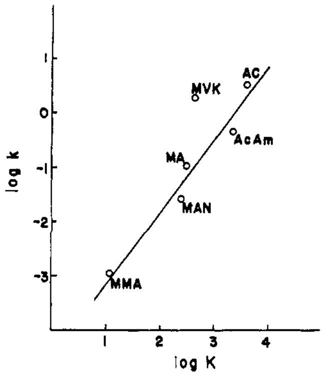

Figure 7. Relation between the stability constants K and the specific rate constants k of the reactions of $R_2Ni(dipy)$ with olefins at 30°.

series of stability constants was obtained for the dealkylated olefin complexes of type **3**. Since the nature of the π bond between the olefin and nickel is considered not to differ significantly between **2** and **3**, stability constants of type-**3** complexes may be used in place of those of **2**. Figure 7 indicates that a linear relation exists between the logarithms of stability constants of **3** and the rate constants[8] for reactions of **1** with olefins at room temperature. This result gives additional support for the proposed reaction mechanism of $R_2Ni(dipy)$ and olefins.[8] The same trend is also found in the polymerization of vinyl monomers by dialkylbis(dipyridyl)iron.[10] The detailed discussion of the polymerization mechanism will be reported separately.

Experimental Section

I. Materials. All materials were prepared, purified, and stored as described in our previous papers.[8,19]

II. Spectral Measurement. Ultraviolet and visible spectra were recorded on a Shimadzu Type SV-50A spectrometer. The complexes and solvents were transferred to the cell under nitrogen and in some cases the solvent and the olefin were distilled into the cell *in vacuo*, but no significant differences were observed between the two procedures.

1. Determination of the Stability Constants of Ni(dipy)(olefin). The temperature of the cell was maintained within 0.3° by circulating thermostated water around the cell. Green solutions obtained by dissolving $Ni(dipy)(olefin)_n$ in tetrahydrofuran in the absence of extra olefin were checked to see if Beer's law was obeyed. Measured amounts of the olefin were added to the green solution and the spectral change was recorded.

2. Determination of the Stability Constants of $R_2Ni(dipy)(olefin)$ at Low Temperatures. A tetrahydrofuran solution containing $R_2Ni(dipy)$ and a measured amount of olefin was first kept at −110° and then gradually warmed to room temperature. The color of the solution is orange at very low temperature, indicating the formation of $R_2Ni(dipy)(olefin)$, and changes at higher temperature to dark green, indicating the dissociation of the coordinated olefin. The complete change of color is observed over a range of about 5°. During this change the solution should pass the point where the concentration of $R_2Ni(dipy)(olefin)$ is equal to that of $R_2Ni(dipy)$. Since the spectra of $R_2Ni(dipy)$ and $R_2Ni(dipy)(olefin)$ are similar to those of Ni(dipy)(solvent) and Ni(dipy)(olefin), respectively, one can prepare a solution containing equimolar amounts of Ni(dipy)(olefin) and Ni(dipy)(solvent) at room temperature and take the color of the solution as that of a solution containing equal amounts $R_2Ni(dipy)(olefin)$ and $R_2Ni(dipy)$ at low temperature. After some training one can observe this equilibrium point with a precision of ±1°. The experiments were carried out with varying amounts of olefin in solution and the stability constants K' were calculated from eq 5.

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Electronic Structures of Thiocyanatopentacyanocobaltate(III) and Related Complexes

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Received August 12, 1970

Abstract: Electronic absorption spectra of the complex series $K_3[Co(CN)_5X]$ ($X = SCN^-$, NCS^-, N_3^-, and $NCSe^-$) in aqueous solution are assigned in terms of a molecular orbital scheme derived from the energy levels of thiocyanate and $M(CN)_6{}^{3-}$. These assignments are supported by spectra of $[(n\text{-}C_4H_9)_4N]_3[Co(CN)_5X]$ ($X = -NCS^-$, N_3^-, and $-NCSe^-$) in low-temperature glasses. The nature of the bonding interactions between the metal ion and the triatomic ligand is discussed. The spectra do not provide any evidence for the participation of π-acceptor orbitals of the triatomic ligand in this bonding.

It has been established that the mode of bonding of thiocyanate to transition metals is subject to a variety of influences, some of which have their origin in intramolecular electronic effects.[1-3] In an effort to sort out certain of the important bonding interactions between metal ions and thiocyanate, we have chosen a model system in which analogous complexes containing N-bonded and S-bonded thiocyanate, as well as azide and selenocyanate, can be investigated. Specifically, the complexes we have studied are the acidopentacyanometalates of cobalt(III) and iron(III). Our attention was originally drawn to this series by the reported preparation[4] of $K_3[Co(CN)_5SCN]$, which is an unusual complex in that it contains a first-row metal

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

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[3] J. L. Burmeister, *Coord. Chem. Rev.*, 1, 205 (1966); 3, 225 (1968).

[4] J. L. Burmeister, *Inorg. Chem.*, 3, 919 (1964).

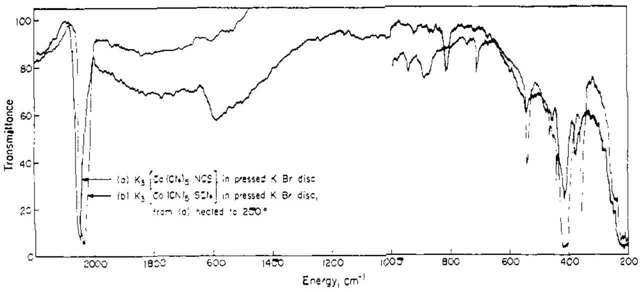

Figure 1. Infrared spectra of $K_3[Co(CN)_5NCS]$ and $K_3[Co(CN)_5SCN]$, 200–2500 cm^{-1}.

