Neither the data of Table I nor Figure 1 show evidence of change over the temperature range in which dehydration would be expected. Further, the infrared spectrum does not show the ν_1 and ν_3 water bands at 3400 and 3220 cm^{-1}.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Ion Association between Quaternary Ammonium Ions and Hexacyanochromate(III) Ion. Study of Proton Transverse Relaxation Times

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A study was made of the changes that occur in the proton transverse relaxation times of aqueous quaternary ammonium ions upon ion-pair formation with hexacyanochromate(III) ions. The observed decrease in transverse relaxation times is attributed to a dipolar interaction, and a previously proposed model is used to explain the observed T_2 values. Tumbling times for the ion pairs and the possibility of tumbling of the separate ions within the ion pair are discussed.

Introduction

Recently, nmr methods have been used to study ion-pair formation in both aqueous[1–3] and nonaqueous solvents.[4,5] When one of the ions in the ion pair is paramagnetic, isotropic hyperfine interactions are present owing to close association between cation and anion.[3] If T_{1e}, the spin-lattice relaxation time of the unpaired electron(s), is relatively short, the large chemical shifts, due to "contact" or "pseudo-contact" interactions,[6] which accompany ion-pair formation may be observed. Aqueous solutions containing quaternary ammonium ions and ferricyanide ion have been shown[3] to exhibit large chemical shifts due to "pseudo-contact" interactions, from which information about the geometry was obtained.

If T_{1e} is relatively long, a decrease[7] in the transverse relaxation time, T_2, of the nucleus in question will accompany ion-pair formation. Aqueous solutions containing quaternary ammonium ions and chromicyanide ion exhibit short T_2 values owing to the relatively long T_{1e} value for the chromicyanide ion. This paper presents detailed experimental T_2 data from nmr measurements. The data are evidence for ion-pair formation, and inferences may be drawn about the geometry within the ion pair.

Experimental Section

Reagents.—The following reagents were used without further purification: quaternary ammonium salts (Eastman Organic Chemicals) and deuterium oxide (Liquid Carbonic). Potassium chromicyanide (K & K Laboratories) was recrystallized twice from water and dried for 1 hr at 100° before use.

Nmr Measurements.—The proton magnetic resonance spectra of D_2O solutions containing R_4N^+ were recorded using a Varian Associates DA-60 nmr spectrometer operating at 60 Mcps. Values of T_2 were determined from the line widths of the recorded spectra. Sets of solutions contained 0.05 *M* quaternary ammonium salts and 0 to $\sim$0.015 *M* potassium chromicyanide.

Results

Determination of T_2 Values.—Addition of $Cr(CN)_6{}^{3-}$ to solutions containing R_4N^+ causes line broadening of the proton spectra which increases with increasing concentration of the paramagnetic anion. The line widths for each set of magnetically equivalent protons in all R_4N^+ systems studied may not be measured directly from the recorded spectra because of the presence of spin–spin coupling.

The proton spectrum of $(CH_3)_4N^+$ is a 1:1:1 triplet[3,8] due to spin coupling with N^{14}, with $J_{N\alpha} = 2.0$ cps.

The spectrum of $(C_2H_5)_4N^+$ is essentially an ethyl pattern (A_2X_3 case[9]) with additional splitting of the methyl resonance due to coupling with N^{14}. Values of coupling constants have been reported:[3,10] $J_{N\alpha} = 0$; $J_{N\beta} = 2.0$; $J_{\alpha\beta} = 7.4$ cps.

The spectrum of the methyl (γ) protons in $(n\text{-}C_3H_7)_4N^+$ is essentially the B part of an A_2B_3 case[9] with $J = 7.0$ cps and $\nu_0\delta = 45$ cps. The spectrum of the α-methylene protons is essentially one-half of an A_2B_2 case[9] with $J \neq J'$. Spin-decoupling experiments indicate that the only observable coupling for both the α-CH_2 and γ-CH_3 sets of protons is to the β-CH_2 protons. It was possible to reduce either the α or the γ multiplet to a sharp Lorentzian singlet by H_2 irradiation

