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Electronic Structure of Isothiocyanatopentacyanoferrate(III) and Related Complexes

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Infrared and Raman spectra indicate that the triatomic ligand in the complexes $[(n\text{-}C_4H_9)_4N]_3[Fe(CN)_5NCS]$ and $[(n\text{-}C_4H_9)_4N]_3[Fe(CN)_5NCSe]$ is bonded to the metal through nitrogen. Esr spectra and magnetic susceptibility data between 40 and 300°K of undiluted powders of $[(n\text{-}C_4H_9)_4N]_3[Fe(CN)_5NCS]$ and $[(n\text{-}C_4H_9)_4N]_3[Fe(CN)_5N_3]$ suggest that the ground-state axial distortion introduced by the triatomic ligand is small compared with the octahedral ligand field splitting and is of the same magnitude as the spin–orbit interaction. Electronic spectra of the $[Fe(CN)_5X]^{3-}$ complexes are interpreted in terms of a molecular orbital scheme derived from the energy levels of ferricyanide. The characteristic low-energy electronic absorption band in these complexes is assigned as a charge-transfer transition from a filled 2π orbital of the triatomic ligand to the hole in the $d\pi$ metal level.

Introduction

In a previous paper[1] we analyzed the electronic absorption spectra of the complexes $[Co(CN)_5X]^{3-}$ ($X^- =$ NCS^-, SCN^-, N_3^-, $NCSe^-$) in terms of a molecular orbital energy level scheme for an axially distorted octahedral system. In each case the analysis indicated that in bonding to the metal, the triatomic ligand functions essentially as a σ and π donor. As a further test of this electronic structural model, we have studied the magnetic susceptibilities and electronic and esr spectra of the d^5 low-spin complexes $[(n\text{-}C_4H_9)_4N]_3[Fe(CN)_5NCS]$ and $[(n\text{-}C_4H_9)_4N]_3[Fe(CN)_5N_3]$. We have also prepared and examined the spectral properties of $[(n\text{-}C_4H_9)_4N]_3[Fe(CN)_5NCSe]$. Here we report a detailed characterization of the nature of the ground-state distortion and assignments for the lowest electronic transitions in the $[Fe(CN)_5X]^{3-}$ complexes.

Experimental Section

Compound Preparations.—$[(n\text{-}C_4H_9)_4N]_3[Fe(CN)_5N_3]$ and $[(n\text{-}C_4H_9)_4N]_3[Fe(CN)_5NCS]$ were prepared by a modification of the method of Jaselskis.[2] An aqueous solution of 5 mequiv of $Na_2[Fe(CN)_5NH_3]$ and 15 mequiv of KN_3 or KSCN was passed over a cation-exchange resin. The eluent was titrated to pH 7 with $[(n\text{-}C_4H_9)_4N]OH$ in methanol, keeping the pH between 4 and 11 during the titration. The solution was extracted with several portions of CH_2Cl_2, the CH_2Cl_2 portions were combined, and the solvent was evaporated. The oily residue of azido complex was dissolved in CH_2Cl_2–ether at −78° and recrystallized by slowly warming the solution to 25° to give deep red crystals.

Recrystallization of the thiocyanate complex was preceded by a step in which the excess $[(n\text{-}C_4H_9)_4N](SCN)$ was removed chromatographically. A suspension in benzene of 30 g of silica gel/g of material was used to pack the column. Ionic thiocyanate was eluted with 5% methanol–benzene until the eluent did not change the color of a ferric nitrate solution. The complex was then eluted from the column with methanol. The methanol was evaporated and the complex recrystallized from CH_2Cl_2–ether, as described above, to give orange needles. Some decomposition occurred on the silica gel to produce a blue material which was insoluble in CH_2Cl_2. This substance was not identified. *Anal.* Calcd for $FeC_{55}H_{108}N_{11}$: C, 66.63; H, 11.40; N, 16.16. Found: C, 66.74; H, 11.41; N, 16.00; molar conductance (2.30×10^{-3} *M*) 394 $cm^2\ ohm^{-1}\ mol^{-1}$. Calcd for $FeC_{56}H_{108}N_9S$: C, 66.76; H, 11.22; N, 12.98; S, 3.30. Found: C, 66.58; H, 11.26; N, 12.55; S, 3.49; molar conductance (1.31×10^{-3} *M*) 374 $cm^2\ ohm^{-1}\ mol^{-1}$.

$[(C_2H_5)_4N]_3[Fe(CN)_5NCS]$ and $[(C_6H_5)_4As]_3[Fe(CN)_5NCS]$ were similarly prepared by titrating with a 10% aqueous solution of $[(C_2H_5)_4N]OH$ or a freshly prepared solution of $[(C_6H_5)_4As]OH$. $[(C_2H_5)_4N]_3[Fe(CN)_5NCS]$ could not be extracted from aqueous solution, and the water was removed under reduced pressure at room temperature. These compounds were not analyzed, but the band positions in both the electronic and infrared spectra were found to match those of the $[(n\text{-}C_4H_9)_4N]^+$ salt except for bands attributable to the cations. $[(C_6H_5)_4As]_3[Fe(CN)_5NCS]$ was not completely separated from $[(C_6H_5)_4As](SCN)$.

$[(n\text{-}C_4H_9)_4N]_3[Fe(CN)_5NCSe]$.—$Na_2[Fe(CN)_5NH_3]$ (0.47 g, 1.67 mequiv), $[(n\text{-}C_4H_9)_4Cl]$ (1.39 g, 5 mequiv), and KSeCN (0.24 g, 1.67 mequiv) were stirred for 3 hr in 50 ml of acetone. The violet solution was filtered and the acetone evaporated. The oily residue was recrystallized from CH_2Cl_2–ether to produce a small yield of dark violet crystals. *Anal.* Calcd for $FeC_{56}H_{108}N_9Se$: C, 63.69; H, 10.69; N, 12.38. Found: C, 63.54; H, 10.96; N, 12.32; molar conductance (1.31×10^{-3} *M*), 377 $cm^2\ ohm^{-1}\ mol^{-1}$; $\mu_{eff}(300°K) = 2.15$ BM.

$Na_3[Fe(CN)_5NH_3]$ from Eastern Chemical Corp. was oxidized with nitrous acid to produce $Na_2[Fe(CN)_5NH_3]$.[3] KSeCN from Alfa Inorganics was treated with decolorizing charcoal and recrystallized from acetone. Cation-exchange columns of Amberlite IR-120 cation-exchange resin were washed with dilute HCl and then with distilled water. A Corning Model 12 pH meter was used to measure titration end points.

