being weighted to allow for sterically hindered rotation about the C_α–C_β bond. The "rigid model," in which the alkyl chains are fully extended in solution with minimal steric interaction among themselves, has been suggested by Larsen as a more reasonable alternative to the isotropic tumbling model, in view of the fact that the anion is bound to restrict the freedom of motion of the cation at the interionic distances expected. In the more recent of a series of papers,[15] a restricted tumbling model has been proposed, in which the cation is placed at the center of the coordinate system, and the anion is permitted to move about on a section of a sphere of radius *A*, characterized by a boundary angle α (Figure 3). This angle is a measure of the freedom of motion of the cation in the ion pair. Calculations have been performed in which *A* and boundary angle have been varied independently

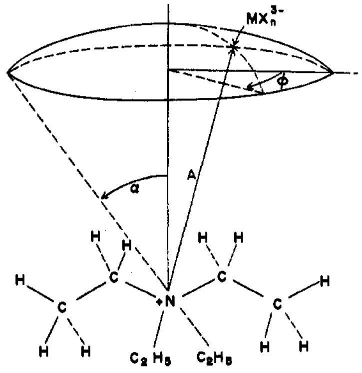

Figure 3.—The "restricted tumbling model" of Larsen.[15] The anion may occupy any position on the spherical section of radius *A*, bounded by angle α.

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(15) D. W. Larsen, *J. Amer. Chem. Soc.*, **91**, 2920 (1969).

and the shift ratios $(\Delta\nu_\alpha/\Delta\nu_\beta)$ for the $(C_2H_5)_4N^+$ ion plotted as functions of both parameters.[15] As the boundary angle is increased to 90°, which corresponds to the isotropic tumbling model, it becomes apparent that there is a serious discrepancy between the predictions of Larsen and those of La Mar.[2] In the former case, $(\Delta\nu_\alpha/\Delta\nu_\beta)$ approaches unity for all physically reasonable A values while the La Mar formula predicts $(\Delta\nu_\alpha/\Delta\nu_\beta)$ to be always greater than unity, becoming increasingly so as A decreases.

In an attempt to resolve the difficulty, we have rederived the general equation for the isotropic tumbling model in such a way that it can be modified to allow for anisotropic tumbling by inserting a distribution function to represent the preferred orientation of different chain protons.

We have also considered the possibility that the anion has rhombic symmetry, *i.e.*, three unequal g tensors, and that the cation is not located on any one of the three orthogonal g-tensor axes.

The expression for the dipolar shift in rhombic symmetry is of the form[16,17]

$$(\Delta\nu_i)_{\text{dip}} = -e \times \left[\mathrm{F}_1(g)\,\frac{(3\cos^2\chi_i - 1)}{R_i^3} - \frac{3\mathrm{F}_2(g)}{2}\,\frac{\sin^2\chi_i\cos 2\Omega_i}{R_i^3}\right] \quad (6)$$

where

$$e = \frac{|\beta|^2 S(S+1)}{45kT}$$

Here, $\mathrm{F}_1(g)$ and $\mathrm{F}_2(g)$ are once again functions of g_1, g_2, and g_3, which are, respectively, the components of the g tensor along the z, x, and y axes.[17] In the axially symmetric case, $g_2 = g_3$, causing $\mathrm{F}_2(g)$ to disappear. This leaves us with eq 3.

The geometrical considerations are shown in Figure 4. A has its usual meaning, while R, χ, and Ω are the instantaneous spherical coordinates for a proton in the metal (M)-centered coordinate system $\{x, y, z\}$. (Q, θ, μ) are the analogous proton coordinates in the cation-centered coordinate system $\{\hat{\imath}, \hat{\jmath}, \hat{k}\}$; angle μ is measured out from the $\hat{\imath}$ axis. We shall proceed to write expressions for $(3\cos^2\chi - 1)/R^3$ and $(\sin^2\chi\cos 2\Omega)/R^3$ in terms of A, ψ, ω, in the $\{x, y, z\}$ coordinate system, which fix the center of the sphere in space, and in terms of θ, μ, over which we must perform the average. It can be seen by reference to Figure 2 that R is independent of μ and is given by[2]

