noted that the variation of this wave with metal is within only 0.2 v. The Re values are least negative, meaning that the Re complex is most easily reduced. This result is consistent with the electron entering the $3a_1'$ level in each case. As discussed above (and illustrated by the spectra), this level should be more stable in Re than in W, and thus we expect it to be easier to put an electron into the $3a_1'$ orbital in the Re complex.[35]

The potential of the $n = -1 \rightarrow n = -2$ wave is quite negative for the Re complexes. There is a change of -1.5 v for the Re complexes, but a change in only -0.6 v for the W or Mo complexes (compared to the voltage of the $n = 0 \rightarrow n = -1$ wave). This is consistent with the electron going into the higher lying (by 8000 cm^{-1} from the spectra) $5e'$ level for the Re complexes and into the $3a_1'$ level for W and Re.

The $n = -2 \rightarrow n = -3$ wave occurs in the Re and Mo complexes but not in the W complexes (below 3.0 v). This wave in each case is interpreted as due to an

(35) This argument assumes that interelectronic-repulsion effects are very small. This is reasonable since we are dealing with molecular orbitals which are thoroughly delocalized over the ReS₆ framework. Furthermore, interelectronic-repulsion parameters for Re are small relative to 3d and 4d series metals, as are the parameters for sulfur compared to lighter donor atoms.

electron entering $5e'$, and its absence in the W complexes indicates a high energy $5e'$ level in this case. This result may be compared to the position of the $2a_2' \rightarrow 5e'$ transition, which is considerably higher energy in the W complexes than in either Mo or Re systems.

Thus it appears that the polarographic and electronic spectral results may be correlated quite satisfactorily using the proposed model of molecular orbitals. When taken together the theoretical and experimental results allow us to present a reasonable description of the electronic structures of these unusual and interesting complexes.

Hydrogen-Bonding Interaction of Chloroform with Metal Complexes. Chloroform Nuclear Magnetic Resonance Contact Shifts

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Contribution from the William A. Noyes Laboratory, Department of Chemistry, University of Illinois, Urbana, Illinois. Received December 11, 1965

Abstract: The complexes [(n-C₄H₉)₄N][(C₆H₅)₃PMI₃] (M = Co(II), Ni(II), and Zn(II)) have been found to interact *via* hydrogen bonding with chloroform. In the CDCl₃ solutions of the complexes, the interaction is accompanied by the appearance of a broad, well-resolved, intense infrared band at 2224 cm⁻¹. The decrease in intensity of the unperturbed chloroform C–H stretching overtone vibration in the presence of the complexes indicates that 4.5 ± 0.5 chloroform molecules are interacting with the complexes. The direct interaction is further manifested in the large upfield contact shifts observed for the chloroform resonance in the presence of both the nickel and cobalt complexes. It is shown that the nmr results are consistent only with a strong dominance of the contact contribution over the pseudo-contact contribution. The calculated chloroform contact shift is found to be +233 or +186 cps for the four- or five-coordinate cases, respectively. Possible distributions of the bonded chloroform molecules are suggested on the basis of the available data. Finally, these contact shifts provide additional evidence, probably the best available to date, to indicate that the hydrogen-bonding interaction is at least partially covalent.

A part of our present interest in nuclear magnetic resonance contact shifts[2] deals with the paramagnetic ion–solvent interaction. We have found evidence for such interactions by means of shifts in the solvent nmr frequency on dissolution of a paramagnetic solute. The complexes found most suitable for this work were tetra-n-butylammonium triiodo(triphenylphosphine)cobaltate(II) and -nickelate(II), prepared

originally by Cotton, *et al.*,[3,4] and more recently studied by La Mar.[5-8] These complexes were chosen for study for two principal reasons: (1) their solubility properties are such that a wide range of concentrations can be studied; and (2) the *g*-value anisotropies are such that

(1) Abstracted in part from the Ph.D. Thesis of M. F. Rettig, University of Illinois, 1967; National Science Foundation Graduate Fellow, 1963 to present.
(2) H. M. McConnell and C. H. Holm, *J. Chem. Phys.*, 27, 314 (1957).
(3) F. A. Cotton, O. D. Faut, D. M. L. Goodgame, and R. H. Holm, *J. Am. Chem. Soc.*, 83, 1780 (1961).
(4) F. A. Cotton, O. D. Faut, and D. M. L. Goodgame, *ibid.*, 83, 344 (1961).
(5) G. N. La Mar, *J. Chem. Phys.*, 41, 2992 (1964).
(6) G. N. La Mar, *ibid.*, 43, 235 (1965).
(7) G. N. La Mar, *ibid.*, 43, 1085 (1965).
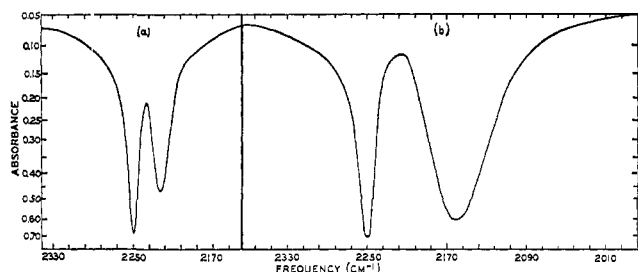(8) G. N. La Mar, *J. Am. Chem. Soc.*, 87, 3567 (1965).

