Ion Pairing and Magnetic Anisotropy in Some Tetrahedral Complexes of Iron(II), Cobalt(II), and Nickel(II)

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Abstract: The proton magnetic resonance spectra of tetrabutylammonium tetrahalometalates(II) have been studied in 0.25 M solution in dichloromethane. Upfield resonance shifts for tetrahedral iron(II) and cobalt(II) complexes and downfield shifts for the nickel(II) complexes were noted. The cations are believed to be extensively ion-paired to the paramagnetic anions in this medium. Since the complexes are expected to be effectively cubic in solution, our observation of nmr shifts is quite surprising, due to the known pseudocontact origin of the cation proton shifts. With the assumption that the cations in the ion pair are in some way responsible for distortions from cubic symmetry, point-charge calculations were performed in an attempt to explain these observations.

The dipolar, or "pseudocontact," shift has been recently employed by several groups[2–8] as a probe in studying ion pairing in solution. When a molecule is situated in the region of a magnetic complex which is distorted from cubic symmetry, a shift in the nmr resonance frequency occurs in accordance with eq 1[9] (valid for $\tau_c \gg T_1$): τ_c and T_1 are the molecular cor-

$$\left(\frac{\Delta\nu}{\nu_0}\right)_i = -\frac{|\beta^2|S(S+1)}{45kT} \times (3g_{\parallel} + 4g_{\perp})(g_{\parallel} - g_{\perp})\frac{3\cos^2\theta_i - 1}{R_i^3} \quad (1)$$

relation and electron spin relaxation times, respectively, ΔH is the shift in resonance frequency, H_0 is the frequency of the spectrometer, and $g_{\parallel}$ and $g_{\perp}$ are the electronic g factors parallel and perpendicular, respectively, to the highest fold molecular symmetry axis. R_i is the distance from the metal atom to resonating proton i, and θ_i is the polar angle which the proton makes with the axis of $g_{\parallel}$. The other symbols used have their usual meanings. The dipolar shift is seen to be critically dependent on the anistropy of the g tensor, *i.e.*, on $(g_{\parallel} - g_{\perp})$, and on θ_i; the expression changes sign as θ_i passes from 0 to 90° and is zero at $\theta_i \sim 55°$.

The dipolar shift contributes to the total isotropic shift of any permanently distorted molecule in solution. The contact shift, on the other hand, depends for its magnitude on direct transmission of unpaired electron density through orbital overlap between metal and ligand. In the case of the alkylammonium cations, it is claimed[2] that there is no effective mechanism whereby direct spin delocalization from anion to cation in an ion pair can take place; therefore, the resonance shifts observed for the cation on ion-pairing to paramagnetic anions are ascribed solely to the dipolar shift.[2]

Among the anions recently studied under ion-pair-producing conditions are $(C_6H_5)_3PMI_3)^-$ (M = Co, Ni),[2] $M(acac)_3^-$ (M = Co, Ni),[6] and $M(CN)_6^{-3}$ (M = Cr, Fe).[4,5] For the ions $(C_6H_5)_3PMI_3^-$, the cobalt and nickel g-tensor anisotropies appear to be roughly equal[2] but of opposite sign. The estimated proton pseudocontact shifts in the complexes $[(C_6H_5)_3P]_2MX_2$ (M = Co, Ni; X = Br, I)[10] are considerably smaller for nickel than for cobalt. However, there is the possibility that cancellation of terms in the pseudocontact shift equation causes the nickel shifts to be drastically reduced, owing to the special form of eq 1 used when the symmetry is reduced from axial to rhombic.[10] Crystal-field theory predicts, in general, that for axially distorted or unsymmetrically substituted complexes, T ground states give rise to large g-tensor anisotropies, since a first-order orbital contribution to the g tensor is present. In A or E ground terms, g-tensor anisotropy arises solely from spin–orbit mixing in second order with excited states; hence the anisotropies are expected to be small or to vanish. On the basis of this oversimplified model, tetrahedral nickel(II), with a triply degenerate $^3T_1$ (F) ground state, is expected to be considerably more anisotropic than the tetrahedral cobalt(II) analog ($^4A_2$).

It has recently been shown[11] that the protons in tetrabutylammonium tetrabromocuprate(II) in $CDCl_3$ solution are shifted downfield relative to the free cation resonances. The tetrahalocuprates are known[12] to be axially distorted tetrahedra from crystal structure studies, and the presence of the ion-pairing shifts in these systems has been interpreted in terms of an inherent electronic property of the copper(II) ion,[11] in which the distortion is preserved on passing from solid state into solution. On the other hand, tetrachloronickelate is known to possess a perfectly regular solid-state geometry in certain lattices,[13] and tetrahalocobaltates(II), possessing a non-Jahn–Teller susceptible ground ($^4A_2$) state, would be expected to show little anisotropy in the g tensor. Many previous studies on tetrahedral cobalt(II) complexes with unsymmetrically substituted ligands have neglected the pseudocontact contribution to the total isotropic shift for this reason. It is therefore most interesting to report that the ions FeX_4^{2-}, CoX_4^{2-}, and NiX_4^{2-} (X = halide,

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[1] National Institutes of Health Postdoctoral Fellow, University of Illinois, 1966–1968.
[2] G. N. LaMar, *J. Chem. Phys.*, 41, 2992 (1964).
[3] G. N. LaMar, *ibid.*, 43, 235 (1965).
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[5] D. W. Larsen, *ibid.*, 5, 1109 (1966).
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[7] G. N. LaMar, R. H. Fischer, and W. D. Horrocks, Jr., *Inorg. Chem.*, 6, 1798 (1967).
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[9] G. N. LaMar, *J. Chem. Phys.*, 43, 1085 (1965).
[10] G. N. LaMar, W. D. Horrocks, Jr., and L. C. Allen, *ibid.*, 41, 2126 (1964).
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[13] P. Pauling, *Inorg. Chem.*, 5, 1498 (1966).

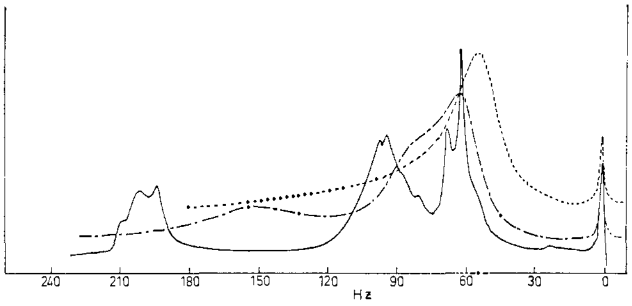

Figure 1. Nmr spectra of tetrabutylammonium cations in dichloromethane solution of $[Bu_4N]_2MCl_4$: ——, 0.25 *M* $[Bu_4N]_2ZnCl_4$; -·-·-·-·-, 0.14 *M* $[Bu_4N]_2ZnCl_4$, 0.11 *M* $[Bu_4N]_2CoCl_4$; --------, 0.25 *M* $[Bu_4N]_2CoCl_4$.

