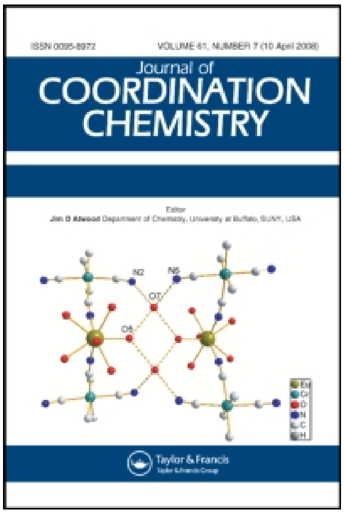

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CONTACT VERSUS DIPOLAR NMR SHIFTS IN ION-PAIRED SYSTEMS:
A Comparison of Lanthanide and First Row Metal Complexes of Organic Cations

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Proton NMR data for a series of unsymmetrically substituted ammonium and phosphonium cations in ion pairs with tetrahalocobaltate(II) and nickelate anions are compared with similar data for lanthanide containing systems. The data suggest that the dominant shift mechanism is the axial (through space) dipolar interaction in the cobalt complexes, and not the Fermi-Contact mechanism postulated in previous articles. The structural parameters for the ion-pairs which are obtained by comparison of theory and experiment are used to infer that the cation orientation with respect to the principal axis of magnetic susceptibility of the anion is roughly the same in both sets of complexes, as is the interionic distance, A.

INTRODUCTION

The origins of the NMR isotropic shifts in quaternary ammonium cations has been the subject of several recent articles.[1,2,3] Such shifts arise when the diamagnetic cation forms contact ion-pairs with paramagnetic anions in low dielectric solvents.

In a system bearing unpaired electrons there are three mechanisms which are capable of producing substantial chemical shifts (isotropic shifts) in the NMR.[3] These are the Fermi Hyperfine Contact shift, $\Delta\nu_{\mathrm{con}}$, the axial dipolar shift, $\Delta\nu_{\mathrm{ax}}$, and the rhombic dipolar shift, $\Delta\nu_{\mathrm{rh}}$. Thus:

$$\Delta\nu_{\mathrm{iso}} = \Delta\nu_{\mathrm{con}} + \Delta\nu_{\mathrm{ax}} + \Delta\nu_{\mathrm{rh}}$$

The axial dipolar term is a useful probe of solution geometry because of its dependence on angles and distances.[4,5,6]

$$\Delta\nu_{\mathrm{ax}} = F(\chi_{11}, \chi_{\perp})[\mathrm{G.F.}] \tag{1}$$

where

$$[\mathrm{G.F.}] = (3\cos^2\alpha - 1)R_i^{-3} \tag{2}$$

and α is the angle between the metal–proton vector, R_i, and the principal magnetic axis on the anion. F is a function of the magnetic susceptibilities of the complex, and is non-zero provided the symmetry is less than cubic.

In many lanthanide-containing systems, the proton isotropic shifts behave as though they are entirely due to the axial dipolar mechanism.[6] This behaviour has been recently explained by Horrocks,[5] and appears to be a property of *any* magnetically anisotropic system in which the ligands exchange rapidly between the large number of different isomeric environments on the NMR time scale. Since most second-sphere coordination phenomena satisfy this condition, it is not surprising that in many instances, a number of workers have been able to derive geometrical information using the geometric factor (G.F.) and a pure axial dipolar interpretation of the observed shift.

Such systems can usually be easily identified since the ratios of any two proton shifts are independent of the metal ion.[6]

This is, unfortunately, not always the case in ion-pair systems. We have found, for instance, that the anions $\mathrm{CoX_4^{2-}}$ and $\mathrm{NiX_4^{2-}}$ (X = halide) induce radically different shift patterns on cation protons.[1,7] Anions of the type $\mathrm{LnCl_6^{3-}}$ (Ln = Ce, Pr, Nd, Sm, Er, Tm, Yb) also fall into this class.[8] On the other hand, the cation shift patterns induced by $\mathrm{(Ph)_3PMX_3^-}$ anions (M = Co, Ni; X = Br, I) appear to be independent of M, and hence can be assigned to a predominantly dipolar mechanism.[9,10,11] This is also the case[12] in the $\mathrm{Co(acac)_3^-}$ and $\mathrm{Ln(NO_3)_5^{2-}}$ complexes.[2,13]

The anomalous shift ratios in the $\mathrm{MX_4^{2-}}$ and $\mathrm{LnX_6^{3-}}$ complexes are obviously due to the presence of more than one mechanism in the overall isotropic shift.