Figure 1. Partial infrared spectra of: (a) 0.250 g of [(n-C₄H₉)₄N]-[(C₆H₅)₃PNiI₃] in 1.00 ml of CDCl₃; (b) 0.100 g of (n-C₄H₉)₄NI in 1.00 ml of CDCl₃. The spectra were obtained in a 0.100-mm CaF₂ cell *vs.* air. A 5X wavelength expansion was used.

it is possible to separate the contact and the pseudo-contact contributions to the observed chemical shifts.

This article presents evidence for chloroform- (or deuteriochloroform-) solvated anions of definite stoichiometry, in which the interacting solvent molecules experience a large nmr contact shift.

Experimental Section

The spectrometers used in this work were as follows: Varian A-60 and DP-60 (nmr), with a Varian variable temperature control unit; Perkin-Elmer 521 (infrared); Cary Model 14M (near-infrared and visible). Conductance data were obtained using an Industrial Instruments conductivity bridge, Model RC 16B2, calibrated with aqueous solutions of potassium chloride.

Microanalyses were performed in the University of Illinois micro-analytical lab, under the supervision of Mr. Josef Nemeth.

The chloroform used was Baker Analyzed reagent quality. Deuteriochloroform (>99.5 atom % D) was obtained from the spectroscopic service laboratory at the University of Illinois. (The purification of CHCl₃ and CDCl₃ is described below.) Fisher Certified nitromethane and nitrobenzene were stored over Linde 4A molecular sieve pellets before use. Matheson Coleman and Bell o-dichlorobenzene was fractionated through a 40-cm column, and a middle fraction (178.5–179°) was collected and stored over Linde 4A molecular sieve pellets. Baker Analyzed dimethyl sulfoxide was dried over molecular sieves prior to use.

Purification of CDCl₃. It was found by infrared analysis that the concentration of both water and ethanol (present as a preservative) could be lowered below 10^{-3} M by allowing 25 ml of CDCl₃ (containing about 0.1% water and 0.75% ethanol) to stir with about 4 g of Linde 4A molecular sieve pellets for 12 hr, followed by filtering the mixture (in a drybox) through a 1-cm × 1-cm column of Woelm neutral alumina. The resultant CDCl₃ showed no infrared absorption from 3900 to 3200 cm⁻¹ using a 2-mm path length NaCl cell.

Purification of CHCl₃. Baker Analyzed CHCl₃ was fractionated through a 40-cm column (separating very little ethanol) and was then treated as described for CDCl₃ to remove ethanol and water. CHCl₃ was always used just after removal of the preservative, a fresh batch being prepared for each experiment.

Preparation of Complexes. The procedures of Cotton, *et al.*,[2,3] for the preparation of [(n-C₄H₉)₄N][(C₆H₅)₃PCoI₃] and [(n-C₄H₉)₄N]-[(C₆H₅)₃PNiI₃] were found less satisfactory than the new procedures reported here. The zinc analog, [(n-C₄H₉)₄N][(C₆H₅)₃PZnI₃], has not been previously reported.

[(n-C₄H₉)₄N][(C₆H₅)₃PNiI₃]. NiI₂·6H₂O (8.41 g, 0.02 mole, City Chemical Co., New York, N. Y.) was dehydrated by stirring for 1 hr with 50 ml of dimethoxypropane (Eastman practical grade). Anhydrous ether (100 ml) was then added with stirring, followed by decantation. Two more 50-ml ether washes followed, the final decantation leaving approximately 25 ml of ether on the yellow-brown powder, to which was added 25 ml of 1-butanol. To this mixture was added (all at once) 7.38 g of (n-C₄H₉)₄NI and 5.26 g of (C₆H₅)₃P (0.02 mole each). On stirring, an immediate color change to red and deposition of red crystals occurred. The mixture was stirred at about 40° for 10 hr, filtered, washed copiously with ether, and dried *in vacuo* over P₂O₅ for 24 hr. A 60% yield of deep red powder was obtained. The melting point was 135.5° (lit.[4,5] 132.5°).
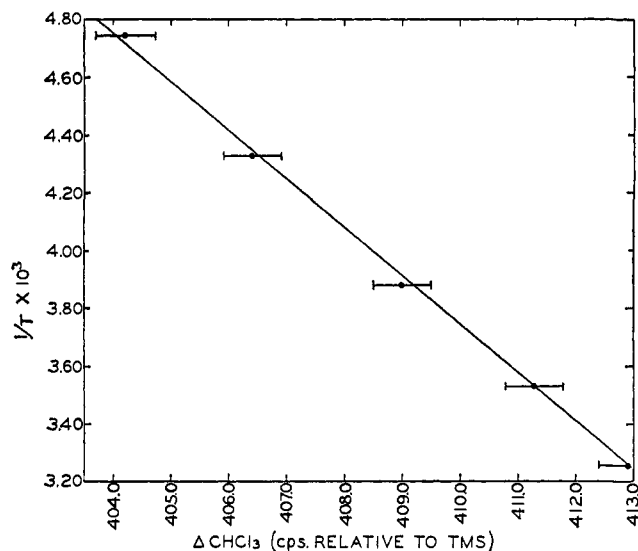
Anal. Calcd for C₃₄H₅₁NiI₃NP: C, 43.25; H, 5.44. Found: C, 43.10; H, 5.48.

