Table III. Some $\nu(CO)$ Frequencies of $C_5H_5Fe(CO)XL$ (cm^{-1})

Compound]	$\nu(CO)$	Medium	Ref
$CF_3C(NH)Fe(CO)(NCCF_3)(C_5H_5)$	1996	CCl$_4$	a
$CF_3C(NH)Fe(CO)(NCCF_3)(C_5H_5)$	1995	KBr	a
$C_5H_5FeCOS_2CSR$			
(R = CH$_3$, C$_2$H$_5$, C$_6$H$_5$)	1965 ± 1	CCl$_4$	b
$C_5H_5Fe(CO)[P(C_6H_5)_3]X$			
(X = Cl, Br, I)	1950 ± 15	CHCl$_3$ or Nujol	c
$C_5H_5Fe(CO)(\pi\text{-}C_3H_5)$	1950	CS$_2$	d
$C_5H_5Fe(CO)[P(OC_6H_5)_3]C_6F_5$	1940	Vaseline	e
$C_5H_5Fe(CO)[P(OC_6H_5)_3]C_6H_5$	1935	Vaseline	e
$CH_3SCH_2CH_2COFe(CO)C_5H_5$	1935	Halocarbon	f
$C_5H_5Fe(CO)[P(C_6H_5)_3]COCH_3)$	1920	CHCl$_3$	c
$C_5H_5Fe(CO)[P(C_6H_5)_3]CH_3$	1905	CHCl$_3$	c
$(CH_3)_2NCH_2CH_2COFe(CO)_3H_5$	1890	KBr	g

a This work. b R. Bruce and G. R. Knox, J. Organometal. Chem. (Amsterdam), 6, 67 (1966). c P. M. Treichel, R. L. Shubkin, K. W. Barnett, and D. Reichard, Inorg. Chem., 5, 1177 (1966). d M. L. H. Green and P. L. I. Nagy, J. Chem. Soc., 189 (1963). e A. Nesmeyanov, Yu. A. Chapovsky, and Yu. A. Ustynyuk, J. Organometal. Chem. (Amsterdam), 9, 345 (1967). f R. B. King and M. B. Bisnette, Inorg. Chem., 4, 486 (1965). g R. B. King and M. B. Bisnette, ibid., 5, 293 (1966).

negatively charged two-coordinate nitrogen atom (Vb) or no bond between the two carbon atoms (Vc). Thus the high π-acceptor strength of the trifluoroacetimino–trifluoroacetonitrile combination must come from the trifluoroacetonitrile ligand rather than the trifluoroacetimino ligand. Further verification of the high π-acceptor strength of the trifluoroacetonitrile ligand will have to await the synthesis of trifluoroacetonitrile complexes with more conventional other ligands.
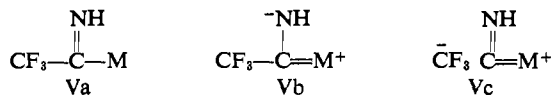
The Influence of Solvent on Ion Association. Proton Nuclear Magnetic Resonance of Trioctylmethylammonium Hexacyanoferrate(III)

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Abstract: The proton magnetic resonance spectra of trioctylmethylammonium hexacyanoferrate(III) and -cobaltate-(III) were obtained in 17 different solvents. The dipolar shift of the N-methyl and N-methylene protons of the ammonium ion were determined for 0.1 M solutions, and the N-methyl shift was found to vary linearly with the dielectric constant of the solvent, ϵ, when ϵ ranges from 2.76 to 47.6. An explanation for this linear relationship is given. The shifts were measured at various concentrations in propylene carbonate, CD_3SOCD_3, $CDCl_3$, CH_3NO_2, and CD_3COCD_3. The temperature variation of the shifts in CD_3SOCD_3 and $CDCl_3$ was determined.

According to the coordination model for nonaqueous solvent behavior, donor strength and solvating ability are two of the essential properties needed for the understanding of these systems. Since these properties cannot be directly measured toward most solutes, one must attempt to estimate them indirectly by procedures which have been described.[2] A qualitative ordering of the solvents as a function of these properties results. The greater the number and types of systems employed to deduce solvating and donor orders, the more complete the understanding and the more sure one is of the ordering. In this connection it was of interest to examine the ion-pairing interaction in $[(C_8H_{17})_3NCH_3]_3Fe(CN)_6$ as a function of solvent by taking advantage of the pseudocontact shift of the

proton nmr. The better solvating solvents will lead to decreased ion pairing and smaller pseudocontact shifts. If such an approach were to prove successful, it would result in a much more convenient procedure for estimating solvating ability of solvents than that offered from the evaluation of association constants.

Several recent articles on ion association, or ion pairing, have dealt with the study of the association of paramagnetic anions with quaternary ammonium cations[3-6] by measuring the nuclear magnetic resonance (nmr) isotropic shifts of the cation protons. The dipolar shift of a given ith proton, $\Delta\nu_{pi}$, is the difference between the measured frequency, ν_{pi}, of the proton in a paramagnetic environment minus the frequency, ν_{Di}, of the proton under diamagnetic conditions. When there is rapid exchange between

(2) (a) R. S. Drago and K. F. Purcell, Progr. Inorg. Chem., 6, 271 (1964); (b) R. S. Drago, D. M. Hart, and R. L. Carlson, J. Am. Chem. Soc., 87, 1900 (1965).