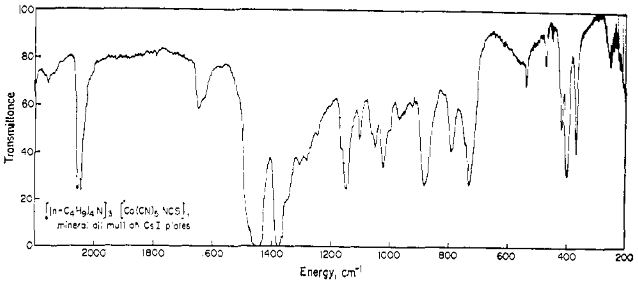

Figure 2. Infrared spectrum of $[(n\text{-}C_4H_9)_4N]_3[Co(CN)_5NCS]$, 200–2500 cm^{-1}.

bonded to the sulfur end of thiocyanate. As an unanticipated bonus, we were able to isolate a pure sample of the linkage isomer $[Co(CN)_5NCS]^{3-}$, and thus allow a comparison of the spectral properties of –SCN and –NCS in the same first-row-metal system. The $[M(CN)_5X]^{3-}$ complexes are also appropriate for a detailed electronic structural investigation because the hexacyanometalates of cobalt(III) and iron(III) have been thoroughly studied[5] and thus the spectral changes that result upon the substitution of a triatomic ligand for a cyanide can readily be determined. Furthermore, the ground states of the paramagnetic d^5 Fe(III) compounds can be studied by esr and magnetic susceptibility methods.

In this paper we shall discuss the electronic energy levels of thiocyanate and propose electronic spectral assignments for the series of pentacyanocobaltates, $[Co(CN)_5X]^{3-}$, where X = $-NCS^-$, $-NCSe^-$, N_3^-, and $-SCN^-$. In a subsequent paper, we shall consider the spectral and magnetic properties of the analogous pentacyanoferrates.

Experimental Section

Preparation of Compounds. $K_3[Co(CN)_5SCN]$ was prepared by the method of Burmeister.[4] To remove a small excess of barium acetate, the salt was passed over a cation-exchange column. The acid eluent was then titrated to pH 7 with KOH and concentrated on a rotary evaporator. Absolute ethanol was added to precipitate an orange oil, leaving potassium acetate in solution. The oil solidified on standing to yield a yellow powder which was collected, washed with ethanol and ether, and dried over P_2O_5. *Anal.* Calcd for $K_3CoC_6N_6S$: Co, 16.17; C, 19.73; S, 8.80; H, 0.0. Found: Co, 16.36; C, 19.47; S, 8.65; H, 0.15.

$K_3[Co(CN)_5NCS]$. $[(n\text{-}C_4H_9)_4N]_3[Co(CN)_5NCS]$ (prepared as in method II below) in a minimum volume of ethanol was filtered into an ethanol solution containing a 10% excess of KNCS. The resulting precipitate was collected on a glass frit, washed with ethanol until the washings did not change the color of a ferric nitrate solution, and dried *in vacuo* over $CaCl_2$. *Anal.* Calcd for $K_3CoC_6N_6S$: see above. Found: Co, 16.19; C, 19.31; S, 8.64; H, 0.28.

$K_3[Co(CN)_5N_3]$ prepared by the method of Fujita and Shimura[6] was recrystallized from dilute HCl by slow addition of methanol to give golden needles.

$K_3[Co(CN)_5NCSe]$ was prepared by the method of Burmeister and Al-Janabi.[7] It was passed over a cation-exchange column, titrated to pH 7 with KOH, and precipitated with ethanol. The acid step apparently removes selenium-containing impurities. *Anal.* Calcd for $K_3CoC_6N_6Se$: Co, 14.33; C, 17.52; N, 20.43; H, 0.00. Found: Co, 14.45; C, 17.41; N, 20.37; H, 0.00.

$[(n\text{-}C_4H_9)_4N]_3[Co(CN)_5NCS]$. Method I. $K_3[Co(CN)_5SCN]$ was passed over a cation-exchange column. The acid eluent was titrated to pH 7 with $[(n\text{-}C_4H_9)_4N]OH$ 25% solution in methanol. The aqueous solution was extracted with several portions of methylene chloride. The CH_2Cl_2 portions were combined and the solvent was removed on a rotary evaporator. The oily yellow residue was dissolved in a small volume of CH_2Cl_2 and the solution filtered. Enough ethyl ether was added to begin precipitation. The flask was cooled in a Dry Ice–acetone bath to dissolve the precipitate. Keeping the flask cold, more ether was added, but not enough to cause precipitation. The salt was precipitated by allowing the solution to warm slowly to room temperature. The precipitate was collected on a glass frit, washed with ether, and dried over P_2O_5. *Anal.* Calcd for $C_{54}CoH_{108}N_9S$: C, 66.55; H, 11.17; N, 12.94; S, 3.29. Found: C, 65.78; H, 11.20; N, 13.08; S, 3.19; molar conductance (1.42×10^{-3} *M*), 357.

$[(n\text{-}C_4H_9)_4N]_3[Co(CN)_5N_3]$ and $[(n\text{-}C_4H_9)_4N]_3[Co(CN)_5NCSe]$ were similarly prepared from the corresponding potassium salts. For the azido complex in particular, this recrystallization procedure yields good crystals. *Anal.* Calcd for $C_{53}CoH_{108}N_{11}$: C, 66.42; H, 11.36; N, 16.07. Found: C, 66.25; H, 11.50; N, 16.02; molar conductance (1.20×10^{-3} *M*), 337. Calcd for $C_{54}CoH_{108}N_9Se$: C, 63.50; H, 10.66; N, 12.34. Found: C, 63.46; H, 10.82; N, 12.28; molar conductance (1.10×10^{-3} *M*), 390.

$[(n\text{-}C_4H_9)_4N]_3[Co(CN)_5NCS]$ was also prepared by the following routes.

Method II. An aqueous solution of $K_3[Co(CN)_5SCN]$ was extracted with several portions of a CH_2Cl_2 solution containing an excess of $[(n\text{-}C_4H_9)_4N]Cl$. The aqueous layer was washed with CH_2Cl_2, the organic portions were combined, and the solvent was evaporated. The oily residue was recrystallized from CH_2Cl_2 and ether, collected, and dried *in vacuo* over $CaCl_2$.

Method III. $K_3[Co(CN)_5NCS]$ prepared by the method of Stotz, *et al.*,[8] was treated as in method II. *Anal.* Calcd for $C_{54}CoH_{108}N_9S$: see above. Found: C, 66.41; H, 11.33; N, 12.90; S, 3.39.

Cation-exchange columns of Amberlite IR-120 cation-exchange resin were washed with dilute HCl followed by distilled water. A Corning Model 12 pH meter was used to measure titration end points. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Conductivities were measured at room temperature in acetonitrile.