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(1) R. P. H. Gasser and R. E. Richards, *Mol. Phys.*, **2**, 357 (1959).
(2) M. Alei, *Inorg. Chem.*, **3**, 44 (1964).
(3) D. W. Larsen and A. C. Wahl, *ibid.*, **4**, 1281 (1965).
(4) R. L. Buckson and S. G. Smith, *J. Phys. Chem.*, **68**, 1875 (1964).
(5) G. N. LaMar, *J. Chem. Phys.*, **41**, 2992 (1964).
(6) H. M. McConnell and R. E. Robertson, *ibid.*, **29**, 1361 (1958).
(7) I. Solomon, *Phys. Rev.*, **99**, 559 (1955).
(8) E. Grunwald, A. Lowenstein, and S. Meiboom, *J. Chem. Phys.*, **25**, 382 (1956).
(9) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, Chapter 6.
(10) J. M. Anderson, J. D. Baldeschwieler, D. C. Dittmer, and W. D. Phillips, *J. Chem. Phys.*, **38**, 1260 (1963).

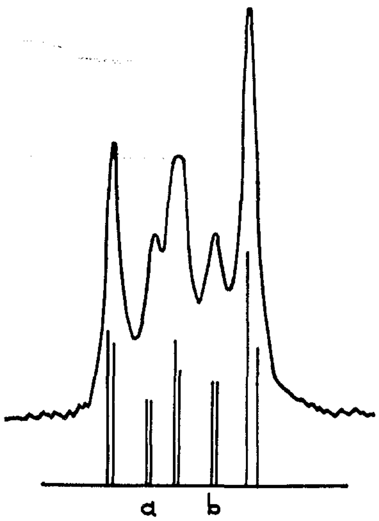

Figure 1.—Observed and calculated spectra for α-methylene protons in $(n\text{-}C_3H_7)_4N^+$. Peaks a and b are degenerate. Separation between peaks a and b is 8.0 cps.

at the proper frequency. The spectrum was subjected to detailed analysis and fitting following the procedure of Pople, Schneider, and Bernstein.[11] The required matrix diagonalizations associated with solution of the eigenvalue problem were conveniently accomplished using an IBM 7072 computer. The spectrum was best fit assuming the values of the parameters: $K = 20$, $M = 0$, $L = 8$, $N = 17$, and $\nu_0\delta = 83$ cps. The observed and calculated spectra are shown in Figure 1. The spectrum of the β-methylene is too complex and poorly resolved to admit analysis.

The spectrum of methyl (δ) protons in $(n\text{-}C_4H_9)_4N^+$ is the same type as that of the methyl protons in $(n\text{-}C_3H_7)_4N^+$. For the methyl (δ) protons, $J = 7.0$ and $\nu_0\delta = 32$ cps. The α-methylene protons in this case likewise exhibit the same type of spectrum as the α-methylene protons in the previous case. The values for the parameters associated with the spectrum fitting for α-methylene protons in $(n\text{-}C_4H_9)_4N^+$ are: $K = 20$, $M = 0$, $L = 8$, $N = 17$, $\nu_0\delta = 100$ cps.

The positions and relative intensities of the component lines of the spectrum of each equivalent set of protons studied were determined as indicated above.

The total multiplet, $g(\nu)_T$, is a sum of Lorentzian curves[12] of the type

$$g(\nu_i) = \frac{2T_{2i}}{1 + 4\pi^2T_{2i}^2(\nu_{0i} - \nu)^2}$$

or

$$g(\nu)_T = \sum_i c_i g(\nu_i) \tag{1}$$

where T_{2i} and $2\pi\nu_{0i}$ are the transverse relaxation time and the resonance frequency of the component, respectively, and $2\pi\nu$ is the applied frequency. The coefficients, c_i, are proportional to the calculated relative intensities, and the resonance frequencies, $2\pi\nu_{0i}$, are the calculated positions of the component lines. The width at half-maximum of each Lorentzian component is given by[12]

$$\Delta\omega_{1/2} = \frac{2}{T_{2i}} \tag{2}$$

The observed line broadening from addition of paramagnetic substance is attributed to a change in line width of each component or a decrease in T_{2i} by eq 2. This is a change in $g(\nu_i)$ which in turn results in a change in $g(\nu)_T$ from eq 1. All values of T_{2i} are equal in the absence of paramagnetic species, and we assume each decreases to the same extent upon addition of paramagnetic substance, so that $T_{2i} = T_{2j}$. We also assume that the values of $2\pi\nu_{0i}$ and c_i remain constant. Under the conditions of the experiments, all multiplets were reduced to broad, irregularly shaped singlets whenever paramagnetic substance was added. Thus, in each case, only total multiplet line width could be measured. Values of total line width of $g(\nu)_T$ were determined from eq 1 as a function of T_{2i} for each equivalent set of protons. An iterative method was employed on the IBM 7072 computer. Plots of total line width of $g(\nu)_T$ *vs.* $1/T_{2i}$ were made, and T_{2i} values were determined from these plots, using the measured half line widths of $g(\nu)_T$ from the recorded spectra.