(3) G. N. LaMar, J. Chem. Phys., 41, 2992 (1964).
(4) G. N. LaMar, ibid., 43, 235 (1965).
(5) W. D. Horrocks, Jr., R. H. Fischer, J. R. Hutchinson, and G. N. LaMar, J. Am. Chem. Soc., 88, 2436 (1966).
(6) D. W. Larsen and A. C. Wahl, Inorg. Chem., 4, 1281 (1965).

protons in the two environments, the measured shift, ν_t, is given by

$$\nu_t = \nu_{\mathrm{p}i}N_{\mathrm{p}} + \nu_{\mathrm{D}i}N_{\mathrm{F}} \tag{1a}$$

where N_{p} is the mole fraction of the cations in a paramagnetic environment, and N_{F} is the mole fraction of the cations in a diamagnetic environment. From eq 1a and $N_{\mathrm{F}} + N_{\mathrm{p}} = 1$, the shift is found to be related directly to N_{p}

$$\Delta\nu_t = \Delta\nu_{\mathrm{p}i}N_{\mathrm{p}} \tag{1b}$$

where $\Delta\nu_t = \nu_t - \nu_{\mathrm{D}i}$ and $\Delta\nu_{\mathrm{p}i} = \nu_{\mathrm{p}i} - \nu_{\mathrm{D}i}$. Thus the amount of ion association of a paramagnetic anion with the cation is directly related to the magnitude of the shifts of the protons in the quaternary ammonium ion. By varying the concentration of the species and by measuring the shift of different cation protons, association constants, mean distances between the associated species, and $\Delta\nu_{\mathrm{p}i}$ have been estimated for several protons.

The nmr shifts in these investigations are considered to be produced by a pseudocontact type of interaction[7] arising from a nonzero dipolar interaction of the electron spin and electron orbit with the proton nuclear spin. This interaction which is transmitted through space is a result of the anisotropy of the g tensor of the metal ion. Since $K_3Fe(CN)_6$, diluted in $K_3Co(CN)_6$, has values of $g_{||}$ and $g_{\perp}$ of 0.92 and 2.22, respectively,[8] large pseudocontact shifts of the protons of the quaternary ammonium ion are expected when ion pairing to this anion occurs.

Most of the reported studies have been confined to one solvent. No work to date has been carried out having as its purpose the study of association in various solvents by employing pseudocontact shift measurements. As previously mentioned, this is the purpose of this study. A relatively satisfactory solute for this study was $[(C_8H_{17})_3N(CH_3)]_3M(CN)_6$, where M = Co(III) or Fe(III). Both the diamagnetic cobalt(III) salt and the paramagnetic iron(III) salt could be prepared, and both were soluble to a high degree in a large number of solvents. The signals due to the N-methyl protons and to the N-methylene protons of the octyl groups could be identified and the shifts of these peaks determined. Some limitations are placed on the number and types of solvents which can be studied because of overlap between solvent and cation resonances. However, 17 different solvents were treated.

Experimental Section

Preparation of $[(C_8H_{17})_3NCH_3]_3Co(CN)_6$. $K_3Co(CN)_6$ (6.52 g, 19.5 mmoles) was dissolved in 100 ml of concentrated ammonium hydroxide. $[(n\text{-}C_8H_{17})_3NCH_3]Cl$ (19.94 g, 49.4 mmoles, from General Mills, Chemical Division, Kankakee, Ill.) was dispersed by vigorous shaking into 100 ml of concentrated NH_4OH. A yellow-white precipitate appeared immediately upon mixing the two solutions. The mixture was stirred with a magnetic stirrer for 0.5 hr, filtered, and washed with concentrated NH_4OH. Air was drawn through the precipitate for a few minutes. The solid was dissolved in 60 ml of 95% EtOH and the solution filtered. The EtOH solution was poured into 600 ml of concentrated NH_4OH containing 3 g of $K_3Co(CN)_6$, and the mixture was stirred for about 0.5 hr in order to produce coagulation. The yellow-white precipitate was treated in the same manner as before. The cycle of precipita-

(7) D. R. Eaton and W. D. Phillips in "Advances in Magnetic Resonance," Vol. 1, Academic Press Inc., New York, N. Y., 1966, p 106.
(8) B. R. Figgis, "Introduction to Ligand Fields, "Interscience Publishers, New York, N. Y., 1966, p 306.

tion in concentrated NH_4OH, filtering off the precipitate, dissolving the precipitate in EtOH, filtering the solution, and reprecipitation in concentrated NH_4OH was carried out a total of three times to remove trapped quaternary ammonium chloride. On the last cycle, the reprecipitation was carried out with no $K_3Co(CN)_6$ present in the concentrated NH_4OH. The triply cycled salt was crushed to a fine powder and placed in a desiccator over concentrated H_2SO_4 and allowed to dry for at least 2 days. After this period, the solid was dissolved in 100 ml of dry CH_2Cl_2 and the solution filtered. The solution was evaporated to one-half its volume using a rotatory evaporator. C_6H_{12} (50 ml) was added, and the solution was evaporated until a solid formed and filtered. The solid was dried in a vacuum desiccator over Drierite; 16.6 g of $[(C_8H_{17})_3\text{-}NCH_3]_3Co(CN)_6$ was prepared. The yield was 69.4% of the theoretical.

Anal. Calcd for $C_{81}H_{162}N_9Co$: C, 73.64; H, 12.36; N, 9.54; Co, 4.46. Found: C, 73.12; H, 12.48; N, 8.37; Co, 3.86. N: Co ratio found, 9.10:1.

Preparation of $[(C_8H_{17})_3NCH_3]_3Fe(CN)_6$. An identical procedure was used to prepare this yellow compound as was used to prepare the analogous Co compound. One special precaution taken with this compound was to ensure that it had only a minimum exposure to light. The compound has a tendency to darken when exposed to light, and this is especially true when moist.

Anal. Calcd for $C_{81}H_{162}N_9Fe$: C, 73.80; H, 12.39; N, 9.57; Fe, 4.24. Found: C, 72.79; H, 12.54; N, 8.44; Fe, 3.75. N: Fe ratio found, 8.98:1.

The amorphous appearing material probably contains a trace of trapped CH_2Cl_2 but, at the concentrations used in the study, the nmr spectra showed no evidence of any contaminant.

Instrumentation. The nmr spectra were obtained on Jeolco C-60H and Varian A-60A spectrometers. Unless otherwise indicated, all temperatures are 34° (±0.5). All variable-temperature studies were carried out with the Jeolco. The temperature measured before and after each spectrum was recorded with a Yellow Springs Instrument Model 42SC Tele-Thermometer, and the temperatures are accurate to $\pm0.5\%$. The N-methyl peak positions are accurate to ±0.5 cps.

The ultraviolet and visible spectra of the solutions were obtained with a Cary 14 recording spectrometer using 0.1-mm quartz cells at room temperature. The molar extinction coefficients are reproducible to about $\pm2\%$.

