

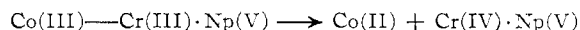
$\times 10^{-6} \text{ sec}^{-1}$ , there is negligible dissociation of this species during the course of the redox reaction.<sup>7</sup>

The most significant difference between the kinetic description of this system, compared to the reaction between the aquated Np(V) and Co(III), is the change in the empirical form of the rate law. An *a posteriori* rationale of the observations would invoke the hydrolytic preequilibrium of one of the reactants followed by the obvious rate-determining step when the Np(V)·Cr(III) complex is the reductant. In this context, *i.e.*, reduction of the net formal charge of the activated complex providing a preferred kinetic path, it is of interest to note that no system has been reported for the actinide ions with formal charge greater than +6.<sup>12</sup>

A calculation of the predicted rate constant  $k_c''$  using the formulas of the Marcus theory is not feasible on the basis of at least two considerations. First, even if the reaction does meet all of the criteria necessary for such a calculation (such as outer-sphere mechanism, favorable interaction between redox orbitals, etc.), the

(12) T. W. Newton and F. B. Baker, Paper O-30, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966.

data presented do not preclude a path in which the Co(III) attacks the complex at the Cr(III) site



Whatever the fate of the Cr(IV) in such a scheme (*i.e.*, direct electron exchange between the Cr(IV) and the Np(V) could occur, or dissociation of the complex followed by subsequent oxidation of the Np(V) and reduction of the Cr(IV)), the over-all stoichiometry and kinetics would fit the data. The data do preclude the formation of Cr(VI) in the reaction,<sup>18</sup> as would be expected from the slow rate of the oxidation of Cr(III) to Cr(VI) by Co(III).<sup>14</sup>

Second, the electron-transfer reaction between Np(VI) and Np(V)·Cr(III) has not been studied. The present work does indicate that this rate must be much slower than the Np(VI)–Np(V) exchange reaction,<sup>10</sup> since second-order kinetics were observed with respect to the metal ions.

(13) In 2 M HClO<sub>4</sub> at 25° there was no detectable oxidation of the complex (*ca.* 10<sup>-3</sup> M) by 0.01 M Cr(VI) after several hours.

(14) J. B. Kirwin, P. J. Proll, and L. H. Sutcliffe, *Trans. Faraday Soc.*, **60**, 119 (1964).

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## Ion Pairing and Interionic Distances in Solution for Paramagnetic Complexes from Proton Magnetic Resonance Shifts<sup>1a</sup>

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The proton magnetic resonance spectra have been observed for deuteriochloroform solutions of the Co(II) and Ni(II) complexes [(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>As][{(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>PM<sup>II</sup>I<sub>3</sub>}. For the cobalt complex, large cation chemical shifts arise from a dipolar (pseudo-contact) interaction between ions in an ion pair. Several models for the ion pair are postulated, and their relative dipolar shifts calculated. Best agreement between the calculated and observed shift ratios was obtained with a model in which the cation lies along the C<sub>3</sub> axis of the anion, with a cation C<sub>2</sub> axis coincident with the unique anion axis and with the two ions separated by 9.0 ± 0.8 Å. Certain other reasonable models give roughly similar results and may contribute to some extent. The validity of this method of analysis is supported both by the precision of the three estimates and by the relative line widths for the proton resonance peaks of the cation. The relative advantages of studying ion pairing from dipolar shifts and line widths are discussed.

### Introduction

It has recently been shown<sup>2</sup> that the large proton chemical shifts observed for the diamagnetic cation of an ionic, paramagnetic complex in solution are the result of a dipolar nucleus–electron interaction<sup>3</sup> between ions in an ion pair. From the pattern of observed isotropic shifts it has also been possible to estimate the interionic distance.<sup>2b</sup> Since then, such dipolar shifts have been observed in some other systems<sup>4,5</sup> where they were also related to ion association.

(1) (a) This work was supported by the National Science Foundation through Grants GP3397 and GP6321; (b) Swiss Federal Institute of Technology; (c) Princeton University.

(2) (a) G. N. LaMar, *J. Chem. Phys.*, **41**, 2992 (1964); (b) G. N. LaMar, *ibid.*, **43**, 235 (1965).

(3) H. M. McConnell and R. E. Robertson, *ibid.*, **29**, 1361 (1958).

