a disruption of the water around the complex would account for the higher entropies and more endothermic enthalpies of the β-mercaptopropionate complexes compared to their α analogs.

Acknowledgment.—This research was supported by the United States Atomic Energy Commission under Contract AT-(40-1)-1797. The NSF assisted *via* a grant to The Florida State University Computer Center.

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Ion Pairing and Interionic Distances in Solution. Proton Magnetic Resonance Shifts of the Butyltriphenylphosphonium Ion in the Presence of Paramagnetic Anions[1]

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Received July 2, 1968

The observation[2-5] of large proton chemical shifts for diamagnetic cations in the presence of certain paramagnetic anions is perhaps the most sensitive technique for detecting ion pairing or aggregation in solution. These shifts (resonance frequency displacements from their diamagnetic positions) result from a dipolar interaction between the unpaired electron spin and the nuclear spin and generally occur when one of the ions in the ion pair exhibits significant magnetic anisotropy and there is a preferred orientation of the partners.[3] Dipolar shifts $\Delta\nu_D$ for axially symmetric octahedral cobalt(II) systems are given by[6-8]

$$\Delta\nu_D = -[\beta^2\nu S'(S'+1)/3kT][f(g)]\langle(3\cos^2\chi - 1)/R^3\rangle_{av} \quad (1)$$

where S' is the effective spin quantum number and $f(g)$ is a function of the g values and g-tensor anisotropy. Its value depends on the relative magnitudes[8] of the Zeeman anisotropy energy, the correlation time for tumbling in solution, and the electron spin-lattice relaxation time. The final factor in eq 1 is known as the geometric factor. χ is the angle made by a vector from the paramagnetic ion to the nucleus in question with the principal ligand field axis; R is the length of this vector. Very likely equations of similar form hold[8] for the present tetrahedral d^7 and d^8 systems. Thus far, dipolar shifts related to ion pairing have been observed for only symmetric cations: tetraalkylammonium ions[2-4] and the tetraphenylarsonium ion.[5] No studies wherein the *anion* size has been varied for related species have been reported. The present investigation deals with complexes of the type $[C_4H_9(C_6H_5)_3P][M(C_6H_5)_3PX_3]$ (M = Co, Ni; X = Br, I), involving an unsymmetrical cation and related anions of differing size.

Preparation of Complexes.—The complexes were prepared by the following general procedure. Equimolar quantities of butyltriphenylphosphonium halide and triphenylphosphine were dissolved in hot butanol and added to a hot, filtered solution of anhydrous metal halide in the same solvent. The resulting crystals were washed with butanol and ether and recrystallized. Analytical and other pertinent data are listed in Table I.

TABLE I
ANALYTICAL[a] AND SYNTHETIC DATA

Compound	Analyses, % Calcd C	Analyses, % Calcd H	Analyses, % Found C	Analyses, % Found H	Recrystallized from	Mp, °C	Color
$[(C_4H_9)(C_6H_5)_3P][Co(C_6H_5)_3PBr_3]$	54.57	4.47	54.27	4.65	Nitromethane–ether	188–188.5	Blue
$[(C_4H_9)(C_6H_5)_3P][Ni(C_6H_5)_3PBr_3]$	54.59	4.47	54.03	4.44	Butanol	182.5–183.5	Green
$[(C_4H_9)(C_6H_5)_3P][Co(C_6H_5)_3PI_3]$	47.04	3.85	47.17	3.97	Chloroform–ethyl acetate	168–169	Dark green
$[(C_4H_9)(C_6H_5)_3P][Ni(C_6H_5)_3PI_3]$[b]	47.05	3.85	46.88	4.03	Nitromethane–ether	160	Green

[a] Galbraith Laboratories, Knoxville, Tenn. [b] The reaction solvent has 3:1 butanol–ethyl acetate.