SCN^-, OCN^-) ion-paired to tetrabutylammonium ion produce substantial pseudocontact shifts in the alkyl protons. We will concern ourselves in this paper with a discussion of the shifts and with a discussion of the errors in the simplified approach to this problem employed above. A discussion of the agencies by which *g*-tensor anisotropy can arise is offered in order to explain the observed data for these apparently symmetrical complexes.

Experimental Section

Preparation of Complexes. Tetrabutylammonium Chloride. Tetrabutylammonium iodide (Bu_4NI) was allowed to react with an excess of freshly precipitated silver chloride in anhydrous methanol. The resulting silver iodide was removed by filtration and the desired salt obtained by evaporation of the filtrate and addition of ether.

Tetrabutylammonium Tetrahalometalates. The tetrachlorometalates were prepared by allowing stoichiometric amounts of metal chloride to react with tetrabutylammonium chloride in hot acetone. Hydrated metal chlorides were first stirred with dimethoxypropane for several hours to remove coordinated water. The solids obtained were then recrystallized twice from acetone. *Anal.* Calcd for $(Bu_4N)_2FeCl_4$: C, 56.31; H, 10.63; N, 4.10. Found: C, 56.08; H, 10.57; N, 3.95. Calcd for $(Bu_4N)_2CoCl_4$: C, 56.05; H, 10.58. Found: C, 55.94; H, 10.44. Calcd for $(Bu_4N)_2NiCl_4$: C, 56.07; H, 10.59; N, 4.09. Found: C, 56.55; H, 10.63; N, 4.10. Calcd for $(Bu_4N)_2ZnCl_4$: C, 55.53; H, 10.49; N, 4.05. Found: C, 55.0; H, 10.56; N, 3.90.

The tetrabromometalates were prepared similarly from metal bromide and tetrabutylammonium bromide. Recrystallization was carried out by adding an equal volume of hot carbon tetrachloride to a boiling acetone solution of the complex. Crystals deposited on cooling. *Anal.* Calcd for $(Bu_4N)_2CoBr_4$: C, 44.51; H, 8.40; N, 3.24. Found: C, 44.20; H, 8.18; N, 3.58. Calcd for $(Bu_4N)_2NiBr_4$: C, 44.52; H, 8.41; N, 3.24. Found: C, 44.58; H, 8.41; N, 3.29. Calcd for $(Bu_4N)_2ZnBr_4$: C, 44.18; H, 8.34; N, 3.22. Found: C, 44.47; H, 8.32; N, 3.10. Calcd for $(Bu_4N)_2MnBr_4$: C, 44.72; H, 8.44; N, 3.26. Found: C, 44.75; H, 8.36; N, 3.05.

The tetraiodocobaltate complex was prepared by a method previously reported[14] as was the tetraiodozincate. The tetraiodonickelate was prepared by allowing anhydrous nickel iodide (Alfa Inorganics) to react with tetrabutylammonium iodide in boiling ethanol. A large volume of ether was added with stirring, and on cooling red crystals of the desired salt appeared. *Anal.* Calcd for $(Bu_4N)_2CoI_4$: C, 36.55; H, 6.90; N, 2.66. Found: C, 37.04; H, 7.02; N, 2.57. Calcd for $(Bu_4N)_2NiI_4$: C, 36.56; H, 6.90; N, 2.66. Found: C, 36.61; H, 6.80; N, 2.75. Calcd for $(Bu_4N)_2ZnI_4$: C, 36.33; H, 6.86; N, 2.65. Found: C, 37.47; H, 7.02; N, 2.61.

Tetrabutylammonium tetracyanatocobaltate(II) and -zincate(II) are prepared as follows. To a rapidly stirred solution of cobalt chloride and potassium cyanate in water (1:4 mole ratio) is added a little less than the stoichiometric amount of tetrabutylammonium bromide in water. Blue crystals form immediately. These are washed with copious quantities of distilled water and rigorously dried under vacuum over phosphorus pentoxide. Recrystallization is accomplished by addition of hot carbon tetrachloride to a boiling solution of the complex in ethanol. Crystals deposit on cooling. The infrared spectrum reveals no water absorptions in the region 3000–4000 cm^{-1}. Elemental analysis reveals that only a very small trace of chloride is present (<0.05%). Tetrabutylammonium tetrathiocyanatocobaltate and -zincate are prepared from aqueous solution by procedures similar to those above. A blue oil results, which crystallizes on standing or rapid stirring in the cold. This is dried and recrystallized as in the case of the tetracyanato complexes. *Anal.* Calcd for $(Bu_4N)_2Co(NCO)_4$: C, 60.74; H, 10.19; N, 11.81. Found: C, 60.83; H, 10.08; N, 11.94. Calcd for $(Bu_4N)_2Zn(NCO)_4$: C, 60.19; H, 10.10; N, 11.70. Found: C, 60.22; H, 9.87; N, 11.68. Calcd for $(Bu_4N)_2Zn(NCS)_4$: C, 55.25; H, 9.27; N, 10.74. Found: C, 55.05; H, 9.21; N, 10.54. Calcd for $(Bu_4N)_2Co(NCS)_4$: C, 55.71; H, 9.35; N, 10.83. Found: C, 55.15; H, 9.14; N, 10.18.

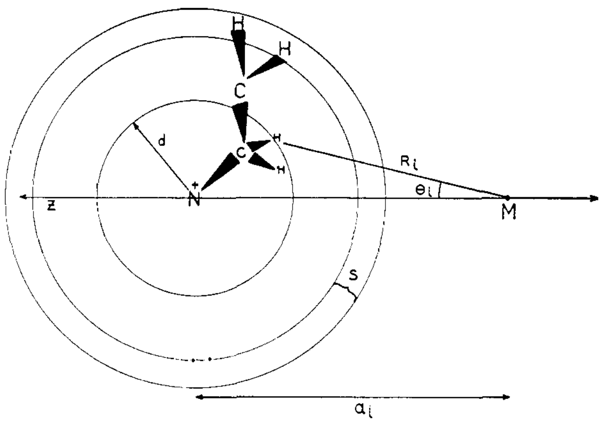

Figure 2. Orientation of cation in the ion-pair model. The cation tumbles with the central nitrogen atom on the highest fold symmetry at a fixed distance, a_i, from the metal atom M. In tumbling, the H_1 protons describe a sphere of radius *d*; the H_i protons describe the spherical shell s (i = 2, 3, 4).

Analyses were performed at the University of Illinois Microanalytical Laboratory under the supervision of Mr. Josef Nemeth.