Spectral Measurements. Infrared spectra were recorded on a Beckman IR-12 or a Perkin-Elmer 225 spectrophotometer. Electronic absorption spectra were measured using a Cary 14 or a Cary 14 RI spectrophotometer. Low-temperature spectra were taken at liquid N_2 temperature with a Cary low-temperature dewar modified to hold a standard 1-cm cell. EPA (5:5:2 ethyl ether, isopentane, ethanol) from Matheson Coleman and Bell was used as the solvent for most of these spectral studies. The $[Co(CN)_5NCSe]^{3-}$ complex reacts with traces of peroxide in the commercial solvent. EPA was therefore mixed as needed from freshly opened containers of the component solvents, all manipulations being performed in a nitrogen atmosphere. Solutions of $[Co(CN)_5NCSe]^{3-}$ prepared in this way are sufficiently stable to obtain reproducible spectra. The low-temperature spectra were corrected for the contraction of the solvent using the data of Passerini and Ross.[9]

Structural Assignments

The mode of bonding of NCS^- and $NCSe^-$ to the $[Co(III)(CN)_5]$ unit in the various solid samples and in solution has been investigated by means of infrared

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[5] J. J. Alexander and H. B. Gray, *J. Amer. Chem. Soc.*, **90**, 4260 (1968); *Coord. Chem. Rev.*, **2**, 1, 29 (1967).

[6] J. Fujita and Y. Shimura, *Bull. Chem. Soc. Jap.*, **36**, 1281 (1963).

[7] J. L. Burmeister and M. Y. Al-Janabi, *Inorg. Chem.*, **4**, 962 (1965).

[8] I. Stotz, W. K. Wilmarth, and A. Haim, *ibid.*, **7**, 1250 (1968).

[9] R. Passerini and I. E. Ross, *J. Sci. Instrum.*, 30, 274 (1953).

Table I. Infrared Spectra of $[Co(CN)_5X]^{3-}$ Complexes in the Range 200–2500 cm^{-1} [a]

Compound	Absorptions of X				Absorptions of $M(CN)_5$				Other peaks
	Sym str	Asym str	δ	2δ	$\nu_{C\equiv N}$	ν_{M-C}	δ_{MCN}	ν_{M-X}	
$K_3[Co(CN)_5NCS]$[e]	2123 (s)	812 (w)	483 (w) 470 (vw)	*b*	2130 (s)	412 (s) 377 (m)	546 (mw)	278 (mw)	458 (vvw) 430 (sh)
$K_3[Co(CN)_5SCN]$	2110 (vs)[d]	718 (w)	472 (w) 461 (vw) 448 (w)	948 w 920 vw 898 w	2144 (ms) 2134 (s) 2129 (vs)[d] 2118 (vs)[d]	420 (s) 361 (m)	547 (m)	265 (mw)	453 (vw) 427 (sh)
$K_3[Co(CN)_5N_3]$	2070 (s, br)	1300	604 (w, sp)	*b*	2130 (s)	418 (s, br) 378 (m)	550 (w, br)	355 (m) 343 (m) 325 (m)	483 (w) 465 (mw)
$K_3[Co(CN)_5NCSe]$[e]	2120 (sh)	*b*	*b*	*b*	2137 (sh) 2128	415 (ms) 365 (m)	562 (w) 546 (m)	*b*	464 (m) 433 (sh) 372 (sh)
$[(n\text{-}C_4H_9)_4N]_3[Co(CN)_5NCS]$	2113 (s)	*c*	475 (mw)	*b*	2140 (s)	421 (ms) 372 (ms)	555 (brw) 540 (mw)	263 (mw)	453 (w)
$[(n\text{-}C_4H_9)_4N]_3[Co(CN)_5N_3]$	2035 (s, br) 2020 (s)	*c*	625 (mw) 598 (w)	*b*	2106 (ms)	415 (s) 372 (m)	538 (mw) 505 (vw)	337 (m)	458 (mw)
$[(n\text{-}C_4H_9)_4N]_3[Co(CN)_5NCSe]$	2108 (s)[d] 2075 (w)[d]	661 (vvw)[d] 620 (vvw)	*c*	*b*	2145 (s) 2115 (vs)[d]	420 (m) 365 (m)	543 (m) 515 (vw)	*b*	462 (w)

[a] Samples prepared as mulls in mineral oil, on CsI plates. [b] Not seen. [c] Obscured by cation or other absorptions. [d] Assignment uncertain. [e] Prepared from a $(n\text{-}C_4H_9)_4N^+$ salt.

and electronic spectroscopy. Sample infrared spectra are shown in Figures 1 and 2. Table I sets out the infrared spectra of mineral oil mulls of the pentacyanocobaltates along with band assignments. In each spectrum there are two bands near 400 cm^{-1} which have been assigned as components of the metal–carbon stretch $\nu_{(M-C)}$ and at least one band near 550 cm^{-1} which has been assigned as the deformation $\delta_{(MCN)}$. This follows the accepted assignment of the $M(CN)_6{}^{3-}$ vibrational modes.[10] The metal–thiocyanate and metal–azide stretching frequencies are similar to those in other octahedral complexes.[11–14] The metal–selenocyanate stretching frequencies apparently occur below 200 cm^{-1}. Band assignments in the cyano stretching region are rather arbitrary, particularly when more than two bands are observed. Spectra of solutions of tetra-*n*-butylammonium salts in the cyano region are reported in Table II.

Table II. Solution Infrared Spectra of $[(n\text{-}C_4H_9)_4N]_3[Co(CN)_5X]$ Complexes in the Region 2000–2300 cm^{-1}

Complex	Solvent	ν, cm^{-1}
$[Co(CN)_5NCS]^{3-}$	$CHCl_3$	2137 (s) 2118 (s)
$[Co(CN)_5NCSe]^{3-}$	CH_2Cl_2	2137 (s) 2118 (vs) 2109 (s) 2067 (wbr)
$[Co(CN)_5N_3]^{3-}$	Acetone	2113 (s) 2025 (vs)
$[Co(CN)_5SCN]^{3-}$ [a]	CH_2Cl_2	2112 (s) 2097 (ms)

[a] An extract of $K_3[Co(CN)_5SCN]$ with a solution of $(n\text{-}C_4H_9)_4NCl$ in CH_2Cl_2 was freshly prepared.