Pmr Results and Discussion.—The cation pmr spectra for the $Co(C_6H_5)_3PBr_3^-$ and $Ni(C_6H_5)_3PBr_3^-$ salts along with that of diamagnetic $[C_4H_9(C_6H_5)_3P][Br]$ are shown in Figure 1. The cation phenyl proton dipolar shifts, together with their widths at half-height, are given in Table II. The cation phenyl proton resonances are shifted upfield for the cobalt and downfield for the nickel complexes owing to the opposite senses of the magnetic anisotropies in the two cases. The cation phenyl resonances of $[C_4H_9(C_6H_5)_3P][Ni(C_6H_5)_3PI_3]$ were not resolved and will not be considered further. The butyl proton resonances (Figure 1) are shifted in the same sense as the phenyl resonances, but the individual methyl and methylene peaks are not as well resolved as they were for the $(C_4H_9)_4N^+$ salts.[2] The resonances observed for the anion triphenylphosphine protons correspond very well with those reported for the $M(C_6H_5)_3PI_3^-$ ions in salts of other cations.[2,5]

Estimates of interionic distances can, in principle at least, be made from observed dipolar shifts or shift ratios (eq 1). Such estimates have been made[5,9] for interionic distances between $Co(C_6H_5)_3PI_3^-$ and the

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[1] This research was supported by the National Science Foundation through Grant GP 6321.

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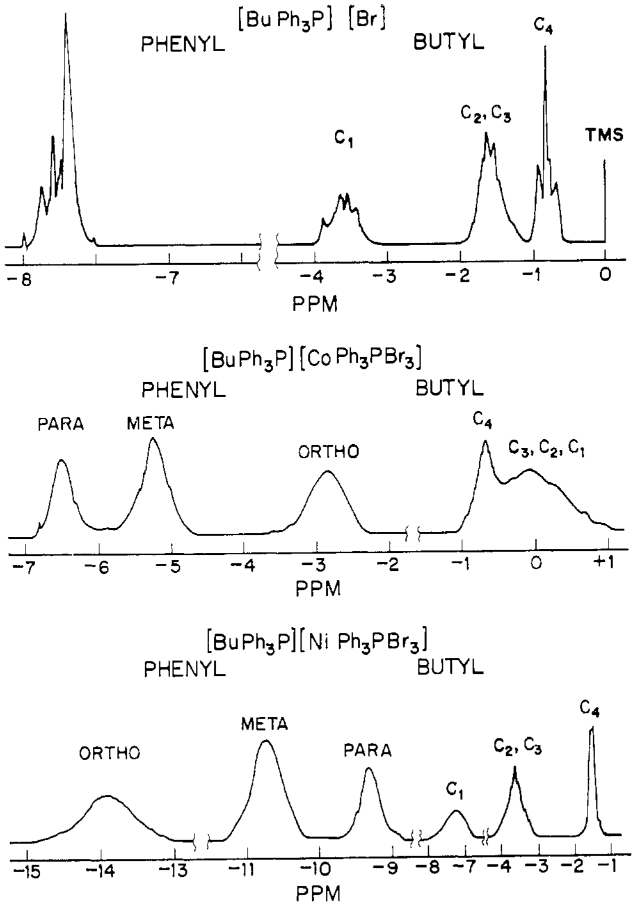

Figure 1.—Spectra of diamagnetic $[C_4H_9(C_6H_5)_3P][Br]$ and paramagnetic $[C_4H_9(C_6H_5)_3P][Co(C_6H_5)_3PBr_3]$ and $[C_4H_9(C_6H_5)_3P][Ni(C_6H_5)_3PBr_3]$ in deuteriochloroform at 30°. The phenyl and butyl resonances have different ordinate scales.