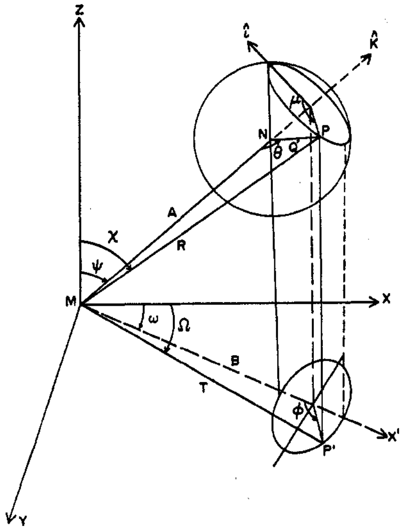

Figure 4.—The "isotropic tumbling model" of La Mar,[2] showing the metal-centered (x, y, z) and cation-centered $(\hat{\imath}, \hat{\jmath}, \hat{k})$ coordinate systems. This model is applicable to paramagnetic anions having rhombic symmetry. The proton may occupy any position on a sphere of radius Q, as before.

$$R(\theta) = (A^2 + Q^2 - 2AQ\cos\theta)^{1/2} \quad (7)$$

For a given value of θ, the proton defines a plane normal to vector A as angle μ is varied. The circle of radius $Q\sin\theta$ lying on this plane when projected onto the xy plane forms an ellipse whose major axis lies normal to the x' axis of Figure 4. The length of the major axis is just $Q\sin\theta$, while the length of the minor axis is $Q\sin\theta\cos\psi$. Angle ϕ is measured out from the x' axis to the projection of point P in the xy plane, P′. The distance between the center of the ellipse and the metal ion, B, is given by

$$B = (A + Q\cos\theta)\sin\psi \quad (8)$$

It can be readily shown that

$$\cos\phi = \frac{\cos\mu\cos\psi}{(\sin^2\mu + \cos^2\mu\cos^2\psi)^{1/2}} \quad (9)$$

Using the law of cosines and the above coordinate transformations, it follows, after a little algebra, that T, the distance between the metal and P′, is given by

$$T^2 = R(\theta)^2\sin^2\chi = Q^2\sin^2\theta + \sin^2\psi(A^2 - Q^2\sin^2\theta \times \cos^2\mu - 2QA\cos\theta + Q^2\cos^2\theta) + 2\sin\psi \times \cos\psi(Q^2\sin\theta\cos\theta\cos\mu - QA\sin\theta\cos\mu) \quad (10)$$

and is independent of ω. Thus

$$\frac{3\cos^2\chi - 1}{R(\theta)^3} = \frac{2R^2 - 3T^2}{R(\theta)^5} \quad (11)$$

By similar arguments, it can be readily shown that

$$\frac{\sin^2\chi\cos 2\Omega}{R^3} = R(\theta)^{-5}\{G\cos 2\omega + 2H\sin 2\omega\} \quad (12)$$

where

$$G = (A^2\sin^2\psi - 2AQ\cos\theta\sin^2\psi + Q^2\cos^2\theta\sin^2\psi - 2AQ\sin\psi\cos\psi\sin\theta\cos\mu + 2Q^2\cos\theta\sin\theta\cos\psi\sin\psi\cos\mu + Q^2\sin^2\theta\cos^2\psi\cos^2\mu - Q^2\sin^2\theta\sin^2\mu) \quad (13)$$

and

$$H = (Q^2\cos\theta\sin\theta\sin\psi\sin\mu + Q^2\sin^2\theta\sin\mu\cos\mu \times \cos\psi - AQ\sin\psi\sin\theta\sin\mu) \quad (14)$$

The average is now taken as

$$\langle\langle \mathrm{f}(R, \chi, \Omega)\rangle\rangle_{\theta,\mu} = \left[\int_{\mu=0}^{2\pi}\int_{\theta=0}^{\pi} \mathrm{f}(R, \chi, \Omega)\sin\theta\,\mathrm{d}\theta\mathrm{d}\mu\right] \times \left[\int_{\mu=0}^{2\pi}\int_{\theta=0}^{\pi}\sin\theta\,\mathrm{d}\theta\mathrm{d}\mu\right]^{-1} \quad (15)$$

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(16) G. N. La Mar, *J. Chem. Phys.*, **43**, 1085 (1965).
(17) G. N. La Mar, W. D. Horrocks, Jr., and L. C. Allen, *ibid.*, **41**, 2126 (1964).

where $\langle\langle f(R, \chi, \Omega)\rangle\rangle_{\theta,\mu}$ represents either of the above geometric factors.