The infrared spectra of the solutions were obtained with a Perkin-Elmer Model 521 spectrophotometer using 0.1-mm NaCl cells at room temperature. The frequencies are accurate to ±5 cm^{-1}.

Solvents. $CDCl_3$ (Brinkman Instruments, Westbury, N. Y.) and CD_3SOCD_3 and CD_3COCD_3 (Diaprep, Inc., Atlanta, Ga.) were used without further purification. CH_2Cl_2 was dried with molecular sieves. The other solvents were reagent grade materials and were used without further purification.

Solutions. The solutions were prepared by weighing out the solute, adding the proper amount of solvent, and adding tetramethylsilane (0.1%). It was found that solutions made by using solvents of low polarity (*e.g.*, $CDCl_3$) did not give reproducible nmr spectra until about 2 hr after preparation. The hexacyanoferrate(III) solutions were exposed to light only when necessary.

Results

In order to show that the anion species in solution are the hexacyano complexes, the infrared and ultraviolet–visible spectra of $CDCl_3$ and CH_3SOCH_3 solutions of the two compounds were obtained. The results from these spectra are given in Table I and may be compared with the ultraviolet–visible spectra of aqueous solutions of $K_3M(CN)_6$ and with their solid-state infrared spectra.

The N-methyl, ν_{CH_3}, and N-methylene, ν_{CH_2}, proton frequencies, relative to tetramethylsilane, were measured at a concentration of about 0.1 M in all of the solvents and are given in Table II. The N-methyl peak is a sharp signal, whereas the N-methylene signal is a broad, flat peak, about 10 cps wide at its maximum height. ν_{CH_2} in Table II is the frequency at the center of the broad peak. The spectra of the cobalt and iron compounds dissolved in C_5H_5N are typical and are

Table I. Infrared and Ultraviolet–Visible Spectral Data

Solvent	Solute	Concn, M	Infrared $\bar{\nu}_{CN}$, cm^{-1}	Ultraviolet and visible, $\bar{\nu}$, cm^{-1} (ϵ_{max})
CH₃SOCH₃	[R₃NR']₃Co(CN)₆	0.0534	2110	31,500 (16.8),[b] 38,000 (17.8)
	[R₃NR']₃Fe(CN)₆	0.0536	2095	23,600 (721), 31,000 (981), 3 2,900 (1240) 38,500 (944)
CDCl₃	[R₃NR']₃Co(CN)₆	0.0533	2110	32,000 (16.8), 38,200 (16.8)
	[R₃NR']₃Co(CN)₆	0.0529	2105	23,700 (706), 30,800 (886), 32,800 (1241), 37,700 (1094)
H₂O	K₃Co(CN)₆	0.0513		32,500 (20.3), 37,900 (21.0)
	K₃Fe(CN)₆	0.0563		23,800 (954), 31,300 (1171), 33,000 (1575), 38,300 (1238)
Solid state[a]	K₃Co(CN)₆		2126, 2129, 2143	. . .
	K₃Fe(CN)₆		2125	. . .

[a] From K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1961, p 166. [b] Molar absorptivity, ϵ_{max}, in parentheses.

Table II. Nmr Spectral Data

Solvent	Dielectric constant ϵ	Solute^{f,g}	Concn, M	$-\nu_{CH_3}{}^m \pm$ 0.5 cps	$\Delta\nu_{CH_3}{}^i$ cps	$-\nu_{CH_2}{}^{i,m}$ cps	$\Delta\nu_{CH_2}{}^k$	$\Delta\nu_{CH_2}/\Delta\nu_{CH_3}$
C₄H₄S	2.76ᵃ	Co	0.1044	219.0	125.4	202	64	2.0
	(16°)ᵈ	Fe	0.1012	93.5		138		
CDCl₃	4.81ᵃ,ᵉ	Co	0.1003	213.2	119.7	204	49	2.4
	(20°)	Fe	0.1006	93.5		155		
CH₂Cl₂	9.08ᵃ	Co	0.1009	205.2	109.7	198	42	2.6
	(20°)	Fe	0.1016	95.5		156		
cis-C₂H₂Cl₂	9.20ᵃ	Co	0.1049	201.9	99.4	198	41	2.4
	(25°)	Fe	0.1032	102.5		157		
C₅H₅N	12.3ᵃ	Co	0.1032	230.5	100.0	220	53	1.9
	(25°)	Fe	0.1098	130.5		167		
C₆H₅CHO	17.8ᵃ	Co	0.1032	231.5	93.1	218	40	2.3
	(20°)	Fe	0.1039	138.4		178		
CH₂=CHCH₂OH	21.6ᵃ	Co	0.1022	194.8	84.3	198	35	2.4
	(15°)	Fe	0.1066	110.5		163		
CD₃COCD₃	20.7ᵃ,ᵉ	Co	0.1029	208.8	76.6	216	43	1.8
	(25°)	Fe	0.1000	132.2		173		
CH₃OH	32.6ᵃ	Co	0.1019	191.0	57.8	199	24	2.4
	(25°)	Fe	0.1019	133.2		175		
HCON(CH₃)₂	37.8ᵇ	Co	0.1041	203.2	55.6	210	25	2.2
	(25°)	Fe	0.1020	147.9		185		
CH₃CN	36.7ᵃ	Co	0.1012	187.2	50.4	196	22	2.3
	(20°)	Fe	0.1039	136.8		174		
CH₃NO₂	35.9ᵃ	Co	0.1012	191.2	40.0	203	16	2.5
	(30°)	Fe	0.1031	151.2		185		
CD₃SOCD₃	46.7ᵇ,ᵉ	Co	0.1079	183.9	28.5	192	11	2.6
	(25°)	Fe	0.1037	155.4		181		
CH₃CHCH₂OC=O[h] (└—O—┘)	69.0ᶜ	Co	0.1018	183.1	15.9	193	5	. . .
	(22°)	Fe	0.1009	167.2		188		
HCONH(CH₃)	182ᵇ	Co	0.1031	197.5	9.0	. . .	. .	
	(25°)	Fe	0.1065	188.5		. . .		
trans-C₂H₂Cl₂[l]	2.14ᵃ	Co	0.1033	. . .	. . .	216	78	
	(25°)	Fe	0.1014	. . .		138		
C₆H₆[l]	2.28ᵃ	Co	0.1014	. . .	. . .	222	80	
	(20°)	Fe	0.1031	. . .		142		
30% (v/v) CD₃SOCD₃		Co	0.1062	201.7	69.2	201	24	2.0
70% (v/v) CDCl₃		Fe	0.1049	132.5		177		
70% (v/v) CD₃SOCD₃		Co	0.1038	188.1	37.7	197	20	1.9
30% (v/v) CDCl₃		Fe	0.1041	150.4		177		