[(n-C₄H₉)₄N][(C₆H₅)₃PCoI₃]. Anhydrous CoI₂ (5.94 g, 0.0189 mole, prepared by reaction of CoCO₃ with 47% HI, followed by dehydration in a drying pistol at 132°) was dissolved in 70 ml of acetone and filtered. (C₆H₅)₃P (5.98 g) and 7.01 g of (n-C₄H₉)₄NI (0.0189 mole each) were then added all at once to the CoI₂ solution. The green solution was stirred briefly, filtered, and treated with about 250 ml of anhydrous ether, resulting in the deposition of green crystals of the complex. The material was filtered, washed copiously with ether, and dried *in vacuo* over P₂O₅. A 79% yield of the green crystalline material was obtained. The observed melting point was 145° (lit. 141.5°,[5] 141°[3]).

Anal. Calcd for C₃₄H₅₁CoI₃NP: C, 43.23; H, 5.43. Found: C, 43.12; H, 5.45.

[(n-C₄H₉)₄N][(C₆H₅)₃PZnI₃]. Anhydrous ZnI₂ (3.19 g, Alfa Inorganics), 2.62 g of (C₆H₅)₃P, and 3.69 g of (n-C₄H₉)₄NI (0.01 mole each) were dissolved in 35 ml of acetone and filtered. Slow addition of 125 ml of anhydrous ether brought about the deposition of well-formed white crystals. The product was filtered, washed copiously with ether, and redissolved in 20 ml of acetone. About 70 ml of anhydrous ether was then added dropwise to reprecipitate the product, which was then filtered, washed copiously with ether, and dried *in vacuo* over P₂O₅ for 8 hr. A 54% yield of the white crystalline powder was obtained, with mp 138.5°.

Anal. Calcd for C₃₄H₅₁ZnI₃NP: C, 42.95; H, 5.41; Zn, 6.87. Found: C, 43.09; H, 5.45; Zn, 6.93.

Results

Table I presents spectral and conductivity data for the complexes in a variety of solvents. Table II shows the effect of the various compounds on the C–D stretching fundamental of CDCl₃. The concentrations of (n-C₄H₉)₄NI and (C₆H₅)₃P used here were roughly equivalent to the concentration of (n-C₄H₉)₄N⁺ and (C₆H₅)₃P in the metal ion containing solutions. Figure 1 illustrates some of these data. The data in Table III demonstrate the effect of concentration of the complexes on the CHCl₃ chemical shift. It will be noted that the CHCl₃ chemical shift changes linearly with the mole ratio change. Table IV presents the results of experiments designed to reveal the "solvation number" for various compounds, *i.e.*, the number of chloroform molecules associated with the species in solution. These numbers were inferred from the decrease in intensity of the first overtone of the C–H stretching vibration, which appears at 1693 mμ. Figure 2 shows

Figure 2. Temperature dependence of the CHCl₃ chemical shift: 0.250 g of [(n-C₄H₉)₄N][(C₆H₅)₃PCoI₃] dissolved in 1.00 ml of CHCl₃.