Experience has shown[3] that the isotropic shift in a given system may usually be resolved into its components along one of the following three lines:

A) axial dipolar and Fermi contact;
B) axial dipolar and rhombic dipolar; and
C) all three mechanisms.

The relative contribution of a given mechanism may of course be very different from one metal to another, since contact and dipolar shifts are not governed by the same electronic factors.

In previous work we attempted to factor the isotropic shift into its component parts on the basis of assumption A.[1,8] The upfield shifts in the CoX_4^{2-} species were assumed to arise from a predominant Fermi contact mechanism, since the ground state of these ions is $^4A_2$ in tetrahedral symmetry. It was therefore felt that they should not possess as large magnetic susceptibility anisotropies as the $NiX_4^{2-}(^3T_1)$ complexes under the same conditions. The smaller shifts in the NiX_4^{2-} systems were presumed to arise from axial dipolar and Fermi contact effects of comparable magnitude, the relative signs being opposed, however. Our arguments were supported by the observation of anomalous shifts in the cation ^{14}N resonance spectrum which implied spin delocalization onto the cation nitrogen atom,[14,15] hence the possibility of a Fermi Contact effect at the protons.

If a contact term is responsible for the greater part of the CoX_4^{2-} shifts, then it is quite surprising that no evidence of a sizeable contact contribution is also present in the similarly constituted $Ph_3PMX_3^-$ systems. In his recent review article, LaMar[3] has noted the similarity between the cation shift patterns in the CoX_4^{2-} ion-pairs and those in systems containing the $Ph_3PCoX_3^-$ anion and has inferred a predominant axial dipolar mechanism from the data in this case. The reversal in the sign of the cation isotropic shifts on passing from cobalt to nickel in the $Ph_3PMX_3^-$ series is consistent with the measured magnetic anisotropies in single crystals of the similarly constituted $(Ph_3P)_2MCl_2$ complexes.[3,11] Since it is unlikely that the Fermi contact effect would be present in the cobalt(II) complexes but not in the corresponding nickel derivatives, this implies that the origins of the anomaly are most likely described by case B, above. Thus it could be argued that the small shifts in the NiX_4^{2-} complexes are caused by nearly cancelling axial and rhombic dipolar terms.

There are thus two conflicting views on the origins of the isotropic shifts in the MX_4^{2-} containing ion-pair systems. The axial dipolar mechanism could be clearly demonstrated in the CoX_4^{2-} case if it could be shown that:

1) The isotropic shift ratios and the geometrical parameters derived from them are at least comparable to those observed in other systems in which the cation-shifts are known with certainty to be dipolar.

2) The observed and calculated shift ratios can be made to agree at sufficiently reasonable values of the interionic distance that the ions are not forced into physically impossible geometries.

Data from our previous work does not lead to an unambiguous resolution of the issue since the cations used were flexible and the time average structure could therefore be a function of the local environment in the ion-pair. In this article we present data on systems containing the N-alkylpyridinium, N,N,N-trimethyl anilinium and n-butyltriphenylphosphonium cations. Each of these cations contains protons which maintain a fixed separation from the central positively charged atom, thus in principle enabling the calculation of reliable shift ratios from Cartesian coordinates.[13]

The shift ratios are compared to those found in the previously studied pentanitratolanthanate complexes,[16] in which conclusions regarding the shift mechanism are considerably more certain.

EXPERIMENTAL

N,N,N-Trimethyl-(4-n-butyl) anilinium Iodide

N,N-Dimethyl-(4-n-butyl) aniline was prepared from 4-n-butylaniline (K & K Laboratories) by the method of Billman, et al.[17] and was purified by distillation. The methiodide was obtained when the aniline was refluxed with methyl iodide in acetone, followed by precipitation with ether.

The preparation of all other materials used follows previously outlined procedures[1,2,8,16] and will therefore not be discussed in detail. The compounds were analyzed gravimetrically for metal in these laboratories; results were satisfactory in all cases.

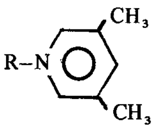
NMR spectra at ambient temperature were obtained in dichloromethane on the Varian A-60 and HA-100 spectrometers.