Conductivities were measured at room temperature in acetonitrile on an Industrial Instruments bridge, Model RC 16B2. Acetonitrile solutions of the $[(n\text{-}C_4H_9)_4N]_3[Fe(CN)_5X]$ com-

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(1) D. F. Gutterman and H. B. Gray, *J. Amer. Chem. Soc.*, **93**, 3364 (1971).

(2) B. Jaselskis, *ibid.*, **83**, 1082 (1961).

(3) K. A. Hoffmann, *Justus Liebigs Ann. Chem.*, **312**, 1 (1900).

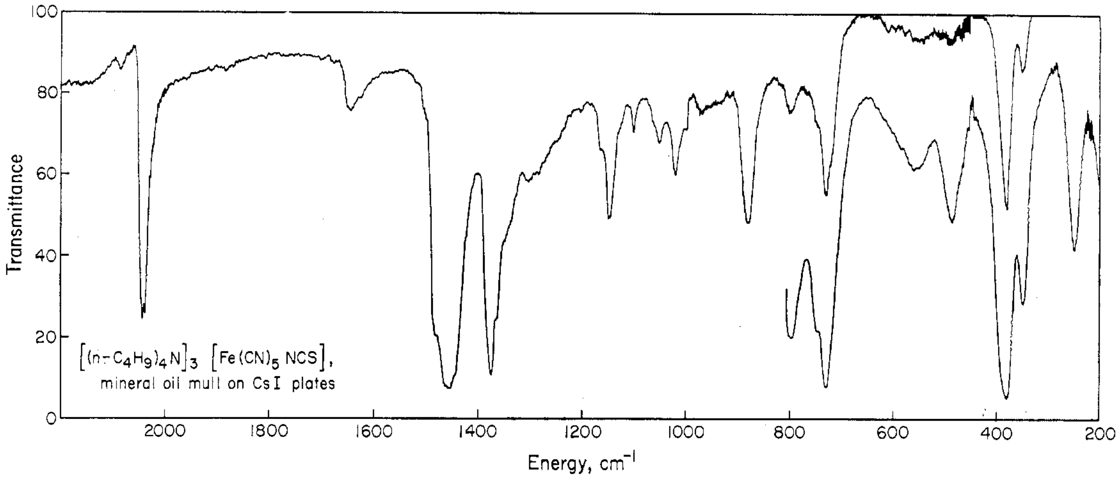

Figure 1.—Infrared spectrum of $[(n\text{-}C_4H_9)_4N]_3[Fe(CN)_5NCS]$ in the region 200–2500 cm^{-1}.

pounds are not stable for long periods and were therefore freshly prepared in each case.

Magnetic Susceptibility Measurements.—Magnetic susceptibilities were measured on a Foner vibrating-sample magnetometer[4] built by Princeton Applied Research. Sample holders machined of Teflon or nylon were designed to attach to the end of the sample rod; these hold a volume of about 0.2 ml. The instrument was calibrated at room temperature with $CuSO_4 \cdot 5H_2O$[5] and with $HgCo(NCS)_4$.[6] The calibrations agreed to within 0.5% in χ. The measured diamagnetisms of KN_3 and of $K_3[Co(CN)_5N_3]$ were found to agree with that calculated from Pascal's constants[7] within experimental accuracy. The diamagnetism of $[(n\text{-}C_4H_9)_4N]_3[Co(CN)_5N_3]$ was then measured to estimate the susceptibility of $[(n\text{-}C_4H_9)_4N]^+$ as -118×10^{-6} cgsu mole^{-1}. Temperature control was achieved with an Andonian Associates liquid helium dewar. The magnetic susceptibility of a weighed sample of $CuSO_4 \cdot 5H_2O$ was measured at five temperatures; the slope of the straight line obtained by plotting temperature *vs.* reciprocal magnetic susceptibility was compared with the Curie–Weiss constants of Figgis and Nyholm[5] to yield instrument calibration constants under these conditions. The susceptibility of a 187-mg sample of $[(n\text{-}C_4H_9)_4N]_3[Fe(CN)_5NCS]$ was then measured at nine points between 40 and 300°K. The susceptibility of a 168-mg sample of $[(n\text{-}C_4H_9)_4N]_3[Fe(CN)_5N_3]$ was similarly measured at four points. These points were used to calibrate a trace of magnetic susceptibility *vs.* thermocouple output which was obtained from an X-Y recorder while the sample was slowly cooled.

Spectral Measurements.—Esr spectra were measured on a Varian 4500 X-band spectrometer equipped with a Varian temperature control unit. Infrared spectra were recorded in the range 200–4000 cm^{-1} on a Beckman IR-12 or a Perkin-Elmer 225 spectrophotometer and in the range 650–4000 cm^{-1} on a Beckman IR-7 or a Perkin-Elmer 421 spectrophotometer. Solution spectra in the cyanide stretching region were taken in a 0.1-mm path length NaCl cell. Raman spectra were recorded on solid samples utilizing a Cary 81 spectrophotometer equipped with a neon–helium laser operating at 6328 Å. Uv, visible, and near-ir absorption spectra were measured on a Cary 14 or a Cary 14 RI recording spectrophotometer. Spectra of solid samples of the $[(n\text{-}C_4H_9)_4N]^+$ salts were obtained either by supporting mineral oil mulls on strips of filter paper or by evaporating a drop of solution on the surface of a silica cell to leave a glassy film. Low-temperature spectra were taken in EPA solution as described previously.[1]

Results and Discussion

Structural Assignments.—The infrared spectrum of a mineral oil mull of $[(n\text{-}C_4H_9)_4N]_3[Fe(CN)_5NCS]$ is shown in Figure 1. The peaks assignable to the complex anion $[Fe(CN)_5NCS]^{3-}$, as well as those for $[Fe(CN)_5N_3]^{3-}$ and $[Fe(CN)_5NCSe]^{3-}$, are summarized in Table I. Bands were assigned by comparing these spectra with infrared spectra of the analogous cobalt compounds[1] and of the tetra-*n*-butylammonium halides. In each case two bands near 400 cm^{-1} have been assigned as ν_{M-C}, the metal–carbon stretch, and a band near 500 cm^{-1} has been assigned as δ_{MCN}, following the accepted assignments for ferricyanide.[8] The metal–thiocyanate and metal–azide stretching frequencies are close to their values in the corresponding cobalt compounds.[1] The metal–selenocyanate stretch is apparently below 200 cm^{-1}.