TABLE II

CATION PHENYL PROTON MAGNETIC RESONANCE DATA[a]

	Anion		
	$Co(C_6H_5)_3PBr_3^-$	$Ni(C_6H_5)_3PBr_3^-$	$Co(C_6H_5)_3PI_3^-$
Concn, *M*	0.0380	0.0432	0.0376
Dipolar shifts,[b,c] ppm			
ortho	4.92	−6.12	3.28
meta	2.48	−2.97	1.82
para	1.28	−1.53	1.00
Dipolar shift ratios			
ortho/meta	1.98 ± 0.10	2.06 ± 0.09	1.81 ± 0.13
meta/para	1.94 ± 0.20	1.93 ± 0.17	1.82 ± 0.25
ortho/para	3.83 ± 0.34	3.99 ± 0.29	3.28 ± 0.39
Line widths at half-height, Hz			
ortho	44	46	32
meta	26	25	21
para	20	14	20
Corrected[d] line width ratios			
meta/ortho	0.43	0.38	0.44
para/ortho	0.27	0.10	0.40

[a] Measured on deuteriochloroform solutions at 30° using TMS as an internal standard and a Varian A-60A instrument. [b] From the diamagnetic chemical shift of −7.75 ± 0.08 ppm from TMS. [c] These resonances follow a reciprocal temperature dependence between −50 and 50°. [d] Spin–spin and diamagnetic contributions of 10 Hz (*meta* and *para*) and 7 Hz (*ortho*) have been subtracted from the measured widths.

$(C_4H_9)_4N^+$ and $(C_6H_5)_4As^+$ ions. The model employed in order to evaluate the geometric factors consisted of the approach of the cation along the C_3 axis of the anion on the side opposite the bulky triphenylphosphine ligand. This model necessarily involves rotational orientations of the cation as it approaches with its center on the C_3 axis of the anion. For comparison purposes, the present results will be analyzed in terms of this model although it is subject to some criticism (*vide infra*).

Within the above framework, two models will be considered for calculation of average values of the geometric factors. The C_3 axis of the anion may be coincident with a "C_3" axis of the pseudo-tetrahedral cation (C_3 model) or with a "C_2" axis of the cation (C_2 model). In both cases the various possible phenyl orientations were weighted to take into account the fact that the butyl group is one of the four cation substituents. No bias was given to configurations with the butyl group either toward or away from the anion. Phenyl groups were allowed free rotation about the *p*-hydrogen–phosphorus axis. Average values of the geometric factors were calculated on an IBM 7094 computer for the three sets of cation phenyl protons (*ortho*, *meta*, *para*). The calculated ratios of these as a function of interionic distance are shown in Figures 2 and 3 for the two models.

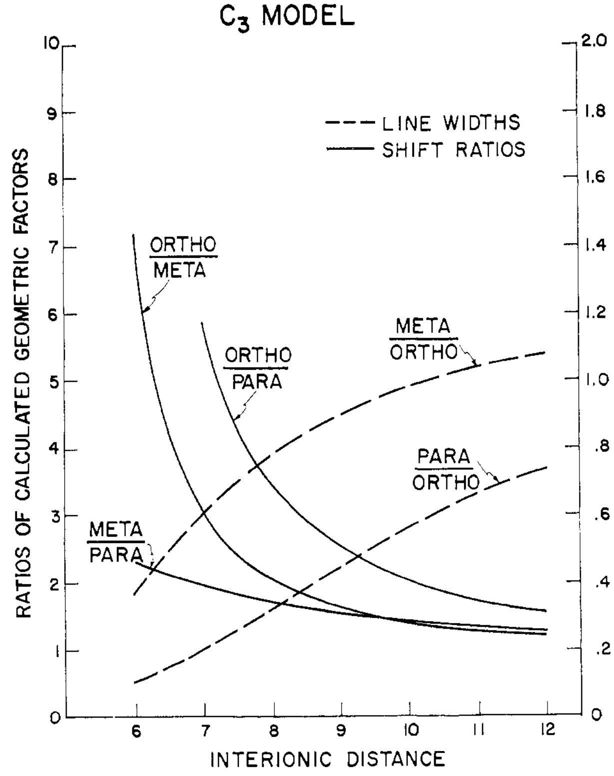

Figure 2.—Ratios of calculated geometric factors and relative line widths *vs.* interionic distance for the C_3 model.

Table III gives the predicted interionic distances (metal to phosphorus) obtained by comparing the observed shift ratios (Table II) with those predicted (Figures 2 and 3). The uncertainties quoted arise primarily from uncertainty in the diamagnetic resonance position.