$[Co(CN)_5SCN]^{3-}$ and $[Co(CN)_5NCS]^{3-}$. The mode of bonding of the thiocyanate group in $K_3[Co(CN)_5SCN]$ and $K_3[Co(CN)_5NCS]$ has been assigned on the basis of the C–S stretching frequencies, which occur at 718 and 812 cm^{-1}, respectively.[4,15] The tetra-*n*-butylammonium salt has been shown to contain only the nitrogen-bonded isomer.[15] It is noteworthy that although the position of the cobalt–thiocyanate stretch in the linkage isomers $K_3[Co(CN)_5NCS]$ and $K_3[Co(CN)_5SCN]$ follows the expected order $\nu_{M-NCS} > \nu_{M-SCN}$, the values 278 and 265 cm^{-1} are not very different. In fact, the band is as sensitive to a change in cation as it is to isomerization; in $[(n\text{-}C_4H_9)_4N]_3[Co(CN)_5NCS]$ it is found at 263 cm^{-1}. Another point of interest is that a freshly prepared solution of $[Co(CN)_5SCN]^{3-}$ in CH_2Cl_2 shows only two band maxima attributable to $C\equiv N$ stretching. This implies that the extensive splitting observed in the cyano region in solid $K_3[Co(CN)_5SCN]$ is a result of crystal effects rather than the effect of a nonlinear metal-thiocyanate bond, as one might have supposed.

$[Co(CN)_5NCSe]^{3-}$. The best evidence that $[(n\text{-}C_4H_9)_4N]_3[Co(CN)_5NCSe]$ contains selenocyanate bonded through nitrogen comes from the electronic spectral comparisons provided in Table III. The first ligand-field band in this complex peaks at 27,900 cm^{-1} (358 nm) in aqueous solution. The band is at slightly higher energy than the corresponding band in $[Co(CN)_5NCS]^{3-}$ and thus strongly suggests an N-bonded selenocyanate.[16–18] In addition, the infrared spectrum of a concentrated mull of $[(n\text{-}C_4H_9)_4N]_3[Co(CN)_5NCSe]$ shows a weak peak at 661 cm^{-1} and a broad band centered near 620 cm^{-1}. Either or both of these may be weak peaks associated with $(n\text{-}C_4H_9)_4N^+$ or ν_{CSe} of an isoselenocyanate ligand.

$K_3[Co(CN)_5NCSe]$ was first reported by Burmeister and Al-Janabi[7] who assigned it as the N-bonded isomer on the basis of their 664-cm^{-1} position of ν_{CSe}. It has

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(10) D. M. Adams, "Metal Ligand and Related Vibrations," E. Arnold, London, 1967, Chapter 3.

(11) D. Foster and D. M. L. Goodgame, *Inorg. Chem.*, **4**, 715 (1965); *J. Chem. Soc.*, 268 (1965).

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(13) D. Foster and W. D. Horrocks, *ibid.*, **5**, 1510 (1966).

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

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

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

Table III. Electronic Absorption Spectra of $[Co(CN)_5X]^{3-}$ Complexes in Aqueous Solution at 300°K

Compound	λ_{max}, nm	ν_{max}, 1000 cm^{-1}	ϵ_{max}	$f \times 10^2$	Assignment
$K_3[Co(CN)_6]$[a]	312	32.1	243	0.30	$^1A_{1g} \rightarrow {}^1T_{1g}$
	260	38.5	180	0.28	$^1A_{1g} \rightarrow {}^1T_{2g}$
	202	49.5	35,400	31.8	$2t_{2g} \rightarrow 4t_{1u}$
$K_3[Co(CN)_5SCN]$	378	26.5	191	0.52	$^1A_1 \rightarrow {}^1E(^1A_2?)$
	265	37.7	17,100	35.2	$4e \rightarrow 3a_1$
	227	44.0	4,300		$2\pi \rightarrow 3\pi$
	200	50.0	16,700	41.5	$(5e,2b_2) \rightarrow 6e$
$[(n\text{-}C_4H_9)_4N]_3[Co(CN)_5NCS]$	363	27.6	500	0.92	$^1A_1 \rightarrow {}^1E(^1A_2?)$
	265	37.7	2,340	7.3	$4e \rightarrow 3a_1$
	202	49.5	28,100	77.6	$(5e,2b_2) \rightarrow 6e$
$[(n\text{-}C_4H_9)_4N]_3[Co(CN)_5N_3]$	383	26.1	743	1.6	$^1A_1 \rightarrow {}^1E(^1A_2?)$
	281	35.6	8,580	22.2	$4e \rightarrow 3a_1$
	220	45.5	11,000 (sh)		$2\pi \rightarrow 3\pi$
	201	49.8	18,800	52	$(5e,2b_2) \rightarrow 6e$
$[(n\text{-}C_4H_9)_4N]_3[Co(CN)_5NCSe]$	358	27.9	484	0.92	$^1A_1 \rightarrow {}^1E(^1A_2?)$
	274	36.5	6,830	15.0	$4e \rightarrow 3a_1$
	203	49.3	32,500	102	$(5e,2b_2) \rightarrow 6e$
$K_3[Co(CN)_5CNSe]$	362	27.6	306 (sh)		*b*
	274	36.5	17,800	34.4	*b*
	230	43.5	5,300 (sh)		*b*

[a] From ref 5. [b] Not explicitly assigned because the solution probably contains both linkage isomers.

not, however, been possible to locate this peak again, although the rest of the infrared spectrum can be reproduced without difficulty. In the ultraviolet spectrum of this compound the band maxima occur at about the same positions as in $[(n\text{-}C_4H_9)_4N]_3[Co(CN)_5NCSe]$, indicating that it does in fact contain $[Co(CN)_5NCSe]^{3-}$. However, the relative intensities of the bands are quite different for the two compounds (Table III): the low-energy band is only 60% as intense in the K^+ salt as it is in the $(n\text{-}C_4H_9)_4N^+$ salt, while the band at 274 nm is three times as intense. These spectral observations are reminiscent of the comparison of the electronic spectrum of $[(n\text{-}C_4H_9)_4N]_3[Co(CN)_5NCS]$ with that of a potassium salt, which revealed[15] that the latter complex contained a mixture of linkage isomers. In addition, the similarity of the pattern of C≡N stretching frequencies in the infrared spectrum to that of $K_3[Co(CN)_5SCN]$[4,7] suggests that some $K_3[Co(CN)_5SeCN]$ may be present in the potassium salt. The $[(n\text{-}C_4H_9)_4N]_3[Co(CN)_5NCSe]$ compound was therefore converted to a potassium salt by metathesis with KNCSe in CH_2Cl_2–acetone. The electronic spectrum of this compound is nearly identical with that of $[(n\text{-}C_4H_9)_4N]_3[Co(CN)_5NCSe]$, and it must therefore be $K_3[Co(CN)_5NCSe]$. It is somewhat lighter in color than the original potassium salt. Its infrared spectrum is simpler than that of the original material in that there are fewer bands above 2000 cm^{-1} and below 600 cm^{-1}. No infrared absorption was found above 570 cm^{-1} which may be assigned as ν_{CSe}, so that the assignment of this compound as the isoselenocyanate rests on the position of the first ligand-field band. Unlike the isothiocyanate,[15] $K_3[Co(CN)_5NCSe]$ does not isomerize detectably in the solid state; it decomposes when heated, apparently with loss of selenium.