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

This dipolar or pseudo-contact interaction<sup>3</sup> arises in a system where the metal ion possesses significant magnetic anisotropy and results in proton resonance shifts from the positions observed in a similar diamagnetic system. For a given complex, the magnitude of the fractional dipolar shift for any proton depends only on the *g* tensor, certain physical constants for the electron and proton, the temperature, and a geometric factor which relates the relative orientation of the proton with respect to the *g* tensor,<sup>3</sup> such that the relative dipolar shifts for a given complex are simply proportional to their geometric factors.<sup>2b</sup> Dipolar shifts for a cation vanish if it does not maintain a preferred orientation

(5) W. D. Horrocks, Jr., R. H. Fischer, J. R. Hutchison, and G. N. LaMar, *J. Am. Chem. Soc.*, **88**, 2436 (1966).

with respect to the complex anion. An ion-pair model was postulated for the cobalt and nickel complexes  $[(n-C_4H_9)_4N][[(C_6H_5)_3PMI_3]]$ ,<sup>2</sup> in which the cation approaches the paramagnetic anion along its  $C_3$  axis, opposite the metal-phosphorus bond.<sup>2b</sup> The more bulky triphenylphosphine ligand inhibits the close approach of the cation from any other direction. The dipolar shift,  $\Delta H_i$ , for such an axially symmetric case is given by<sup>2,6</sup>

$$\frac{\Delta H_i}{H} = -\frac{\beta^2 S(S+1)}{45kT} (3g_{\parallel}^2 + g_{\perp}^2 - 4g_{\perp}^2) \times \frac{3 \cos^2 \chi_i - 1}{R_i^3} \quad (1)$$

where  $R_i$  is the radius vector to the  $i$ th proton,  $\chi_i$  is the angle of this vector with the unique axis of the  $g$  tensor, and the other symbols have their conventional meanings.<sup>2a</sup> Based on the assumption that an ion-paired cation may take any rotational position with respect to its central atom, the averaged geometric factor for a spherical cation was shown to be<sup>2b</sup>

$$\left\langle \frac{3 \cos^2 \chi_i - 1}{R_i^3} \right\rangle_{av} = \frac{2[A^2 - 1.250Q_i^2]}{A^3[A^2 - Q_i^2]} \quad (2)$$

where  $A$  is the distance between centers in the ion pair and  $Q_i$  is the distance of a set of equivalent protons from the cation center. From a comparison of the ratios of calculated geometric factors and the observed ratios of the dipolar shifts, the equilibrium interionic separation was estimated to be 3.8 Å.<sup>2b</sup>

However, the tetra- $n$ -butylammonium cation is not an ideal subject for such calculations<sup>2b</sup> since the configuration of the alkyl chain during ion pairing is not known, and the internal rotations significantly alter the calculated geometric factors. It was previously assumed that the internal rotations about the innermost carbon-carbon bond of the butyl chain were essentially unhindered.<sup>2b</sup> This extreme case was selected owing to the lack of precedence for a more realistic model. The protons bonded to the outer two carbon atoms in the alkyl chains were not included in the calculations, since their average positions are highly uncertain. In a more recent similar analysis<sup>4</sup> of a system with tetra- $n$ -alkylammonium cations, the interionic separations were estimated by assuming another extreme, namely, that the alkyl chains were perfectly extended, with no internal rotation at all. It was also assumed that the cation had one unique rotational position with respect to the complex anion during pairing.

Our inability to calculate accurately the geometric factors for any ion-pair model due to the uncertainty of the alkyl chain configuration prompted us to look for similar ionic complexes, in which three or more equivalent sets of cation protons are rigidly disposed with respect to the center of the cation. For such a case accurate geometric factors can be calculated, and the observation of more than just two sets of inequivalent protons allows at least two independent estimates

of the interionic separation. For this purpose, the tetraphenylarsonium salts of the previously studied anions,  $[(C_6H_5)_4As][[(C_6H_5)_3PM^{II}I_3]]$ , were prepared and their pmr spectra recorded.

### The Geometric Factors

For the tetraphenylarsonium cation, the only internal rotation which could affect the geometric factor is that of a phenyl group about the As-C bond. The ion-pair model will be identical with that assumed previously,<sup>2b</sup> except that a variety of restricted orientations of the cation will be adopted as it approaches along the  $C_3$  axis of the anion, in order to ascertain which orientation accounts most satisfactorily for the observed shifts. The first case is that where the cation can take up any rotational position during ion pairing and is designated as  $S$ . This is identical with that assumed previously, except that in this case the geometric factors will *not* be affected by any internal bond rotations, so that the geometric factors can be evaluated accurately.