Table III

Estimated Interionic Distances and Predicted Line Width Ratios

	Anion		
	$Co(C_6H_5)_3PBr_3^-$	$Ni(C_6H_5)_3PBr_3^-$	$Co(C_6H_5)_3PI_3^-$
	C_3 Model		
Interionic separation obtained from ratio, Å			
ortho/meta	8.1 ± 0.2	8.0 ± 0.2	8.5 ± 0.4
meta/para	7.0 ± 0.9	7.1 ± 0.8	7.6 ± 1.4
ortho/para	7.8 ± 0.2	7.7 ± 0.2	8.2 ± 0.4
Mean separation, Å	7.6 ± 1.0	7.6 ± 1.0	8.1 ± 1.0
Predicted line width ratio at mean separation			
meta/ortho	0.71	0.71	0.80
para/ortho	0.28	0.28	0.34
	C_2 Model		
Interionic separation obtained from ratio, Å			
ortho/meta	7.3 ± 0.1	7.2 ± 0.1	7.5 ± 0.2
meta/para	8.3 ± 0.5	8.3 ± 0.5	8.6 ± 0.8
ortho/para	7.7 ± 0.1	7.7 ± 0.1	7.9 ± 0.2
Mean separation, Å	7.8 ± 1.0	7.7 ± 1.0	8.1 ± 1.0
Predicted line width ratio at distance of mean separation			
meta/ortho	1.85	1.84	1.86
para/ortho	0.65	0.63	0.70

Several features are noteworthy. The three ratios obtained from the C_3 model predict interionic distances which are within the uncertainties of each other while this is not true for the C_2 model. However, the mean interionic separation obtained from each model is identical within the uncertainties quoted. Two features attest to the validity, or at least the consistency, of the present approach. First, despite the fact that the dipolar shifts are in ***opposite*** directions for the $Co(C_6H_5)_3PBr_3^-$ and $Ni(C_6H_5)_3PBr_3^-$ ions, the estimates of interionic distance are identical. Second, in the comparison afforded by the results on anions containing different halogens, the counterion separation was greater for $Co(C_6H_5)_3PI_3^-$ than for $Co(C_6H_5)_3PBr_3^-$. The estimated difference of 0.5 Å is roughly that which one would expect from a consideration of the difference in van der Waals radii[10] of bromine and iodine atoms. For the $Co(C_6H_5)_3PI_3^-$ systems the estimated interionic distance for $C_4H_9(C_6H_5)_3P^+$ (8.1 Å) is slightly less than that estimated[5] for $(C_6H_5)_4As^+$ (9.0 Å); this is reasonable in view of the smaller covalent radius of phosphorus and the lesser steric requirements of the butyl group.

The observed line widths are less useful in estimating the interionic distances. The uncertainties in the relatively narrow measured line widths and the corrections which must be applied for intrinsic diamagnetic width and the effect of spin–spin coupling render the ratios particularly uncertain. The predicted line width ratios for a $\langle 1/R^6\rangle_{av}$ line width dependence are given in Figures 2 and 3 and the values obtained for the interionic distances estimated from the shifts are listed in Table III. Qualitatively the agreement is better for the C_3 model; however, little can be concluded from the lack of quantitative agreement in view of the large uncertainties involved. Furthermore it has been shown theoretically[11] and confirmed experimentally[12] that there is an angular dependence on dipolar relaxation in the presence of *g*-tensor anisotropy. For the relatively small anisotropy expected for the present tetrahedral species[2,3] this angular dependence is probably negligible.