One may, at this stage, allow for anisotropic tumbling by introducing a distribution function $D(\theta, \mu)$ in the usual manner.[18]

For isotropic tumbling, the integration over μ yields

$$\left\langle\frac{\sin^2\chi\cos 2\Omega}{R^3}\right\rangle_\mu = \left[\frac{\sin^2\psi\cos 2\omega}{4}\right]J \tag{16}$$

$$\left\langle\frac{3\cos^2\chi - 1}{R^3}\right\rangle_\mu = \left[\frac{3\cos^2\psi - 1}{4}\right]J \tag{17}$$

where

$$J = (2A^2 - Q^2)\int_0^\pi \frac{\sin\theta\, d\theta}{R(\theta)^{5/2}} - 4AQ\int_0^\pi \frac{\cos\theta\sin\theta\, d\theta}{R(\theta)^{5/2}} + 3Q^2\int_0^\pi \frac{\cos^2\theta\sin\theta\, d\theta}{R(\theta)^{5/2}} \tag{18}$$

The behavior of J depends on the values of A and Q chosen. There are three possible cases, *i.e.*, $A < Q$, $A = Q$, and $A > Q$, of which only the last has any physical meaning in the present context. For $A < Q$ and $A > Q$, J was evaluated both by analysis and by computer, using three different integrating routines, in view of the extremely tedious algebra involved. The results are

$$J = \frac{4}{A^3} \quad (A > Q) \tag{19}$$

$$J = \text{undefined} \quad (A = Q) \tag{20}$$

$$J = 0 \quad (A < Q) \tag{21}$$

We thus find, for the special case[2] of a proton situated on the principal magnetic axis of an axially symmetric cation ($\chi = 0°$), that

$$\left\langle\frac{3\cos^2\chi - 1}{R^3}\right\rangle_{\theta,\mu} = \frac{2}{A^3} \tag{22}$$

The important feature revealed by the calculation is that the shift is independent of the distance between the proton and the cation center, Q. Even for the β, γ, δ protons in tetrabutylammonium ions, which describe spherical shells, with a distribution function $D(Q)$ to allow for the various conformational preferences, a brief inspection of eq 18 and 22 shows that $|\Delta\nu_\alpha| = |\Delta\nu_\beta| = |\Delta\nu_\gamma| = |\Delta\nu_\delta|$ in agreement with the results of Larsen for $\alpha = 90°$. We will now examine the experimental data, with a view to testing these predictions.

The Isotropic Shift.—Due to the very small perturbations provided by external crystal fields in rare earth complexes the magnetic properties are approximately those which one would predict for the free ions. The electronic states are well characterized by the total quantum number J; each J level splits in a magnetic field into $2J + 1$ levels characterized by the Lande g factor, g_L. The contact shift, to first order, for rare earth ions becomes[19]

$$(\Delta\nu_f)_i = \frac{A_i}{3kT}[J(J + 1)g_L(g_L - 1)]\frac{\beta^2}{g_N\beta_N} \tag{23}$$

where the term in $(g_L - 1)$ represents the fact that only the electron spin magnetic moment at the nucleus is important in producing a contact shift. Since g_L is less than unity for the ground states of ions in the first half of the rare earth series and greater than unity for the second half of the series, the contact shift changes sign at gadolinium (III) (f^7), $g_L = 2$.

Isotropic shift data have been reported thus far for rare earth complexes of phenanthroline,[20] pyridine,[21] water,[19,22] and tropolonate ligands.[23] Due to the similarities in chemical bonding which the lanthanides show to a given ligand, the hyperfine coupling constant is not believed to vary greatly across the series.[22] This proposition, although quite reasonable, remains to be adequately tested, since data on a complete series of complexes are available only for the aquo and tropolonato derivatives; furthermore the spectra of the latter compounds have not been scrutinized in detail. The change in sign of the contact shift with $(g_L - 1)$ is evident in the aquo complexes,[22] as well as in the isotropic shift of the resonances of solvent DMSO and water coordinated to the tropolonates.[23]

It is apparent from previous experimental studies[24,25] that spin delocalization in σ systems proceeds with attenuation as the number of bonds separating the spin-containing orbital from the resonant protons increases. Thus we find, for instance, 100-fold attenuation in the spin densities on going from α to γ protons in the $Ni(n\text{-}C_3H_7NH_2)_6^{2+}$ complexes.[24]