Table I. Visible and Near-Infrared Spectra and Conductance Data

Compound	Solvent	Concn, M	λ_{max} (ϵ)									Λ,[a] ohms⁻¹
(Bu₄N)[(C₆H₅)₃PCoI₃]	CHCl₃	7.54 × 10⁻²	447 (>2000)	583 (64)	635 (76)	691 (831)	708 (798)	734 sh[e] (891)	749 (1040)	777 (1455)	1350 (130)	...
	o-C₆H₃Cl₂	7.45 × 10⁻²	448 (>2000)	583 (68)	633 (79)	691 (905)	707 (862)	737 sh (920)	751 (1080)	779 (1556)	1350 (140)	...
	C₆H₅NO₂	1.55 × 10⁻³	445 (2550)	580 (65)	630 (55)	690 (820)	710 (800)	755 (1030)	765 sh (1230)	778 (1450)	1350 (—)	19.7
	Nujol mull	...	450 str[e]	580 w[e]	630 w[e]	690 str[e]	710 str[e]	745 sh[e]	{775 str,[e] broad}		1375 m[e]	...
	CH₃NO₂	1.06 × 10⁻³	405 (>1000)	625 sh (66)	665 (217)	690 sh (339)	705 (367)	740 (500)	...	775 sh (217)	1450 (55)	...
	Reflectance[b]	...	...	590 w	645 w	...	...	730 sh	...	790	...	...
	CH₃NO₂[b]	10⁻³	...	...	...	...	700 (648)	720 (689)	760 (880)	790 (890)	...	72
(Bu₄N)[(C₆H₅)₃PNiI₃]	CHCl₃	2.14 × 10⁻¹	<600 (CTB)[c]	700 sh (374)	745 (452)	1055 (256)	...	...	...	...	...	...
	o-C₆H₃Cl₂	1.71 × 10⁻²	<600 (CTB)	705 sh (380)	745 (466)	1060 (248)	...	...	...	...	...	...
	C₆H₅NO₂	1.55 × 10⁻³	<600 (CTB)	705 sh (400)	745 (495)	1062 (265)	...	...	...	...	...	19.6
	Nujol mull	...	570 str	{745, broad, str}		1065 str	...	...	...	...	...	...
	C₆H₆	1.50 × 10⁻³	<600 (CTB)	700 sh (360)	745 (459)	1060 (247)	...	...	...	...	...	...
	Reflectance[d]	...	...	...	770	1100	...	...	...	...	...	...
	C₆H₆[d]	1.5 × 10⁻³	<600 (CTB)	...	765 (450)	1095 (233)	...	...	...	...	...	...
	CH₃NO₂[d]	1 × 10⁻³	...	...	...	...	...	...	...	...	...	71.6
(Bu₄N)[(C₆H₅)₃PZnI₃]	CH₃NO₂	1.00 × 10⁻³	...	...	...	...	...	...	...	...	...	74.3
	C₆H₅NO₂	1.59 × 10⁻³	...	...	...	...	...	...	...	...	...	21.2

[a] All conductances (this work) measured at 26°. [b] Data from ref 3. [c] Charge-transfer band. [d] Data from ref 4. [e] sh = shoulder; str = strong; m = medium; w = weak.

Table II. Effect of Compounds on the C–D Stretching Vibration[a]

Compound	Concn, g/ml of CDCl₃	ν_{max}, free, cm⁻¹ [b]	ν_{max}, H-bonded, cm⁻¹	$\Delta\nu$, cm⁻¹
(Bu₄N)[(C₆H₅)₃PCoI₃]	0.250	2249 (0.61)	2224, (0.41)	25
(Bu₄N(C₆H₅)₃PNiI₃]	0.250	2249 (0.62)	2223 (0.41)	26
(Bu₄N)[(C₆H₅)₃PZnI₃]	0.250	2249 (0.61)	2224 (0.41)	25
(Bu₄N)I	0.100	2249 (0.65)	2160 (0.55)	89
Triphenylphosphine	0.0695	2249 (0.68)	...	...
Dimethyl sulfoxide	~0.05	2249 (0.79)	2234 (0.90)	15
...	Neat CDCl₃	2249 (0.70)	...	...

[a] 0.100 mm of CaF₂ vs. air, 5× wavelength expansion. [b] The numbers in parentheses are absorbances. Only absorbance values for similar compounds should be compared, as the free and H-bonded peaks overlap to different extents.

Table III. Dependence of CHCl₃ Chemical Shift on the Concentration of Dissolved Solute

Solute	Wt, g	CHCl₃, ml	ν_{CHCl_3}, cps	$\Delta\nu_{CHCl_3}$, cps	Mole ratio, CHCl₃/solute
(Bu₄N)[(C₆H₅)₃PCoI₃]	0.100	1.00	−427	+8	117
	0.200	1.00	−418	+17	59
	0.300	1.00	−410	+25	39
	0.400	1.00	−402	+33	29
	0.500	1.00	−394	+41	23
	0.600	1.00	−386	+49	19
	0.700	1.00	−378	+57	17
(Bu₄N)[(C₆H₅)₃PNiI₃]	0.100	1.00	−427	+8	118
	0.200	1.00	−417	+18	59
	0.300	1.00	−408	+27	40
(Bu₄N)[(C₆H₅)₃PZnI₃]	0.300	1.00	−438	−3	40
...	...	Neat CHCl₃	−435	...	...