Two specific orientations for the tetrahedral cation were also chosen—one in which its  $C_3$  axis coincides with the unique anion axis, the other in which the cation  $C_2$  and anion  $C_3$  axes are coincident. For each of these two cases, several angles of "pitch,"  $\theta$ , for the phenyl groups were included, with zero pitch indicating that the plane of the phenyl rings oriented toward the anion will become tangent to a sphere centered on the anion as the cation approaches the anion along its unique axis. These cases are designated by  $C_2$ - $\theta$  and  $C_3$ - $\theta$ . When the angle of pitch is unrestricted, that is, the phenyl groups are free to rotate, then the models are designated just  $C_2$  and  $C_3$ .

Geometric factors were calculated as a function of interionic distance,  $A$ , for the three inequivalent sets of cation protons and for each specified orientation of the cation. The  $S$  model was calculated using eq 2, employing the bond lengths from the literature.<sup>7</sup> For the other models, no analytic formula exists, so the calculations were performed on an IBM 7094 computer.

### Experimental Section

The proton magnetic resonance spectra of tetraphenylarsonium iodide and the complexes were obtained in deuteriochloroform solution on a Varian A-100 spectrometer, operating at 100 Mc/sec. The very low solubility necessitated the use of this more sensitive spectrometer over a 60-Mc/sec machine. The solution temperature was 34°, and tetramethylsilane was used as the internal reference. The isotropic shifts are given in ppm, defined as the difference in resonance position between that observed in the paramagnetic complex and in diamagnetic tetraphenylarsonium iodide, where upfield shifts are positive.

**Preparation of Compounds. Tetraphenylarsonium Iodide.**—This compound was synthesized by a method proposed by Blick and Moore.<sup>8</sup>

**Tetraphenylarsonium Triiodotriphenylphosphinecobaltate(II).**—Equal molar quantities of tetraphenylarsonium iodide and triphenylphosphine were dissolved in butanol and a separate solution containing a 50% molar excess of cobalt(II) iodide dihydrate in butanol was prepared. (A larger amount of solvent may be

(6) G. N. LaMar, *J. Chem. Phys.*, **43**, 1085 (1965).

(7) R. C. L. Mooney-Slater, *Acta Cryst.*, **12**, 187 (1959).

(8) F. E. Blick and E. Moore, *J. Am. Chem. Soc.*, **57**, 720 (1935).

necessary for the cobalt(II) iodide than for the tetraphenylarsonium iodide and triphenylphosphine.) The solutions were filtered and combined while hot. The green crystals were separated and washed twice with butanol and twice with carbon tetrachloride; mp 236°. *Anal.* Calcd for  $[(C_6H_5)_4As][(C_6H_5)_3PCoI_3]$ : C, 46.48; H, 3.25. Found: C, 46.44; H, 3.25.

**Tetraphenylarsonium Triiodotriphenylphosphinenickelate(II).**—Equal molar quantities of tetraphenylarsonium iodide and triphenylphosphine were dissolved in butanol as was an excess of nickel(II) iodide in a separate vessel. (It was necessary to add a small quantity of water to make the nickel(II) iodide dissolve.) The solutions were filtered and mixed while hot. The resulting solution was boiled down gently until the volume was approximately one-fourth the initial volume. The hot solution and precipitate were filtered into a preheated vacuum filter. The dark red crystals were washed twice with small portions of boiling butanol and were vacuum dried at 58°; mp 237°. *Anal.* Calcd for  $[(C_6H_5)_4As][(C_6H_5)_3PNiI_3]$ : C, 46.48; H, 3.25. Found: C, 46.46; H, 3.25.

### Results and Discussion

The pmr spectrum for the cation protons of  $[(C_6H_5)_4As][(C_6H_5)_3PCoI_3]$  in deuteriochloroform is illustrated in Figure 1. The nickel complex exhibited only a single peak for the cation protons which was shifted less than 0.6 ppm downfield from its diamagnetic value. Though it is apparent that the peak is composed of two or more overlapping peaks, it is impossible to decompose the broad peak and assign the components with any certainty. The isotropic shifts for the triphenylphosphine ligand protons in both complexes correspond very well with those observed previously<sup>2</sup> and will not concern us further here.