[a] A. A. Maryott and E. A. Smith, "Table of Dielectric Constants of Pure Liquids," National Bureau of Standards Circular 514, U. S. Government Printing Office, Washington, D. C., 1951. [b] R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworth and Co., (Publishers) Ltd., London, 1959, p 458. [c] V. Gutmann and E. Wychera, *Rev. Chim. Minerale*, 3, 941 (1966). [d] Numbers in parentheses are the temperatures at which ϵ was measured. [e] Values of ϵ are for the protonated compounds. [f] Co represents [(C₈H₁₇)₃NCH₃]₃Co(CN)₆. [g] Fe represents [(C₈H₁₇)₃NCH₃]₃Fe(CN)₆. [h] All measurements made on the solutions of CH₃CHCH₂CO₃ were made at 22°; others at 34°. [i] $\Delta\nu_{CH_3} = \nu_{CH_3}{}^{Fe} - \nu_{CH_3}{}^{Co}$. [j] Center of a band about 10 cps wide. [k] $\Delta\nu_{CH_2} = \nu_{CH_2}{}^{Fe} - \nu_{CH_2}{}^{Co}$. [l] Only one very broad band observed. [m] All frequencies are relative to tetramethylsilane as an internal standard. (A resonance frequency of 60 MHz was used.)

illustrated in Figure 1. The pseudocontact shifts of the two proton types, $\Delta\nu_{CH_3}$ and $\Delta\nu_{CH_2}$, are given in Table II. For several of the solvents the concentration was varied and the nmr spectra were obtained. These data are presented in Figure 3.

In some instances (especially dilute solutions), peaks were not observed because of overlap by solvent or solvent side bands.

The nmr spectra of several solutions were measured at various temperatures. The solvents for these
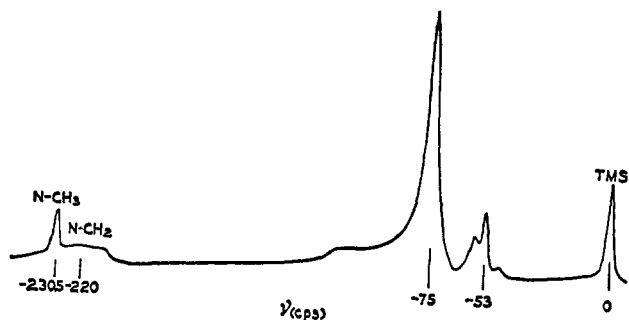
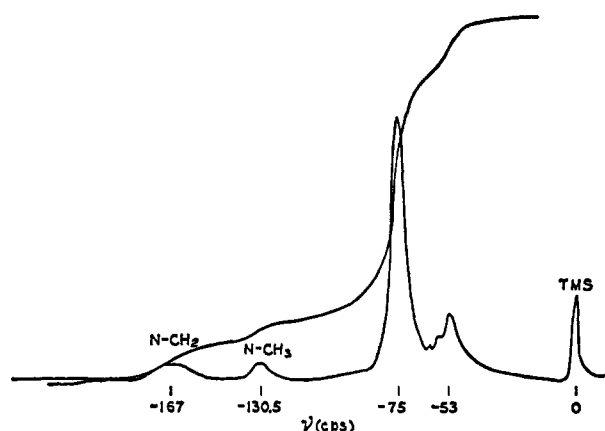Figure 1a. Nmr spectra of C_5H_5N solution of $[(C_8H_{17})_3NCH_3]_3$-$Co(CN)_6$.

Figure 1b. Nmr spectra of C_5H_5N solution of $[(C_8H_{17})_3NCH_3]_3$-$Fe(CN)_6$.

solutions were $CDCl_3$ and CD_3SOCD_3. The data are given in Table III.

Table III. Effect of Temperature Change on Nmr Spectra

Solute[a]	Temp, °C	$-\nu_{CH_3}$, ±0.5 cps	$\Delta\nu_{CH_3}$, cps	$-\nu_{CH_2}$, cps	$\Delta\nu_{CH_2}$, cps	$\Delta\nu_{CH_3}/\Delta\nu_{CH_2}$
A. Solvent, CD_3SOCD_3						
Co (A)	22.5	179.6		191		
			25.1		12	2.1
Fe (B)	22.5	154.5		179		
Co	36.8	178.5		189		
			21.7		9	2.4
Fe	36.8	156.8		180		
Co	47.8	178.4		188		
			20.9		8	2.6
Fe	47.8	157.5		180		
Co	64.0	179.2		183		
			20.8		4	...
Fe	64.0	158.4		179		
B. Solvent, $CDCl_3$						
Co (C)	22.3	206.4	125	198		
					52	2.4
Fe (D)	22.3	81		146		
Co	34.4	206.1		197		
			117.2		52	2.3
Fe	34.4	88.9		145		
Co	49.0	208.4		199		
			108.3		48	2.3
Fe	49.0	100.1		151		
Co	59.8	207.8		200		
			102.4		46	2.2
Fe	59.8	108.4		154		

[a] Concentrations of solutes in respective solvents: (A) $[R_3NR']_3$-$Co(CN)_6$, 0.0801 $M;$ (B) $[R_3NR']_3Fe(CN)_6$, 0.0834 $M;$ (C) $[R_3$-$NR']_3Co(CN)_6$, 0.0808 $M;$ (D) $[R_3NR']_3Fe(CN)_6$, 0.0795 $M.$

Discussion

Spectral Assignments. All of the spectra of the cobalt complex had a relatively sharp peak in the region of -190 cps usually superimposed upon a broad, flat peak about 10 cps wide (see Figure 1). The sharp peak was assigned to the N-methyl protons and the broad peak to the N-methylene protons. When thiophene was used as a solvent, the two peaks were sufficiently separated to integrate their areas. The ratio of integrated areas of the methylene peak to methyl peak are in the ratio of 2:1, as would be expected based on the assignment. Larsen and Wahl[6] found that the chemical shift of the protons on a carbon atom adjacent to the nitrogen atom of quaternary ammonium ions is around -180 cps from tetramethylsilane. The N-methyl and N-methylene would both be expected to be broadened by the quadrupole moment of the nitrogen, but the N-methylene would be broadened still further by spin-spin coupling with adjacent methylene groups.