Nmr spectra were recorded on the JEOLCO C-60-H spectrometer at a probe frequency of 60 MHz and a temperature of 22 ± 0.5°. The solvent, AR grade dichloromethane, was dried several days over Linde 4A molecular sieves before use. Special precautions against air oxidation were taken in making up the tetrahaloferrate(II) solutions. All work including filling of nmr tubes was done in a drybag under a nitrogen atmosphere.

Results

The proton nmr spectrum of the tetrabutylammonium $(Bu_4N)^+$ cation has been assigned previously[5,7] using this numbering system

$$N{-}(\underset{1}{C}{-}\underset{2}{C}{-}\underset{3}{C}{-}\underset{4}{C})_4^+$$

The H_1 protons occur furthest downfield (−202 Hz); H_2 and H_3 form an unresolved peak at −95 and the terminal methyl protons occur near −65 Hz. A typical spectrum is shown in Figure 1. The H_1 protons show a partially resolved N^{14} splitting, which serves as a check on the assignment.[5] In all of the studies to date, it has been noted that ion pairing to paramagnetic anions produced the greatest shift at the H_1 proton, followed by H_2, H_3, H_4 in that order. If the cation is assumed[3] to sit with its central nitrogen on the highest fold symmetry axis of the molecule, then the H_1 protons describe a sphere of radius *d* during the tumbling motion of the cation, as in Figure 2. The protons further

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[14] F. A. Cotton, D. M. L. Goodgame, and M. Goodgame, *J. Am. Chem. Soc.*, **83**, 4690 (1961).

from the nitrogen describe spherical shells, for which the average pseudocontact shifts are increasingly reduced. The H_1 protons experience the largest pseudocontact shift because of their relatively close position to the axis of maximum pseudocontact shift.

Spectra. The nmr spectra of the $(Bu_4N)_2MnX_4$ salts in CH_2Cl_2 could not be observed, owing to the particularly long electron relaxation time of manganese(II). Dilution of the manganese complexes with the corresponding zinc salts gave only one broad peak at −58 Hz from TMS, with no other detectable resonances attributable to the cation. Much of this region is obscured by an extensively broadened and shifted dichloromethane resonance. No attempt has been made, therefore, to study this ion in greater detail.

The tetrahaloferrate(II) and tetrahalocobaltate(II) salts in CH_2Cl_2 give one broad resonance signal 60–90 Hz from TMS (see Figure 1). It is impossible to obtain information of the individual protons from such a spectrum. Therefore, the resonance positions of the cation protons were studied by preparing solutions of transition metal complexes with varying amounts of the zinc analog, keeping the total molarity of complex in solution constant. The resonance positions for the protons were plotted as a function of mole fraction n of paramagnetic ion. The straight lines which result confirm that the cations exchange rapidly between the paramagnetic and diamagnetic sites as has been observed in previous work.[2,6] Absolute values of the shifts ($\Delta\nu$) are obtained by subtracting the frequency of the diamagnetic site ($\Delta\nu_{n=0}$) resonance from that of the extrapolated paramagnetic site resonance ($\Delta\nu_{n=1}$) for each type of proton. The absolute shifts for each anion are listed directly beneath the mole fraction data for each anion in Table I. A positive sign indicates an upfield shift relative to the same proton in a diamagnetic environment. The plot of resonance frequency *vs.* n reveals that the extrapolated $\Delta\nu_{n=1}$'s fall quite close to the observed broad resonances for pure tetrahalometalate(II) solutions ($n = 1$), indicating that the broad peak contains all four types of protons. The data for all complexes studied are presented in Table I. Representative spectra are shown in Figure 1, indicating the size and direction of the observed shifts at different n. The shifts are slightly concentration dependent. Holding the mole ratio n constant at 0.3, the pseudocontact shifts of the H_1 protons decrease somewhat (10 Hz) on lowering the total concentration of complex. This represents a decrease in the fraction of ion pairs at lower concentrations, as would be expected. Similar behavior has been noted by Fanning and Drago[8] in low dielectric constant solvents. Little variation of shift with concentration is found beyond $M = 0.25$, which represents a practical solubility limit. The proton resonance line widths increase from $CoI_4^{2-} < CoBr_4^{2-} < CoCl_4^{2-} < Co(NCO)_4^{2-} < Co(NCS)_4^{2-}$, or directly with the crystal-field splittings of these ions. This strongly suggests that electron relaxation effects are responsible for the resonance line broadenings. In the case of $Co(NCS)_4^{2-}$ the lines are sufficiently broad to introduce considerable difficulty in determining the exact resonance positions.

Discussion

The Agency of the Pseudocontact Shift. The complexes we are studying here are something of a paradox

Table I. Butyl Proton Resonance Data for $[Bu_4N]_2MX_4$ Complexes

Anion	M^{a}	n^{b}	$\Delta\nu$-$(H_1)^{c}$	$\Delta\nu$-$(H_{2,3})^{c}$	$\Delta\nu$-$(H_4)^{c}$
$FeCl_4^{2-}$	0.25	0.152	178	89	60
		0.318	144	75	56
		0.434	122	54^{d}	
		0.596	90	49^{d}	
		1.0		37^{e}	
		1	187^{g}	65^{g}	23^{g}
$FeBr_4^{2-}$	0.25	0.151	167	81	56
		0.283	143	74	56
		0.457	95	52^{d}	
		0.712		45^{e}	
		1.0		33^{e}	
		1	202^{g}	75^{g}	24^{g}
$CoCl_4^{2-}$	0.10	0.299	171	87	62
	0.25	0.166	182	88	61
		0.299	165	83	61
		0.440	149	79	61
		0.604	126	60^{d}	
		1.0		55^{e}	
		1	125^{g}	38^{g}	4^{g}
$CoBr_4^{2-}$	0.11	0.263	173	87	62
	0.25	0.114	185	90	60
		0.189	173	86	60
		0.508	127	67	58
		1.0		54^{e}	
		1	147^{g}	56^{g}	12^{g}
CoI_4^{2-}	0.11	0.278	169	85	
	0.25	0.101	191	93	
		0.201	178	87	
		0.349	153	77	
		0.400	148	76	
		0.501	134	59^{d}	
		1.0	51^{e}		
		1	140^{g}	56^{g}	4^{g}
$Co(OCN)_4^{2-}$	0.25	0.147	196	97	63
		0.256	192	96	62
		0.430	185	94	63
		0.639	177	93	60
		1.0	...^{f}		
		1	39^{g}	5^{g}	5^{g}
$Co(SCN)_4^{2-}$	0.10	0.282	205	108	67
	0.25	0.150	205	106	67
		0.300	205	106	67
		0.600	203	109	68
		1.0	...^{f}		
	0.25	1	0^{g}	0^{g}	0^{g}
$NiCl_4^{2-}$	0.1	1.0	260	153	101
	0.1	1.0	-58^{g}	-57^{g}	-38^{g}
	0.25	1.0	252	156	105
	0.25	1.0	-53^{g}	-60^{g}	-44^{g}
$NiBr_4^{2-}$	0.25	0.175	210	104	68
		0.247	211	108	72
		0.404	216	113	76
		0.663	224	125	84
		1.0	235	139	95
		1	−33	−43	−32
NiI_4^{2-}	0.1	1.0	187	109	75
	0.25	1.0	185	108	76
	0.1	1.0	$+15^{g}$	-17^{g}	-12^{g}
	0.25	1.0	$+17^{g}$	-16^{g}	-13^{g}
$ZnCl_4^{2-}$	0.25	0.00	202	93	63
$ZnBr_4^{2-}$	0.25	0.00	202	93	63
ZnI_4^{2-}	0.25	0.00	202	93	63