For the cobalt complex, three cation peaks all shifted upfield are observed, with relative intensities 1:2:2 reading upfield, none of them displaying any multiplet structure. The least shifted resonance is easily identified as that due to the *para* position protons, but no experimental technique allows a definite assignment of the other two peaks. No multiplet structure appeared even upon the addition of excess diamagnetic cation, though the resonance positions shifted downfield toward those of the pure diamagnetic cation. However, on the basis of experience with the tetra-*n*-butylammonium cation, where it was noted that the dipolar shifts increase with decreasing<sup>2,5</sup> distance between the cation center and the resonating proton, an order of the shifts *ortho* > *meta* > *para* is expected. This order of shifts is clearly predicted by eq 2, such that the farthest upfield peak belongs to the *ortho* position protons. This assignment is verified by the calculation of geometric factors for every model considered except one (*vide infra*). The one exception is the  $C_3$  model with the unique phenyl group pointing toward rather than away from the anion. This model predicts *ortho* < *meta* < *para*, which is inconsistent with the observed spectrum. Therefore this model was discarded. The exact values of the dipolar shifts are given in Table I along with the ratios of shifts for any two positions. The uncertainties in the shifts arise primarily from the uncertainty in the diamagnetic resonance positions.<sup>9</sup> The ratios of the calculated geometric factors as a function of interionic distance for the models  $S$ ,  $C_2$ ,

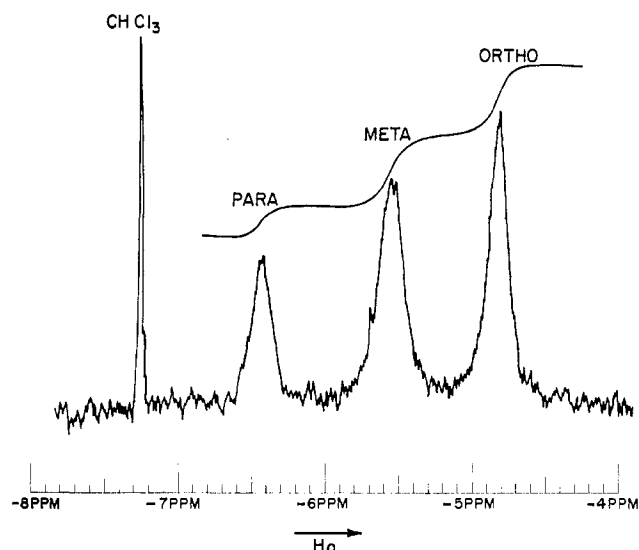


Figure 1.—Pmr spectrum of cation phenyl protons of  $[(C_6H_5)_4As][(C_6H_5)_3PCoI_3]$  in deuteriochloroform solution at 34° and integrated intensities.

TABLE I  
DIPOLAR SHIFTS FOR CATION PROTON RESONANCES IN  
 $[(C_6H_5)_4As][(C_6H_5)_3PCoI_3]^a$

Ring position	Obsd shift <sup>b</sup>	Dipolar shift <sup>c</sup>	Line width <sup>d</sup>	Obsd shift ratios
<i>ortho</i>	$-4.82 \pm 0.03$	$+2.98 \pm 0.10$	14	<i>o/p</i> $2.14 \pm 0.25$
<i>meta</i>	$-5.55 \pm 0.03$	$\pm 2.25 \pm 0.10$	22	<i>m/p</i> $1.62 \pm 0.20$
<i>para</i>	$-6.41 \pm 0.03$	$+1.39 \pm 0.10$	16	<i>o/m</i> $1.32 \pm 0.11$

<sup>a</sup> Measured in deuteriochloroform solution at 34° (<0.01 *M*).

<sup>b</sup> In ppm, recorded at 100 Mc/sec, referenced to tetramethylsilane.

<sup>c</sup> In ppm, referenced to diamagnetic  $[(C_6H_5)_4As][I]$ , whose resonance positions for all protons fall in the region  $-7.80 \pm 0.07$  ppm from TMS. <sup>d</sup> In cps at 100 Mc/sec.

and  $C_3$  are illustrated in Figures 2, 3, and 4, respectively. It is interesting to note that even though the three cation peaks for the nickel complexes are not clearly resolved, which precludes an analysis, their dipolar shifts are of opposite sign to those for the cobalt complex, as observed previously.<sup>2</sup>

In order to estimate the interionic separation for each cation orientation, that value of  $A$  was chosen for which the calculated ratios of geometric factors coincide with the observed ratios. Thus three estimates of  $A$ , two of them independent, result for each case, and the consistency of the model can be checked. The interionic distances so obtained are listed in Table II, together with the mean of the three estimates,  $A_m$ . These points are shown in Figures 2–4 by means of arrows.