The multiplet pattern for α-CH_2 protons in $(n\text{-}C_3H_7)_4N^+$ depends upon $\nu_0\delta$, the chemical shift between α-CH_2 and β-CH_2 protons. This parameter decreases with increasing concentration of chromicyanide ion.[3] Evidence has been obtained[3] which indicates that the "pseudo-contact" shifts are similar in magnitude for corresponding $R_4N^+Fe(CN)_6^{3-}$ and $R_4N^+Cr(CN)_6^{3-}$ systems. An estimate of the change in $\nu_0\delta$ for the range of chromicyanide ion used in this study was made from the data for the $(n\text{-}C_3H_7)_4N^+Fe(CN)_6^{3-}$ system. The estimated change in $\nu_0\delta$ is less than 2 cps or less than 2%. The change in multiplet pattern corresponding to this small change in $\nu_0\delta$ is unobservable, and errors due to its neglect are unobservable.

T_2 Values for Ion Pairs.—The features of nmr spectra of systems containing ion pairs have been discussed previously.[3] In general, rapid exchange of R_4N^+ between the ion-pair sites and the bulk solution reduces each component i of the multiplet to a collapsed singlet with half line width, $1/T_{2i}$, given by[13]

$$\frac{1}{T_{2i}} = \frac{[R_4N^+]}{[R_4N^+]_T}\left(\frac{1}{T_2}\right) + \frac{[R_4N^+Cr(CN)_6^{3-}]}{[R_4N^+]_T}\left(\frac{1}{T_{2ip}}\right) \tag{3}$$

where $1/T_2$ and $1/T_{2ip}$ are the half line widths of a proton in the bulk solution and the ion pair, respectively, and $[R_4N^+]_T = [R_4N^+] + [R_4N^+Cr(CN)_6^{3-}]$. According to eq 3, values of $1/T_{2i}$ are concentration dependent.

Plots of $1/T_{2i}$ *vs.* $[K_3Cr(CN)_6]$ were found to approximate linearity up to $[K_3Cr(CN)_6] \approx 0.015$ *M* and to deviate markedly from linearity above this concentration, approaching zero slope at high concentrations

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[11] See ref 9, pp 138–144.

[12] See ref 9, pp 25–40.

[13] H. S. Gutowsky and A. Saika, *J. Chem. Phys.*, **21**, 1688 (1953).

TABLE I

INITIAL SLOPES OF LINE WIDTH *vs.* CONCENTRATION PLOTS AND VALUES OF $(1/T_{2ip} - 1/T_2)$ FOR PROTONS IN TETRAALKYLAMMONIUM CHROMICYANIDE ION PAIRS

Position	Group			
	CH_3[a]	C_2H_5	n-C_3H_7	n-C_4H_9
α[b]	1600 ± 50[c] (160)[d]	2100 ± 100 (350)	2320 ± 300 (460)	3200 ± 300 (640)
β		1360 ± 100 (230)	. . .	. . .
γ			1720 ± 250 (340)	. . .
δ				1710 ± 250 (340)

[a] Refers to ions of the type R_4N^+. [b] Refers to position with respect to N. [c] Estimated possible error. [d] $(1/T_{2ip} - 1/T_2)$ values in parentheses, cps.

of $K_3Cr(CN)_6$. The initial slopes of the plots are presented in Table I.