[a] Total molarity of MX_4^{2-} and ZnX_4^{2-} in H_2CCl_2 solution. [b] Mole fraction of paramagnetic complex. [c] All shifts are in Hz, downfield from TMS. All values are accurate to ±2 Hz, unless otherwise indicated. [d] Composite peak includes H_2, H_3, H_4, accurate to ±5 Hz, relative to TMS. [e] Composite peak includes H_1, H_2, H_3, H_4, relative to TMS. [f] Too broad to be accurately measured. [g] Shifts for protons H_1, H_2, H_3, H_4 relative to the corresponding proton resonance position in 0.25 M $[Bu_4N]_2ZnX_4$ solutions. Upfield shifts are shown as positive.

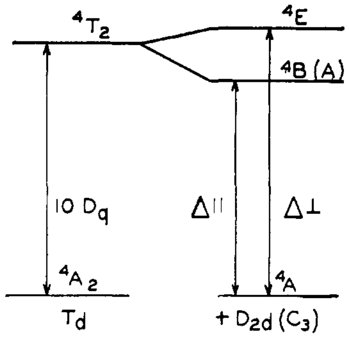

Figure 3. The electronic structure of the lowest quartet states of tetrahedral cobalt(II) complexes.

because the pseudocontact shift should vanish if both cation and anion have no preferred orientation relative to one another and are thus free to tumble independently. One expects a preferred orientation of the cation in $(C_6H_5)_3PMI_3^-$-$(Bu_4N)^+$ but this is not the case in MX_4^{2-}. The stereochemical features leading to noncubic molecular anions, such as chelate ring distortions in the $M(acac)_3^-$ complexes, or the nonequivalence of the ligand field in $(C_6H_5)_3PMI_3^-$, are also absent in the MX_4^{2-} system. It is, therefore, very interesting that pseudocontact shifts are observed in this system, and we shall consider several alternative explanations for the behavior encountered here which are of significance to this entire area. We can quickly dismiss ground-state distortions due to the Jahn–Teller effect. Distortions are not expected in CoX_4^{2-} because the ground state is an orbital singlet. In NiX_4^{2-}, spin–orbit coupling is large and should oppose the natural Jahn–Teller instability of the $^3T_1$ ground term. A symmetrical configuration is expected because the true ground state is an orbital singlet ($J = 0$) under the influence of spin–orbit coupling.[15a] Ham[15b] cites experimental evidence to the contrary, based on the observed distortions of tetrahedral nickel in cubic sites in spinels.[16] Because of the impossibility of separating intrinsic from lattice-induced distortions, however, we prefer the explanation of Liehr,[15a] since it is in accord with the observed structural regularity of tetrachloronickelate ion.[13] In FeX_4^{2-}, on the other hand, the small value of spin–orbit coupling requires a more serious consideration of Jahn–Teller effects, as can be found in a later section discussing the individual ions.

Dynamic Jahn–Teller effects involving orbital triplet terms have been investigated theoretically[15b] and have been shown to reduce the expectation values of orbital angular momentum operators, in much the same way as do covalency effects. We do not believe, however, that dynamic Jahn–Teller effects involving equivalent energy minima have a significant effect on the magnitude of the pseudocontact shift in the present case, since that portion of the g-tensor anisotropy due to these effects will go to zero since the rate of vibrational transfer from one equivalent distorted configuration to the other is expected to be very rapid in the nmr time scale.

The only contribution to the shift which occurs in all of the complexes is the axial field due to the presence of the cations ion-paired to the anion. The effect of ion pairing may be to lock in a ground- or excited-state Jahn–Teller distortion, to provide an axial field resulting in a splitting of the ground or excited states, or to cause *via* electrostatic interactions a distortion in the complex. First let us consider whether or not anisotropies of the appropriate order of magnitude could arise simply from the d-orbital perturbation by the cations. In our treatment we have calculated the g-tensor anisotropy from the ionic model and compared it to the g-tensor anisotropy obtained from the observed dipolar shift of the H_1 protons in $FeCl_4^{2-}$ and $CoCl_4^{2-}$.

In order to test the point-charge model, let us first turn to the case of cobalt(II). We shall calculate Δg from eq 4 using the $^4T_2$ matrix elements, with empirical spectroscopic parameters $10Dq$ and λ. The calculated Δg values will be compared with those required to give the pseudocontact shifts observed in the experiments. For tetrahedral cobalt(II), the ground state is $^4A_2$ and the anisotropy in the g tensor arises by admixture of the split $^4T_2$ and $^2T_2$ levels *via* spin–orbit coupling. Considering just the $^4T_2$ level, we obtain, in a field of tetragonal or trigonal symmetry

$$g_{\|} = 2 - (8\lambda/\Delta_{\|}) \qquad (2)$$

$$g_{\perp} = 2 - (8\lambda/\Delta_{\perp}) \qquad (3)$$

$\Delta_{\|}$ and $\Delta_{\perp}$ are the energies of the $^4A_2 \rightarrow {}^4B_1$ ($^4T_2$) and $^4A_2 \rightarrow {}^4E$ ($^4T_2$) transitions, respectively, as shown in Figure 3. The g-tensor anisotropy is now written as

$$\Delta g = g_{\|} - g_{\perp} = \frac{8\lambda(\Delta_{\|} - \Delta_{\perp})}{\Delta_{\|}\Delta_{\perp}} = \frac{8\lambda\Delta(^4T_2)}{100Dq^2} \qquad (4)$$

since $\Delta_{\|}\Delta_{\perp} \simeq 100Dq^2$ for small axial distortions. $\Delta(^4T_2)$, the splitting of the excited state, is defined as $E(^4A\ (T_2)) - E(^4E\ (^4T_2))$, and the magnitude of this energy difference will be evaluated from the crystal-field calculation (see Figure 3).