TABLE I

INFRARED SPECTRA OF $[(n\text{-}C_4H_9)_4N]_3[Fe(CN)_5X]$ AS MINERAL OIL MULLS ON CsI PLATES

	$\bar{\nu}$, cm^{-1}		
Assignments	NCS	N_3	NCSe
Absorptions of X			
Sym str	2103 vs 2070 sh[a]	2031 s	2065 s
Asym str	*b*	*b*	655 vvw[a] 620 vvw[a]
δ	475 sh	623 m 590 sh	*b*
Absorptions of $[Fe(CN)_5]$			
$\nu_{C\equiv N}$	2117 sh 2113 vs	2096 s	2118 sh 2112 s 2102 s 2096 m
ν_{M-C}	390 s 355 m	388 s 360 sh	384 ms 348 mw
δ_{MCN}	495 m	500 mw	493 m
Metal–ligand str, ν_{M-X}	258 m	338 m	*c*
Unassigned absorptions	565 mw		560 vw 533 vw 455 vw

[a] Uncertain assignment. [b] Obscured by other absorptions. [c] Not observed.

$[Fe(CN)_5NCS]^{3-}$.—Jaselskis, who first isolated[2] $[(n\text{-}C_4H_9)_4N]_3[Fe(CN)_5NCS]$, made no attempt to assign the mode of bonding of the thiocyanate ligand. This assignment is complicated by the presence in the infrared spectrum of absorptions due to $[(n\text{-}C_4H_9)_4N]^+$ and to the $[Fe(CN)_5]^{2-}$ unit. In the region between 680 and 850 cm^{-1}, in which ν_{CS} is expected, infrared spectra of $[(n\text{-}C_4H_9)_4N]_3[Fe(CN)_5NCS]$, $[(n\text{-}C_4H_9)_4N]_3[Fe(CN)_5N_3]$, and $[(n\text{-}C_4H_9)_4N]Br$ are indistinguishable. Since it has not been possible to isolate $[Fe(CN)_5$-

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[4] S. Foner, *Rev. Sci. Instrum.*, **30**, 7, 548 (1959).

[5] B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 331 (1959).

[6] B. N. Figgis and R. S. Nyholm, *ibid.*, 4190 (1958).

[7] J. Lewis and R. G. Wilkins, Ed., "Modern Coordination Chemistry," Interscience, New York, N. Y., 1960, p 403.

[8] D. M. Adams, "Metal Ligand and Related Vibrations," E. Arnold Publishing Co., London, 1967, Chapter 3.

$NCS]^{3-}$ as the salt of an inorganic cation, it was instead prepared with two other cations whose bands in this region are shifted somewhat from those of $[(n\text{-}C_4H_9)_4N]^+$.

Several lines of infrared evidence indicate that the thiocyanate in these three compounds is bonded through nitrogen. First, in the ν_{CS} region the infrared spectrum of $[(C_2H_5)_4N]_3[Fe(CN)_5NCS]$ in a pressed KBr disk shows only a cation band above 750 cm^{-1} and nothing between 750 and 650 cm^{-1}. Thus, no absorption is observed which may be assigned as ν_{CS} of a sulfur-bonded thiocyanate.[9,10] Second, in the infrared spectrum of $[(C_6H_5)_4As]_3[Fe(CN)_5NCS]$ there is a shoulder at 805 cm^{-1} which is not present in the spectrum of $[(C_6H_5)_4As]Cl$ and which may be assigned as ν_{CS} of a nitrogen-bonded thiocyanate.[9,10] Finally, in the spectrum of $[(n\text{-}C_4H_9)_4N]_3[Fe(CN)_5NCS]$ the thiocyanate bending frequency, δ_{NCS}, is observed as a shoulder at 475 cm^{-1} on the low-energy side of the M–C–N bending frequency. The position of δ_{NCS} and the absence of additional components of δ_{NCS} at low energy are consistent with a nitrogen-bonded thiocyanate.[10,11] However, the low-energy end of this region is partly obscured by the tail of a strong, broad band at 393 cm^{-1}.

The N-bonded assignment is confirmed by the Raman spectrum of $[(n\text{-}C_4H_9)_4N]_3[Fe(CN)_5NCS]$. Raman spectral data for this compound and for several other thiocyanates are listed in Table II. The positions of the Raman bands are close to the corresponding infrared frequencies. However, the apparent intensities of $\nu_{C\equiv N}$ and ν_{CS} are more nearly equal in the Raman spectra than they are in the infrared and ν_{CS} is more easily discernible. In addition, the Raman spectrum of $[(n\text{-}C_4H_9)_4N]_3[Fe(CN)_5NCS]$ between 600 and 900 cm^{-1} is simpler than the infrared spectrum so that ν_{CS} can be distinguished from the cation peaks. In a number of $[(n\text{-}C_4H_9)_4N]^+$ salts, Raman scattering frequencies are found near 605, 800, and 888 cm^{-1} with relative peak heights 1:4:8. In $[(n\text{-}C_4H_9)_4N]_3[Fe(CN)_5NCS]$ the peaks are at 603, 803, and 888 cm^{-1} with relative peak heights 1:16:8. There are no other peaks in this region. The peak at 803 cm^{-1} is about 4 times as intense as for $[(n\text{-}C_4H_9)_4N]^+$ alone and is assigned primarily to ν_{CS} of a nitrogen-bonded thiocyanate.

TABLE II

RAMAN SPECTRA OF SOME THIOCYANATES IN POWDER SAMPLES

Compd	$\bar{\nu}$, cm^{-1} δ_{NCS}	ν_{CS}	$2\delta_{NCS}$	ν_{CN}
KSCN	481 w	757 ms	974 w	2078 ms
			958 w	2070 s
				2027 vs
$[(n\text{-}C_4H_9)_4N]_3[Fe(NCS)_6]$	488 br, w	830 w		2120 w
				2080 w
				2060 s
$K_3[Co(CN)_5SCN]$	465 sh, w	728 m		2123 m[a]
$[(n\text{-}C_4H_3)_4N]_3[Co(CN)_5NCS]$	475 m	800 m		2097 m[a]
$[(n\text{-}C_4H_9)_4N]_3[Fe(CN)_5NCS]$	478 m	803 m		2114 s[b]

[a] Overlaps the cyano stretching frequency which is at higher energy. [b] There is only one peak in this region of the spectrum; $\nu_{C\equiv N}$ from isothiocyanate falls at the same position as the coordinated cyanide stretching frequency.