If the equilibrium quotients for the $R_4N^+Cr(CN)_6{}^{3-}$ systems are assumed to be similar to those for the $R_4N^+Fe(CN)_6{}^{3-}$ systems, the initial linearity of the plots is predicted. The two anions, $Fe(CN)_6{}^{3-}$ and $Cr(CN)_6{}^{3-}$, have equal charges and very nearly equal sizes, so the association constants and geometries of their ion pairs should be essentially the same.[3] Also presented in Table I are estimated values of $(1/T_{2ip} - 1/T_2)$ for the $R_4N^+Cr(CN)_6{}^{3-}$ systems. These were calculated from the initial slopes using the equilibrium quotients which apply to the corresponding $R_4N^+Fe(CN)_6{}^{3-}$ systems.

Mechanisms of Interaction.—Two types of interactions between unpaired electrons in a paramagnetic anion and protons may be considered as giving rise to the observed line broadenings. The first of these is the spin-exchange interaction[14] for which the line broadening is given by[15]

$$\left(\frac{1}{T_{2i}} - \frac{1}{T_2}\right) = \frac{1}{3}\frac{S(S+1)A^2p}{\hbar^2}\left[\tau_e + \frac{\tau_e}{1 + \omega_s{}^2\tau_e{}^2}\right] \tag{4}$$

where A is the hyperfine coupling constant, p is the fraction of protons in ion pairs, ω_s is the Larmor precession frequency of the unpaired electron(s), and τ_e is the correlation time for the exchange interaction.

The second type of interaction is the dipolar spin-spin interaction[7] for which the line broadening is given by[15]

$$\left(\frac{1}{T_{2i}} - \frac{1}{T_2}\right) = \frac{S(S+1)\gamma_I{}^2g^2\beta^2p}{15r^6}\left[7\tau_c + \frac{13\tau_c}{1 + \omega_s{}^2\tau_c{}^2}\right] \tag{5}$$

where γ_I is the gyromagnetic ratio of the proton, g is the spectroscopic splitting factor of the unpaired electron(s), r is the distance between the electron(s) and the proton, and τ_c is the correlation time for the dipolar interaction. The correlation time τ_c is presumably related to τ_r, the ion-pair tumbling time, and to T_{1e} according to the relationship[16]

$$\frac{1}{\tau_c} = \frac{1}{\tau_r} + \frac{1}{T_{1e}} \tag{6}$$

Rate processes may contribute to the line width if the lifetimes of the ion pairs and ions in the bulk solution are long compared to the inverse frequency separation of the protons in the two environments.[17] Broadening due to the chemical-exchange process was ruled out because (1) there is no observable line broadening in the $R_4N^+Fe(CN)_6{}^{3-}$ system,[3] where the frequency separations (between protons in ion pairs and in bulk solution) and presumably the lifetimes are comparable to those in the $R_4N^+Cr(CN)_6{}^{3-}$ systems and (2) doubling the concentrations of $(CH_3)_4N^+$ and $(C_2H_5)_4N^+$ showed only the narrowing of the lines which is expected from a shift in the equilibrium, and not the additional narrowing which is expected on the basis of a second-order exchange process. If the exchange is second order, doubling the concentration of each component should result in a twofold decrease in average lifetimes, which in turn results in a twofold decrease in the line broadening.

Ion-Pair Geometry.—A model has been proposed for the $R_4N^+Fe(CN)_6{}^{3-}$ ion pair, and evidence has been presented which indicates that the "pseudo-contact" or dipolar interaction is predominant in both $R_4N^+Fe(CN)_6{}^{3-}$ and $R_4N^+Cr(CN)_6{}^{3-}$ ion pairs.[3] We propose to interpret the data in this study in terms of the same dipolar interaction,[18] which is given by eq 5. We further propose to use the same model for the ion-pair geometry.

Inspection of eq 5 shows that for any given ion with more than one equivalent set of protons, the relative line broadenings for the various sets will be given by

$$\left(\frac{1}{T_{2i}} - \frac{1}{T_2}\right):\left(\frac{1}{T_{2j}} - \frac{1}{T_2}\right):\cdots = \frac{\left[7\tau_c + \dfrac{13\tau_c}{1 + \omega_s{}^2\tau_c{}^2}\right]_i}{r_i{}^6}:\frac{\left[7\tau_c + \dfrac{13\tau_c}{1 + \omega_s{}^2\tau_c{}^2}\right]_j}{r_j{}^6}:\cdots \tag{7}$$