Table IV. Determination of CHCl₃ Solvation Numbers for Various Donors

Sample solution	Absorbance at 1693 mμ[a]	Absorbance expected for no interaction[b]	Moles of CHCl₃ associated/mole solute[c]
12.35 M CHCl₃ (neat)	1.557	...	...
2.10 × 10⁻¹ M (Bu₄N)-[(C₆H₅)₃PZnI₃]– 10.81 M CHCl₃	1.237	1.365	4.7 ± 0.5
3.68 × 10⁻¹ M (Bu₄N)-[(C₆H₅)₃PZnI₃]– 9.630 M CHCl₃	1.007	1.215	4.5 ± 0.5
3.00 × 10⁻¹ M Bu₄NI– 11.31 M CHCl₃	1.273	1.426	4.1 ± 0.5
3.10 × 10⁻¹ M (C₆H₅)₃P–11.47 M CHCl₃	1.356	1.450	2.4 ± 0.5
3.08 × 10⁻¹ M (C₆H₅)₃CH–11.51 M CHCl₃	1.365	1.452	2.2 ± 0.5
4.175 M DMSO– 8.625 M CHCl₃	0.488	1.088	1.14 ± 0.05

[a] The spectra were obtained vs. the same solute molarity in CDCl₃, which does not absorb in this region. Thus all solute absorptions (all of which were very weak) were compensated. The path length was 0.1 cm. [b] The numbers in this column are calculated on the basis of the CHCl₃ molarity in the solution. The difference in the absorbance for columns 2 and 3 was used to derive column 4. [c] The error limits assume a maximum error of ±0.01 in the absorbance measurement.

the linear temperature variation of the chloroform chemical shift in the presence of [(n-C₄H₉)₄N] [(C₆H₅)₃-PCoI₃]. Because of the small changes involved, these shifts were measured by the side-band technique.

Discussion

Characterization of Complexes. Cotton and co-workers[3,4] found that the magnetic moments, spectra,

and conductivities of $[(n\text{-}C_4H_9)_4N][(C_6H_5)_3PCoI_3]$ and $[(n\text{-}C_4H_9)_4N][(C_6H_5)_3PNiI_3]$ are consistent with their formulation as C_{3v} complexes and 1:1 electrolytes in nitromethane. We have repeated their spectral work and report new data obtained in chloroform, o-dichlorobenzene, and nitrobenzene. Both transition energies and intensities in these three solvents are self-consistent, and the absorption maxima agree with our Nujol mull spectra (see Table I). In the case of the nickel complex, an identical spectrum was also obtained in benzene. Both our nitromethane spectrum of the cobalt complex and that determined by Cotton, et al.,[3] are in sharp disagreement with each other and with the results obtained in the other solvents. This situation is not surprising in view of the well-known tendency of nitromethane (or the impurities of this solvent) to decompose certain complexes. In view of the spectral results, it was considered necessary to determine conductances for the Co(II), Ni(II), and Zn(II) complexes in a solvent other than nitromethane, i.e., nitrobenzene. The results are consistent with the formulation of the complexes as 1:1 electrolytes, for which the range of conductivities can be taken as 18–30 ohms^{-1}.[9–12] The latter data, together with the elemental analysis, permit us to formulate the zinc complex as $[(n\text{-}C_4H_9)_4N][(C_6H_5)_3P\text{-}ZnI_3]$. These results leave little doubt that in chloroform the C_{3v} anions $[(C_6H_5)_3PMI_3]^-$ of cobalt(II), nickel(II), and zinc(II) are intact.

Nature of the Chloroform Solvation. A. Infrared Results. In the case of each of the tetra-n-butylammonium salts dissolved in $CDCl_3$ (listed in Table II and shown also in Figure 1), a broad, high intensity band appears at a frequency lower than the C–D stretching vibration. There is no comparable band for $(C_6H_5)_3P$ dissolved in $CDCl_3$, the only noticeable effect in this case being a slight broadening at the base of the C–D absorption. Inasmuch as these intense bands are not present in $CHCl_3$ solutions of the salts (and are therefore not absorptions due to the salts), their appearance is attributed to a hydrogen-bonding interaction with $CDCl_3$. The analogous absorptions in $CHCl_3$ are obscured by C–H vibrations of $[(n\text{-}C_4H_9)_4]^+$ and $(C_6H_5)_3P$, but can be noticed as an increase in intensity and loss of resolution in this region. High-intensity bands shifted to frequencies lower than that for the unperturbed vibration are considered to be diagnostic of H- (or D-) bonding interactions.[13,14] π-Interactions with aromatic systems, e.g., benzene, are generally accompanied by an increase in intensity at the unperturbed C–D stretching frequency, with no resolution of a new band.[14]

As can be seen from Table II, the three anionic complexes behave identically in $CDCl_3$, giving rise to bands 25–26 cm^{-1} lower than that of the unperturbed C–D stretching frequency. The identity of the spectra for the different complexes indicates that *the solvated species is of the same stoichiometry in each case.* Triphenylphosphine at a concentration comparable to that of the complexes gives rise to no significant change

in the infrared spectrum, while $(n\text{-}C_4H_9)_4NI$ at a similar concentration shows an intense peak at 2160 cm^{-1}. We consider these results to indicate that $CDCl_3$ certainly interacts in part with the complexes via the coordinated iodides. Interaction with the phosphine moiety cannot be ruled out, however, since the infrared experiment may well be insensitive to this low concentration of triphenylphosphine.