Although crystalline $[(n\text{-}C_4H_9)_4N]_3[Fe(CN)_5NCS]$ is orange, its solutions in organic solvents range in color from orange, in aprotic solvents such as acetone, to purple in ethanol or methanol. Aqueous solutions are either blue or purple depending on the other species present. The different colors in protic solvents could indicate some linkage isomerization has occurred. In fact, it has been suggested[12] that in aqueous solution the purple color is due to $[Fe(CN)_5NCS]^{3-}$ and the blue to $[Fe(CN)_5SCN]^{3-}$. Another reasonable possibility is that varying mixtures of the two linkage isomers are present in different protic solvent media. Turning to infrared spectral data in the cyano stretching region, we find that the solid and solutions in both protic and aprotic organic solvents show either two overlapping peaks or a broad band with a shoulder. The spectrum of a chloroform solution, for example, is given in Table III. The exact band positions change slightly from solvent to solvent but are always within about 5 cm^{-1} of the principal peak positions (2103, 2113 cm^{-1}) in the solid. These solvent shifts are comparable to those observed[1] for $\nu_{C\equiv N}$ of $[(n\text{-}C_4H_9)_4N]_3[Co(CN)_5NCS]$ and thus it would appear that appreciable linkage isomerization of $[Fe(CN)_5NCS]^{3-}$ does not take place in nonaqueous solutions. Infrared spectral evidence, however, is not available bearing on the question of linkage isomerization in aqueous solution.

TABLE III

INFRARED SPECTRA IN SOLUTION IN THE REGION 2000–2300 CM^{-1}

Compd	Solvent	$\bar{\nu}$, cm^{-1}	ϵ, M^{-1} cm^{-1}	$\Delta\nu_{1/2}$, cm^{-1}	$10^{-4}A$,[a] M^{-1} cm^{-2}
$[(n\text{-}C_4H_9)_4N]_3[Fe(CN)_5NCS]$	$CHCl_3$	2111	1160	b	
		2106		b	
$[(n\text{-}C_4H_9)_4N]_3[Fe(CN)_5NCSe]$	Acetone	2118	780	23	6.5
		2110 sh			
		2065	590	19	3.9
$[(n\text{-}C_4H_9)_4N]_3[Fe(CN)_5N_3]$	Acetone	2103	835	16	4.8
		2028	654	18	4.3
KSeCN	Acetone	2069	690	12	2.9
$[(C_2H_5)_4N](SeCN)$	Acetone	2068	746	11	3.1

[a] Values calculated by the method given by D. A. Ramsay, *J. Amer. Chem. Soc.*, **74**, 72 (1952). [b] Strongly overlapping peaks.

$[Fe(CN)_5NCSe]^{3-}$.—The infrared spectrum of a concentrated mull of $[(n\text{-}C_4H_9)_4N]_3[Fe(CN)_5NCSe]$ shows several weak peaks in the region of ν_{CSe}. Of these, a peak at 534 cm^{-1} is assigned to the $[(n\text{-}C_4H_9)_4N]^+$ cation and a broad band near 570 cm^{-1} is identified with a similar band in $[(n\text{-}C_4H_9)_4N]_3[Fe(CN)_5NCS]$. This leaves unaccounted for the absorptions at 623 and 655 cm^{-1}. These two frequencies are close to those seen in the infrared spectrum of the corresponding cobalt compound.[1] Assuming that at least one of these peaks is due to ν_{CSe}, the complex in question must be N bonded.

The magnitude of the integrated absorption coefficient (A) of the C≡N stretching band of coordinated selenocyanate ($\nu_{C\equiv N}$) shows that nonaqueous solutions contain primarily $[Fe(CN)_5NCSe]^{3-}$. The integrated intensity of $\nu_{C\equiv N}$ in aprotic solvents has been shown to be roughly an order of magnitude greater when NCS^- or $NCSe^-$ is bonded through nitrogen than when it is bonded through sulfur or selenium, whereas an intermediate A value is found in the uncomplexed ion.[13] The integrated intensities of the bands in the cyano

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[9] A. Turco and C. Pecile, *Nature (London)*, **191**, 66 (1961).

[10] J. Lewis, R. S. Nyholm, and P. W. Smith, *J. Chem. Soc.*, 4590 (1961).

[11] A. Sabatini and I. Bertini, *Inorg. Chem.*, **4**, 1665 (1965).

[12] R. Stasiw and R. G. Wilkins, *ibid.*, **8**, 156 (1969).

[13] C. Pecile, *ibid.*, **5**, 210 (1966).

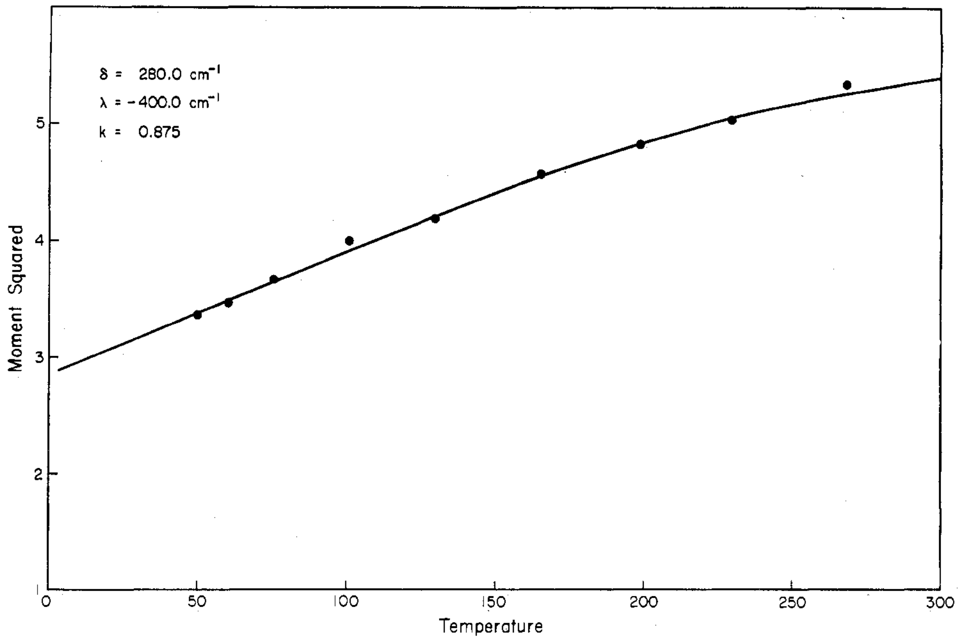

Figure 2.—Temperature dependence of the square of the magnetic moment for $[(n\text{-}C_4H_9)_4N]_3[Fe(CN)_5NCS]$.