If we assume there is no contribution to τ_c from internal motion of the alkyl chain, then eq 7 becomes

$$\left(\frac{1}{T_{2i}} - \frac{1}{T_2}\right):\left(\frac{1}{T_{2j}} - \frac{1}{T_2}\right):\cdots = r_i{}^{-6}:r_j{}^{-6}:\cdots \tag{8}$$

and relative line broadenings can be described solely in terms of molecular geometry. Values of $r_i{}^{-6}$ were calculated from the model as a function of R, the internuclear distance between the Cr in $Cr(CN)_6{}^{3-}$ and the N in R_4N^+. The relative broadenings were calculated for each ion from eq 8. These values, which are line broadenings for protons in ion pairs or

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(14) I. Solomon and N. Bloembergen, *J. Chem. Phys.*, **25**, 261 (1956).

(15) R. A. Bernheim, T. H. Brown, H. S. Gutowsky, and D. E. Woessner, *ibid.*, **30**, 950 (1959).

(16) N. Bloembergen and L. O. Morgan, *ibid.*, **34**, 842 (1961).

(17) H. S. Gutowsky, D. W. McCall, and C. P. Slichter, *ibid.*, **21**, 279 (1953).

(18) See T. J. Swift and R. E. Connick, *ibid.*, **37**, 307 (1962), for a discussion of limiting cases in paramagnetic broadening. The present case corresponds to their eq 10d, although they consider systems in which concentration of diamagnetic species ≫ concentration of paramagnetic species.

$(1/T_{2ip} - 1/T_2)$, are equal to $(1/T_{2i} - 1/T_2)$ when $p = 1$. The values were normalized to fit the α-CH_2 protons for each ion except $(CH_3)_4N^+$. In this case, the normalized value for α-CH_2 in $(C_2H_5)_4N^+$ was used to calculate the broadening in $(CH_3)_4N^+$. The values of $(1/T_{2ip} - 1/T_2)$ were calculated for various values of R from the data in Table I and are presented in Table II. For any given ion, the initial slopes and calculated values of $(1/T_{2ip} - 1/T_2)$ are proportional to one another, so that absolute values need not be known. For comparison between different ions, absolute values of line broadenings must be used, and these depend upon a knowledge of the correct equilibrium quotients. Thus, the comparison made between $(CH_3)_4N^+$ and $(C_2H_5)_4N^+$ may be in error.

It can be seen by comparison of the calculated values of $(1/T_{2ip} - 1/T_2)$ in Table II with the observed values in Table I that a value of $R = 11$ A gives satisfactory agreement between observed and calculated data.

TABLE II

CALCULATED VALUES OF $(1/T_{2ip} - 1/T_2)$ FOR PROTONS IN TETRAALKYLAMMONIUM CHROMICYANIDE ION PAIRS

Position	Group			
	CH_3	C_2H_5	n-C_3H_7	n-C_4H_9
		$R = 9^a$		
α	300	350^b	460^b	640^b
β		190	...	...
γ			220	...
δ				180
		$R = 10$		
α	310	350^b	460^b	640^b
β		210	...	...
γ			240	...
δ				230
		$R = 11$		
α	310	350^b	460^b	640^b
β		230	...	...
γ			290	...
δ				270

^{a} N–Cr internuclear distance in A. ^{b} Normalized value.

Discussion

One of the purposes of this paper is to compare results obtained from line-broadening studies with those obtained previously,[3] using two systems in which ion-pair geometry is expected to be very nearly identical. The value of R reported[3] for the $R_4N^+Fe(CN)_6{}^{3-}$ system is 8 A; relative chemical shifts were calculated for this system for larger values of R. Table III shows observed values and values calculated for $R = 8$ and 9 A. The calculations showed that values of R larger than 9 A need not be considered.

It is seen from inspection of Table III that $R = 9$ A gives as good a fit of the data as does $R = 8$ A. We conclude that line-broadening studies indicate that $R = 11$ A for the $R_4N^+Cr(CN)_6{}^{3-}$ system and that chemical shift studies indicate that $R = 9$ A for the $R_4N^+Fe(CN)_6{}^{3-}$ system. The agreement may be considered satisfactory, since the ion-pair model is a crude one.