In summary, $[(n\text{-}C_4H_9)_4N]_3[Co(CN)_5NCSe]$ and the potassium salt prepared from it contain chiefly, if not exclusively, N-bonded selenocyanate, whereas the potassium salt prepared by the method of Burmeister and Al-Janabi[7] appears to contain a significant amount of $[Co(CN)_5SeCN]^{3-}$. Since $[Co(CN)_5NCSe]^{3-}$ does not itself rapidly isomerize in water, either $[Co(CN)_5]^{3-}$, which is present in the reaction mixture, catalyzes the linkage isomerization, or the reaction of $[Hg(SeCN)_4]^{2-}$ with $[Co(CN)_5]^{3-}$ does not proceed exclusively through the $[(NCSe)_3\text{–}Hg(II)\text{–}SeCN\text{–}Co(II)(CN)_5]^{5-}$ bridged intermediate, as was proposed.[7]

Electronic Energy Levels

Thiocyanate belongs to the general class of linear triatomic molecules that includes CO_2, CS_2, COS, N_2O, NCO^-, as well as N_3^- and $NCSe^-$. The electronic structures of these molecules have been described by Mulliken[19] and by Walsh[20] in terms of molecular orbital (MO) theory. There exists in addition a large body of experimental information concerned with the energy levels of the neutral molecules, as well as spectroscopic data on many of the singly ionized radical species. In these molecules, the highest filled level is 2π, a combination that is localized on the end atoms and is essentially nonbonding. The energy of this level may be estimated from the first ionization potential of the molecule, which is 10.4 eV (84,300 cm^{-1}) in NCS radical and 10.6 eV (86,000 cm^{-1}) in HNCS.[21]

The lowest unfilled level is 3π, which is a combination that is antibonding between neighboring atoms and is concentrated on the central atom. The energy of this 3π level can be estimated from the position of the first allowed electronic transition. This unfortunately occurs at over 51,000 cm^{-1} in KNCS. In addition to the allowed $^1\Sigma_g^+ \rightarrow {}^1\Sigma_u^+$ component, two forbidden components of the $\pi_g \rightarrow \pi_u$ transition can also be seen in the spectrum of CO_2. The lower of these, about 16,000 cm^{-1} below the main band, is assigned as a component of $^1\Delta_u$ which is split because the molecule is bent in the excited state.[20,22] This is the probable origin of the shoulder at 45,600 cm^{-1} in the spectrum of aqueous NCS^- and of the bands between 40,000 and 42,000 cm^{-1} in the spectra of alkyl thiocyanates and alkyl isothiocyanates.[23,24] The 3π level in thiocyanate is

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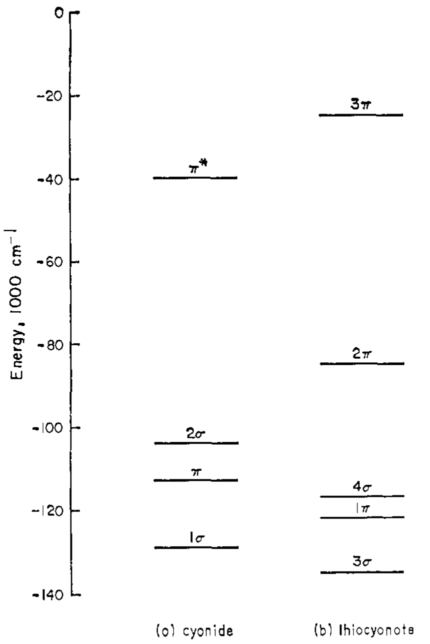

Figure 3. Estimated energies of selected molecular orbitals of cyanide and thiocyanate.

thus estimated as roughly 60,000 cm^{-1} above 2π, or at about $-25{,}000$ cm^{-1}.

The order of the lower filled orbitals apparently depends on the specific atomic makeup of the triatomic molecule. Most of the experimental information on these levels comes from the ionization potentials of the neutral molecules which have been measured in a variety of ways,[25-28] although only the CO_2 data have been interpreted in detail.[27,28] The most useful measurements have been the photoelectron spectra of Turner and coworkers[28] which make it possible to locate the vertical single ionizations and to distinguish nonbonding from bonding or antibonding levels. The spectra of CO_2, CS_2, COS, and N_2O in each case show at least four ionization potentials at energies less than 21.21 eV, of which one is a bonding electron and three are nonbonding ones. The first nonbonding level is the 2π which has already been discussed. The bonding level must be identified with the lowest π combination (1π), which is bonding between all pairs of atoms. In CO_2, CS_2, and COS, the 1π level corresponds to the second ionization potential, and is, therefore, just below 2π. In N_2O it corresponds to the third ionization potential.

The two remaining ionizations must be from the two highest filled σ orbitals, which correspond to nonbonding lone pairs in sp hybrid orbitals localized essentially on the end atoms. The highest filled σ level and the 1π level are in each case fairly close in energy and the order can apparently reverse, as observed on going from CO_2 to N_2O. Another means of obtaining the energy level order is from the emission spectrum of a radical species with less than 16 valence electrons. In the emission spectra of CO_2^+,[29] CS_2^+,[30] N_2O^+,[31] and N_3 radical,[32] each with 15 valence electrons, the lowest energy band is a $^2\Pi \leftarrow {}^2\Sigma^+$ transition; in NCN radical,[33] with 14 valence electrons, the lowest band is a $^3\Sigma_g \leftarrow {}^3\Pi_u$ transition. This can be understood as a transition between the nonbonding π level and the highest filled σ orbital. In these radicals the apparent energy level order is $\pi_u < 2\sigma_g < \pi_g$; the order of the filled levels may therefore depend on the state of ionization of the molecule as well as on its chemical identity. There is no well-established experimental information concerning the two remaining lowest filled σ orbitals; they are, however, necessarily strongly bonding.