RESULTS AND DISCUSSION

N-Alkyllutidinium Complexes

Due to the extensive line broadening induced by the CoX_4^{2-} species, cation isotropic shifts cannot be

TABLE I
Proton isotropic shifts in 1-alkyl-3,5 lutidinium salts



R	Anion	$\Delta\nu^a_{\alpha-CH_2}$	Shift Ratios[b] o	m	p
$n-C_{14}H_{29}$	$CoBr_4^{2-}$	170[c]	1.02	0.34	0.44
$n-C_{14}H_{29}$	$CoBr_4^{2-}$	151[d]	1.05	0.50	0.52
$n-C_8H_{17}$	$CoBr_4^{2-}$	131[d]	1.27	0.44	0.51
$n-C_8H_{17}$	CoI_4^{2-}	144[d]	1.01	0.40	0.52
$n-C_4H_9$	$CoBr_4^{2-}$	135[d]	1.10	0.41	0.50
$n-C_4H_9$	$NiBr_4^{2-}$	−13[d]	−0.85	3.10	1.0
$n-C_4H_9$	$Er(NO_3)_5^{2-}$	−634[e,i]	0.88	0.35	0.28
$n-C_8H_{17}$	$PrCl_6^{3-}$	46[f]	1.22	0.28	0.09
$n-C_8H_{17}$	$ErCl_6^{3-}$	292[f]	1.89	0.51	1.62
$n-C_8H_{17}$	$TmCl_6^{3-}$	−55[f]	1.43	0.74	0.55
$n-C_8H_{17}$	$YbCl_6^{3-}$	−60[f]	1.73	0.20	0.17
		Calculated			
A(Å)	ϕ(deg.)				
7.0	0	–g	1.10	0.52	0.51
7.0	5	–g	1.02	0.45	0.45
6.0	20	–h	1.01	0.31	0.26
7.0	15	–h	1.05	0.38	0.35

[a] Shift in Hz at 60 MHz. An upfield shift is defined as positive.

[b] $\Delta\nu_i/\Delta\nu_{\alpha-CH_2}$.

[c] 0.2 mol/l. in H_2CCl_2.

[d] 0.4 mol/l. in H_2CCl_2.

[e] 0.1 mol/l. in H_2CCl_2.

[f] 0.2 mol/l. in $HCCl_3$.

[g] Pyridine ring protons avoid close contact with anion. (Restricted rotation model).

[h] Pyridine ring permitted to rotate freely about X-axis of coordinate system of Fig. 7. (Isotropic rotation model).

[i] Data taken from Ref. 16.

obtained from the spectrum of the pure complex in solution. The fast exchange law is therefore utilized by recording the chemical shifts of solutions of constant cation concentration, with the mole fraction of diamagnetic (Br^- or $ZnBr_4^{2-}$) anion varying the plot of observed shift vs. mole fraction of paramagnetic species is then used to identify the isotropic shift in the fully paramagnetic solution.[1,2,7]

The isotropic shift data, expressed as ratios $\Delta\nu_i/\Delta\nu_{\alpha-CH_2}$ for the 1-alkyl-3,5-lutidinium complexes may be found in Table I. It can be seen that the nickel and cobalt shift patterns are quite different, as is usually observed,[1,8] while on the other hand, the CoX_4^{2-} and $Ln(NO_3)_5^{2-}$ shift patterns, while not identical in every detail, are quite similar. As has been seen previously,[8] the shift ratios for the $LnCl_6^{3-}$ containing ion-pairs bear no correspondence to one another, nor do they bear any obvious similarity to the $CoCl_4^{2-}$ or $Ln(NO_3)_5^{2-}$ shift patterns; this indicates the contribution of more than one mechanism to the isotropic shift.

If the CoX_4^{2-} isotropic shifts are predominantly axial dipolar in origin, one ought to be able to reproduce the observed shift ratios through model calculations. Using the known cartesian coordinates for the pyridine ring protons, the ratios $(G.F.)_i/(G.F.)_{\alpha-CH_2}$ were calculated assuming that the Co^{+2} cation sits at a fixed distance, A, from the central nitrogen of the pyridine ring. The relative orientation of the C_2 axis of the pyridine ring with respect to vector A is as shown in Fig. 1. As in previous attempts to reproduce the observed shift ratios,[13,16] the ring is permitted varying degrees of rotational freedom in the ion pair.