A model structure through which spin density can reach the cation has been suggested by Burkert, *et al.*[7] Upon formation of the ion-pair complex the central nitrogen of the cation rehybridizes to a trigonal bipyramid, one apex of which is occupied by a spin-containing ligand orbital; direct delocalization onto the α carbon is thus possible through the axial p_z orbital of the nitrogen. It might also be argued that the strongly electron-withdrawing central nitrogen atom of the cation will impart a certain degree of polarity to the α-C–H bond, thus introducing the possibility of hydrogen bonding to the anion *via* the α protons. Spin delocalization through hydrogen bonds has already been clearly demonstrated in the case of chloroform interacting with the anions $CoI_3P(C_6H_5)_3^-$ and $NiI_3P(C_6H_5)_3^-$.[26]

In sum, these considerations lead us to believe that the contact shift will be largest at the α protons, attenuating sharply along the chain. It follows that the δ-resonance shift where it occurs is due predominantly to the dipolar term. Provided the tumbling motion of the cation is reasonably isotropic, the latter will not attenuate so rapidly down the chain. We further expect that the ratios of the dipolar shifts, depending as they do solely on the cation geometry, will be a function of the electrostatic charge on the anion and thus approximately independent of the metal ions in this series.

The presence of dipolar shifts in the $LnCl_6^{3-}$ complexes is at first sight surprising, since the anions, having formally cubic symmetry, should have isotropic g tensors; thus from eq 3, $\Delta\nu_{dip} = 0$. The theory has already been discussed.[5] In brief, the effect is due to the cations, which provide a noncubic crystal field at

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(18) D. R. Eaton, *Can. J. Chem.*, **47**, 2645 (1969).

(19) W. B. Lewis, J. A. Jackson, J. F. Lemons, and H. Taube, *J. Chem. Phys.*, **36**, 694 (1962).

(20) F. A. Hart, J. E. Newbery, and D. Shaw, *Chem. Commun.*, 45 (1967).

(21) E. R. Birnbaum and T. Moeller, *J. Amer. Chem. Soc.*, **91**, 7274 (1969).

(22) J. Reuben and D. Fiat, *J. Chem. Phys.*, **51**, 4909 (1969).

(23) E. L. Muetterties and C. M. Wright, *J. Amer. Chem. Soc.*, **87**, 4706 (1965).

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

(25) D. R. Eaton, A. D. Josey, and R. E. Benson, *ibid.*, **89**, 4040 (1967).

(26) M. F. Rettig and R. S. Drago, *ibid.*, **88**, 2966 (1966).

TABLE V

FACTORING OF THE ISOTROPIC SHIFTS IN THE COMPLEXES $[(C_4H_9)_4N]_3LnCl_6^{3-}$ IN DICHLOROMETHANE

	Obsd shifts,[a] ppm				Isotropic tumbling contact shifts,[b] ppm			Anisotropic tumbling contact shifts,[c] ppm		
Anion	$\Delta\nu_\alpha$	$\Delta\nu_\beta$	$\Delta\nu_\gamma$	$\Delta\nu_\delta$	$\Delta\nu_\alpha$	$\Delta\nu_\beta$	$\Delta\nu_\gamma$	$\Delta\nu_\alpha$	$\Delta\nu_\beta$	$\Delta\nu_\gamma$
$NdCl_6^{3-}$	0.45	0.19	0.10	0.03	0.42	0.16	0.07	0.33	0.10	0.04
$ErCl_6^{3-}$	0.50	0.54	1.11	0.66	−0.16	−0.12	0.45	−2.14	−1.44	−0.21
$TmCl_6^{3-}$	−1.13	−0.19	0.29	0.22	−1.35	−0.41	0.07	−2.01	−0.85	−0.15
$YbCl_6^{3-}$	−0.75	−0.29	0.21	0.17	−0.92	−0.46	0.04	−1.43	−0.80	−0.13

[a] Total isotropic shift relative to diamagnetic lanthanum complex. The data are taken from the most concentrated solutions (0.15–0.22 *M*). [b] Fermi contact shift calculated by assuming $(\Delta\nu_\alpha)_{\text{dip}} = (\Delta\nu_\beta)_{\text{dip}} = (\Delta\nu_\gamma)_{\text{dip}} = \Delta\nu_\delta$. [c] Fermi contact shifts calculated by assuming dipolar shift ratios $\alpha:\beta:\gamma:\delta = 4:3:2:1$.

the anion, with a resulting *g*-tensor anisotropy. This, in turn, manifests itself as a dipolar shift on the cations.

In the present case, the possibility of a rhombic dipolar shift (eq 6) cannot be wholly discounted. We believe, however, that the rhombic component is small, as is shown in the following argument.