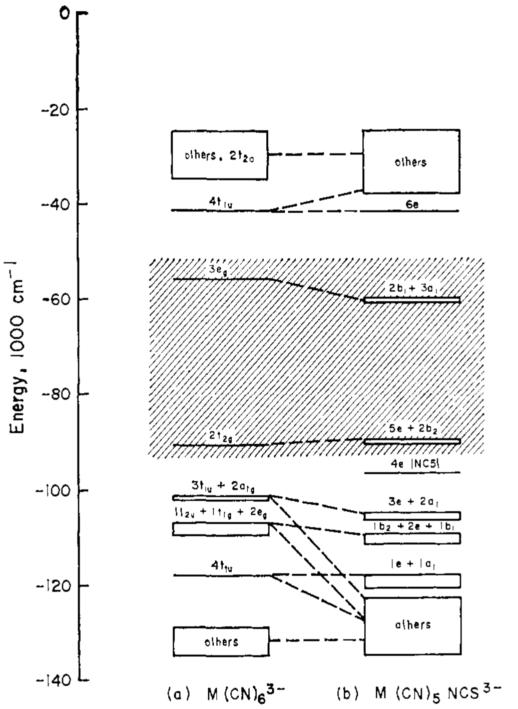

Figure 4. Estimated energies of selected molecular orbitals of $M(CN)_6{}^{3-}$ and $M(CN)_5NCS^{3-}$.

Thiocyanate *vs.* Cyanide

Although there is no published experimental information about the inner ionization potentials of thiocyanates, it is possible to estimate the orbital energies from the pattern of energies in the triatomic molecules that have been measured. In Figure 3 one such attempt is compared with an energy level diagram for CN. The cyanide energy levels were estimated from a combination of spectroscopic and ionization potential data and were used in the input of MO calculations of the $M(CN)_6{}^{n-}$ complexes.[5] For the filled levels of thiocyanate, the $3\sigma < 1\pi < 4\sigma < 2\pi$ order we have chosen is in agreement with a published MO calculation.[34] The strongly bonding and strongly antibonding σ

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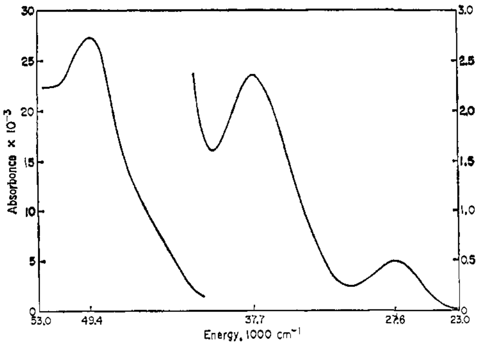

Figure 5. Electronic spectrum of $[(n\text{-}C_4H_9)_4N]_3[Co(CN)_5NCS]$ in aqueous solution.

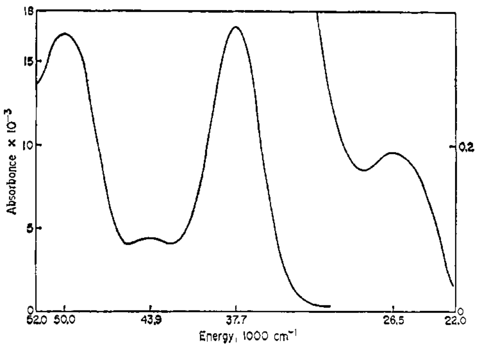

Figure 6. Electronic spectrum of $K_3[Co(CN)_5SCN]$ in aqueous solution.

levels of NCS and of CN are omitted as being too stable or too unstable to contribute to metal–ligand bonding. This comparison between thiocyanate and cyanide is not expected to be correct in any absolute sense. It is intended to provide a framework in which to discuss the electronic structure of $[M(CN)_5NCS]^{3-}$ complexes.

The most prominent difference between the thiocyanate and cyanide energy level schemes is the presence in thiocyanate of the filled nonbonding 2π level at relatively high energy. In the complex this can be expected to give rise to ligand-to-metal charge-transfer absorption at readily accessible energies. The unfilled 3π level in thiocyanate is spatially and energetically less suited for metal-to-ligand bonding than the π^* level in cyanide; we can therefore expect that cyanide will be the more important π acceptor. The lower thiocyanate levels have the same pattern of energies as the cyanide levels but are somewhat more stable. The thiocyanate basis set for metal–ligand bonding is thus similar to the cyanide basis set, but with slightly more stable filled levels, less stable unfilled levels, and with the addition of a filled 2π level at relatively high energy.

The Complex. $[M(CN)_5NCS]^{3-}$

The energy level scheme for $[M(CN)_6]^{3-}$ [5] and a suggested level diagram for $[M(CN)_5NCS]^{3-}$ are shown in Figure 4. When thiocyanate replaces a cyano ligand, the symmetry about the metal is reduced from O_h to at least C_{4v}. The effect on the primarily d metal orbitals is shown in the shaded area of Figure 4. The triply degenerate $2t_{2g}$ is split into e and b_2 components and the doubly degenerate $3e_g$ is split into a_1 and b_1 components. Experience with substituted ammine complexes suggests that these splittings will be small relative to Δ, the octahedral splitting of $2t_{2g}$ and $3e_g$.

The major difference between $[M(CN)_6]^{3-}$ and $[M(CN)_5NCS]^{3-}$ is the placement in the latter case of the thiocyanate 2π orbital immediately below the metal levels. If the metal–ligand bonds are all linear, ligand orbital degeneracies will not be lifted in the complex; 2π (NCS) remains a level of e symmetry. If the thiocyanate–metal bond is not linear, all orbital degeneracies in the complex are lifted.

The unfilled π^* acceptor levels of $[M(CN)_6]^{3-}$ will be split with the axial components at higher energies. The equatorial component of the lowest ligand acceptor level in $[M(CN)_6]^{3-}$, the $4t_{1u}\pi^*CN$ combination, is expected at nearly unchanged energy in $[M(CN)_5NCS]^{3-}$. This equatorial component, of e symmetry in the pentacyano complex, will be the lowest orbital available for metal-to-ligand charge transfer. Similarly, the filled ligand levels of $[M(CN)_6]^{3-}$ should split on going to $[M(CN)_5NCS]^{3-}$, with the axial components more stable and the equatorial components nearly unchanged.

Electronic Spectra of the $[Co(CN)_5X]^{3-}$ Complexes

The electronic spectra of the pentacyanocobaltates in aqueous solution are set out in Table III. Each spectrum displays a relatively weak band near 30,000 cm^{-1}, a more intense peak about 10,000 cm^{-1} higher, and a very intense peak near 50,000 cm^{-1}. Several complexes also exhibit a shoulder or peak of medium intensity near 44,000 cm^{-1}. The spectra of $[(n\text{-}C_4H_9)_4N]_3[Co(CN)_5NCS]$ and $K_3[Co(CN)_5SCN]$ are shown in Figures 5 and 6, respectively. Spectra of the tetra-*n*-butylammonium salts at 300 and 77°K in EPA solution are summarized in Table IV and are shown in Figures 7–9.