Angles θ and ϕ specify the anion orientation in the cation based coordinate system. Angle θ is set at 90° in what follows. The dihedral angle λ between the xy plane and the plane of the pyridine ring is varied from 0° to 360°, a geometric factor being calculated for each value of λ in five degree steps.

In the "isotropic rotating model" no weight is attached to any particular value of λ. In the "restricted rotating model" a distribution function $D(\lambda) = \sin^2\lambda$ is incorporated in the calculation. This has the effect of making the pyridine ring protons avoid close contact with the anion.[16] The results of

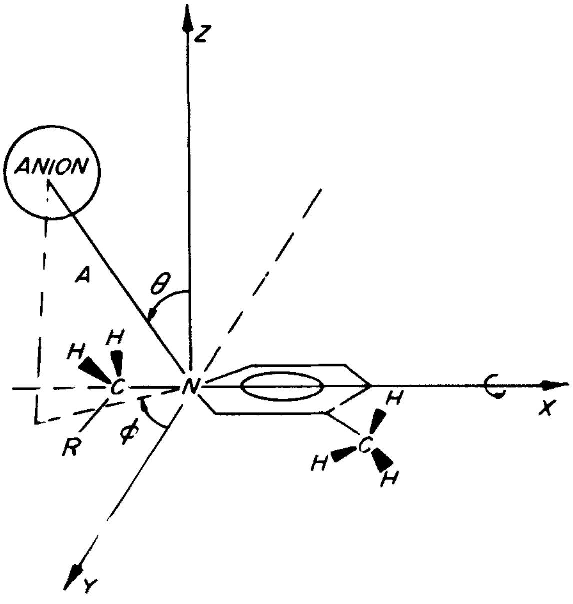


FIGURE 1 Coordinate system used in calculating geometric factor ratios of cation protons.[13,16]

the calculations may be found in Table I. As can be seen, the calculations fit the CoX_4^{2-} data best at A = 7Å and $\phi = 0^\circ$ or 5° in the restricted rotation model. These results are in good agreement with the parameters which gave best agreement in the case of $Ln(NO_3)_5^{2-}$ anion (A = 7Å, $\phi = 10^\circ$).

The isotropic shifts in the CoI_4^{2-} containing ion-pair are very similar to those in the $CoBr_4^{2-}$ complex. This is at first sight surprising, since the interionic distance would be expected to be greater here than in the $CoBr_4^{2-}$ case due to the greater VanderWaals radius of I^-. The theory is in accord with these findings, however, since for the pyridine ring protons the calculated shift ratios are quite insensitive to the value of A when A is greater than 6Å.[13] The results imply that the anion sits directly perpendicular to the symmetry axis of the pyridine ring, above the nitrogen atom. As in the $Ln(NO_3)_5^{2-}$ complexes, the pyridine ring does not appear to be completely free to rotate in the CoX_4^{2-} ion pairs. This phenomenon has been attributed to a steric effect from the 3,5 methyl substitution.[16]

Line-Width Studies

As an independent test of our choice of ion-pair structure parameters, the line-width at half height, $(1/\pi T_2)_{obs}$ was recorded for the pyridine protons in the CoX_4^{2-} complex. Since the line-widths could not be properly measured in solutions of the pure complex, the experimental procedure was similar to that used in obtaining the isotropic shifts. Thus, $(1/\pi T_2)_{obs}$ was recorded as a function of f_{para} for solutions of constant total cation concentration. The system was found to obey the fast exchange equation:[19]

$$\Delta\omega_{obs} = (1/\pi T_2)_{obs} - (1/\pi T_2)_{dia} = f_{para}[(1/\pi T)_{para} - (1/\pi T_2)_{dia}] \tag{3}$$

where $\Delta\omega_{obs}$ is the line broadening in an ion paired system for which the mole-fraction of paramagnetic anions is f_{para}. The 3,5 lutidine system is ideal for this type of study since the proton–proton couplings are all less than the line-width under diamagnetic conditions, $(1/\pi T_2)_{dia}$, hence errors in estimating the paramagnetic line width, $(1/\pi T_2)_{para}$, are minimized.

TABLE II

NMR line-broadening data for lutidinium cation protons

Ratio[a]	Observed	Calculated b	 c	 d
o/p	4.0	4.2	2.6	6.8
m/p	1.4	1.9	1.1	3.1

[a] Ratios of line widths at half height in 0.4M H_2CCl_2 solutions of $[C_{14}H_{29}NC_5H_3(CH_3)_2]_2CoBr_4$ corrected for line width in diamagnetic $ZnBr_4^{2-}$ salt. Estimated uncertainty = 0.3 for all ratios.