Two "tightly bound" cations are assumed to lie on a common axis containing the central metal atom, with the third cation more weakly held for steric as well as electrostatic reasons. The third cation will of course provide a small fluctuating rhombic field, whose magnitude, like that of the axial field, falls off as $1/A^3$ or $1/A^5$ with distance[5] (Figure 4). Examination of eq 17 and 6 for the situation depicted reveals that for two "tightly held" cations on the *z* axis the term in $\sin^2\chi$ $\cos 2\Omega$ vanishes. For the weakly bound cation, this term fluctuates about zero due to the motion of the cation, since, when g_1 and g_2 become equal, $F_2(g)$ goes to zero. Due to fast exchange, the rhombic shift is at most one-third of that expected for closest approach along the *x* axis.

Factoring the Isotropic Shift.—The aquo complexes studied by Reuben and Fiat[22] were factored into contact and dipolar contributions using the shift of the gadolinium complex, which has an isotropic (^8S) ground state, hence no dipolar component. Assuming the constancy of A_i across the lanthanide series, it was possible to calculate $\Delta\nu_f$ values for protons in the other aquo complexes using the shift in the Gd^{3+} complex and eq 23. Use of eq 1 and the calculated $\Delta\nu_f$ value resulted in an estimated dipolar shift. This method is not feasible in our case, due to the severe characteristic broadening of the nmr lines by Gd^{3+} ion. Examination of a solution of the samarium complex at 220 MHz in H_2CCl_2 containing as little as 0.02 mol % of $GdCl_6^{3-}$ reveals only a broad hump with maximum at 220 Hz corresponding to the δ protons. In the absence of a clear spectrum whose shifts are unambiguously contact in origin, we are forced to proceed as follows.

The shift results of the other σ systems discussed previously make it possible to attribute the δ-proton shifts in our case to a predominantly dipolar origin. Thus the strong attenuation of shift observed in the Ce^{3+}, Pr^{3+}, and Nd^{3+} complexes, coupled with the absence of large δ-proton shifts, suggests that the contact interaction is dominant here.

For those complexes having significant δ-proton shifts, we will calculate a trial value for the dipolar shift at the other protons using the relations

$$(\Delta\nu_i)_{\text{dip}} = P_i(\Delta\nu_\delta) \qquad (i = \alpha, \beta, \gamma) \tag{24}$$

Using eq 1 and the observed shifts then allows us to estimate the contact shift at the α, β, γ protons for each metal ion complex in the series. The dipolar shift ratios, P_i, are characteristic of the ion-pair geometry and can vary upward from unity (isotropic tumbling). P_i is then varied until the ratios of the contact shifts, *i.e.*, $(\Delta\nu_i)_f/(\Delta\nu_j)_f$, so obtained are independent of the metal ion chosen. This assumed independence of Fermi contact shift on details of the electronic structure of the metal ion is our cardinal assumption and one which has been employed with notable success in the factoring of the isotropic shift in complexes of first-row transition metal ions.[27,28]

This method has the obvious disadvantage that small errors in the measurement of $\Delta\nu_\delta$ markedly affect the predicted $(\Delta\nu_i)_f$ values, this error being proportional to P_i.

We may now estimate the Fermi contact contribution in the isotropic tumbling model by simply subtracting the δ-proton shift from the shifts of the other protons. The results are summarized in Table V. While the contact shifts for the Nd^{3+} complex attenuate in accord with our expectations, we find a distinct lack of attenuation in the contact shifts calculated for erbium, in addition to the unwelcome changes of sign at the γ proton in the calculated Er, Tm, and Yb contact shifts. The isotropic tumbling model is thus not in accord with our observations.

Upon varying the central chain proton dipolar shift ratios, P_β and P_γ, it becomes apparent that the contact shift ratios for the central chain protons are most consistent with $P_\beta = 3$ and $P_\gamma = 2$. Using a value of $P_\alpha = 4$ gives α-proton contact shifts which have the correct sign, *i.e.*, consistent with those of the β,γ protons in a given ion aggregate and with $(g_L - 1)$. It should be noted that the fit is more approximate for the β,γ protons than for the α proton, due to the small size of the shifts and the accompanying error of measurement. The contact shifts obtained with these *P* values may be seen in the last three columns of Table V.

We will test the predictions of Reuben and Fiat by evaluating the number $K = 10^6(\Delta\nu_f)_\alpha/[\nu g_L J(g_L - 1)\cdot(J + 1)]$, which is proportional to A_α. The *K* values for the metal ions studied are collected in Table VI.