The uncertainties in  $A$  arise solely from uncertainties in the observed shifts, since for a given model the geometric factor ratios may be evaluated very accurately. Thus if the three values for  $A$  obtained from the three ratios are not within their respective uncertainties, the model is discarded as unrealistic, and therefore we discard  $C_2-0^\circ$ ,  $C_3-0^\circ$ , and  $C_3-30^\circ$ . The cases  $C_3-60^\circ$ ,

(9) The diamagnetic tetraphenylarsonium iodide produced a peak with a complicated multiplet structure even at 100 Mc/sec, centered at  $-7.80$  ppm from TMS. The width of the peak indicated that all three resonances occur at  $-7.80 \pm 0.07$  ppm.

TABLE II  
 ESTIMATED INTERIONIC DISTANCES FROM THE CALCULATED GEOMETRIC FACTORS

Model	Interionic separations from obsd shift ratios, A				Calculated relative $\langle R^{-3} \rangle_{av}$ for $A_m$		
	$o/p$	$o/m$	$m/p$	$A_m^a$	$o$	$m$	$p$
$S$	$7.0 \pm 0.1$	$6.9 \pm 0.2$	$7.0 \pm 0.1$	$7.0 \pm 0.2$	1.00	10.4	65
$C_2-0^\circ$	$8.3 \pm 0.3$	$8.5 \pm 0.3$	$7.7 \pm 0.2$	$b$	...	...	...
$C_2-30^\circ$	$8.6 \pm 0.3$	$9.0 \pm 0.5$	$8.1 \pm 0.5$	$8.6 \pm 1.0$	1.00	$1.48 \pm 0.07$	$1.77 \pm 0.12$
$C_2-60^\circ$	$9.3 \pm 0.3$	$9.2 \pm 0.7$	$9.8 \pm 0.8$	$9.4 \pm 1.2$	1.00	$1.84 \pm 0.10$	$0.79 \pm 0.17$
$C_2$	$9.0 \pm 0.3$	$8.8 \pm 0.6$	$9.2 \pm 0.4$	$9.0 \pm 0.8$	1.00	$1.77 \pm 0.09$	$0.89 \pm 0.17$
$C_3-0^\circ$	$8.7 \pm 0.5$	$10.5 \pm 0.5$	$7.4 \pm 0.5$	$b$	...	...	...
$C_3-30^\circ$	$9.2 \pm 0.5$	$10.5 \pm 0.5$	$7.9 \pm 0.5$	$b$	...	...	...
$C_3-60^\circ$	$10.2 \pm 0.6$	$10.5 \pm 0.5$	$9.5 \pm 1.0$	$10.1 \pm 1.6$	1.00	$0.98 \pm 0.10$	$0.47 \pm 0.06$
$C_3$	$9.8 \pm 0.6$	$10.8 \pm 1.5$	$9.1 \pm 0.7$	$9.9 \pm 2.4$	1.00	$0.96 \pm 0.26$	$0.53 \pm 0.28$

<sup>a</sup> Mean value for the interionic distance. <sup>b</sup> The three estimates for  $A$  are not within each other's uncertainties, so the model is discarded as unrealistic.

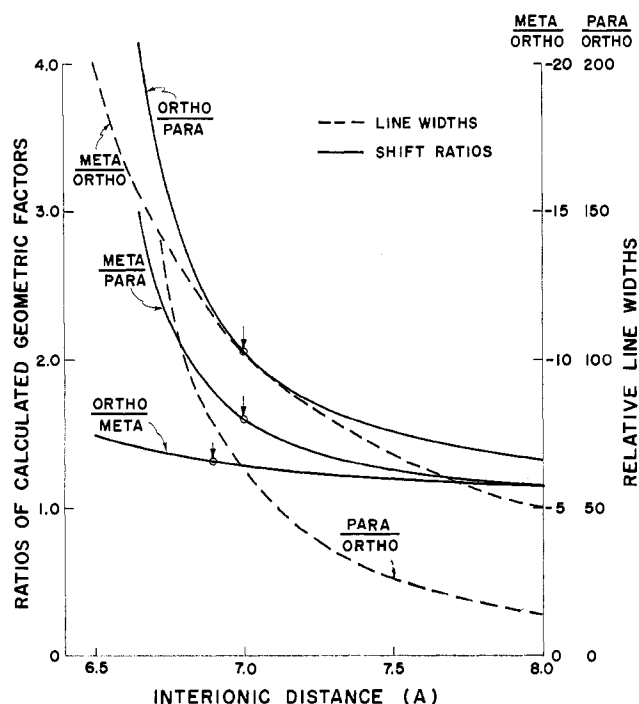


Figure 2.—Ratios of calculated geometric factors and relative dipolar line widths vs. interionic distance for the spherical ( $S$ ) model.