[b] Ratio of $\langle 1/R^6\rangle_i/\langle 1/R^6\rangle_j$ calculated presuming restricted rotation about x-axis in Fig. 1. A = 7.0A, $\phi = 10^\circ$.

[c] Ratio calculated presuming no relative cation–anion motion. A = 7Å, $\phi = 10^\circ$.

[d] Ratio calculated presuming cation is totally free to rotate about x-axis in the ion-pair. A = 7Å, $\phi = 10^\circ$.

For protons i, j, it can be shown that the ratio of the paramagnetic broadenings depends only on the ratio of the inverse sixth powers of the average metal–proton distances.[19] Thus:

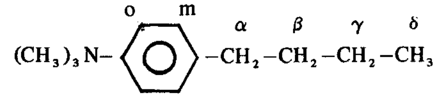
$$\frac{(\Delta\omega_{obs})_i}{(\Delta\omega_{obs})_j} = \frac{\langle R^{-6}\rangle_i}{\langle R^{-6}\rangle_j} \tag{4}$$

The line-broadening ratio data may be found in Table II, where it is compared to calculated values of $\langle R^{-6}\rangle_i/\langle R^{-6}\rangle_j$. Data for the α–$CH_2$ protons are not included since the extensive spin–spin coupling renders all conclusions meaningless. The calculated ratios are in reasonably good agreement with experiment for the restricted ($D(\lambda) = \sin^2\lambda$) rotation model at A = 7Å, $\phi = 10^\circ$; while the ratios calculated on the assumption of either isotropic rotation or fixed relative orientation disagree markedly with experiment. Table II thus shows that comparison of calculated with observed line-broadening ratios distinguish far better than shift ratios between alternative model structures.

N,N,N-Trimethylanilinium Complexes

Further evidence for the dipolar hypothesis comes from an inspection of the shift pattern in the anilinium (QA) system (Table III). It can be seen that the phenyl ring proton shifts attenuate uniformly, in the $CoCl_4^{2-}$ complex with increasing separation from the nitrogen atom in a fashion very similar to what was observed in the pyridinium complexes. The terminal methyl (t–CH_3) shift of the butyl chain is in the opposite direction to the phenyl ring shifts, however. The reversal in sign at t–CH_3 is well reproduced by the $Er(NO_3)_5^{2-}$ complex. Unfortunately, however, the central portions of the alkyl chain were not resolved in the $CoCl_4^{2-}$ complex, so that a more detailed comparison cannot be made.

TABLE III
Proton isotropic shift ratios in N,N,N-trimethylanilinium salts



Anion	$\Delta\nu^{a}_{N-CH_3}$	Shift ratios[b] o	m	α	β	γ	δ
$CoCl_4^{2-}$	237	0.72	0.10	c	c	c	–0.047
$NiCl_4^{2-}$	–93	0.53	0.32	0.17	0.13	0.11	0.075
$Er(NO_3)_5^{2-}$	–526	0.69	0.19	0.021	0.015	–0.036	–0.047

[a] Shift in Hz at 100 MHz. Positive sign indicates an upfield shift.
[b] $\Delta\nu_i/\Delta\nu_{N-CH_3}$. All data obtained in H_2CCl_2 at ~0.2 Mol/l conc'n.
[c] Isotropic shift could not be determined due to poor resolution.

The reversal in sign at t–CH_3 can be reproduced by model calculations, assuming an axial dipolar model with the butyl chain fully extended in trans-configuration. Quantitatively, the fit between theory and experiment is not particularly good for the remaining protons. If the N-alkylpyridinium cation may be thought of as a rod in which the positive charge is located near the centre, then the anilinium cation resembles a rod in which the charge is located close to one end; the theory does not handle the latter case very well, since a variety of angles ϕ is available to the attacking anion. We interpret the reversal in sign to mean that the t–CH_3 protons lie outside the positive cone of the geometric factor on a time-average. The t–CH_3 shift in the NiX_4^{2-} complex is in the same direction as the ring proton shifts. This is not surprising since, if there is a sizeable rhombic contribution to the shift, the rhombic term is not required to vanish in the same region of space as the axial term. In other words, the rhombic shift is dominant clearly at this position in the $NiCl_4^{2-}$ complex.

