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Solvent and Countercation Effects on Ambidentate Bonding Patterns in Thiocyanato- and Selenocyanatopentacyanocobaltate(III) Complexes*

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The complexes $[Co(NH_3)_5NCS]^{2+}$ *and* $[Co(CN)_5SCN]^{3-}$ *have frequently been cited as classic examples of symbiotic bonding in terms of the Hard/Soft Acid/Base Principle. The results of infrared and electronic spectral studies in our laboratory have revealed that this comparison is appropriate only in protic solvents, for the* $[Co(CN)_5SCN]^{3-}$ *complex isomerizes to its N-bonded isomer in* CH_2Cl_2*, acetone, and nitrobenzene. In DMF, an equilibrium is established involving the N-bonded isomer and a species resulting from the dissociation of the* SCN^- *group. Dissociation is essentially complete in* CH_3CN *and DMSO. S-bonding prevails in the protic solvent ethylene glycol, emphasizing the importance of H-bonding in stabilizing the S-bonded isomer. We have succeeded in preparing the corresponding* $[Co(CN)_5SeCN]^{3-}$ *complex via an inner-sphere redox reaction between* $[Co(NH_3)_5NCSe]^{2+}$ *and* $[Co(CN)_5]^{3-}$ *and find that it follows the same bonding pattern as a function of solvent as its thiocyanate analog. Infrared data indicate that the* $[Co(CN)_5XCN]^{3-}$ *complexes isomerize via a dissociative mechanism, possibly involving the formation of an ion pair, in* CH_2Cl_2*, acetone, nitrobenzene, and DMF, the thiocyanate complex isomerizing at a faster rate. The rates of dissociation of the four* $[Co(CN)_5CNX]^{3-}$ *linkage isomers in* CH_3CN *and DMSO vary in the order: Co–SCN > Co–SeCN > Co–NCS ~ Co–NCSe. The size of the countercation can determine the bonding mode adopted by the complexes in the solid state. S-bonding prevails when* K^+*,* Cs^+*, and* $CH_3NH_3^+$ *are present, a mixture (25% N-bonded) is obtained with* $(CH_3)_2NH_2^+$ *and* $(CH_3)_4N^+$*, like the previously reported* $(n\text{-}C_4H_9)_4N^+$*, yields only the N-bonded isomer.*

Introduction

The $[Co(CN)_5]^{2-}$ moiety has proved to be an exceedingly valuable probe for studies concerning the nature of metal–ligand bonding, especially those involving the ambidentate thiocyanate and selenocyanate ions*. Some of the most significant results include a classic example[1] of inorganic symbiosis[2], $[Co(CN)_5SCN]^{3-}$ *versus* $[Co(NH_3)_5NCS]^{2+}$, the discovery[3] of countercation bonding mode control, $K_3[Co(CN)_5SCN]$ *versus* $[(n\text{-}C_4H_9)_4N]_3[Co(CN)_5NCS]$, and one of the earliest examples[3] of solvent bonding mode control[4], $[Co(CN)_5SCN]^{3-}$ (aq) *versus* $[Co(CN)_5NCS]^{3-}$ (CH_2Cl_2). The nature of the bonding interactions between the metal and the thiocyanate and selenocyanate ions has been convincingly interpreted by Gutterman and Gray[5] on the basis of electronic absorption spectral studies. However, several points of issue have remained unresolved, among them being the ambiguity surrounding the synthesis[5,6] of the Se-bonded isomer, $K_3[Co(CN)_5SeCN]$, and the nature and extent of the effects of solvents and countercations on the bonding modes adopted by the thiocyanate and selenocyanate groups in the $[Co(CN)_5CNX]^{3-}$ complexes in, respectively, solution and in the solid state. This paper describes the results of our attempts to resolve these issues, which have led to the discovery of a very important limitation on the concept of symbiotic bonding in coordination complexes.

Experimental

Preparation of Complexes

The syntheses described in detail in this section involve the following reaction scheme, with suitable variations:

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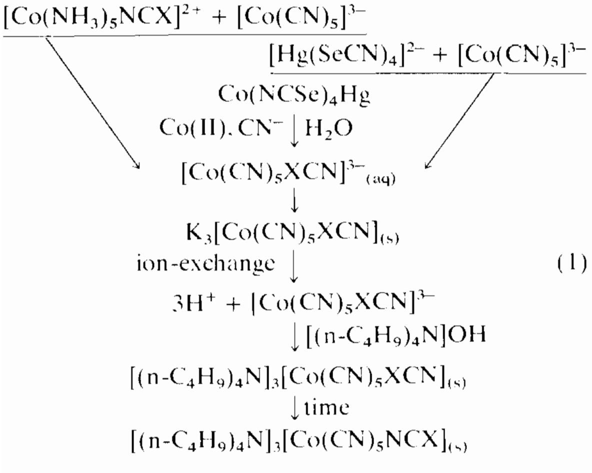
* Throughout this paper, the archaic symbolism CNX will be used to specify the presence of the thiocyanate or selenocyanate ions without regard to their bonding modes. The formulas MNCX, MXCN, MXCNM, and $\mathrm{M}\underset{\underset{\mathrm{N}}{\mathrm{C}}}{\mathrm{X}}\mathrm{M}$ will be used to indicate, respectively, N-bonding, S- (or Se-) bonding, triatomic bridging and monatomic bridging via the S (or Se) atom.



(1)

The following compounds were prepared by methods given in the literature: $[Co(NH_3)_5NCS]SO_4 \cdot 2H_2O$[7], $K_3[Co(CN)_5SCN]$[1], $[(n\text{-}C_4H_9)_4N]_3[Co(CN)_5NCS]$[5], $K_2[Hg(SeCN)_4]$[8], $Co(NCSe)_4Hg$[8], $[(n\text{-}C_4H_9)_4N]_3[Co(CN)_5NCSe]$[5], $K_3[Co(CN)_5N_3]$[9], and $K_3[Co(CN)_5NCO]$[10].