TABLE III

OBSERVED AND CALCULATED SHIFTS FOR PROTONS IN TETRAALKYLAMMONIUM FERRICYANIDE ION PAIRS

Position	Group			
	CH_3	C_2H_5	n-C_3H_7	n-C_4H_9
		Observed		
α	63	106	104	99
β		64	88	...
γ			56	...
δ				31
		$R = 8^a$		
α	95	103^b	103^b	103^b
β		67	71	...
γ			49	...
δ				30
		$R = 9$		
α	96	103^b	103^b	103^b
β		71	78	...
γ			57	...
δ				38

^{a} N–Fe internuclear distance in A. ^{b} Normalized values.

Examination of the data for α-CH_2 protons in Table II shows that $(1/T_{2ip} - 1/T_2)$ increases appreciably with length of the alkyl chain. This indicates that τ_c varies from ion to ion (see eq 7) since $r_i{}^{-6}$ factors are identical for CH_2 protons at any one position. The dipolar correlation time is related to the tumbling time for the ion pair, τ_r, and T_{1e} by eq 6. Estimates of τ_c from eq 5 indicate that τ_c values range from 10^{-8} to 10^{-9} sec for the various ion pairs studied. Electron magnetic resonance studies indicate[19] that T_{1e} is of the order of 10^{-9} sec in these systems. Since there is no reason to suspect that T_{1e} varies from one ion pair to another in these systems, we attribute the change in τ_c to a change in τ_r. Presumably, τ_r is also of the order of 10^{-9} sec and varies with length of the alkyl chain. The presumed variation is toward longer τ_r for longer alkyl chains or a longer tumbling time for a more bulky ion pair, which is reasonable.

A model for ion pairs has been proposed[20] in which the R_4N^+ tumbles unrestricted about the N at a fixed distance from the anion. Free rotations about C–C single bonds were also assumed. An interionic distance of 3.8 A was calculated for $(C_4H_9)_4N^+(C_6H_5)_3PMI_3{}^-$ systems, where M is Co or Ni. Unrestricted tumbling is not a reasonable assumption[3] at the small interionic distance calculated since there would be much steric hindrance. Also, unrestricted rotation about a C–C single bond presumably does not occur.[21] Three configurations, one *trans* and two *gauche*, are considered to be predominant for each C–C single bond. Unfortunately, no change in the multiplet pattern could be detected at a temperature of 90° or with use of acetone-d_6 as a solvent. Thus, no estimate of fractions of *trans* and *gauche* forms was made. Calculations made from the model used in this paper show that the shifts in the $(C_4H_9)_4N^+(C_6H_5)_3PMI_3{}^-$ systems[20] are consistent with an interionic distance of 6 A.

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(19) A. Wolberg, private communication.

(20) G. N. LaMar, *J. Chem. Phys.*, **43**, 235 (1965).

(21) See ref 9, pp 377–385.

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Coordination Complexes of the Selenocyanate Ion[1]

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A series of new selenocyanate complexes of transition metal ions has been prepared. The basic preparative technique involves the reaction of the appropriate metal salt with potassium selenocyanate and $[(n\text{-}C_4H_9)_4N]SeCN$ in absolute ethanol. The complexes were characterized by elemental analyses, conductivity measurements in nitrobenzene solution, and infrared spectra of Nujol mulls and acetone solutions. Examples of both bonding modes of the selenocyanate were found: $[M(NCSe)_4]^{2-}$ (M = Fe(II), Zn(II)), $[M(NCSe)_6]^{n-}$ (M = Mn(II), Fe(III), Ni(II), Y(III)), $[Rh(SeCN)_6]^{3-}$, and $[M(SeCN)_4]^{2-}$ (M = Pd(II), Pt(II)). The Cd(II) complex prepared is unique in its constitution, $[(n\text{-}C_4H_9)_4N]_2[Cd_2(NCSe)_6]$. Its infrared spectrum supports a structure involving Cd–NCSe–Cd bridges and terminal Cd–NCSe groups. The ranges of integrated absorption intensities of the C–N stretching bands for Se- and N-bonded complexes were found to be, respectively, $0.5\text{–}1 \times 10^4$ and $5\text{–}10 \times 10^4$ M^{-1} cm^{-2}. The visible spectrum of the Pd(II) complex indicates that the ligand field strength of –SeCN is less than that of –SCN, the former being slightly below –Br in the spectrochemical series.