When the quaternary ammonium cation is in the presence of the paramagnetic $Fe(CN)_6^{3-}$, the methyl and methylene protons are shifted upfield. The dipolar shift separates the two peaks, and area ratios may be determined. They are, as expected, in the ratio of 2:1 (Figure 1). The N-methyl peak shifts more than the N-methylene peak. The addition of the cobalt(III) compound to a solution of the iron compound moves the signals downfield as would be expected (eq 1b), for the shift should decrease as the mole fraction of paramagnetic complex decreases. The resonances in the paramagnetic complex can be traced back to those in the diamagnetic complex and assignments made by this procedure. Using $CDCl_3$ and CD_3SOCD_3 as solvents and about equal amounts of the two solutes, solutions at an over-all cation concentration of about 0.3 M were prepared and the N-methyl peak position was measured. In the fast exchange approximation (eq 1a), the N-methyl frequency, ν_{CH_3}, may be calculated from the values of the frequencies found for the 0.1 M cobalt solution, $\nu_{CH_3}^{Co}$, and for the 0.1 M iron solution, $\nu_{CH_3}^{Fe}$, by use of the equation

$$\nu_{CH_3} = \nu_{CH_3}^{Co}N_{Co} + \nu_{CH_3}^{Fe}N_{Fe} \qquad (2)$$

where $\nu_{CH_3}^{Fe}$ is an average free and ion-paired frequency, N_{Co} is the mole fraction of the cation added with the cobalt anion, and N_{Fe} is the mole fraction added with the iron anion. Agreement between the calculated and the measured values is found when the sum of the Fe and Co complex concentrations is held constant, so fast exchange does occur between the associated species and the free cation in solution. It is interesting that $\nu_{CH_3}^{Fe}$ remains constant, indicating the extent of dissociation is constant when the total ionic strength is held constant with the same salt type and the ferricyanide concentration varied. The dipolar shift changes when the ferricyanide concentration is varied without excess cobalticyanide present to maintain constant ionic strength.

The positions of the N-methyl and N-methylene peaks in the diamagnetic hexacyanocobaltate(III) spectra are dependent on the nature of the solvent. In solvents of low dielectric constant, ν_{CH_3} is further downfield than ν_{CH_2}, but the reverse is true for solvents of higher dielectric constant. Using benzene and

trans-$C_2H_2Cl_2$ only one very broad peak was observed under both paramagnetic and diamagnetic conditions. For these reasons, all dipolar shifts for the iron complex are calculated relative to the cobalt complex.

The cation nmr spectra in the presence of $Co(CN)_6{}^{3-}$ and $Fe(CN)_6{}^{3-}$ exhibit a large, intense peak around -78 cps and another less intense peak about -54 cps (Figure 1). Based on comparison with spectra of other similar cations,[5] the peak at -78 cps is assigned to the protons of the other six methylene groups of the octyl group. The peak at -54 cps is due to the end methyl groups of the octyl chains. An integration, approximate because of the overlap of the bands, indicates that this assignment is correct. These two peaks are not influenced by solvent changes or by the presence of a paramagnetic anion.

Effect of Solvent on the Observed Dipolar Shift. As a means of comparing the data in different solvents, $\Delta\nu_{CH_3}$ values for approximately 0.1 M solutions were plotted against ϵ, the dielectric constants of the solvents (Figure 2). An unexpected result of this plot was the apparent linear relationship between $\Delta\nu_{CH_3}$ and ϵ. A linear plot was not obtained for the more conventional plot of $-\log \Delta\nu_{CH_3}$ *vs.* $1/\epsilon$ or for $-\log \Delta\nu_{CH_3}$ *vs.* ϵ. Certainly $\Delta\nu_{CH_3}$ would be expected to decrease as dielectric constant increases since less association, and thus a smaller N_p, would be expected in solvents with the higher dielectric constant. Using all of the data at a concentration of 0.1 M, except that for propylene carbonate and $HCONH(CH_3)$, the points were fitted to a straight line by means of the least-squares technique, and the resulting equation is

$$\Delta\nu = 127.4 - 2.14\epsilon \qquad (3)$$

The dielectric constants used to calculate this equation were those measured at or near room temperature. The ϵ values for the protonated solvents were used for the deuterated compounds, but this should not influence the linear relationship to any marked extent. Points 10 and 12 correspond to solvents that are extremely difficult to purify, and this could be the cause of their deviation. Since we feel that the existence of this linear relation provides the key to interpreting the solution behavior, we shall attempt to rationalize this observation next.