Experimental evidence from polarized spectra of the transition $^4A_2 \rightarrow {}^4T_2$ in Cs_3CoCl_5 seems to indicate that the simple theory is insufficient to give consistent results;[17] the measured sign of Δg is different from the one predicted from the excited-state splittings, although order of magnitude agreement is good. Since there is no covalency in our case, these shortcomings are not expected for the ionic ion-pairing interaction. The excited-state splittings are, from the diagonal matrix elements

$$\Delta(^4T_2) = \frac{35}{4}Dt \qquad (5)$$

in tetragonal (D_{2d}) symmetry, and

$$\Delta(^4T_2) = \frac{3}{2}Ds + \frac{10}{3}Dt \qquad (6)$$

in trigonal symmetry.

Out of the vast number of conceivable ion-pair models for the calculation we have selected two for consideration. These are as shown in Figure 4. Both have the advantage of producing strictly axial fields

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[15] (a) A. D. Liehr, *J. Phys. Chem.*, **67**, 389 (1963); (b) F. Ham, *Phys. Rev.*, **A138**, 1727 (1965).

[16] R. J. Arnott, A. Wold, and D. B. Rogers, *J. Phys. Chem. Solids*, **25**, 161 (1964).

[17] R. P. Van Stapele, H. G. Belgers, P. F. Bongers, and H. Zijlstra, *J. Chem. Phys.*, **44**, 3719 (1966).

at the metal atom, thus reducing the number of terms in the point-charge expansion. A rhombic model, in which the cations sit equidistant from the metal ion on two adjacent triangular faces of the anion, is also possible. In view of the complexity of the species in solution (double, triple, etc. aggregates), an exact solution of this problem is not feasible, and the main concern is to gain some appreciation of the order of magnitude of this effect. In the two models considered, the cations are placed 180° apart on a line joining their centers with the metal atom. Perhaps somewhat unrealistically, we have set them equidistant from the metal, although the calculation can be extended without difficulty to accommodate an infinite number of other possibilities. As previously shown, the existence of micelles makes previous estimates,[4,5] of the ion-pairing distance unreliable, so this is treated as an independent variable in this calculation. In an attempt to ascertain the most stable configuration of a simple 2:1 ion pair, rough calculations of the balance of electrostatic attractive and repulsive forces were performed for the two models. The results indicate that both have very nearly the same energy, as does the rhombic model proposed above.

The matrix elements of the generalized axial potential[18]

$$\langle \mathrm{p}|V_{\mathrm{ax}}|\mathrm{q}\rangle = \sum_{i}\sum_{l=0}^{\infty}\sum_{M=-l}^{l}\frac{4\pi Z_{\mathrm{i}}e^2}{2l+1}Y_l^m(\theta_i,\phi_i) \times \int_0^{\infty} R_{3\mathrm{d}}{}^2\frac{r^n}{a^{n+1}}r^2\mathrm{d}r\int_0^{\pi}\int_0^{2\pi}\psi_{\mathrm{p}}{}^* Y_l^m(\theta,\phi)\psi_{\mathrm{q}}\sin\theta\ \mathrm{d}\theta\mathrm{d}\phi \quad (7)$$

were obtained within the manifold of d orbitals (p, q) for the models discussed. Here, for d orbitals, l takes on the values 0, 2, 4. ψ_{p} and ψ_{q} refer to the angular portions of the d orbitals p and q. θ_i and ϕ_i refer to the angular coordinates of the point charges, while θ and ϕ refer to the angular coordinates of the d electron. The resulting orbital energies are written most conveniently in terms of the radial parameters *Ds* and *Dt* (eq 8 and 9). We have used the angular matrix elements of Piper and Carlin[19] in our calculations, while the *Ds* and *Dt* values which we use are of opposite sign to those of the above authors,[19] since Z_i, the charge of the ith perturbing "ligand" (*i.e.*, cation), is *positive.*

$$Ds = (2/7)Ze^2\langle r_<{}^2\rangle/a_i{}^3 \quad (8)$$

$$Dt = (2/21)Ze^2\langle r_<{}^4\rangle/a_i{}^5 \quad (9)$$

$\langle r_<{}^n\rangle$ is defined as $\int R(r)^2r^nr^2\mathrm{d}r$, $R(r)$'s are normalized Slater d orbitals, and in our case a_i represents the distance between the tetraalkylammonium nitrogen atom and the central metal atom. Since a_i is large, and the degree of covalent overlap between anion and cation is virtually zero, a point-charge treatment describes the anion–cation interaction quite well. The $\langle r_<{}^n\rangle$'s were evaluated using Burns' exponents[20] calculated for cobalt(II). The results in terms of *Ds* and *Dt* are listed in Table II. The calculated $\langle r_<{}^n\rangle/a_i{}^{n+1}$'s are in reasonable agreement with the values quoted by Piper and Carlin[19] for which Hartree–Fock radial wave functions were used. It can be seen that, at the large distances with which we are concerned, *Ds* is by far the more important parameter. For distortions in the nearest neighbor ligands, *Dt* is far more significant than in the present case. The $\Delta g_{\mathrm{calcd}}$ values in Table II were calculated for the $\mathrm{CoCl_4}^{2-}$ ions using eq 4 with $\Delta(^4\mathrm{T}_2)$ as given by eq 5 and 6 for the two models. *Ds* and *Dt* values as a function of a_i are reported in colums 2 and 3. The literature values of Dq = 300 cm^{-1} and $\lambda = -180$ cm^{-1} were employed.[14]

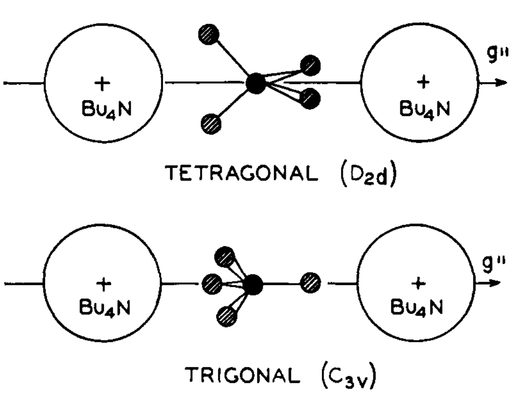

Figure 4. Ion-pair models selected for point-charge calculations.

Table II. Comparison of Experimental and Calculated *g*-Tensor Anisotropies in $[\mathrm{Bu_4N}]_2\mathrm{CoCl_4}$

a_i,[c] Å	*Ds*, cm^{-1} [d]	*Dt*, cm^{-1} [d]	$-\Delta g_{\mathrm{calcd}}$,[a] Tetragonal	$-\Delta g_{\mathrm{calcd}}$,[a] Trigonal	$-\Delta g_{\mathrm{exptl}}$[b]
4	271	4.34	6.1×10^{-3}	6.7×10^{-2}	2.6×10^{-2}
5	133	1.42	2.0×10^{-3}	3.3×10^{-2}	4.8×10^{-2}
6	76.8	0.566	7.9×10^{-4}	1.9×10^{-2}	8.1×10^{-2}
8	32.4	0.135	1.9×10^{-4}	7.8×10^{-3}	1.9×10^{-1}
10	16.6	0.044	6.2×10^{-5}	4.6×10^{-3}	3.6×10^{-1}

[a] Calculated from the ionic model, using tetragonal and trigonal excited-state diagonal matrix elements, eq 5 and 6. [b] The *g*-tensor anisotropy required to account for the experimental shifts at the ion-pairing distances indicated. [c] Ion-pairing distances, N$^+$–metal. [d] Radial parameters calculated from eq 8 and 9.