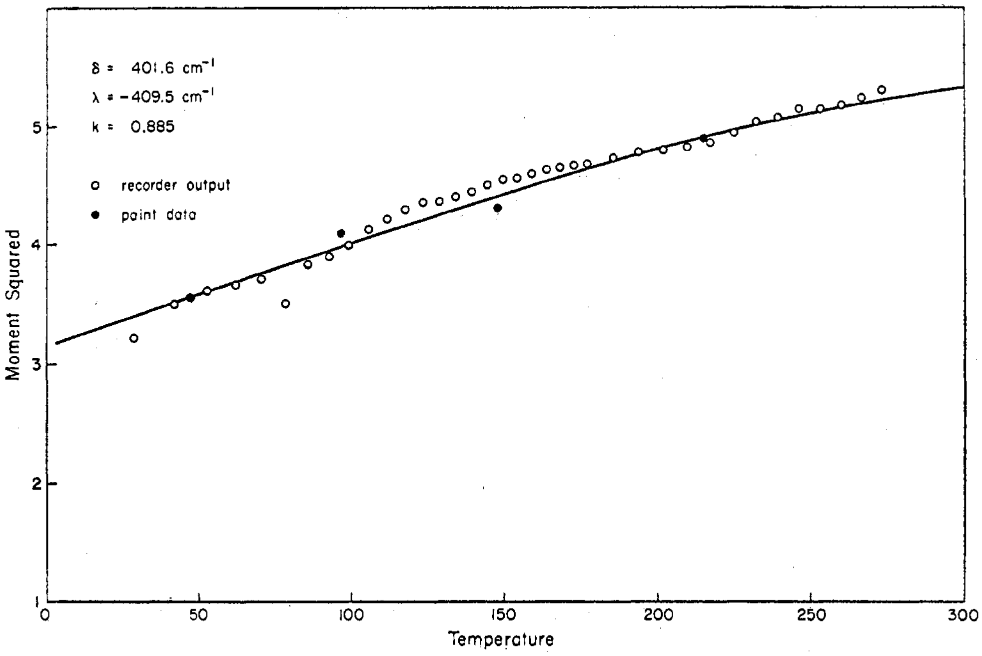

Figure 3.—Temperature dependence of the square of the magnetic moment for $[(n\text{-}C_4H_9)_4N]_3[Fe(CN)_5N_3]$.

stretching region for $[(n\text{-}C_4H_9)_4N]_3[Fe(CN)_5NCSe]$ in acetone solution, which were calculated using Ramsay's method,[14] are given in Table III. The band at 2119 cm^{-1} ($A = 6.5 \times 10^4\ M^{-1}\ cm^{-2}$) is assigned to the cyano ligands and the peak at 2065 cm^{-1} ($A = 3.9 \times 10^4\ M^{-1}\ cm^{-2}$) is attributed to coordinated selenocyanate. The value $A = 3.9 \times 10^4\ M^{-1}\ cm^{-2}$ is below the range suggested for N-bonded selenocyanate[13,15] but is higher than A for ionic $NCSe^-$. The predominant species in acetone solution is therefore the nitrogen-bonded isomer $[Fe(CN)_5NCSe]^{3-}$.

Solutions of $[(n\text{-}C_4H_9)_4N]_3[Fe(CN)_5NCSe]$, like those of the isothiocyanate, exhibit different colors in protic and aprotic solvents. Acetone solutions and solid samples of $[(n\text{-}C_4H_9)_4N]_3[Fe(CN)_5NCSe]$ are purple, and both have infrared peaks at 2065 and 2110 cm^{-1}; in the solid the high-energy peak is extensively split. Ethanol solutions are blue, and the cyano stretching peaks are broader. The low-energy peak, as has been observed for $\nu_{C\equiv N}$ of other selenocyanates in protic solvents,[13] is particularly broad. The peak positions, however, are roughly the same as in acetone and the predominant species is probably still $[Fe(CN)_5NCSe]^{3-}$.

It should be noted that $[(n\text{-}C_4H_9)_4N]_3[Fe(CN)_5NCS]$ and $[(n\text{-}C_4H_9)_4N]_3[Fe(CN)_5NCSe]$ were isolated under conditions which give nitrogen-bonded cobalt complexes,[1] that is, using organic solvents and large organic cations.

Magnetic Susceptibility and Esr Results.—The magnetic susceptibilities and magnetic moments of

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(14) D. A. Ramsay, *J. Amer. Chem. Soc.*, **74**, 72 (1952).

(15) J. L. Burmeister and L. E. Williams, *Inorg. Chem.*, **5**, 1113 (1966).

$[(n\text{-}C_4H_9)_4N]_3[Fe(CN)_5NCS]$ and $[(n\text{-}C_4H_9)_4N]_3[Fe(CN)_5N_3]$ at several temperatures are given in Table IV. These data were fitted by calculating the average susceptibility as a function of temperature for a cubic $^2T_{2g}(d^5)$ term subject to the combined effect of spin–orbit coupling, λ, and an axial field component, δ.[16] The axial field is defined as positive if, in the absence of spin–orbit coupling, the orbitally nondegenerate $^2B_2$ state lies lowest. The Zeeman Hamiltonian is taken as $\mathcal{H}_z = (kL + 2S)\beta \cdot H$, where k is the orbital reduction factor. Theoretical susceptibility *vs.* temperature curves that give the best agreement[17] with the experimental data for $[(n\text{-}C_4H_9)_4N]_3[Fe(CN)_5NCS]$ and $[(n\text{-}C_4H_9)_4N]_3[Fe(CN)_5N_3]$ are shown in Figures 2 and 3, respectively. The best values of λ, δ, and k for these two compounds are compared in Table V with the corresponding parameters for several other low-spin ferric compounds.

TABLE IV
MAGNETIC SUSCEPTIBILITIES AND MAGNETIC MOMENTS AS FUNCTIONS OF TEMPERATURE

Temp, °K	$10^6\chi_g$, cgsu	$10^6\chi_M^{cor}$, cgsu	μ_{eff}, BM	Temp, °K	$10^6\chi_g$, cgsu	$10^6\chi_M^{cor}$, cgsu	μ_{eff}, BM
		$[(n\text{-}C_4H_9)_4N]_3[Fe(CN)_5NCS]^a$					
268	1.81	2496	2.31	101	4.36	4973	2.00
229	2.07	2752	2.25	75	5.53	6105	1.91
199	2.38	3046	2.20	60	6.66	7207	1.86
165	2.82	3469	2.14	50	7.92	8430	1.84
129	3.42	4056	2.05				
		$[(n\text{-}C_4H_9)_4N]_3[Fe(CN)_5N_3]^b$					
215	2.21	2843	2.21	97	4.77	5290	2.02
148	3.05	3648	2.08	47	9.09	9416	1.88

[a] Mol wt 970.7. Diamagnetic correction -740×10^{-6} mol^{-1}. [b] Mol wt 955.7. Diamagnetic correction -730×10^{-6} mol^{-1}.