TABLE VI[a]

VALUES OF $10^6\Delta\nu_\alpha/\nu J g_L(g_L - 1)(J + 1)$ FOR $P_\alpha = 4$ AND $P_\alpha = 10$

Anion	$P_\alpha = 4$	$P_\alpha = 10$
$CeCl_6^{3-}$	−0.16 (−0.16)	−0.16 (−0.16)
$PrCl_6^{3-}$	−0.15	−0.15
$NdCl_6^{3-}$	−0.06	−0.03
$ErCl_6^{3-}$	−0.14 (−0.21)	−0.40 (−0.38)
$TmCl_6^{3-}$	−0.25 (−0.41)	−0.41 (−0.47)
$YbCl_6^{3-}$	−0.56 (−0.39)	−0.95 (−0.39)

[a] Values in parentheses are from data taken in deuteriochloroform.

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(27) W. D. Horrocks, Jr., R. C. Taylor, and G. N. La Mar, *J. Amer. Chem. Soc.*, **86**, 3031 (1964).

(28) R. W. Kluiber and W. D. Horrocks, *ibid.*, **87**, 5350 (1965); **88**, 1399 (1966).

TABLE VII

FACTORING OF THE ISOTROPIC SHIFT AT 60 MHz FOR COMPLEXES $[(C_4H_9)_4N]_2CoX_4$ AND $[(C_4H_9)_4N]_2NiX_4$

				Obsd isotropic shift,[b] ppm			Calcd dipolar shift, ppm				
Anion	μ_{eff}, BM	R[a]	Ref	$\Delta\nu_\alpha$	$\Delta\nu_{\beta,\gamma}$	$\Delta\nu_\delta$	$\Delta\nu_\alpha$	$\Delta\nu_{\beta,\gamma}$	$\Delta\nu_\delta$	$\left[\frac{\Delta\nu_\alpha}{\Delta\nu_\delta}\right]_{dip}$	$\left[\frac{\Delta\nu_{\beta,\gamma}}{\Delta\nu_\delta}\right]_{dip}$
$CoCl_4^{2-}$	4.85	1.04	*c*	2.08	0.63	0.07					
$NiCl_4^{2-}$	3.88		*f*	−0.97	−0.95	−0.63	−2.97	−1.56	−0.63	4.7	2.5
$CoBr_4^{2-}$	4.85	1.08	*c*	2.45	0.93	0.20					
$NiBr_4^{2-}$	3.80		*e, f*	−0.55	−0.72	−0.53	−2.82	−1.58	−0.53	5.3	3.0
CoI_4^{2-}	5.01	1.38	*c*	2.33	0.93	0.07					
NiI_4^{2-}	3.47		*d*	0.28	−0.27	−0.22	−1.42	−0.94	−0.22	6.4	4.3

[a] Room-temperature magnetic moments were used to calculate $R = {}^2/_3(\mu_{eff}^2)_{Co}/(\mu_{eff}^2)_{Ni}$. [b] Data taken from ref. 5. Shifts are measured relative to the zinc salt. Only one broad resonance was observed for β,γ protons. A positive sign indicates an upfield shift. [c] R. Holm and F. A. Cotton, *J. Chem. Phys.*, **32,** 1168 (1960). [d] D. M. L. Goodgame, M. Goodgame, and F. A. Cotton, *J. Amer. Chem. Soc.*, **83,** 4161 (1961). [e] F. A. Cotton and D. M. L. Goodgame, *ibid.*, **82,** 2967 (1960). [f] N. S. Gill and R. H. Nyholm, *J. Chem. Soc.*, 3997 (1959).

The choice of $P_\alpha = 4$ apparently does not lead to constant K; the most serious disagreement being between the K values in the light metals *vs.* those for the heavy metals. Better agreement with theory can, in general, be obtained by assuming negative P values, since this leads to larger positive Nd contact shifts and smaller negative Tm and Yb contact shifts. The erbium contact shift becomes increasingly positive however, which is out of line with the results expected from eq 23.

The discrepancy between the K values at the beginning and end of the series may be due to differences in anion solvation. The larger ions (Ce, Pr, Nd) presumably do not neutralize the negative charge from the first coordination sphere as effectively as the smaller ones (Yb, Tm, Er). Thus, the nucleophilicity of the chloride lone pairs toward solvent is greater for the larger metal ions, leading to tighter solvation, and the number of intimate ion pairs, in which the α cation protons are in direct contact with spin-containing lone-pair orbitals, would be smaller in the case of the Ce, Pr, and Nd complexes.