Before we attempt to assign these spectra, it will be useful to consider the established assignments of the spectrum of the parent hexacyanide.[5] The absorption spectrum of $K_3[Co(CN)_6]$ in aqueous solution consists of two relatively weak bands at 32,050 (ϵ 243) and 38,500 cm^{-1} (ϵ 180) and an intense peak at 50,500 cm^{-1} (ϵ 35,400). The two weak bands are assigned as the spin-allowed components ($^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$) of the $2t_{2g} \rightarrow 3e_g$ transition. The intense, high-energy peak is assigned as a charge-transfer transition from the metal $2t_{2g}$ to the $4t_{1u}\pi^*CN$ level.

The low-energy absorption band in $[Co(CN)_5X]^{3-}$ is logically identified primarily as the $^1A_1 \rightarrow {}^1E$ C_{4v} component of the octahedral $^1A_{1g} \rightarrow {}^1T_{1g}$ transition. Although the band does not appear to split in any of the $[Co(CN)_5X]^{3-}$ spectra, in $K_3[Co(CN)_5SCN]$ it is quite broad and asymmetric. The latter observation can be interpreted either in terms of a further lowering of symmetry in the –SCN complex, removing the degeneracy of the ^1E excited state, or an indication that the orbitally forbidden $^1A_1 \rightarrow {}^1A_2$ component of $^1A_{1g} \rightarrow {}^1T_{1g}$ is part of the lowest band system. Further evidence that the $^1A_1 \rightarrow {}^1A_2$ transition may contribute to the intensity in the region of the first band is the fact that at 77°K the integrated intensity of the band decreases in each case by about 30% from the 300°K value, suggesting a vibronic intensity-giving mechanism.[35] The first ligand-field band in $[Co(CN)_5X]^{3-}$

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[35] C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill, New York, N. Y., 1962, p 185ff.

Table IV. Electronic Absorption Spectra of $[(n\text{-}C_4H_9)_4N]_3[Co(CN)_5X]$ Complexes in EPA at 300 and 77°K

	300°K				77°K			Change in integrated intensity
	λ_{max}[a]	$\bar{\nu}$[b]	ϵ	$f \times 10^2$	λ_{max}[a]	$\bar{\nu}$[b]	$f \times 10^2$	
-NCS	365	27.4	420	0.83	362	27.6	0.66	Decrease
	266	37.6	2140	4.9	267	37.5	3.5	Apparent decrease
-NCSe	364	27.5	394	0.78	361	27.7	0.58	Decrease
	275	36.4	6390	11.3	273	36.6	11.4	No change
$-N_3$	388	25.8	770	1.50	382	26.2	1.22	Decrease
	285	35.1	4010	9.1	278	36.0	9.2	No change

[a] In nm. [b] In 1000 cm^{-1}.

is shifted from its position in $[Co(CN)_6]^{3-}$ by 4500–6000 cm^{-1} to lower energy, as summarized in Table V. The spectrochemical ordering found is: $-CN^- \gg -NCSe^- \sim -NCS^- > SCN^- \sim -N_3^-$. In nonaqueous solvents and in solid samples the ligand-field band in each case shifts slightly to lower energy, but the spectrochemical order is preserved.

Table V. Position of the Lowest Spin-Allowed Ligand-Field Band for $[Co(CN)_5X]^{3-}$ Complexes

X	$\bar{\nu}$, 1000 cm^{-1}
-CN	32.1
-NCSe	27.9
-NCS	27.6
-SCN	26.5
$-N_3$	26.1

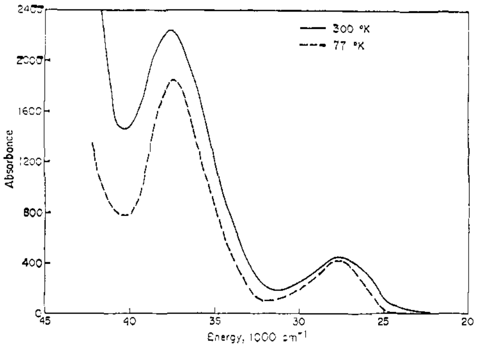

Figure 7. Electronic spectra of $[(n\text{-}(C_4H_9)_4N]_3[Co(CN)_5NCS]$ in EPA, 300 and 77°K.

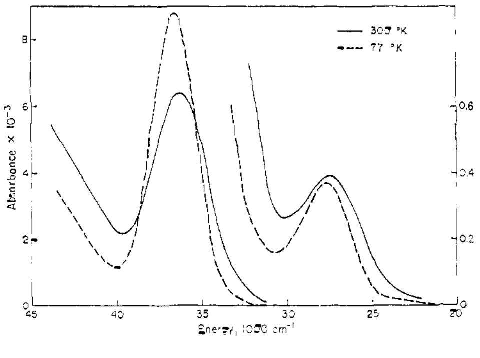

Figure 8. Electronic spectra of $[(n\text{-}C_4H_9)_4N]_3[Co(CN)_5NCSe]$ in EPA, 300 and 77°K.

We can identify the relatively intense second band in each spectrum as the ligand-to-metal transition from the nonbonding 2π orbital on X^- to the unfilled metal $3a_1$ level. The bands occur approximately at the energies predicted from the optical electronegativities of Co(III) and X.[36] Consistent with the assignment as a $^1A_1 \rightarrow {}^1E$ charge transfer, which is fully allowed in C_{4v} symmetry, the integrated absorbance of the second band in either $[(n\text{-}C_4H_9)_4N]_3[Co(CN)_5N_3]$ or in $[(n\text{-}C_4H_9)_4N]_3[Co(CN)_5NCSe]$ is unchanged on going from room temperature to 77°K. However, the intensity of the second band in $[(n\text{-}C_4H_9)_4N]_3[Co(CN)_5NCS]$ appears to decrease significantly at the lower temperatures. Since this is clearly not a ligand-field band, the apparent decrease is probably the result of not taking into account the narrowing of the very intense high-energy band. This effect is more important in the isothiocyanate than in the azide or isoselenocyanate because the second band in the isothiocyanate is of lower intensity and is closer to the high-energy peak.