A solution having as a solute $[(C_8H_{17})_3NCH_3]_3M(CN)_6$, where M is Fe(III) or Co(III), might be expected to exhibit the following equilibria involving cation–anion association.

$$Q^+ + A^{3-} = QA^{2-} \qquad (4a)$$

$$Q^+ + QA^{2-} = Q_2A^- \qquad (4b)$$

$$Q^+ + Q_2A^- = Q_3A \qquad (4c)$$
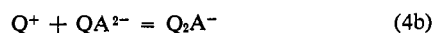
Q represents $[(C_8H_{17})_3NCH_3]^+$ and A^{3-}, $M(CN)_6{}^{3-}$. If the above equilibria are important, then

$$N_F + N_1 + N_2 + N_3 = 1$$

where N_n is the mole fraction of the cation present as the associated species, Q_nA, and N_F is that for the free cation. Since there is more than one paramagnetic environment for the protons of Q^+, eq 1a and 1b should be rewritten as

$$\nu_i = \nu_{Di}N_F + \nu_{1i}N_1 + \nu_{2i}N_2 + \nu_{3i}N_3 \qquad (5a)$$

$$\Delta\nu_i = N_1(\Delta\nu_{1i}) + N_2(\Delta\nu_{2i}) + N_3(\Delta\nu_{3i}) \qquad (5b)$$
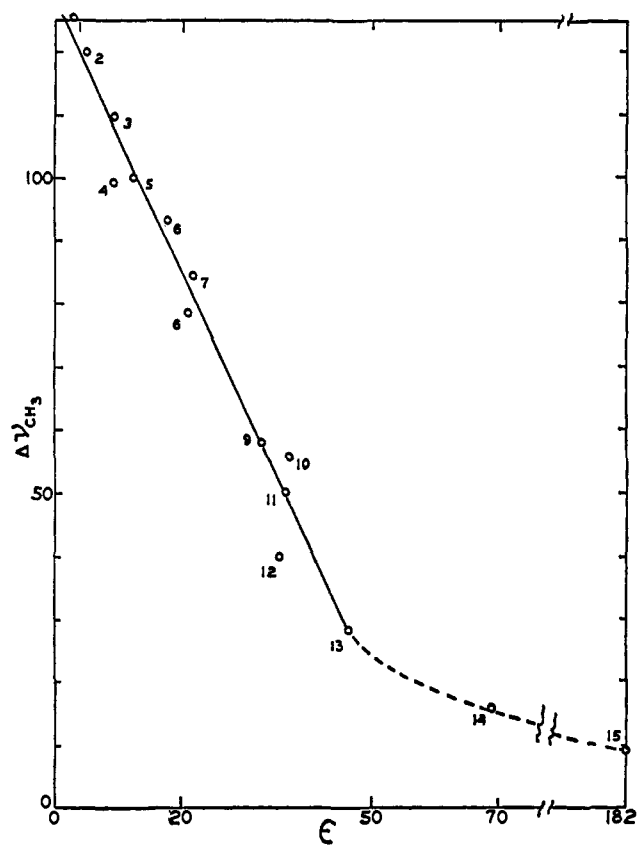

Figure 2. Plot of $\Delta\nu_{CH_3}$ *vs.* ϵ, the dielectric constants of the solvents at a solute concentration of 0.1 M at 34°. The equation, $\Delta\nu_{CH_3} = 127.4 - 2.13\epsilon$, is represented by the solid line: (1) C_4H_4S, (2) $CDCl_3$, (3) CH_2Cl_2, (4) *cis*-$C_2H_2Cl_2$, (5) C_5H_5N, (6) $C_6H_5C(H)O$, (7) $CH_2=CHCH_2OH$, (8) $CD_3C(O)CD_3$, (9) CH_3OH, (10) HC-$(O)N(CH_3)_2$, (11) CH_3CN, (12) CH_3NO_2, (13) $CD_3S(O)CD_3$, (14) $CH_3CHCH_2OC=O$, (15) $HC(O)N(H)CH_3$.

where ν_{ni} is the frequency of the ith proton in the species, Q_nA, and $\Delta\nu_{ni} = \nu_{ni} - \nu_{Di}$. Considering only the CH_3 protons and dividing eq 5b by $\Delta\nu_{3i}$, then

$$\frac{\Delta\nu_{CH_3}}{\Delta\nu_3} = N_1\frac{\Delta\nu_1}{\Delta\nu_3} + N_2\frac{\Delta\nu_2}{\Delta\nu_3} + N_3$$

If it is assumed that $\Delta\nu_1 \sim \Delta\nu_2 \sim \Delta\nu_3$, then

$$\Delta\nu_{CH_3}/\Delta\nu_3 = N_1 + N_2 + N_3$$

and

$$\Delta\nu_{CH_3}/\Delta\nu_3 = 1 - N_F \qquad (6)$$

(Equations 1a,b apply if $\Delta\nu_1 \sim \Delta\nu_2 \sim \Delta\nu_3$.)

Some justification for the assumption will be given below. If it is also assumed that N_F is directly proportional to the thermal energy and inversely proportional to the energy of attraction of the cations and anions, then

$$N_F = \frac{BkT}{e^2/d\epsilon} \qquad (7)$$

where e is the electronic charge, d the mean distance of closest approach for the ions, k Boltzmann's constant, and T the absolute temperature. B is a proportionality constant which includes an average ionic charge. In any given solution, there will be many different types of
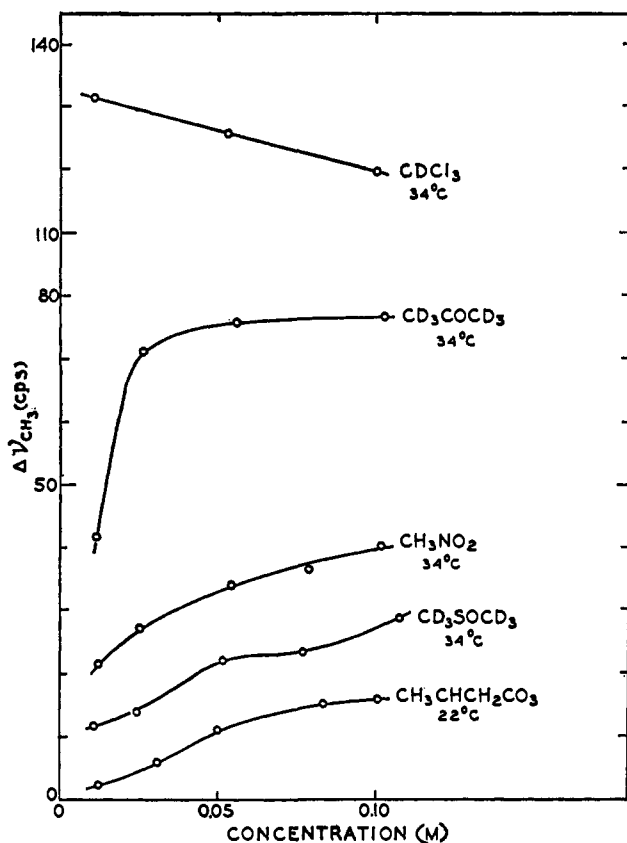
Figure 3. Effect of concentration changes on $\Delta\nu_{CH_3}$.