This explanation correlates well with the observed tendency of the La, Ce, Pr, and Nd anions to decompose in hydrogen-bonding solvents like $HCCl_3$ and in H_2CCl_2 at low concentrations. In other words the metal ion is competing with the solvent for the halide ion.

The P values expected for intimate and solvent-separated ion pairs in 1:1 electrolytes can be obtained by examining the particularly favorable case of the tetrabutylammonium tris(acetylacetonato)metalate(II) complexes, which were studied in both chloroform and carbon tetrachloride.[3] The absence of cation shifts in the magnetically isotropic $Ni(acac)_3^-$ complex enables us to postulate pure dipolar cation shifts in the isostructural $Co(acac)_3^-$ compound. The shift ratios $P_\alpha = 7.8$, $P_\beta = 3$, and $P_\gamma = 2.2$ obtained in carbon tetrachloride agree well with our best-fit values for the β,γ protons, while the P_α value is much higher. The value of $P_\alpha = 5.3$ for chloroform corresponds to a less tightly bound ion pair or one in which a layer of solvent exists between anion and cation. This is expected from the known tendency of chloroform to hydrogen bond to acetylacetonato complexes.[29]

It appears, from this study at any rate, that the cation tumbling is more anisotropic in the intimate ion pair, so that we expect larger P_α values in the heavy rare earth complexes. We have calculated K values for $P_\alpha = 10$, which allows for the larger anionic charge; the results are to be found in Table VI. The results for the heavy rare earth are more internally consistent than for $P_\alpha = 4$, and good agreement between chloroform and dichloromethane data should be noted. It is apparent, however, that the presence of a contact shift does not permit us to set more than a lower limit to P_α at the present time.

Having thus treated the observed shifts for the rare earth complexes, we now offer a few comments on the proton shifts in the previously studied tetrabutylammonium tetrahalometalate series[5] (Table VII). Despite the very strongly broadened cation resonances in the CoX_4^{2-} series, the shifts of the α and δ protons are clearly identifiable. The very large (2–2.5 ppm) upfield α-proton shifts and very small (0.07 ppm) δ-proton shifts suggest that the pseudocontact mechanism is far less important in the cobalt complexes than we had previously thought.[5] In the NiX_4^{2-} series, the δ shifts are far larger (0.2–0.6 ppm) and are downfield. In the case of $[(C_4H_9)_4N]_2NiI_4$ the α resonance shifts upfield by 0.28 ppm while the remainder of the chain protons shift downfield. This behavior is not exhibited by the $NiCl_4^{2-}$ or $NiBr_4^{2-}$ complexes but can also be seen[30] in solutions of $[(n\text{-}C_7H_{15})_4N]_2NiI_4$.

It follows from the preceding discussion that there is both an upfield contact and a downfield dipolar shift operating on the cation protons in the NiX_4^{2-} ion pairs, with the latter effect dominant in every case except that of α protons of the NiI_4^{2-} ion pair. In factoring the isotropic shift in this series of complexes we will use a somewhat different procedure than that used for the rare earth complexes.

We will obtain first an estimate of the magnitude of the contact shift at the various protons using the cobalt data. Use of these estimates in eq 1 along with the observed shifts will give us the dipolar shifts for the NiX_4^{2-} ions. Our principal assumption, therefore, will be that the observed CoX_4^{2-} isotropic shifts are completely Fermi contact in origin. We tend to discount the observed δ-proton shifts in the cobalt complexes and will present evidence in a future publication to the effect that these shifts should be zero.

The estimation of the nickel contact shifts proceeds as follows. From eq 2, with the usual definition of the magnetic moment,[31] μ_{eff}, we obtain

$$(\Delta\nu_f)_i = \nu A \mu_{eff}^2\left(\frac{\beta^2}{3g_N\beta_N kT}\right) \qquad (25)$$

The other symbols have their usual meanings.[2] The hyperfine coupling constant, A_i, is usually defined in

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(29) K. Watenpaugh and C. N. Caughlan, *Inorg. Chem.*, **6,** 963 (1967); G. Steinbach and J. Burns, *J. Amer. Chem. Soc.*, **80,** 1839 (1958).

(30) I. M. Walker, unpublished data.