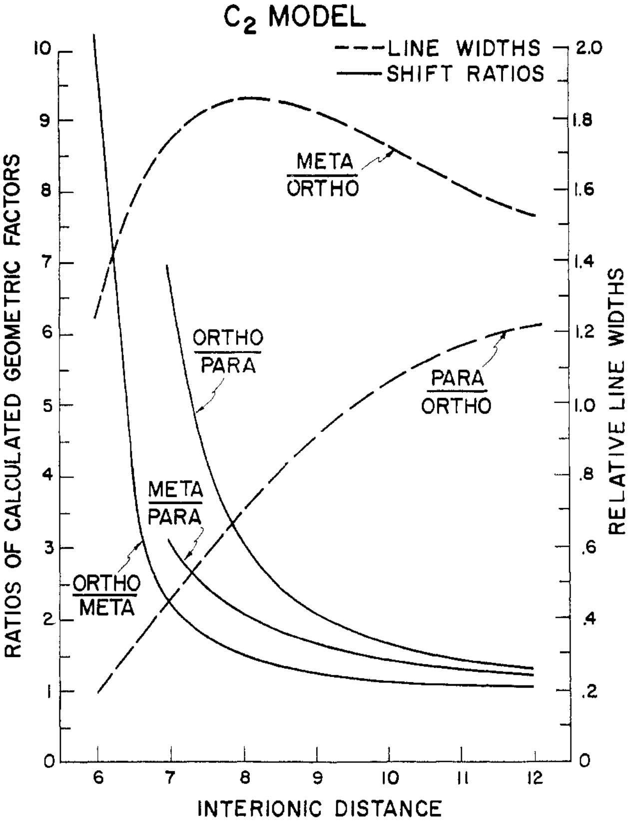

Figure 3.—Ratios of calculated geometric factors and relative line widths *vs.* interionic distance for the C_2 model.

The ion-pair model used here and previously may not be entirely realistic, particularly with respect to restriction of the mode of approach of the cation to along the C_3 axis of the anion A recent crystal structure determination of $[(C_6H_5)_4As][Ni(C_6H_5)_3PI_3]$[13] has shown the following features to be true in the *solid state.* Four symmetry-related cations approach a particular anion to within 6.6–8.0 Å, values which are all less than the solution-state estimate of 9.0 Å.[5] Furthermore, none of these cations approaches exactly along the C_3 axis of the anion, although the two closest do occupy positions on either side of this axis in "front" of the anion. The other two nearest neighbor cations approach almost as close, but from the side, *i.e.*, between the iodine atoms and the triphenylphosphine. Thus, while C_3 axis approach *may* be the favored one in solution, other modes of ion pairing cannot be dismissed. Insofar as these other

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modes are present, average values derived from a model which ignores them will be in error. It is not feasible to take such other modes into account in the analysis since a number of unknown parameters would be involved. It is felt, however, that while the absolute values of interionic distances predicted by the present model may be inaccurate, comparisons of sizes of related species obtained in this way are meaningful.

That the cation nuclear resonance shifts in systems like the present are of dipolar origin at all has recently been challenged. Burkert, *et al.*,[14] state that their ^{14}N resonance studies indicate that these shifts result from the Fermi contact interaction *via* direct counterion electron transfer. However, the fact that the protons of three different cations—$(C_4H_9)_4N^+$, $(C_6H_5)_4As^+$, and $C_4H_9(C_6H_5)_3P^+$—show, respectively, upfield and downfield shifts when ion paired to $Co(C_6H_5)_3PX_3^-$ and $Ni(C_6H_5)_3PX_3^-$ is unimpeachable evidence that they are predominantly dipolar in origin. Burkert, *et al.*,[14] offer no explanation for this decisive observation and in fact give no data or details of their own experiments. Their interpretation cannot be accepted.

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Stabilization of the Hexachloroferrate(III) Anion by the Methylammonium Cation

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Received July 3, 1968

In 1963 Piper and coworkers[1] prepared several compounds which they postulated as containing the hexachloroferrate(III) anion, an ion whose existence had not previously been confirmed. X-Ray powder data for one of their compounds, $[Co(NH_3)_6][FeCl_6]$, were compared with similar data for $[Co(NH_3)_6][TlCl_6]$, where the octahedral $TlCl_6^{3-}$ is known to exist from a detailed X-ray study. The very similar powder patterns suggested that the two compounds were isomorphous. In the compounds prepared by Piper, *et al.*,[1] the $FeCl_6^{3-}$ species was stabilized in the crystal lattice by a cation of similar size and equal and opposite charge. This paper reports evidence that the $FeCl_6^{3-}$ entity can exist in the solid state in association with a smaller, univalent cation.