charged species interacting with one another. From eq 6 and 7

$$\frac{\Delta\nu_{CH_3}}{\Delta\nu_3} = 1 - \frac{BkTd\epsilon}{e^2}$$

and comparing this with the empirical eq 3, $\Delta\nu_3 = 127.4$ and $BkTd\Delta\nu_3/e^2 = 2.14$. B probably has a value close to 1, T is 300°K, and e and k are constant. Solving for d gives 9.3×10^{-8} cm, a not too unreasonable value for the distance of closest approach of ions. In this way we are able to rationalize the linear plot of $\Delta\nu_{CH_3}$ vs. ϵ, as well as (eq 6) the slope and intercept of this plot. We are faced with two problems as yet unresolved. (1) Why does $\Delta\nu_1 = \Delta\nu_2 = \Delta\nu_3$ and (2) why do the hydrogen-bonding solvents fall on this plot?

The ion $[(C_8H_{17})_3NCH_3]^+$ at high concentration, especially in the presence of highly charged counterions, should form micelles, or large, bulky clusters of positive ions, which vary in size as the concentration changes.[9] Thus, cation–anion association would not lead to simple ion pairs, but association leading to high molecular weight cationic or anionic species might occur. The equilibria would be more complex than shown in eq 4a–c. The Q^+ ions and the Q_nA^{n-3} groups would be part of a large cluster rather than being relatively independent, single species. Formation of this cluster could account for the fact that hydrogen-bonding solvents obey the empirical relationship 3, because specific hydrogen-bonding interactions between the solvent and the anions would be sterically inhibited.

(9) C. W. Davies, "Ion Association," Butterworth Inc., Washington, D. C., 1962, Chapter 11.

In the absence of formation, such interaction would tend to enhance dissociation of the ion pairs, and contrary to what is observed hydrogen-bonding solvents, e.g., chloroform and methanol, would not be expected to fall on the dielectric constant plot.

The assumption that $\Delta\nu_1 \sim \Delta\nu_2 \sim \Delta\nu_3$ would not be expected to be true if the Q_nA^{n-3} species were independent groups (vide infra, eq 9). If the Q_nA^{n-3} and Q^+ species were independent, then the Q^+ ions attracted to the A^{3-} ion would be placed about the anion in positions minimizing repulsions and maximizing attractions. The cation locations and induced distributions of the anions by the cations would lead to different values of $\Delta\nu_1$, $\Delta\nu_2$, and $\Delta\nu_3$ for the QA^{2-}, Q_2A^- species. Deviation of eq 6 would then be impossible without a very fortuituous change in the magnitudes of all the K's in direct proportion to ϵ. In the micelle model it is also difficult to see why the dipolar shift should be independent of the ratio of the numbers of cations to anion in the cluster i.e., why $\Delta\nu_p$ should be the same for a composition of two cations per anion or one cation per anion. If this occurred, the counterpart of $\Delta\nu_1$, $\Delta\nu_2$, and $\Delta\nu_3$ for the more complex equilibria would be constant and eq 6 would result. It seems more reasonable that as the average composition of the cluster units vary continuously from Q_3A to QA^{2-}, the average dipolar shift varies in a continuous manner. Such changes if roughly linear would not effect the linearity of eq 6 but would effect the slope rendering our estimate of the ion-pair distance approximate depending on the extent of change in $\Delta\nu_p$.

All attempts to use the equilibria 4a–c and the "sphere in continuum" model in order to describe these systems failed.[10] In this model, $\log K_n$ is a function of $1/\epsilon$, where K_n's are the equilibrium constants for (4a–c) and, thus, gives no direct relationship between N_F and ϵ.

Studies of this type have a potential application in providing effective dielectric constants for mixed solvents. The wide variations possible are illustrated by the last two examples in Table II involving the mixed solvent dimethyl sulfoxide–chloroform.

Studies of the Effect of Solute Concentration. Concentration changes using five solvents were found not to influence ν_{CH_3} and ν_{CH_2} in the cobalt systems to any great degree. However, the dipolar shifts $\Delta\nu_{CH_3}$ and $\Delta\nu_{CH_2}$ of hexacyanoferrate(III) were affected by concentration changes as shown in Figure 3. The shifts $\Delta\nu_{CH_3}$ in solvents of high dielectric constant increase slowly as solute concentration increases, while for solvents of moderate dielectric constant $\Delta\nu_{CH_3}$ increases markedly at low concentration and then remains essentially constant. For solvents of low dielectric constant, $\Delta\nu_{CH_3}$ decreases slightly as concentration increases. The increase in $\Delta\nu_{CH_3}$ in solvents of moderate dielectric constant is due to an increase in cation–anion association as concentration increases. The decrease in low dielectric constant solvents is probably due to an activity effect. In other words, the introduction of the solute into the low dielectric solvent makes the solution slightly more ionizing, and thus more anion dissociation occurs. An increase of conductivity of solutions at high con-

(10) J. T. Denison and J. B. Ramsey, J. Am. Chem. Soc., 77, 2615 (1955); W. R. Gilkerson, J. Chem. Phys., 25, 1197 (1956); R. M. Fuoss, J. Am. Chem. Soc., 80, 5059 (1958); R. M. Fuoss and E. Hirsch., ibid., 82, 1013 (1960).

centration with an increase in concentration has been interpreted in terms of such activity effects.[11]