Introduction

The coordination chemistry of the selenocyanate ion was, until this decade, an area almost completely devoid of research. Recent studies[2–6] have emphasized the analogous coordination behavior of the selenocyanate and thiocyanate ions. However, at the inception of this study, complexes containing selenocyanates as the only ligands had been prepared for only five different transition metal ions: $[Co(NCSe)_4]^{2-}$,[2,4] $[Cr(NCSe)_6]^{3-}$,[5] $[Pt(SeCN)_6]^{2-}$,[2] $[Hg(SeCN)_4]^{2-}$,[2] and AgSeCN (bridged).[2] In an effort to obtain a more complete picture, we have synthesized a number of hitherto unknown selenocyanate complexes. As this paper was being written, Forster and Goodgame[7] published the results of a study involving selenocyanate complexes of several transition metal ions which we had included in our work. However, no two of the compounds prepared from ions common to both studies are identical and the results are, on the whole, complementary.

Experimental Section

Preparation of Compounds. $[(n\text{-}C_4H_9)_4N]SeCN$.—This salt was prepared metathetically from the corresponding bromide and KSeCN in ethanol. After the potassium bromide which precipitated was removed by filtration, the desired product was precipitated from solution by the addition of ethyl ether.

Selenocyanate Complexes.—The preparative technique employed was essentially the same for all of the complexes, with the exception of those of Y(III) and Rh(III). To a solution of the hydrated metal nitrate (Fe(III), Ni(II), Zn(II), Cd(II)), sulfate (Fe(II)), chloride (Mn(II)), or complex chloride (Pd(II), Pt(II)) in absolute ethanol was added an ethanolic solution of a stoichiometric amount (with respect to metathesis) of KSeCN. The resulting mixture was filtered into an ethanolic solution of the calculated amount of $[(n\text{-}C_4H_9)_4N]SeCN$, and the solution thus obtained was stored at $-20°$ until the complex crystallized. The crystals were isolated by filtration, washed with absolute ethanol and anhydrous ethyl ether, dried *in vacuo*, and recrystallized from absolute ethanol. Water was added initially to dissolve the Fe(II), Pd(II), and Pt(II) salts completely. The Ni(II) complex was first precipitated by the addition of anhydrous ethyl ether. The initial Pt(II) reaction mixture was warmed gently on a steam bath in order to complete the substitution reaction.

The Y(III) and Rh(III) complexes were prepared by the direct reaction in ethanol of, respectively, $Y(NO_3)_3 \cdot 6H_2O$ and $K_3[RhCl_6] \cdot H_2O$ with excess $[(n\text{-}C_4H_9)_4N]SeCN$. Water was added to complete the dissolution of the Rh(III) salt. The reaction mixtures were warmed on a steam bath to complete the reactions, then cooled in an ice bath and treated as above.

Infrared Spectra.—Infrared spectra, in the 4000–400 cm^{-1} range, of complexes held in Nujol suspension between KBr plates were measured on a Perkin-Elmer Model 421 recording spectrophotometer. The same instrument was used to record high-resolution spectra of Spectro Grade acetone solutions of the complexes in the selenocyanate C–N stretching range (2200–2000 cm^{-1}). Matched 0.1-mm NaCl cells were employed.

The integrated absorption intensities, A (M^{-1} cm^{-2}), of the C–N stretching bands were determined by Ramsay's method of direct integration.[8] Beer's law plots were made for all of the solutions.

Visible and Ultraviolet Spectra.—Visible and ultraviolet absorption spectra of ethanolic solutions of complexes were measured

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(2) A. Turco, C. Pecile, and M. Nicolini, *Proc. Chem. Soc.*, 213 (1961); *J. Chem. Soc.*, 3008 (1962).

(3) S. M. Nelson, *Proc. Chem. Soc.*, 372 (1961).

(4) F. A. Cotton, D. M. L. Goodgame, M. Goodgame, and T. E. Haas, *Inorg. Chem.*, **1**, 565 (1962).

(5) K. Michelson, *Acta Chem. Scand.*, **17**, 1811 (1963).

(6) M. E. Farago and J. M. James, *Inorg. Chem.*, **4**, 1706 (1965).

(7) D. Forster and D. M. L. Goodgame, *ibid.*, **4**, 1712 (1965).

(8) D. A. Ramsay, *J. Am. Chem. Soc.*, **74**, 72 (1952).