Experimental *g*-tensor anisotropies ($\Delta g_{\mathrm{exptl}}$) were calculated using the nmr data for the $\mathrm{H_l}$ proton. For $\mathrm{CoCl_4}^{2-}$ we have $\Delta\nu_{\mathrm{l}}$ = 125 Hz. Values of $\langle(3\cos^2\theta - 1)/R_i{}^3\rangle$ for $\mathrm{H_l}$ were calculated from the relation of LaMar[3] (eq 10), where d, the nitrogen–$\mathrm{H_l}$ distance, is

$$\langle(3\cos^2\theta - 1)/R_i{}^3\rangle = \frac{2[a_i{}^2 - 1.25d^2]}{a_i{}^3[a_i{}^2 - d^2]} \quad (10)$$

2.11 Å. $g_{\parallel} - g_{\perp}$ was then obtained from the dipolar shift equation (1) using $\beta = 0.927 \times 10^{-20}$ erg/G, $k = 1.38 \times 10^{-16}$ erg/deg, with T = 300°K, and $\nu_0 = 60 \times 10^6$ Hz. Since the trigonal splitting is far larger than the tetragonal splitting, Δg for the trigonal model is far larger than that for the tetragonal at equal distances. Thus, good agreement between observed and calculated Δg's occurs at an ion-pairing distance between 6 and 4 Å in the trigonal model, while unreasonably close distances are required in the tetragonal case for agreement. Of course, these comparisons are only order of magnitude, for the $\mathrm{CoCl_4}^{2-}$ is most probably rapidly rotating and the pseudocontact shift arises

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(19) T. S. Piper and R. L. Carlin, *J. Chem. Phys.*, **33**, 1208 (1960).

(20) G. Burns, *ibid.*, **41**, 1521 (1964).

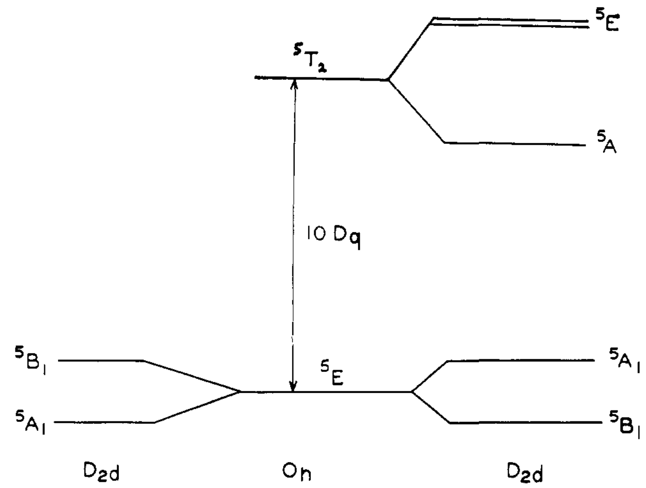

Figure 5. The effect of tetragonal fields on the quintet states of tetrahedral iron(II).

from some average g-tensor anisotropy of some complex structure.

A correction for off-diagonal matrix elements and configuration interaction with the excited states $E(^4T_1)$ in the tetragonal model for cobalt(II) was applied using a matrix diagonalization program.[21] Inclusion of the $E(^4T_1)(e^3t^4)$ and $E(^4T_1)(e^2t^5)$ states in the calculation causes a doubling of the splitting of $^4T_2$ obtained from the diagonal elements. The improvement thus introduced is not sufficiently marked to warrant a more extended treatment of the problem.

Cation-Induced Distortion of the Anion. It is possible that the cations may cause an elongation of the tetrahedron because of their electrostatic attraction for the residual charge on the coordinated halides. Evaluation of the axial field matrix elements for a distorted tetrahedron[22] follows the same lines discussed above. If we assume a 4.7° reduction in the polar angle (as a limiting case) and we use[19] values of $\langle r_<^2/a_i^3\rangle$ and $\langle r_<^4/a_i^5\rangle$ for cobalt(II), we find that the T_2 state is now split by 163 cm^{-1}, giving rise to a g-tensor anisotropy of -2.6×10^{-2}, certainly sufficient to explain the shifts observed in the tetrahalocobaltates. Although the net induced distortion is unknown, it is clear that a combination of the cation perturbation of the d orbitals and distortion induced axial fields is sufficient to explain our data. Studies[11] of the complexes $[Et_4N]_2CuCl_4$ and $[Et_4N]_2$ $CoCl_4$ in the region 200–400 cm^{-1} in nitromethane reveal that the infrared-active ν_3 and ν_4 modes (T_2 in T_d symmetry) are split in the case of copper(II) but not in the case of cobalt(II). The inference is that angular distortions produced by ion pairing are probably not of sufficient magnitude to result in a splitting of these modes.

We have attempted to verify the existence of ion-pair-induced excited-state splittings by studying the optical spectra of $[Bu_4N]_2CoBr_4$ at 0.25 M in dichloromethane and in propylene carbonate (ϵ 69), in which little ion pairing is expected. Comparison of spectra in the two solvents reveals no differences either in band positions or widths. Optical spectra therefore appear too insensitive to detect excited-state splittings of the magnitude found in this work.

Effect of Micellar Structures. In polyelectrolyte solutions, such as the present case, the role of highly aggregated anion–cation clusters (micelles) is probably a large one. The simple ion-pair model is probably a fair model for these systems. A consideration of the form of the expressions for Ds and Dt reveals that the contributions of point charges drops off as a_i^{-3} and a_i^{-5}, respectively. This indicates that only the nearest neighbors for which a_i = 6–10 Å have a significant contribution to the axial potential. (A cation 20 Å from the anion contributes only $^1/_8Ds$, or $^1/_{32}Dt$ of a cation 10 Å away.) Thus the ion-pair model is accurate in this situation and the significant ambiguity is that we do not know the exact arrangement and number of near neighbors.

We shall proceed to a discussion of the specific complexes providing examples which illustrate the amount of information that can be obtained about the electronic structure of complexes with this technique.

Iron(II). The ground state in purely tetrahedral symmetry is ^5E. The effect of spin–orbit coupling is to give rise to A_1, A_2, E, T_1, and T_2 terms, but since spin–orbit coupling is small (λ 100 cm^{-1}), the possibility of Jahn–Teller distortion arises.