$C_3$ ,  $C_2-30^\circ$ , and  $C_2-60^\circ$  all produced  $A$ 's consistent with all three ratios, though the fairly large variations in  $A$  indicate that the models are perhaps not as reliable as  $S$  or  $C_2$ . It should be noted that all models predict interionic distances in the range 8.6–10.1 Å, except  $S$ , which predicts 7.0 Å.

The value of 7.0 Å obtained for the spherical case agrees well with interionic separations reported<sup>10</sup> for other complexes with the same cation, as determined from X-ray analysis. However, such an interionic separation is totally inconsistent with free rotation of this rigid cation. It therefore appears that the consistency of the three values for  $A$  and their agreement with other data is merely accidental.

The various assumed models for orientation of the cation in the ion pair can be further subjected to experimental verification by considering line-width data.

(10) R. C. L. Mooney, *J. Am. Chem. Soc.*, **62**, 2955 (1940); B. Zaslav and R. E. Rundle, *J. Phys. Chem.*, **61**, 440 (1957); F. A. Cotton and S. J. Lippard, *Inorg. Chem.*, **5**, 416 (1966).

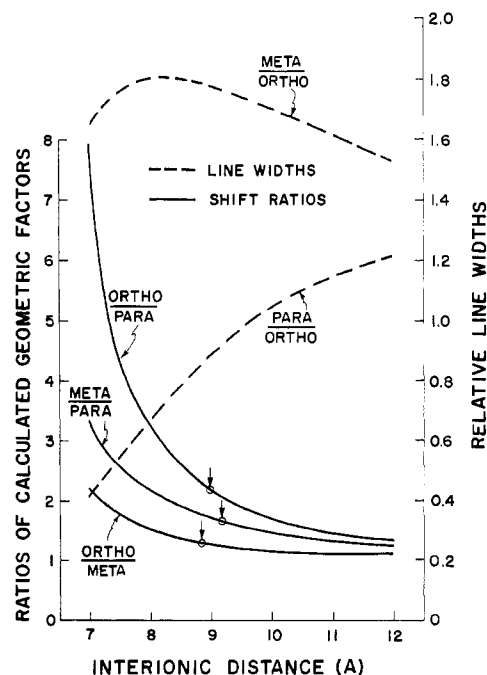


Figure 3.—Ratios of calculated geometric factors and relative dipolar line widths vs. interionic distance for the  $C_2$  model.

In the absence of paramagnetism, the line widths for the cation would be determined by the diamagnetic line width, 1–2 cps, and the spin-spin coupling. It has been shown<sup>11</sup> for similar phenyl rings that  $J_{o-m}$  and  $J_{m-p}$  are equal within experimental error and are about 7–7.5 cps. Both *meta* and *para* resonances are triplets in a first-order spectrum and, hence, would be essentially identical, such that both would have line widths of 15–16 cps. Identical multiplet widths in the absence of dipolar broadening have been observed<sup>11b</sup> for *meta* and *para* triplets in other paramagnetic complexes. Cross-ring coupling is small or absent (<2 cps) and has not been observed in these spectra. The *ortho* peak should be a doublet and, hence, narrower, ~8 cps. Experimentally, it is observed that the *para* line width is approximately that expected for the diamagnetic cation, though the multiplet structure is not resolved. The *meta* and *ortho* peaks, however, are some 6 cps wider than expected, indicating that a paramag-

(11) (a) W. D. Horrocks, Jr., R. C. Taylor, and G. N. LaMar, *J. Am. Chem. Soc.*, **86**, 3031 (1964); (b) E. W. Randall and D. Shaw, *Mol. Phys.*, **10**, 41 (1965).

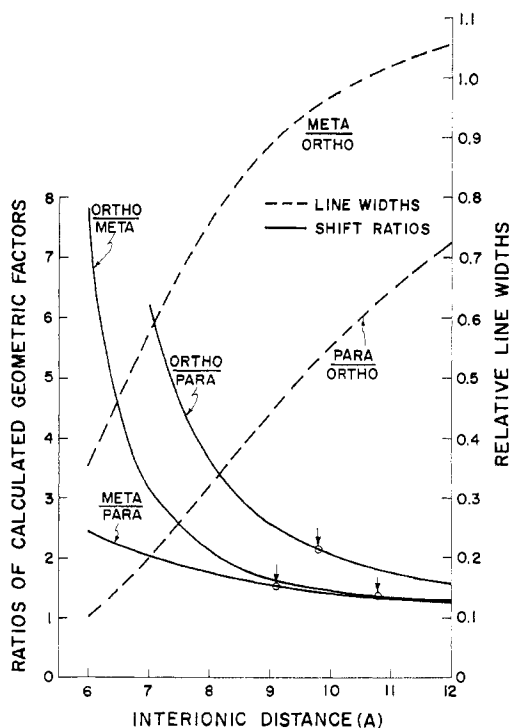


Figure 4.—Ratios of calculated geometric factors and relative dipolar line widths vs. interionic distance for the  $C_3$  model.