TABLE V
VALUES OF THE PARAMETERS USED TO DESCRIBE THE MAGNETIC BEHAVIOR OF SOME LOW-SPIN FERRIC COMPOUNDS

Compd	δ, cm^{-1}	λ, cm^{-1}	δ/λ	k	μ_{eff} (300°K), BM
$[(n\text{-}C_4H_9)_4N]_3[Fe(CN)_5NCS]$	280	−400	−0.70	0.88	2.27
$[(n\text{-}C_4H_9)_4N]_3[Fe(CN)_5N_3]$	402	−409	−0.98	0.89	2.33
$K_3[Fe(CN)_6]^a$	0	−400	0.0	0.8	2.25
$K_3[Fe(CN)_6]^b$	150–300	−325	−0.5 to −1.0	0.75	2.25
$[Fe(o\text{-phen})_3](ClO_4)_3 \cdot 3H_2O^a$	600	−400	−1.50	1.00	2.40
$[Fe(o\text{-phen})_2(CN)_2](ClO_4)^c$	393	−437	−0.9	0.95	2.40
$[Fe(o\text{-phen})_2(CN)_2](NO_3) \cdot 4H_2O^c$	644	−460	−1.4	1.00	2.35

[a] B. N. Figgis, *Trans. Faraday Soc.*, **57**, 204 (1961). [b] B. N. Figgis, M. Gerloch, and R. Mason, *Proc. Roy. Soc., Ser. A*, **309**, 91 (1969). [c] B. N. Figgis, J. Lewis, F. E. Mabbs, and G. A. Webb, *J. Chem. Soc.*, 422 (1966).

For $[(n\text{-}C_4H_9)_4N]_3[Fe(CN)_5NCS]$ the best fit to the data points is found for $\delta = +280$ cm^{-1}, $\lambda = -400$ cm^{-1}, and $k = 0.875$. The fit is nearly as good if $\delta = -305$ cm^{-1}, $\lambda = -435$ cm^{-1}, and $k = 0.90$. Each point is within 1.0% of the curve in either case and this is much smaller than the experimental error. For $[(n\text{-}C_4H_9)_4N]_3[Fe(CN)_5N_3]$ the best fit is found for $\delta = 402$ cm^{-1}, $\lambda = -409$ cm^{-1}, and $k = 0.885$. Each point is within 2.0% of the curve. The best fit for a negative value of δ is considerably poorer and requires a value of $|\lambda|$ which is unexpectedly large. The susceptibility data thus suggest, but do not prove, that both complexes under consideration have a $^2B_2(+\delta)$ ground state.

The esr spectra of the $[Fe(CN)_5X]^{3-}$ complexes confirm that the ground state is $^2B_2$ and are consistent with a model in which the axial distortion is relatively small. The esr spectrum of $[(n\text{-}C_4H_9)_4N]_3[Fe(CN)_5NCS]$ at 85°K shows a typical three-line pattern with $g_1 = 2.51$, $g_2 = 2.29$, and $g_3 = 1.8$. The lines are quite broad and strongly overlapping. The esr spectrum of this complex in the diamagnetic host $[(n\text{-}C_4H_9)_4N]_3[Co(CN)_5NCS]$ is less intense but otherwise identical with that of the undiluted powder. The esr spectrum of $[(n\text{-}C_4H_9)_4N]_3[Fe(CN)_5N_3]$ as an undiluted powder is similar, with two overlapping lines at $g_1 = 2.64$ and $g_2 = 2.28$ and a weaker line at $g_3 \approx 1.8$. The pattern of g values displayed in each case requires[18] a negative value of δ/λ. In addition, $|\delta/\lambda|$ cannot be very large because the g values are significantly different from 2.0.

The observation of three g values clearly demonstrates that the symmetry about the Fe(III) is less than axial. Bleaney and O'Brien have derived general expressions for the g values of a $(t_{2g})^5$ configuration in a rhombic field.[19] When the parameters obtained from the temperature dependence of the magnetic susceptibility of $[(n\text{-}C_4H_9)_4N]_3[Fe(CN)_5NCS]$ are substituted into these expressions, $^1/_2(g_x + g_y)$ is calculated to be 2.38, in reasonable agreement with the experimental value of 2.40. However, g_z is calculated to be 0.5, which is much smaller than the observed 1.8. All three g values can be fitted with $\delta/\lambda = -4.4$, $k = 0.95$, and a rhombic distortion of 2°. Similarly, the g values of $[(n\text{-}C_4H_9)_4N]_3[Fe(CN)_5N_3]$ can be fitted with $\delta/\lambda = -4.1$, $k = 1.0$, and a rhombic distortion of 3°. Thus the esr spectra require axial distortions that are considerably greater than those predicted by the magnetic susceptibility treatment, although the splitting of the $^2T_{2g}$ term is still small relative to the excitation energies from $^2T_{2g}$ to the lowest spin-doublet ligand field excited states.

Electronic Spectra.—The electronic absorption spectra of the $[Fe(CN)_5X]^{3-}$ complexes in thin films and the spectrum of $[Fe(CN)_5NCS]^{3-}$ in acetonitrile solution are set out in Table VI. Table VII gives spectral data for EPA solutions at 300 and 77°K. Sample spectra of $[Fe(CN)_5NCS]^{3-}$ are shown in Figures 4 and 5. In each complex there is a fairly intense band in the visible region of the spectrum and a number of shoulders and poorly resolved peaks on the tail of rising uv absorption. The spectrum of $[(n\text{-}C_4H_9)_4N]_3[Fe(CN)_5NCS]$ in acetonitrile is similar in appearance and band po-

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[16] B. N. Figgis, *Trans. Faraday Soc.*, **56**, 1556 (1960); **57**, 198, 204 (1961); *Nature (London)*, **203**, 1138 (1964); *J. Chem. Soc. A*, 1411 (1966).

[17] D. F. Gutterman, Ph.D. Thesis, Columbia University, 1969.

[18] H. Kamimura, *J. Phys. Soc. Jap.*, **11**, 1171 (1956).

[19] B. Bleaney and M. C. M. O'Brien, *Proc. Phys. Soc., London, Sect. B*, **69**, 1216 (1956).