Triphenylbutylphosphonium Complexes

A further test of the dipolar mechanism lies in comparing the cation isotropic shifts observed[9] in the salts $[Ph_3Pbu]^+ Ph_3PMBr_3^-$ with the corresponding $Ln(NO_3)_5^{2-}$ salts. The data may be found in Table IV. Caution must be used in comparisons between the two systems, since the solvents are not the same in both studies.

It can be seen that the shift ratios within the phenyl ring compare very well between the $(Ph)_3PMBr_3^-$ and $Ln(NO_3)_5^{2-}$ series. This evidence suggests that the cation phenyl rings have very nearly the same orientations with respect to the anion in both series of salts. On the other hand, the ratio $(\Delta\nu_0/\Delta\nu_{\alpha-CH_2})$ is quite different between the two series. The values of $\Delta\nu_0/\Delta\nu_{\alpha-CH_2}$ which we quote were not tabulated by the original authors; they may, however, be estimated to within 1.5 ppm from Figure 1 of Reference 9. These authors were able to obtain the best fit between theory and experiment for the phenyl ring proton ratios when the C_3 axes of both counterions were coincident. Rotational freedom of the phenyl rings was allowed for; in addition, it was assumed that the butyl group could be oriented either toward or away from the anion with equal likelihood. An interionic distance, A = 7.6 ± 1.0 Å, was obtained.[9] Interestingly, this value is within

TABLE IV
Proton isotropic shift ratios in triphenyl-n-butyphosphonium salts

Anion	$\Delta\nu_{\alpha-CH_2}$[a]	Shift ratios °/α–CH_2[e]	o/p[e]	m/p[e]
$Ho(NO_3)_5^{2-}$	–5.9[b]	0.50	5.2	2.0
$Er(NO_3)_5^{2-}$	–3.1[b]	0.49	4.2	1.6
$Yb(NO_3)_5^{2-}$	2.6[b]	0.42	4.3	1.8
$Ph_3PCoBr_3^-$	3.6[c,d]	1.4 ± 0.2	3.8	1.9
$Ph_3PNiBr_3^-$	–3.7[c,d]	1.6 ± 0.2	4.0	1.9

[a] Shift in ppm relative to corresponding protons in $Ph_3PC_4H_9Br$.
[b] The solvent was dichloromethane; saturated (~0.05 mol/l) solutions used in all cases.
[c] Data in $HCCl_3$ taken from Ref. 9.
[d] Value estimated from Figure 1 of Ref. 9. (±0.5 ppm).
[e] Estimated uncertainties in the shift ratios are 0.3 (o/p) and 0.2 (m/p).

experimental error of that obtained for the $Ln(NO_3)_5^{2-}$ complexes [13,16] (7 Å) and with the best fit values for the CoX_4^{2-} complexes presented above. Nonetheless, the cation behaves differently in $(Ph_3PMBr_3)^-$ ion pairs than it does in $Ln(NO_3)_5^{2-}$ systems. One explanation which is consistent with the known dipolar character of the shifts in both series of complexes is that the more highly charged anion favours ion-pair structures in which the less-sterically hindering butyl chain of the cation is in close proximity to the anion. This is a consequence of the "trapping" of the most accessible (least sterically hindered) site on the cation in order to produce a minimum potential energy structure.

Trapping has been observed by Tan and Lim[18] from the cation proton isotropic shift ratio $\Delta\nu_{N-CH_3}/\Delta\nu_{N-CH_2}$ in the system $(n\text{–}bu_3NCH_3)^+$ $(Ph_3PCoBr_3)^-$. In chloroform, the $N\text{–}CH_3$ protons are believed to be closer to the anion on a time average than $N\text{–}CH_2$, while in higher dielectric solvents, the preference decreases dramatically.