In the course of studying the reaction of methylammonium chloride with ferric chloride in concentrated hydrochloric acid, a compound with the stoichiometry $(CH_3NH_3)_4FeCl_7$ was obtained. Upon checking the literature, it was found that a compound corresponding to this stoichiometry was first prepared and reported by Remy in 1925.[2] We propose to show that this was the first reported synthesis of the hexachloroferrate(III) anion, where the complex exists as a double salt with the formula $[CH_3NH_3]_3[FeCl_6]\cdot CH_3NH_3Cl$.

Experimental Section

Compounds.—$(CH_3NH_3)_4FeCl_7$ was obtained by dissolving 5 g of anhydrous $FeCl_3$ and 8.4 g of CH_3NH_3Cl in 50 ml of concentrated HCl, concentrating the resulting solution over a water bath, and subsequently cooling in ice. The yellow-orange product obtained was recrystallized from absolute ethanol. The resulting crystals were very hygroscopic. *Anal.* Calcd for $(CH_3NH_3)_4FeCl_7$: Cl, 57.5; Fe, 12.9. Found: Cl, 57.0; Fe, 12.6.

The compounds prepared for comparative purposes were hexaamminecobalt(III) hexachloroferrate(III), $[Co(NH_3)_6][FeCl_6]$, and tris(1,2-propanediamine)rhodium(III) hexachloroferrate(III), $[Rh(pn)_3][FeCl_6]$. Both were prepared by the method outlined by Piper, *et al.*[1] The analysis of these compounds agreed with their theoretical composition within experimental error.

Magnetic Susceptibility Measurements.—Magnetic susceptibilities were obtained at 295°K by the Gouy method on a magnetic balance of standard design using $HgCo(NCS)_4$ as a calibrant. Diamagnetic corrections were made in the usual manner and the magnetic moments were calculated using the Curie law.

Ir Measurements.—Samples were prepared in pressed polyethylene disks and their spectra were obtained on a Beckman IR-11 spectrophotometer.

Mössbauer Measurements.—Spectra were taken using an Austin Science Associates drive unit and a 30-Mc source of ^{57}Co in chromium, which gave a line width of 0.28 ± 0.01 mm/sec with a thin nitroprusside absorber. Absorbers contained about 7 mg of iron/cm^2 and were mounted in a Teflon holder maintained at 78°K in a stainless steel dewar. The results were statistically analyzed, assuming Lorentzian line shapes, using an IBM 7040 computer.

Electronic Spectral Measurements.—The electronic spectra of KBr disks containing 5% sample were recorded by a Perkin-Elmer 450 spectrophotometer. Temperature of the sample disks was maintained at 78°K.

Results and Discussion

The data obtained for the $(CH_3NH_3)_4FeCl_7$ species and for the comparative compounds, $[Co(NH_3)_6][FeCl_6]$ and $[Rh(pn)_3][FeCl_6]$, are given in Tables I and II.

The magnetic data confirm that the ground state of the iron ion in $(CH_3NH_3)_4FeCl_7$ is the expected high-spin Fe(III). The positions of the peaks in the far-infrared region for ν_3 and ν_4 are identical within experimental error for the established hexachloroferrate species and for $(CH_3NH_3)_4FeCl_7$. The Mössbauer data show agreement between the isomer shifts for the established hexachloroferrates and $(CH_3NH_3)_4FeCl_7$ and are further proof of the existence of an octahedral arrangement of chloride ions about the central iron atom. The absence of detectable quadrupole splitting and the typical width Mössbauer lines indicate a symmetrical octahedral arrangement of the chlorides about the iron atom. The electronic spectrum of $(CH_3NH_3)_4FeCl_7$ consisted of a band at 18,700 cm^{-1} and a broader, more intense band with maximum intensity at 22,400 cm^{-1} which was unsymmetrical and trailed off toward the uv region. The band at 18,700 cm^{-1} for $(CH_3NH_3)_4FeCl_7$ agrees with the band at 18,730 cm^{-1} for

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