TABLE VI

ELECTRONIC SPECTRA OF $[(n\text{-}C_4H_9)_4N]_3[Fe(CN)_5X]$ COMPLEXES

X		λ_{max}, nm	$10^{-3}\bar{\nu}$, cm^{-1}	ϵ, M^{-1} cm^{-1}
NCS	Acetonitrile soln[a]	479	20.9	3,600
		393	25.5	720
		352	28.4	900
		~320	~31.3 sh	1,000
		302	33.1	1,180
		~275	~36.4 sh	1,670
		~260	~38.5 sh	
		225	44.4	15,500
NCSe	Thin film	550	18.2	
		406	24.6	
		357	28.0	
		327	30.6	
		~305	32.8 sh	
		255	39.2 sh	
N_3	Thin film	532	18.8	
		423	23.6 sh	
		400	25.0	
		322	31.1 sh	
		304	32.9 sh	
		283	35.3 sh	
		261	38.3 sh	
		248	40.3 sh	
		208	48.1 sh	

[a] Band positions are similar in a thin film.

TABLE VII

ELECTRONIC SPECTRA OF $[(n\text{-}C_4H_9)_4N]_3[Fe(CN)_5X]$ IN EPA AT 300 AND 77°K

	300°K			77°K			
X	λ_{max}, nm	$10^{-3}\bar{\nu}$, cm^{-1}	ϵ, M^{-1} cm^{-1}	λ_{max}, nm	$10^{-3}\bar{\nu}$, cm^{-1}	ϵ, M^{-1} cm^{-1}	Assignment
CN[a]	426	23.5[b]	493				$\sigma(CN) \rightarrow d\pi(Fe)$ $[^2T_{2g} \rightarrow {}^2T_{1u}]$
	326	30.7 sh	876				LF $[^2T_{2g} \rightarrow {}^2A_{1g}, {}^2T_{1g}]$
	303	33.0	1338				$\pi(CN) \rightarrow d\pi(Fe)$ $[^2T_{2g} \rightarrow {}^2T_{2u}]$
	286	35.0 sh	864				LF $[^2T_{2g} \rightarrow {}^2E_g]$
	260	38.5	1157				$\pi(CN) \rightarrow d\pi(Fe)$ $[^2T_{2g} \rightarrow {}^2T_{1u}]$
NCS	521	19.2	3600	552	18.1	5390	$2\pi(NCS) \rightarrow d\pi(Fe)$
	395	25.3 sh	520	390	25.6 sh	412	LF
	350	28.6	995	352	28.4	1100	$\sigma(CN) \rightarrow d\pi(Fe)$
	323	31.0 sh	1090	318	31.4 sh	1261	$\pi(CN) \rightarrow d\pi(Fe)$
	300	33.3 sh	1360	300	33.3	1242	LF
	~270	37.0 sh	2130	271	36.9 sh	1702	$\pi(CN) \rightarrow d\pi(Fe)$
	~260	38.5 sh	2280	260	38.5 sh	1758	
NCSe	598	16.7	2180	669	14.9	5400	$2\pi(NCSe) \rightarrow d\pi(Fe)$
	397	25.2 sh	595	396	25.3 sh	700	LF
	353	28.4	870	355	28.2	1080	$\sigma(CN) \rightarrow d\pi(Fe)$
	323	31.0 sh	1150	323	31.0	1215	$\pi(CN) \rightarrow d\pi(Fe)$
				302	33.1	1700	LF
	275	36.4 sh	3226	270	37.0	3290	$\pi(CN) \rightarrow d\pi(Fe)$
N_3	556	18.0	1580	551	18.1	2070	$2\pi(N_3) \rightarrow d\pi(Fe)$
	418	23.9	990	417	24.0	1020	$\sigma(CN) \rightarrow d\pi(Fe)$
	~405	24.7 sh		400	25.0 sh	880	LF
	322	31.1 sh	1650	324	30.9	1156	LF
	305	32.8 sh	2455	303	33.0 sh	2130	
	283	35.3 sh	2910	283	35.3 sh	2750	
				265	37.7 sh	3500	
	240	41.7 sh	5000	243	41.2 sh	5300	

[a] From ref 20. [b] There is a shoulder on the high-energy side of the 23,500-cm^{-1} band. This shoulder, which appears at 25,300 cm^{-1}, is probably part of a vibrational progression in the totally symmetrical C≡N stretching mode on the $^2T_{2g} \rightarrow {}^2T_{1u}$ band and not a forbidden charge-transfer transition as was proposed[20] earlier.

sitions to the thin-film spectrum. However, $[(n\text{-}C_4H_9)_4N]_3[Fe(CN)_5N_3]$ and $[(n\text{-}C_4H_9)_4N]_3[Fe(CN)_5\text{-}NCSe]$ decompose significantly in acetonitrile in the time required to make dilutions, and in Table VI only the spectra of the two solids are reported to 52,000 cm^{-1}. Room-temperature spectra in ethanol and in EPA are identical for each compound. Solutions of the azide and the selenocyanate complexes in ethanol decompose slowly. In the presence of excess $[(n\text{-}C_4H_9)_4N]X$ these solutions are stable and the low-energy regions of the spectra agree with those of freshly prepared solutions in ethanol alone.

Although the electronic absorption spectra of the $[Fe(CN)_5X]^{3-}$ complexes are rather complicated, reasonable assignments may be made on comparison with the spectrum of the parent hexacyanoferrate(III). The spectrum of $[Fe(CN)_6]^{3-}$ in EPA solution includes three moderately intense bands at 23,500, 33,000, and 38,460 cm^{-1} which have been assigned[20] as ligand-to-metal (L → M) charge-transfer transitions from the three highest filled ligand levels $[t_{1u}(\sigma(CN)),\ t_{2u}(\pi(CN)),\ t_{1u}(\pi(CN))]$ to the hole in the metal $t_{2g}(d\pi)$ level. Shoulders on both sides of the 33,000-cm^{-1} band have been assigned[20,21] as ligand field (LF) transitions. An intense shoulder at 45,500 cm^{-1} represents the first metal-to-π^*(CN) charge-transfer transition.[20]

The most prominent feature in the $[(n\text{-}C_4H_9)_4N]_3[Fe(CN)_5NCS]$ spectrum is an intense peak at low energy (20,900 cm^{-1} in acetonitrile) which gives the compound its characteristic color. This band is absent in the spectrum of either $[Fe(CN)_6]^{3-}$ or $[Co(CN)_5NCS]^{3-}$ and thus may be firmly assigned as the L → M charge-transfer transition from an occupied thiocyanate 2π orbital to the metal $d\pi$ level. This assignment is in complete agreement with our earlier conclusion[1] that the major change in the energy level scheme in going from $[M(CN)_6]^{3-}$ to $[M(CN)_5NCS]^{3-}$ is the placement of the filled 2π(NCS) level immediately below the metal $d\pi$ orbitals.

The strong absorptions which are placed at 28,600,

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(20) J. J. Alexander and H. B. Gray, *J. Amer. Chem. Soc.*, **90**, 4260 (1968).