(31) J. Lewis and R. G. Wilkins, "Modern Coordination Chemistry," Interscience, New York, N. Y., 1960, p 404.

terms of the spin density, ρ, by the equation

$$A_i = Q\rho/2S \tag{26}$$

where the spin density represents the fraction of an unpaired electron in the hydrogen 1s orbital of proton *i*, and *Q* is a proportionality constant. *S* represents the total spin quantum number of the ground state of the complex. We now make our second assumption, namely, that the spin densities are the same for a given cation proton in the cobalt ($S = {}^3/_2$) and nickel ($S = 1$) ion-pair complexes of the same anion, *i.e.*

$$(\rho_i)_{\mathrm{CoX_4}} = (\rho_i)_{\mathrm{NiX_4}} \tag{27}$$

After a few rearrangements, it is readily shown that, for data taken at the same temperature

$$\frac{(\Delta\nu_{\mathrm{f}})_{i,\mathrm{CoX_4}}}{(\Delta\nu_{\mathrm{f}})_{i,\mathrm{NiX_4}}} = \frac{2}{3}\,\frac{(\mu_{\mathrm{eff}}{}^2)_{\mathrm{Co}}}{(\mu_{\mathrm{eff}}{}^2)_{\mathrm{Ni}}} = R \tag{28}$$

Thus we obtain from eq 28 the desired estimate of the contact shift in the nickel complexes.

Table VII contains the dipolar shifts for the nickel complexes calculated from eq 28 and 1. The *R* factors were computed using data from the literature. It is seen that the dipolar shifts attenuate uniformly in the expected manner. The dipolar shift ratios are, in addition, quite comparable to those obtained for the rare earth ions using the completely different procedure outlined above.

Since the tetrahalometalate(II) anions are known to interact *via* hydrogen bonding with dichloromethane, as well as chloroform,[30] the evidence thus far accumulated lends credence to the suggestion that $(\Delta\nu_\alpha)_{\mathrm{dip}}/(\Delta\nu_\delta)_{\mathrm{dip}}$ ratios of between 4 and 6 may well be appropriate to the tetrabutylammonium cation in solvent-separated ion pairs.

Summary

The magnetic resonance shifts of the tetra-*n*-butylammonium cation ion paired to a number of paramagnetic anions have been factored into their Fermi contact and dipolar components. Two different factoring methods were used, each one having its own definite set of assumptions.

For the rare earth complexes, the factoring procedures are as follows. (1) The shifts of the δ protons of the cation are assumed to be completely dipolar in nature. (2) The dipolar shifts at the other protons are treated as variables. The correct values of the dipolar shifts are those which give Fermi contact shifts which decrease in the order $\alpha > \beta > \gamma$ when subtracted from the observed isotropic shift. (3) The Fermi contact shifts are required to change sign on passing from the light ($n < 7$) to the heavy ($n > 7$) end of the rare earth ($4f^n$) series, and the ratios of the Fermi contact shifts $(\Delta\nu_{\mathrm{f}})_i/(\Delta\nu_{\mathrm{f}})_j$ for any two protons on the cation must be the same for all metals in the series. The resulting α-proton contact shifts are then tested against the equation of Reuben and Fiat[22] for internal consistency.

For the cobalt and nickel complexes, the assumptions in the factoring procedure are as follows. (1) The cation shifts in the $\mathrm{R_4N^+CoX_4{}^{2-}}$ ion pairs are assumed to be completely Fermi contact in origin, based on the accumulated evidence. (2) The Fermi contact contribution to the total isotropic shift in the nickel ion pair complexes is estimated from the cobalt data by use of the formula

$$\frac{(\Delta\nu_{\mathrm{f}})_{i,\mathrm{CoX_4}}}{(\Delta\nu_{\mathrm{f}})_{i,\mathrm{NiX_4}}} = \frac{2(\mu_{\mathrm{eff}}{}^2)_{\mathrm{CoX_4}}}{3(\mu_{\mathrm{eff}}{}^2)_{\mathrm{NiX_4}}}$$

in which it is assumed that the spin density on a given cation proton is the same in cobalt and nickel complexes of the same halide anion.

The results are interpreted as indicating that a solvent-separated ion pair gives dipolar shift ratios $(\Delta\nu_\alpha)_{\mathrm{dip}}/(\Delta\nu_\delta)_{\mathrm{dip}}$ between 4 and 6, while a contact ion pair gives ratios in excess of this range.

Acknowledgments.—The Authors are grateful for the financial support of the National Research Council of Canada. We also thank Mr. David Weeden, of York University, for performing the metal analyses and Dr. Arthur Clark of the Ontario Research Foundation for the use of the 220-MHz nmr facility.