The esr results on a number of trigonally coordinated complexes of copper(II) (^2E), whose electronic structures are essentially analogous to that of tetrahedral iron, indicate the existence of Jahn–Teller distortions. Since trigonal chelation should preserve the degeneracy of the ^2E ground state, the observation of rhombic symmetry at low temperatures can be attributed to the intrinsic tendency of this ion to distort.[23,24]

The solution spectra of tetrachloroferrate(II)[25] indicate that the excited $^5T_2$ state is not greatly split; however, results obtained in the $[Et_4N]_2Fe[NCS]_4$[26] and FeS[27] lattices indicate that this state is split by 1100 and 900 cm^{-1}, respectively. The effect of axial distortions on the quintet levels is as shown in Figure 5. Although the size of the ground-state splitting can only be guessed, we shall treat the Jahn–Teller splitting as a dynamic one in the free ion MX_4^{2-}.

We assume that the resulting distortion leads to D_{2d} symmetry or lower. One potential minimum results on expansion of the X–M–X angle from tetrahedral; the other results on compression of the X–M–X angle. At ordinary temperatures, both minima can probably be very nearly equally populated. The two minima correspond to the probable A_1 (^5E) or B_1 (^5E) ground states. The introduction of cations in close proximity to the anion can alter the anion potential surface, causing preferential population of either the A_1 or B_1 levels. The expressions for the g factors for these levels are as follows.[28]

For A_1 (^5E)

$$g_{\parallel} = 2 \tag{11a}$$

$$g_{\perp} = (2 - 6\lambda)/(10Dq + C) \tag{11b}$$

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[28] J. S. Griffith, "The Theory of Transition Metal Ions," Cambridge University Press, London, 1961, p 352.

and for B_1 (^5E)

$$g_{\|} = (2 - 8\lambda)/10Dq \tag{12a}$$

$$g_{\perp} = (2 - 2\lambda)/(10Dq + C') \tag{12b}$$

where C and C' are linear functions of the axial field parameters Ds and Dt and are so small compared to $10Dq$ as to be insignificant.

The g-tensor anisotropies can be written in this approximation as

$$g_{\|} - g_{\perp} = 6\lambda/10Dq \text{ for } A_1\,(^5E) \tag{13a}$$

$$g_{|} - g_{\perp} = 6\lambda/10Dq \text{ for } B_1\,(^5E) \tag{13b}$$

It is now possible to assign the ground state in tetragonal fields from the direction of the nmr shift, a particularly interesting result in the absence of esr studies on tetrahedral iron(II) salts. The upfield nmr shifts require a negative value of ($g_{\|} - g_{\perp}$). Since spin-orbit coupling is negative, this condition requires $^5A_1$ (^5E) to lie lowest in ion-paired $FeCl_4^{2-}$. The same reasoning applied to the g values in pseudotetragonal $Cr(H_2O)_5SO_4$ leads to the opposite conclusion, namely that $^5B_1$ (^5E) lies lowest.[29] This is also found to be the case in the great majority of tetragonal and square-planar copper(II) compounds studied.[30]

We will now use the point-charge model to calculate the proton shifts for the iron(II) complexes, by analogy with cobalt(II). The solution spectral data of Furlani[25] give $Dq = 400\ \text{cm}^{-1}$ with $\lambda = -90\ \text{cm}^{-1}$, which, when substituted into eq 13a give a calculated Δg of -0.135. Inclusion of the positive tetragonal field parameters reduces this to -0.125, a correction of only 10%, and therefore not very significant. Experimental Δg values were calculated as for the cobalt(II) case, using $S = 2$ and $\Delta\nu = 187$ Hz; $3g_{\|} + 4g_{\perp}$ was estimated from $g_{\perp} \simeq g_{\|} = 2.1$ (this is a good approximation for $\Delta g = 0.1$).

The experimental Δg's are compiled in Table III as a function of ion-pairing distance. Internal consistency with our previous discussion of cobalt(II) is seen, for the agreement occurs over the same range of ion-pairing distances as for cobalt(II).

Table III. Comparison of Observed and Calculated g-Tensor Anisotropies for $[Bu_4N]_2FeCl_4$

a_i, Å[a]	$-\Delta g_{\text{exptl}}$[a]	$-\Delta g_{\text{calcd}}$[a,b]
4	2.71×10^{-2}	
6	8.54×10^{-2}	1.25×10^{-1}
10	3.87×10^{-1}	

[a] All definitions are as in Table II. [b] Calculated using eq 13a.

Cobalt(II). Now we shall consider variation in the magnitude of the pseudocontact shifts for various cobalt(II) complexes in the framework of the point-charge model. One of the principal effects on Δg, hence on the dipolar shifts, will be the position of the ligand in the spectrochemical series, and we expect the shifts to vary inversely with $10Dq$. We thus expect for a constant axial splitting that the results for $\Delta\nu$ will be $CoI_4^{2-} > CoBr_4^{2-} > CoCl_4^{2-} > Co(NCO)_4^{2-}$. Since the term ($3g_{\|} + 4g_{\perp}$) follows the same order, it is not surprising that the shifts for the halides observed in Table I correspond roughly to these predictions. It is most unlikely that the interionic distances can be pinpointed with any accuracy for this system of compounds. We estimate that for MCl_4^{2-}, MBr_4^{2-}, and MI_4^{2-}, the interionic distances increase only slightly with increasing size of halide ion.

The splitting of the $^4T_2$ state is critically dependent on the ion-pair distance a_i as is evident from Table II. A tabulation of the anionic radii estimated from crystallographic metal–ligand distances is contained in Table IV. The considerably greater radius of the tetrathiocyanato ion is readily apparent. The greater ion-pairing distance in this ion produces a smaller axial field at the cobalt atom, and in addition, the $\langle(3\cos^2\theta - 1)/R_i^3\rangle$ term will be smaller at the cation protons. These two effects reinforce one another and account successfully for the drastically reduced proton shifts in the $Co(SCN)_4^{2-}$ complex. It is somewhat surprising to note that the proton shifts for $Co(NCO)_4^{2-}$ are larger than those for the corresponding $Co(NCS)_4^{2-}$ ion. Thiocyanate ion is a slightly stronger field ligand than cyanate toward cobalt(II) (OCN^-, $Dq = 4150\ \text{cm}^{-1}$; SCN^-, $Dq = 4550\ \text{cm}^{-1}$ [31]). Both complexes are known to bond to Co(II) through nitrogen.[31] Although our knowledge of the bond angles in solution is sketchy at best, it seems possible that the ion-pairing distance is somewhat shorter in $Co(NCO)_4^{2-}$ than in $Co(NCS)_4^{2-}$. A possible explanation lies in the greater van der Waals radius of sulfur. An additional complication arises from the known variation[26,32] in the M–N bond length and the M–N–C angle in coordinated thiocyanates.