(21) C. S. Naiman, *J. Chem. Phys.*, **35**, 323 (1961); **39**, 1900 (1963).

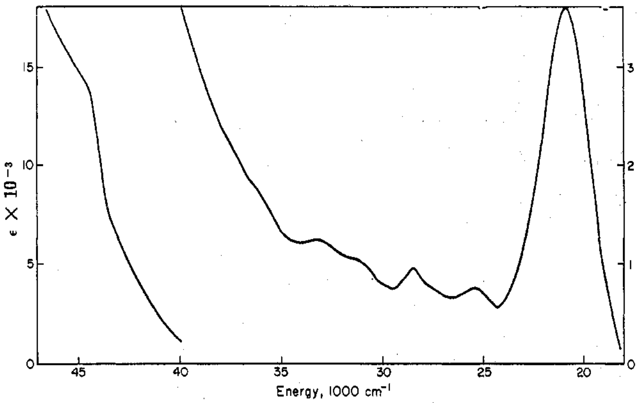

Figure 4.—Electronic spectrum of $[(n\text{-}C_4H_9)_4N]_3[Fe(CN)_5NCS]$ in acetonitrile solution.

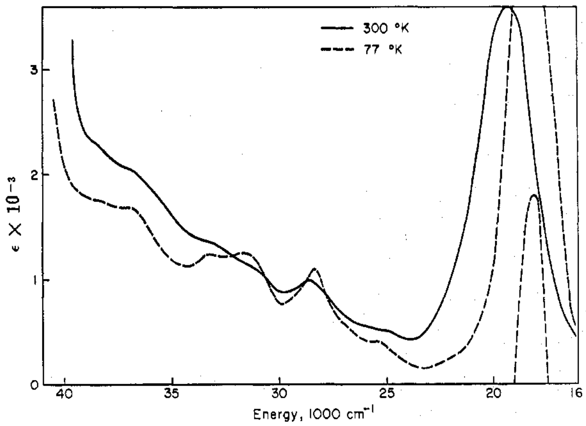

Figure 5.—Electronic spectra of $[(n\text{-}C_4H_9)_4N]_3[Fe(CN)_5NCS]$ in EPA solution at 300 and 77°K.

31,000, and 38,500 cm^{-1} in EPA logically correspond to the three CN → $d\pi(Fe)$ charge-transfer transitions observed in $[Fe(CN)_6]^{3-}$. A shoulder at 37,000 cm^{-1} is probably also primarily a L → M transition. The weaker shoulders which fall at 25,300 and 33,300 cm^{-1} in EPA can then be identified as ligand field bands. In going from room temperature to 77°K these shoulders decrease in intensity, as do the lowest LF bands in $[Fe(CN)_6]^{3-}$.

The electronic spectrum of $[(n\text{-}C_4H_9)_4N]_3[Fe(CN)_5NCSe]$ is very similar to that of $[(n\text{-}C_4H_9)_4N]_3[Fe(CN)_5NCS]$. In the thin-film spectrum the $2\pi(NCSe) \rightarrow d\pi(Fe)$ band appears at 18,200 cm^{-1}, which is 2700 cm^{-1} below the $2\pi(NCS) \rightarrow d\pi(Fe)$ band. The CN → $d\pi(Fe)$ bands in EPA are at 28,400, 31,000, and 36,400 cm^{-1}. The lowest LF transitions are assigned to the bands which are resolved at 25,300 and 33,100 cm^{-1} in EPA at 77°K.

The spectrum of $[(n\text{-}C_4H_9)_4N]_3[Fe(CN)_5N_3]$ in EPA consists of the $2\pi(N_3) \rightarrow d\pi(Fe)$ band at 18,000 cm^{-1} (ϵ 990) and a number of shoulders on the tail of an intense absorption in the ultraviolet. The peak at 23,900 cm^{-1} is logically attributed to the first CN → $d\pi(Fe)$ transition, whereas the shoulders at 24,700 and 31,100 cm^{-1} are assigned to LF excitations. The rest of the rich spectrum of this complex is apparently dominated by L → M transitions.

The color changes in different solutions observed for the $[Fe(CN)_5X]^{3-}$ complexes (*vide supra*) are due to the strong solvent dependence of the $2\pi(X) \rightarrow d\pi(Fe)$ charge-transfer band. Data for a variety of solvents set out in Table VIII establish that the band is significantly red-shifted in protic solvents. Our earlier conclusion that the color changes in organic solvents (and associated band shifts) are not due to linkage isomerization for $X^- = NCS^-$ or $NCSe^-$ is supported by the fact that the $2\pi(N_3) \rightarrow d\pi(Fe)$ band shows the same type of solvent dependence. In addition, the relative energetic relationship of the lowest LF bands in the three complexes is $NCS^- \sim NCSe^- > N_3^-$ in EPA solution. This relationship is consistent with N bonding for both NCS^- and $NCSe^-$. Thus it is likely that a specific hydrogen-bonding interaction with the complexes leads to the relatively lower $2\pi(X) \rightarrow d\pi(Fe)$ charge-transfer energies in alcohol solutions.

TABLE VIII

POSITIONS OF THE LOW-ENERGY BAND OF $[Fe(CN)_5X]^{3-}$ IN VARIOUS SOLVENTS

X	Solvent	λ_{max}, nm	$10^{-3}\bar{\nu}$, cm^{-1}
NCS	Methanol	535	18.7
	Ethanol	521	19.2
	Nitromethane	490	20.4
	Solid	486	20.6
	Chloroform	486	20.6
	Acetonitrile	479	20.9
	Acetone	473	21.1
NCSe	Ethanol	596	16.7
	Solid	550	18.2
	Acetonitrile	550	18.2
	Acetone	517	19.3
N_3	Ethanol	556	18.0
	Solid	532	18.8
	Acetonitrile	520	19.2

The structural situation for $[Fe(CN)_5NCS]^{3-}$ in aqueous solution remains unresolved. Our work has shown[22] that $[Co(CN)_5SCN]^{3-}$ is stabilized relative to $[Co(CN)_5NCS]^{3-}$ in aqueous solution, in agreement with the general conclusion of Burmeister and coworkers[23] that increasing solvent polarity favors S bonding. Thus it would not be unreasonable to find substantial amounts of $[Fe(CN)_5SCN]^{3-}$ in aqueous equilibrium mixtures. Electronic spectral studies now in progress in our laboratory should help to settle this question.

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[22] D. F. Gutterman and H. B. Gray, *J. Amer. Chem. Soc.*, **91**, 3105 (1969).

[23] J. L. Burmeister, R. L. Hassel, and R. J. Phelan, *Inorg. Chem.*, **10**, 2032 (1971).