B. Nmr Results. The nmr results (Table III and Figure 2) are found to be consistent with the infrared results. It is seen from Table III that while the Zn(II) complex causes a small *downfield* shift, both the cobalt-(II) and nickel(II) complexes cause a large upfield shift of the $CHCl_3$ resonance, and the upfield shifts are of comparable magnitude for comparable cobalt(II) and nickel(II) concentrations. In contrast to this behavior, La Mar[5] has shown that the ion-paired butyl protons are shifted upfield in the case of $[(n\text{-}C_4H_9)_4N]\text{-}[(C_6H_5)_3PCoI_3]$, and downfield in the case of $[(n\text{-}C_4H_9)_4\text{-}N][(C_6H_5)_3PNiI_3]$. The butyl proton shifts were identified as pseudo-contact shifts, the different directions of these shifts being ascribed to different signs for $(g_{||} - g_\perp)$ in the complexes. This pseudo-contact behavior was also found for the phenyl protons, positive pseudo-contact shifts being noted for the cobalt complex and negative ones for nickel. Indeed, for the two complexes being considered, the pseudo-contact term must have a different sign at every point in space for which it is not zero. We therefore must conclude that the shifts observed in the $CHCl_3$ resonance are in fact contact shifts, resulting from a direct interaction of $CHCl_3$ with the anions. If the pseudo-contact term were dominant, we would expect shifts in opposite directions for the two complexes. The similarity of the results for cobalt(II) and nickel(II) further indicates that any pseudo-contact contribution must be very small.

In addition to showing the H-bonding nature of this interaction, our nmr results show that the $CHCl_3$ shift is linearly dependent upon the concentration of paramagnetic solute. We interpret this linearity to mean that the solvation number does not change over the wide range of mole ratios studied. Figure 2 reinforces this result in that the expected linearity of the $CHCl_3$ shift with $1/T$ is observed.

C. Stoichiometry of the Solvated Species. In an attempt to elucidate further the nature of this H-bonding interaction, we undertook to determine the number of $CHCl_3$ molecules bound to the solutes. The results are presented in Table IV. In these experiments, the disappearance of the first overtone of the C–H stretching vibration was studied as a function of added solute, assuming that H-bonded $CHCl_3$ molecules do not contribute to the absorption at 1693 mμ.[15] Since the nmr results indicate a constant stoichiometry over a wide range of concentrations, and the infrared results (Table II) show the same stoichiometry for the Co(II), Ni(II), and Zn(II) complexes, we chose to study the Zn(II)

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(10) C. M. Harris and R. S. Nyholm, *ibid.*, 63 (1957).
(11) A. Kabesh and R. S. Nyholm, *ibid.*, 38 (1951).
(12) M. E. Foss and C. S. Gibson, *ibid.*, 3063 (1949).
(13) G. C. Pimentel, "The Hydrogen Bond," W. H. Freeman Co., San Francisco, Calif., 1960.
(14) C. M. Huggins and G. C. Pimentel, *J. Chem. Phys.*, **23**, 896 (1955).

(15) A similar approach has been used for phenol interactions with various lone-pair and π donors. For these determinations, the intensity of the O–H overtone vibration was considered a quantitative measure of the amount of free phenol in solution. The results obtained by this method are in good agreement with results obtained by other methods. See, for example, D. L. Powell and R. West, *Spectrochim. Acta*, **20**, 983(1964); R. West, D. L. Powell, L. S. Whatley, M. K. T. Lee, and P. von R. Schleyer, *J. Am. Chem. Soc.*, **84**, 3221 (1962); R. West, D. L. Powell, M. K. T. Lee, and L. S. Whatley, *ibid.*, **86**, 3227 (1964); J. Rubin, B. Z. Senkowski, and G. S. Panson, *J. Phys. Chem.*, **68**, 1601 (1964); J. Rubin and G. S. Panson, *ibid.*, **69**, 3089 (1965).

complex at "arbitrary" concentrations. Both the Co(II) and Ni(II) complexes show strong "tailing" absorptions at 1693 mμ from near-infrared d–d transitions. Accordingly, the Co(II) and Ni(II) complexes were deemed less desirable for this study than the Zn(II) complex, which exhibits weak, easily compensated absorptions in the near-infrared region.