Table IV. Radii of CoX_4^{2-} Ions

X^-	Radius,[b] Å	Ref
Cl^-	2.34	*c*
I^-	2.63	*d*
NCS^- ($\theta = 120°$)[a]	4.35	*a*
NCS^- ($\theta = 180°$)[a]	8.1	

[a] The radius of the $Co(NCS)_4^{2-}$ ion was calculated from a known Co–N distance of 2.15 Å in $K_2Co(NCS)_4\cdot 4H_2O$ (G. S. Zhadanov and Z. V. Zvonkova, *Zh. Fiz. Khim.*, **24**, 1339 (1950)) and Co–N–C angles (θ) of 120 and 180°. The NCS distances are N–C = 1.25 Å and C–S = 1.59 Å (Z. V. Zvonkova and G. S. Zhdanov, *ibid.*, **23**, 1495 (1949)). The angular variation is necessary due to the seemingly large variation seen in complexes of coordinated thiocyanate.[29] [b] The radius quoted here is the crystallographic radius between centers and does not include halide–ligand van der Waals contributions. [c] M. M. Powell and A. F. Wells, *J. Chem. Soc.*, 359 (1935). [d] T. I. Malinovskii, *Kristallografiya*, **2**, 734 (1957).

The effect of variation in the M–N–C angle on the anion radius is dramatically illustrated in Table IV. If for some unknown reason, the Co–N–C angle is close to 180° for $Co(NCS)_4^{2-}$ in solution while in the $Co(NCO)_4^{2-}$ ion it is bent toward 120°, a smaller shift would be expected in the thiocyanate complex.

The shifts of the H_1 protons were calculated for the ion pairs in CoI_4^{2-} and $Co(NCS)_4^{2-}$. For CoI_4^{2-}, the ion-pair distance was arbitrarily set at 6 Å, yielding,

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from Table II, $Ds = 76.8\ \text{cm}^{-1}$ and $Dt = 0.566\ \text{cm}^{-1}$. Using $\lambda = 180\ \text{cm}^{-1}$ and $10Dq = 2650\ \text{cm}^{-1}$, eq 4 gives in the trigonal model $\Delta g = 2.40 \times 10^{-2}$. $3g_{\parallel} + 4g_{\perp}$ was set equal to $7g_{\text{av}}$; g_{av} was obtained from $\mu_{\text{eff}} = g_{\text{av}}\sqrt{S(S + 1)}$. Since $\mu_{\text{eff}} = 4.77$ BM,[14] $7g_{\text{av}} = 17.3$. Since, at 6 Å, $\langle(3 \cos^2 \theta - 1)/R_i^3\rangle$ for $H_1 = 8.95 \times 10^{-3}$ Å^{-3}, eq 1 yields $\Delta\nu = 38.6$ Hz.

For $Co(SCN)_4^{2-}$, $10Dq = 4550\ \text{cm}^{-1}$ and, assuming ion-pairing distance of 8 Å, we get $Ds = 32.4\ \text{cm}^{-1}$, $Dt = 0.135\ \text{cm}^{-1}$, and $(\langle 3 \cos^2 \theta - 1)/R_i^3\rangle = 3.70 \times 10^{-3}$ Å^{-3}. Since $\Delta(^4T_{2g})$ is 49 cm^{-1}, Δg is 3.25×10^{-3}. From magnetic data, $7g_{\text{av}} = 16.0$, and eq 1 yields $\Delta\nu_1 = 2$ Hz.

Despite the crudity of the models we have selected, the above crystal field calculation certainly differentiates between the halo and thiocyanate complexes, as is required by experiment.

Nickel(II). Several features are particularly apparent on examining the pseudo-contact-shift data for tetrahedral nickel complexes. The *g*-tensor anisotropies are of opposite sign to those found in cobalt(II) and iron(II) as evidenced by the downfield shifts. The same behavior was found by LaMar[3] in the series $[Bu_4N]^+(C_6H_5)_3PMI_3^-$. They are also smaller in magnitude in nickel, as compared to the corresponding cobalt(II) complex, as can be seen from Table V. The magnitudes of the proton shifts decrease regularly from chloride to iodide, in the opposite direction from the observed pattern for cobalt(II) and the expected behavior for an orbital singlet ground state.

Table V. Calculated *g*-Tensor Anisotropies for Some Co(II) and Ni(II) Complexes

Anion	$-\Delta g_{\text{exptl}}$[a]	$\Delta g(\text{Ni})/\Delta g(\text{Co})$[b]
$CoCl_4^{2-}$	8.1×10^{-2}	0.69
$NiCl_4^{2-}$	5.6×10^{-2}	
$CoBr_4^{2-}$	9.4×10^{-2}	0.50
$NiBr_4^{2-}$	4.6×10^{-2}	

[a] Calculated from eq 1, using $\langle(3 \cos^2 \theta - 1)/R_i^3\rangle = 8.95 \times 10^{21}$ cm^{-3} for an ion-pair distance of 6 Å. [b] This ratio is the same for all ion-pairing distances.

The key to this behavior lies in the complexity of the magnetic interactions for an orbitally degenerate ground state. For nickel(II), the spin-orbit coupling and axial field simultaneously perturb the low-lying tetrahedral $^3T_1(F)$ state making any simple predictions concerning the arrangement of perturbed levels dangerously inadequate; it is thus impossible to rationalize the observed shift order with a simple theoretical approach, as was possible in the case of cobalt(II).[33] In fact, owing to the complex effects of the changes in the parameters *B* and *Dq*, and the extent of p-d mixing on the magnetic properties of tetrahedral nickel[34] with changes in halide, it is surprising that a trend in the shifts exists at all.

A particularly interesting feature of the shifts in the nickel(II) complexes is the peculiar behavior of the H_1 proton. The theory of LaMar,[3] as applied to axially symmetric complexes, requires that $\Delta\nu_1 \gtrless \Delta\nu_2$; *i.e.*, all the cation protons should shift in one direction. Examination of molecular models reveals the possibility of close halide ion approach to the H_1 protons for several relatively strain-free cation configurations. It is therefore possible for a small contact shift opposite in sign to the pseudocontact shift to occur here, *via* direct overlap with spin-containing orbitals of the anion. Such an effect would also presumably be present in the cobalt(II) complexes but is not identifiable as such due to the far larger pseudocontact shift in the same direction. The contact effect at H_1 is largest in NiI_4^{2-} where H_1 moves 17 Hz *upfield* and decreases to $NiCl_4^{2-}$, where the expected pseudocontact shift behavior is observed. This effect can perhaps be best understood in terms of the decreasing spatial extension of the spin-containing orbital in the order iodide > bromide > chloride. A further treatment of this behavior in hydrogen-bonding systems will be the subject of a future publication from this laboratory.

Acknowledgment. The authors acknowledge partial support of this research by the National Science Foundation through Grant GP 5498. I. M. Walker is grateful to the National Institute of General Medical Sciences for a Postdoctoral Research Fellowship.

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