If, as previously suggested, cluster formation is important, the concentration data should not be amenable to an ion-pair formation constant evaluation. If eq 6 applies to the 0.1 M solutions over a dielectric constant range of 2.76–46.7, then N_F varies from 0.0465 to 0.782, since N_F would be equal to 2.14ϵ. In CD$_3$-SOCD$_3$ ($\epsilon = 46.7$) most of the Q$^+$ ions would not be associated with the A^{3-} and the primary associated species is QA^{2-}. Thus, in this case, and in the absence of cluster formation, only equilibrium 4a is important, and the following equations apply

$$K_1 = \frac{[QA^{2-}]}{(QT - [QA^{2-}])\left(\frac{QT}{3} - [QA^{2-}]\right)}$$

$$[QA^{2-}] = \frac{\Delta\nu_{CH_3}}{\Delta\nu_1}QT$$

where QT is the total cation concentration. From these equations

$$K_1^{-1} = \frac{\Delta\nu_1}{3\Delta\nu_{CH_3}}QT - (^4/_3)QT + \frac{\Delta\nu_{CH_3}}{\Delta\nu_1}QT \quad (8)$$

For each of the five CD$_3$SOCD$_3$ solutions, various values of $\Delta\nu_1$ were chosen and K_1^{-1} was calculated for each value. K_1^{-1} was plotted as a function of $\Delta\nu_1$ for each solution, and this resulted in five straight lines. A single point of intersection of the lines would be expected if only one $\Delta\nu_1$ and one K_1 applied.[12] No such result was obtained. Cluster size does vary with concentration, and this may produce a variation in $\Delta\nu_p$ as the concentration varies and also make a simple formulation of the equilibrium incorrect. It may be possible to fit the shift data in these solvents with different values for $\Delta\nu_1$, $\Delta\nu_2$, and $\Delta\nu_3$ and with multistep equilibrium constants. It would then require a very fortuitous cancellation of several effects to get eq 6. For this reason, we prefer to think that eq 6 applies to such a wide range of solvent types because these 0.1 M solutions contain positively charged clusters of similar geometry varying in size and composition with the dielectric constant of the solvent. The size and charge of the clusters varies with concentration in different solvents, but at a concentration of 0.1 M the extent of Q$^+$ dissociation is a linear function of ϵ. In the very polar solvents propylene carbonate and N,N-dimethylformamide, the clusters either do not exist at 0.1 M solute or their geometry is radically different.

Cluster Geometry. Shifts produced by ion association to a paramagnetic ion are due, as mentioned earlier, to pseudocontact interaction. The pseudocontact shift in solution is given by the relation[7]

$$\left(\frac{\Delta\nu_p}{\nu}\right)_i = -\frac{\beta^2 S(S + 1)}{45kT}\left[\frac{3\cos^2\chi_i - 1}{r_i^3}\right]f(g) \quad (9)$$

where ν is the resonance frequency, r_i is the distance between the paramagnetic anion and the proton i, χ_i is the angle between the radius vector r_i and the highest fold symmetry of the paramagnetic anion, β is the Bohr magneton, S is the total spin of the unpaired electron

in the paramagnetic anion, and f(g) is some function of the g tensor of the anion. The function to apply in this case is not known, and, since ratios of contact shifts will be used, it will not be necessary to propose an equation for f(g). However, since the contact shift is an upfield shift, f(g) is a negative quantity. By eq 1 and 9 at constant temperature, the measured frequency shift for the ith proton may be expressed as

$$\Delta\nu_i = KF_i f(g)N_p$$

where K is a constant and $F_i = (3\cos^2\chi_i - 1)/\nu_i^3$. Thus the measured ratio, $\Delta\nu_{CH_3}/\Delta\nu_{CH_2}$, should only be a function of F_{CH_3}/F_{CH_2} and should be dependent only upon the distance between the associated ions. If the proper model of the associated ions were known, then possibly the geometric factors for both proton types might be calculated as a function of the distance of closest approach of the ions.[13] We question proposing a model for such highly associated clusters of ions, but it is possible to compare the experimental ratios of $\Delta\nu_{CH_3}/\Delta\nu_{CH_2}$ (Tables II and III). An average value of them is 2.2 ± 0.3. The apparent consistency of the ratio under such a wide range of conditions indicates similar micellular nature, and the distance of closest approach of the ions is nearly constant. This supports the conclusions made by Ramsay and coworkers[14] who found that there was a straight-line relationship between log K values of tetra-n-butylammonium perchlorate in several solvents and $1/\epsilon$ which indicated a constancy in d.

The ratios for the CD$_3$COCD$_3$ solutions are noticeably smaller than those for the other solvents. The reason for their discrepancy is not known.

Temperature Dependence of the Dipolar Shift in Different Solvents. The influence of temperature on the position of $\Delta\nu_{CH_3}$ was found to be very different in the two solvents studied (Table III). The value of $\Delta\nu_{CH_3}$ for the CD$_3$SOCD$_3$ solution was found not to decrease very much with an increase in temperature, whereas the value for the CDCl$_3$ solution decreased linearly as a function of $1/T$ decreasing. As the temperature increases, the dipolar shift should decrease (eq 9) and the dielectric constant should also decrease.[15] The decrease in dielectric constant would produce greater association and an increase in $\Delta\nu_{CH_3}$ at the higher temperature. If the enthalpy of association is negative as expected in the absence of unusual solvent effects, a decrease in association would be expected as the temperature increases. For the low dielectric constant solvent, CDCl$_3$, a $1/T$ relationship is found (eq 9) and thus little change in association probably occurs with an increase in temperature. For the high dielectric constant solvent, CD$_3$SOCD$_3$, an increase in association at the higher temperature must counterbalance the decrease in $\Delta\nu_p$ to produce only a small change in $\Delta\nu_{CH_3}$.

(11) C. W. Davies, ref 9, Chapter 10.
(12) N. J. Rose and R. S. Drago, *J. Am. Chem. Soc.*, **81**, 6138 (1959); T. F. Bolles and R. S. Drago, *ibid.*, **87**, 5015 (1965).
(13) G. N. LaMar, R. H. Fischer, and W. D. Horrocks, Jr., *Inorg. Chem.*, **6**, 1798 (1967).
(14) Y. H. Inami, H. K. Bodenseh, and J. B. Ramsay, *J. Am. Chem. Soc.*, **83**, 4745 (1961).
(15) R. W. Gurney, "Ionic Processes in Solution," McGraw-Hill Book Co., Inc., New York, N. Y., 1953, p 16.