Each of the materials studied shows evidence of interaction with CHCl$_3$. Significantly, the $(C_6H_5)_3P$ result indicates that $(C_6H_5)_3P$ associates with two to three molecules of CHCl$_3$, as does $(C_6H_5)_3CH$. The latter compound was investigated as a "model" for coordinated $(C_6H_5)_3P$, i.e., no phosphine lone pair. Thus, while we could not definitely show $(C_6H_5)_3P$ interaction on the basis of the infrared results in Table II, the present results suggest that this interaction may be important in the coordinated phosphine. Perhaps not surprisingly, the negative iodide ion in $(n\text{-}C_4H_9)_4NI$ shows evidence of associating with about four molecules of CHCl$_3$ at the concentration studied. Of course, for $(C_6H_5)_3P$, $(C_6H_5)_3CH$, and $(n\text{-}C_4H_9)_4NI$ at the concentrations studied, there may be equilibria involving, say, two and three or three and four chloroforms of solvation. Our primary interest was to determine whether or not any interaction takes place. The Zn(II) complex appears to be associated with four to five molecules of CHCl$_3$, and it is noticed that essentially the same result is obtained over a wide concentration range for the complex. This result is consistent with the nmr results for the cobalt(II) complex. Finally, as a check on the method, we determined the average number of CHCl$_3$ molecules associated with dimethyl sulfoxide (DMSO). McClellan, et al.,[16] studied this interaction by nmr and derived equilibrium constants for the formation of CHCl$_3$·DMSO and (CHCl$_3$)$_2$·DMSO. For the CHCl$_3$ mole fraction used here (0.674), we calculate from McClellan's results an average of 1.27 CHCl$_3$/DMSO, which we consider to be in satisfactory agreement with our result of 1.14 ± 0.05 CHCl$_3$/DMSO.

D. The Chloroform Contact Shift. The infrared determinations indicate that the Zn(II), Co(II), and Ni(II) complexes are associated with four to five hydrogen-bonded chloroforms, within the estimated precision of the data. The concentration and temperature dependence of the nmr spectra indicate further that the solvation number is integral; i.e., an equilibrium between, say, four and five hydrogen-bonded chloroform molecules, is inconsistent with both the linear $1/T$ dependence of the chloroform resonance and the similar linear concentration dependence. Consequently, we suggest that each complex anion is intimately associated with either four or five hydrogen-bonded CHCl$_3$ molecules, and, using eq 1, we have calculated the chemical shift of the chloroforms H-bonded to the Co(II) complex.

$$\Delta_o = N_f\Delta_f + N_H\Delta_H \tag{1}$$

in which Δ_o = observed CHCl$_3$ chemical shift (relative to TMS), N_f and N_H = mole fractions of free and H-bonded chloroform molecules, respectively, and Δ_f and Δ_H = chemical shifts of free and H-bonded chloroform molecules, respectively.

(16) A. L. McClellan, S. W. Nicksic, and J. C. Guffy, *J. Mol. Spectry.*, 11, 340 (1963).

For the four-coordinate case, $\Delta_H = -201$ cps ($\Delta_H - \Delta_f = +233$ cps); and for the five-coordinate case, $\Delta_H = -248$ cps ($\Delta_H - \Delta_f = +186$ cps). It should be noted that there may be more than one H-bonded CHCl$_3$ environment. In this instance the calculation of Δ_H results in a weighted average of all the environments which are different from free chloroform.

On the basis of our present results, the CHCl$_3$ molecules cannot be precisely located around the complex anion. The results in Table IV suggest that CHCl$_3$ could interact both with the π system of the phosphine and with the coordinated iodides. Further evidence of the latter interaction is afforded by the C–D infrared frequency shift of 25–26 cm^{-1}, which is not expected for interaction with a ring π system, and is therefore ascribed to interaction with iodide. In any event, the bonded chloroforms must experience a *small* pseudo-contact shift, as the observed shifts have already been shown to be strongly dominated by the contact term. As can be seen from eq 2,[6] which describes the pseudo-contact shift in these complexes (where $\Delta\nu/\nu$ = observed pseudo-contact shift, $\omega = |\beta|^2 S(S + 1)/45kT$, $g_{||}$ and

$$(\Delta\nu/\nu) = -\omega(3g_{||}^2 + g_{||}g_\perp - 4g_\perp^2)[(3\cos^2 X_i - 1)/R_i^3] \tag{2}$$

$g_\perp = g$ tensors of complex, X_i = angle between the radius vector to the ith proton and the C$_3$ axis, and R_i = length of the ith radius vector), the pseudo-contact term vanishes when $3\cos^2 X_i = 1$, i.e., when $X_i \approx 55°$. As an aid in visualizing the possible bonding sites, Figure 3 shows the approximate dimensions of the ion pair. In the figure, only two phenyl groups (labeled A and B) are shown for clarity. Phenyl-A is perpendicular to the plane of the paper, while phenyl-B is in the plane of the paper. The cation is shown on the C$_3$ axis, as suggested by La Mar,[5,6] and the coordinated iodides are shaded. The dotted lines are drawn at angles of 55° to the C$_3$ axis, indicating the "cone" of zero pseudo-contact shift, while the + and − signs correspond to the sign of the pseudo-contact term (in the Co(II) complex) for other angles. The C–P–C, P–Co–I, and I–Co–I angles are assumed to be tetrahedral, and the distances C–C = 1.40, C–H = 1.08, C–P = 1.90, and Co–P = 2.32 A were taken from ref 5. The Co–I distance in diiodobis(p-toluidine)cobalt(II) is 2.6 A,[17] and it seemed reasonable to use this distance here. The radius of the ion-paired $(n\text{-}C_4H_9)_4N^+$ was taken to be about 3 A, after La Mar.[6] The chloroform dimensions in the inset to Figure 3 are taken from ref 18: C–H = 1.073 A, C–Cl = 1.762 A, and the Cl–C–Cl angle is 110.9°.