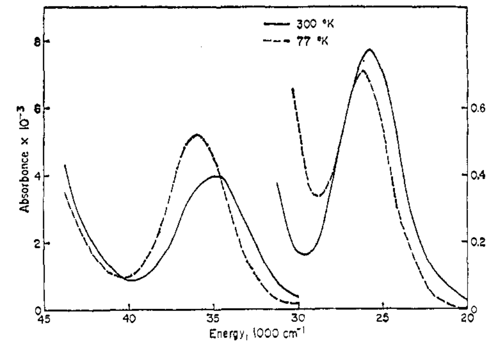

Figure 9. Electronic spectra of $[(n\text{-}C_4H_9)_4N]_3[Co(CN)_5N_3]$ in EPA, 300 and 77°K.

The third band, near 50,000 cm^{-1}, is identified with the third band in the cobalticyanide spectrum as a M → L transition from $2t_{2g}$ to the $4t_{1u}\pi^*CN$ level. In C_{4v} symmetry the transition is from $(5e, 2b_2)$ to the 6e level.

The only band left to account for is the medium-intensity absorption which appears as a well-resolved peak only in the spectrum of $K_3[Co(CN)_5SCN]$, where it is at 44,000 cm^{-1} (ϵ 4300). In the spectrum of $[Co(CN)_5N_3]^{3-}$, there is a well-defined shoulder at 45,500 cm^{-1}. However, there is only a poorly defined shoulder near 45,000 cm^{-1} in the $[Co(CN)_5NCSe]^{3-}$ spectrum. Evidence for absorption near this energy in $[Co(CN)_5NCS]^{3-}$ lies in the shape of the broad, non-Gaussian tail of the high-energy band. From these observations we conclude that the likely contributor to absorption at these energies is the low-energy component of the

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(36) H. H. Schmidtke, *Ber. Bunsenges. Phys. Chem.*, 71, 1138 (1967).

ligand $2\pi \rightarrow 3\pi$ transition, which occurs at about this position in the free-ion spectra. The low-energy component of the $2\pi \rightarrow 3\pi$ transition is orbitally forbidden as long as axial symmetry in the complex is maintained. It is interesting that in $[Co(CN)_5SCN]^{3-}$ and $[Co(CN)_5N_3]^{3-}$, where a bent Co–X bond removes this axial symmetry, the band in question is much more prominent.

Discussion

The molecular orbital description of a thiocyanate complex which was constructed above has been shown to be consistent with the electronic spectra of the model system $[Co(CN)_5X]^{3-}$. Only the highest filled level, the 2π, of thiocyanate, selenocyanate, or azide contributes significantly to the absorption spectrum of the system below 52,000 cm^{-1}. Thus the electronic spectral data, as expected from the discussion of orbital energies, *provide no evidence for the participation of π-acceptor orbitals of the triatomic ligand in the metal–ligand bonding.*

The spectrochemical series observed for $[Co(CN)_5X]^{3-}$ is $-CN \gg -NCSe^- \sim -NCS^- > -SCN^- \sim -N_3^-$. This is similar to the order observed for other types of complexes which include linkage isomers of thiocyanate. The order observed for the complexes $[Cr(H_2O)_5X]^{2+}$ [37] and $[Rh(NH_3)_5X]^{2+}$ [38] differs from that reported here only in that azide lies closer to isothiocyanate than to thiocyanate.

The orbitals relevant to a discussion of thiocyanate bonding are necessarily the nonbonding 2π level and the pair of nonbonding sp hybrid σ orbitals which are labeled 3σ and 4σ in Figure 3. DiSipio, *et al.*,[34] have performed an MO calculation on thiocyanate which indicates that the 2π level is largely localized on the sulfur atom of the molecule. We have also carried out MO calculations of the type used to provide CN and CO basis functions[5,39,40] on both NCS and NCS^- using bond distances found in $(NH_4)(NCS)$ and $(NH_4)[Cr(NH_3)_2(NCS)_4]$. The composition of the 2π orbital, as indicated by a Mulliken population analysis, is particularly sensitive to the choice of bond distances. In the ion, the calculated 2π orbital is approximately equally divided between the nitrogen and sulfur ends; in the isothiocyanate complex it is primarily on the sulfur. As reflected in the bond distances, and as suggested by other authors, considerable electronic rearrangement must occur upon complex formation. That the 2π level of an isothiocyanate is largely localized on sulfur is consistent with the ionization potential of HNCS (10.6 eV)[21] which is close to that of CS_2 (10.11 eV).[28]

The position of –SCN at the low-field end of the spectrochemical series places it among ligands known to be good π donors. The spectroscopic and theoretical considerations thus suggest that –SCN acts as both a σ and a π donor, whereas –NCS behaves essentially as a σ donor. The bent M–SCN bond must result from overlap of the thiocyanate 2π orbital with metal σ orbitals; conversely, the linear M–NCS bond reflects the larger role of a nitrogen sp hybrid σ orbital in metal–isothiocyanate bonding. The 2π level in the free azide ion is necessarily equal on both ends. The properties of azide as a ligand reflect this in that azide produces a weaker ligand field than does –NCS and, like –SCN, forms bent metal–ligand bonds.

The above discussion of thiocyanate bonding orbitals leads to the expectation that –NCS will prefer to bond to hard or class a metals and –SCN to soft or class b metals, and this is apparently true of the unsubstituted tetra- and hexathiocyanates. The isoelectronic series $[Mn(I)(CO)_5X]$ and $[Co(III)(CN)_5X]^{3-}$ both exhibit class b behavior toward halides and both form sulfur-bonded thiocyanates.

The above compounds also illustrate another effect which has been generally overlooked in discussions of the stability of thiocyanate linkage isomers. Thiocyanate is known to be able to function as a bridge between two atoms in stable compounds.[41] It must be expected, then, that the uncoordinated end of a thiocyanate ligand will interact with whatever is available and that the stable isomer will reflect a competition between the metal and the environment for each end of the ligand. This environmental effect has been used to account for the relative stabilities of $K_3[Co(CN)_5SCN]$ and $[(n\text{-}C_4H_9)_4N]_3[Co(CN)_5NCS]$.[15] The isomerization of $[Mn(CO)_5SCN]$ to $[Mn(CO)_5NCS]$ in acetonitrile[42] can be similarly rationalized. The operation of environmental effects probably obscures some expected hard–soft relationships, particularly in the borderline area.

Acknowledgments. This research was supported by the National Science Foundation. We thank Professor John Burmeister for several stimulating discussions and for allowing us access to unpublished data from his laboratory.

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