netic relaxation mechanism is operative. Although it is not possible to state the magnitude of the dipolar contribution to the observed widths, it appears reasonable to attribute the line-width difference between *meta* and *para* resonances to a paramagnetic effect inasmuch as their line widths are usually identical to within experimental error in the absence of paramagnetic relaxation. Thus since both *meta* and *para* line widths are equal to or greater than the expected multiplet widths and the *meta* is broader, it appears safe to conclude that paramagnetic relaxation is more effective at this position. For a dipolar relaxation mechanism, the excess line width over that for the diamagnetic state is proportional to  $\langle R_i^{-6} \rangle_{av}$ <sup>12,13</sup> and to the per cent ion pairing. For the spherical model, it can easily be shown that

$$\langle R_i^{-6} \rangle_{av} = \frac{1 + P_i^2}{A^6(1 - P_i^2)^4} \quad (3)$$

where  $P_i = Q_i/A$  evaluated at  $A = A_m$  in each case. The relative line widths, predicted by eq 3 with *ortho* normalized to unity, are also plotted in Figure 2. For the remaining cases,  $\langle R_i^{-6} \rangle_{av}$  was evaluated by computer, and the results are shown in Table II and in Figures 3 and 4. The relative dipolar line widths were always evaluated at  $A = A_m$ .

Inspection of Table II reveals that the observed excess line widths are quite inconsistent with the spherical model,  $S$ , as it predicts a dipolar line-width contribution six times greater for the *para* than the *meta* protons. This confirms our previous rejection of this ion-pair model. For the  $C_2$  and  $C_3$  models, the excess line

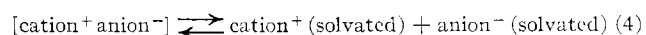
width is predicted to be greater at the *ortho* and *meta* positions than for the *para* proton, as observed, but the analysis does not allow a convincing discrimination between the two models. The  $C_2$ - $30^\circ$  model could be eliminated, as it also incorrectly predicts that the *para* protons will experience the greatest dipolar relaxation. Thus both the  $C_2$  and  $C_3$  models can account quantitatively for the observed dipolar shifts and qualitatively for the observed line widths. On the basis of the precision of the independent estimates, the  $C_2$  model appears most realistic, indicating an interionic separation of  $9.0 \pm 0.8$  A. (It should be pointed out that the line-width data serve only to confirm the elimination of the spherical model.)

If one assumed that the magnetic properties of the complex anion are independent of cation, then the estimate for  $(3g_{||}^2 + g_{\perp}^2 - 4g_{\perp}^2)$  of  $-1.28$  previously obtained<sup>2,6</sup> for  $[(C_6H_5)_3PCoI_3]^-$  and the calculated geometric factors for the present  $C_2$  ion-pair model can be inserted into eq 1 to obtain the value of the dipolar shift for the case of 100% ion pairing. This procedure predicts dipolar shifts of 10.4 (*o*), 8.13 (*m*), and 4.80 (*p*) ppm for total pairing. The observed shifts for the three positions yield per cent ion pairing estimates of 28.7% (*o*), 27.7% (*m*), and 29.0% (*p*), or an average of 28.5%. The reliability of this figure is, however, tainted because the determination of the magnitude of the  $g$ -tensor anisotropy depended<sup>2,6</sup> strongly on the cobalt-phosphorus distance, which had to be a rough estimate in the absence of any X-ray data.

### Comments

It is to be noted that in the present system the spherical cation model predicts an interionic separation significantly shorter than any of the cases where the cation occupies definite preferred rotational positions with respect to the anion. Thus if the spherical model for the previously studied tetra-*n*-butylammonium ion is indeed unrealistic, as now suspected, the interionic distance calculated earlier<sup>2b</sup> would be too small.<sup>13</sup> However, the unknown configuration of this cation precludes an analysis such as here undertaken for the tetraphenylarsonium cation.