CONCLUSIONS

The data presented in this study allow us to state with greater firmness that the proton isotropic shifts in the CoX_4^{2-} complexes contain a sizeable axial dipolar term. Thus our previous interpretation of the cation shift data in terms of a dominant Fermi contact mechanism *at all protons* appears to be in error. Since the cation ^{14}N NMR shifts probably contain a sizeable Fermi contact component, however, as originally claimed,[14,15] the unpaired spin density appears to be localized on the central atom to a large extent, as suggested recently by LaMar.[3]

We cannot exclude the possibility, however, that a *small* amount of spin density reaches the protons in the immediate vicinity of the central nitrogen atom. Unambiguous experimental demonstration of spin density at these protons requires the use of an anion possessing no susceptibility anisotropy (e.g. an S-state ion such as $MnCl_4^{2-}$, $GdCl_6^{3-}$). The electron relaxation times for such ions are such that cation proton resonance shifts cannot be accurately recorded due to the line-broadening effect.[8] It is therefore unlikely that the issue will be resolved using proton spectra, although the use of ^2D NMR in such difficult cases has been found to be promising.[20]

The origins of the sizeable axial and rhombic dipolar shifts in the MX_4^{2-} and $LnCl_6^{3-}$ complexes require comment. Significant distortions from tetrahedral symmetry are sometimes found for the MX_4^{2-} species in the solid state,[21,22] presumably as a consequence of crystal packing effects. On the other hand, the available IR–Raman data for the $LnCl_6^{3-}$ salts in the solid state seem to indicate very nearly regular octahedral geometries.[23] If one presumes that the structural integrity of these species is maintained in solution, then the anisotropy-producing low symmetry ligand field can only be provided by the cations.[7] One cannot predict in advance from a knowledge of the solid state structures the angles and distances in the ion pairs. However, it can be shown that an axial crystal field of positive charges placed at reasonable distances from the paramagnetic centre in an otherwise tetrahedral anion can account for the order of magnitude of the g-tensor (and hence susceptibility) anisotropy. One cannot rule out tetragonal or trigonal distortion of the first coordination sphere ligands as a result of the ion-pairing process. Similarly, one cannot, of course, preclude the alternative possibility that the shift-producing species results from substantial replacement or dissociation of first coordination sphere ligands to produce anionic species of less than cubic symmetry.

It is tempting to try to correlate the signs of the observed shifts in the MX_4^{2-} ion-pairs with single-crystal magnetic anisotropy data for these anions,[24] as was done successfully by Horrocks and Greenberg[11] for the $(Ph_3P)_2MCl_2$ complexes. There are several reasons why we may expect such an approach to be at best only partially successful in our case.

First, since the primary ligand field contains but one species of ligand, the sign of the magnetic anisotropy, $\chi_{\parallel}-\chi_{\perp}$, will depend on the placement of cations in the lattice, and on the manner in which the anion is distorted from tetrahedral symmetry. For example, we will find positive or negative signs depending on whether the $CoCl_4^{2-}$ tetrahedron is elongated or flattened in the Cs_3CoCl_5 and Co_2CoCl_4 lattices, respectively.[24a] In the case of the $(Ph_3P)_2MCl_2$ compounds, on the other hand, the anisotropy may be thought of as being primarily a property of a molecular unit in the lattice.

Thus, there is little evidence that the anisotropy measured in MX_4^{2-} containing crystals will correspond in any way to that observed in solution.

Second, we cannot determine the positions of the protons by means of an independent X-ray experiment, as was possible in the case of the $[Ph_3P]_2MCl_2$ complexes. Thus, due to the lability of the ion-pairs, we cannot infer the location of the magnetic axes in the ion-pair complex.

Taken together, the facts seem to suggest that whenever the anion possesses a permanent low symmetry ligand field from the *first* coordination sphere ligands, as in $(Ph_3P)MX_3^-$ or $Ln(NO_3)_5^{2-}$, the cation shifts have a predominantly axial dipolar nature. On the other hand, the cation shifts in the presence of the "cubic" anions, very obviously do not. These facts are not well explained by the current theories, and should provide the basis for some interesting future theoretical investigations. In the absence of quantitative ideas, we propose the following explanation.

In its present state, the theory indicates[5,25] that non-axial dipolar contributions are most likely to occur either when the ligand is restricted to a few distinct rotamers in the complex,[25] or alternatively cannot exchange rapidly between large numbers of *magnetically* distinguishable isomeric forms.[5] If the primary ligand field is cubic, then the outer sphere ligands are presumably the only source of anisotropy. The anisotropy and the magnetic axes of the complex thus tend to "travel with" the outer sphere ligands in the ion-pair. Thus the rhombic shift would not be expected to average out.

In the non-cubic anions, however, the cation is in rapid motion with respect to a set of magnetic axes which are fixed by the symmetry of the *first* coordination sphere. The agreement with the axial model for such cases can thus be explained.

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