Figure 3 indicates that the coordinated iodides lie close to the "cone" of small pseudo-contact shift, and it therefore seems plausible that some of the bonded chloroforms are in fact bonded to the iodides, which is consistent with the infrared frequency shifts. It is also possible that a chloroform molecule interacting with (say) phenyl-A would experience a small pseudo-contact shift, particularly if the interaction were on the side facing the cation. Clearly, however, there are numerous rotamers for the phosphine moiety, some of which would involve sizeable pseudo-contact terms for the bonded CHCl$_3$.

(17) T. I. Malinovskii, *Kristallografiya*, 3, 364 (1958).
(18) P. N. Wolfe, *J. Chem. Phys.*, 25, 976 (1956).

Considering all the pertinent evidence, we propose two modes of interaction. The first involves all the bonded chloroforms interacting with the iodides close to the "cone" of zero pseudo-contact shift. This concept is reasonable, considering the result that (n-C_4H_9)$_4$NI can associate with several molecules of $CHCl_3$. Secondly, we suggest that the results are also consistent with (say) three chloroform molecules interacting with the three iodides, with the remaining one (or two) chloroform molecules associating with the phenyl groups.

We now should consider mechanisms whereby negative spin density (spin aligned antiparallel to the applied field) may reach the hydrogen-bonded chloroform proton. The triphenylphosphine contact shifts indicate that both positive and negative spin density reaches the phenyl protons via the π system.[5] However, it seems clear that the π system carries a net positive spin density, the observed negative spin density appearing at the *meta* position as a result of electron correlation effects.[19,20] Accordingly, we expect that a proton hydrogen bonded to the ring would sense the net positive spin density in the π system, contrary to the experimental observation. On the other hand, hydrogen bonding to a coordinated iodide ion could lead to a negative spin density on the chloroform proton. In this case, positive spin density would be transferred to the iodide ion through the M–I σ bond. Spin-exchange effects between the M–I σ-bonding orbital and the iodide lone-pair orbitals could then lead to a stabilization of negative spin density near the hydrogen-bonded proton. Such a spin-polarization mechanism is very similar to that proposed in explaining the very large upfield nmr shifts of the amino hydrogens in coordinated ethylenediamines.[21]

A possible alternative explanation for the observed nmr shifts would involve direct overlap of metal orbitals containing unpaired spin with solvating chloroform

(19) E. A. LaLancette and D. R. Eaton, *J. Am. Chem. Soc.*, **86**, 5145 (1964).
(20) G. N. LaMar, W. De W. Horrocks, Jr., and L. C. Allen, *J. Chem. Phys.*, **41**, 2126 (1964).
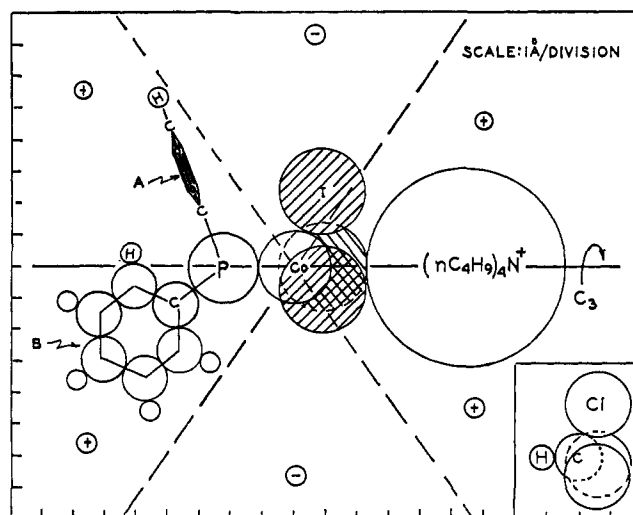(21) R. S. Milner and L. Pratt, *Discussions Faraday Soc.*, **34**, 88 (1962).

Figure 3. Composite scale drawing of [(n-C_4H_9)$_4$N][(C_6H_5)$_3$PCoI$_3$] as it might appear as an ion pair. The inset indicates the size of a $CHCl_3$ molecule in relation to that of the ion pair.

molecules. However, since the unpaired spin on the metal is aligned with the field, this mechanism clearly predicts a *downfield* shift at the chloroform proton. The observed *upfield* shifts rule out this type of interaction.

Conclusions

The data presented show that hydrogen bonds are formed to the complex anions, and that the nmr shifts observed are primarily contact shifts, indicating that the spin is transmitted to the $CHCl_3$ molecules through a partially covalent link. This information, as well as studies of similar systems, should contribute to the further elucidation of the electrostatic and/or covalent character of the hydrogen bond. Accordingly, we are continuing our investigations in this area.