The relative merits of the isotropic shift and line-broadening methods of estimating interionic distances in solution deserve some comment. In both methods, as heretofore applied,<sup>2b,4,13</sup> a tacit assumption has been made that ion pairs in equilibrium with solvated ions (eq 4) are the only significant species present in solution.



Complications due to the presence of higher aggregates have been generally ignored although their presence has been suspected.<sup>5,14</sup> Indeed, clusters are to be expected in solvents of low dielectric constant such as chloroform and at relatively high salt concentrations.<sup>15</sup> For a simple system (eq 4) the absolute values of the

(12) N. Bloembergen and L. O. Morgan, *J. Chem. Phys.*, **34**, 842 (1961).

(13) D. W. Larsen, *Inorg. Chem.*, **5**, 1109 (1966).

(14) R. H. Fischer, unpublished results.

(15) C. W. Davies, "Ion Association," Butterworth and Co. Ltd., London, 1962.

isotropic shifts would be expected to increase with increasing salt concentration and to decrease with temperature. The ratios of isotropic shifts should be essentially independent of these variables. Peak widths should show the same general behavior as the shifts for simple systems.

In chloroform solution the cation protons of  $[(C_4H_9)_4N][Co(C_6H_5)_3PI_3]$  systems show resonance shifts which decrease with increasing concentration and the shift ratios exhibit a small but definite dependence on concentration.<sup>14</sup> In analogous systems where the anion is  $[Co(acac)_3^-]$  the shifts increase with concentration, but the magnitudes of the shifts and their ratios show complicated temperature dependencies<sup>5</sup> indicating that this system is far from ideal. For chloroform solutions of the salt  $[(C_4H_9)(C_6H_5)_3P][Co(C_6H_5)_3PI_3]$  the shifts generally decrease with increasing salt concentration, and the shift ratios are by no means constant.<sup>14</sup> The above observations may be taken as evidence for ion clustering in these solutions.

In cases where one is interested in ion pairing rather than ion clustering it is important to assess the effect of clustering on the experimental observations. The anions of interest here have only one position at which a cation can approach closely;<sup>2</sup> all other models of approach will be more or less equally favored. A cluster will consist of an ion pair with other cations (and anions) more or less randomly oriented with respect to the principal paramagnetic anion. For such random orientation the dipolar shift averages to zero<sup>2b,3</sup> and this would be expected to decrease the magnitude of the observed isotropic shifts, but not much affect the shift ratios. Preferred orientation within a cluster would,

however, tend to modify both the shift magnitude and ratios. Comparison of isotropic shift ratios over a range of concentration is a good experimental test for this effect. The measured line broadening, which depends on  $\langle R^{-6} \rangle_{av}$ , will, unlike the dipolar shifts, not tend to average to zero. The observed broadenings will represent a weighted average over clusters and pairs and thus estimates of ion-pair interionic distances using this method will be affected by ion aggregation, perhaps to a greater extent than the shift measurements. Because of the limited solubility of  $[(C_6H_5)_4As][Co(C_6H_5)_3PI_3]$  in chloroform ( $<0.01 M$ ), the variation of the shift ratios and line-width ratios with concentration could not be assessed; however, the small concentration of this salt present in solution militates against extensive clustering.

Experimentally, isotropic shifts can be measured more accurately than line widths, particularly in cases where the spectra are complex. Both the shift and peak width methods of estimating interionic distance will be affected by ion clustering, the latter probably more so than the former. To best advantage, both methods should be employed.

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## The Reaction of the Hydroxoaquobis(ethylenediamine)cobalt(III) Ion with Amino Acids and Dipeptides and Their Esters and Amides

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Reactions between  $cis-[Co(en)_2OH(H_2O)]^{2+}$  and amino acid esters, amino acid amides, and dipeptides have been studied. Amide or ester hydrolysis is usually accompanied by ligand disproportionation leading to mixtures of products which were separated and characterized.

We have recently reported that the  $\beta-[Co(trien)OH(H_2O)]^{2+}$  ion (trien = triethylenetetramine) rapidly hydrolyzes amino acid esters and amides and acts selectively in the N-terminal hydrolysis of small peptide molecules.<sup>1</sup> These reactions have been interpreted on the basis of initial rate-controlling chelate for-

mation by the amino acid derivative followed by rapid hydrolysis.<sup>2</sup>

Earlier attempts made in one of our laboratories to carry out the above hydrolysis reactions using the  $[Co(en)_2OH(H_2O)]^{2+}$  ion were less successful, but the results of these experiments are, we feel, of some interest and are reported here.

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