$[(n\text{-}C_4H_9)_4N]_3[Co(CN)_5XCN]$ (X = S, Se)

Three-tenths of a gram of $K_3[Co(CN)_5XCN]$, dissolved in 10 ml of H_2O, was passed over a cation-exchange column (Dowex 50-8X). The acid eluent was titrated to pH 7 with a methanolic solution of $[(n\text{-}C_4H_9)_4N]OH$. The aqueous solution was extracted with two 40 ml portions of dichloromethane. Excess anhydrous diethyl ether was immediately added to the dichloromethane solution to precipitate the product. This was quickly isolated by filtration, washed with anhydrous diethyl ether and dried *in vacuo* for 15 min. Solvent studies were initiated in less than two hr before appreciable solid state isomerization could take place.

$[Co(NH_3)_6][Co(CN)_5XCN]$ (X = S, Se)

$[Co(NH_3)_6]Cl_3$ (2.67 g) was dissolved in 100 ml of H_2O and to this was added 4.91 g of silver acetate. After stirring for 0.5 hr, the resulting silver chloride was removed by filtration. The volume of the filtrate was reduced almost to dryness by boiling under reduced pressure. The residue was redissolved in 250 ml of methanol and filtered. The volume of the filtrate was reduced to about 50 ml and the first crystal crop of product ($[Co(NH_3)_6](CH_3CO_2)_3$) was recovered. Further reduction of volume to 25 ml yielded a second crop. The combined product was washed with isopropyl alcohol, followed by anhydrous diethyl ether and dried *in vacuo*. A portion of the product (0.464 g) was then dissolved in 20 ml of methanol and 10 ml of H_2O. One-half gram of $K_3[Co(CN)_5SCN]$ or 0.564 g of $K_3[Co(CN)_5SeCN]$ was dissolved in 10 ml of H_2O and passed over a cation-exchange column (Dowex 50-8X). When the two solutions were mixed together, the product precipitated immediately. This was isolated by filtration, washed with methanol and then anhydrous diethyl ether and dried *in vacuo*.

$[Co(NH_3)_6][Co(CN)_5NCS]$

Tetra-n-butylammonium isothiocyanatopentacyanocobaltate(III) (0.975 g) was dissolved in 25 ml of methanol. To this solution was added 0.338 g of $[Co(NH_3)_6](CH_3CO_2)_3$ dissolved in 25 ml of H_2O. The product was precipitated by the addition of 75 ml of methanol. The product was isolated by filtration, washed with methanol and then anhydrous diethyl ether, and dried *in vacuo*.

$Cs_3[Co(CN)_5XCN]$ (X = S, Se)

One-half gram of $K_3[Co(CN)_5SCN]$ or 0.564 g of $K_3[Co(CN)_5SeCN]$ was dissolved in 10 ml of H_2O and passed over a cation-exchange column (Dowex 50–8X). Cesium iodide (1.10 g) was added to the acid and the volume of the solution was reduced under a vacuum until near dryness. To this was added 100 ml of ethanol to precipitate the product. This was isolated by filtration, washed with ethanol and air dried. The yellow complex was redissolved in 20 ml of H_2O and filtered into 200 ml of ethanol. The product was isolated by filtration, washed with ethanol followed by anhydrous diethyl ether, and dried *in vacuo*.

$Cs_3[Co(CN)_5NCS]$

Tetra-n-butylammonium isothiocyanatopentacyanocobaltate(III) (0.975 g) was dissolved in 15 ml of methanol and passed over a cation-exchange column (Dowex 50-8X). The acid was titrated with aqueous CsOH to pH 7. The volume was reduced under a vacuum to ~ 10 ml. The remaining solution was filtered into 200 ml of ethanol to precipitate the product and kept at 0° C overnight. The complex was isolated by filtration, washed with ethanol and then anhydrous diethyl ether and dried *in vacuo*.

$[(CH_3)_4N]_3[Co(CN)_5XCN]$, $[(CH_3)_4N]_3[Co(CN)_5NCX]$ (X = S, Se), and $[(CH_3)_3NH]_3[Co(CN)_5SCN]$

One-half gram of $K_3[Co(CN)_5XCN]$ was dissolved in 10 ml of H_2O and passed over a cation-exchange column (Dowex 50-8X). The acid was titrated with $[(CH_3)_4N]OH$ or aqueous $(CH_3)_3N$ to pH 7. Acetone (250 ml) was added to precipitate the product, which was isolated by filtration, washed with ethanol and then anhydrous diethyl ether, and air dried. The product was recrystallized from methanol/ethanol. The $[(CH_3)_4N]^+$ salts thus isolated undergo an X→N-bonded isomerization in the solid state.

$[(CH_3)_3NH]_3[Co(CN)_5NCS]$

Sodium perchlorate (0.367 g) was dissolved in 15 ml of H_2O. To this solution was added 0.975 g of $[(n\text{-}C_4H_9)_4N]_3[Co(CN)_5NCS]$ and the resulting $[(n\text{-}C_4H_9)_4N]ClO_4$ removed by filtration. The yellow filtrate was passed over a cation-exchange column (Dowex 50-8X). The acid eluent was titrated to pH 7 with a methanolic solution of $(CH_3)_3N$ and taken to dryness under a vacuum. The product was dissolved in 25 ml of methanol and precipitated by the addition of 50 ml of anhydrous diethyl ether. The pale yellow solid was filtered out, washed with anhydrous diethyl ether and dried *in vacuo*.

$[(CH_3)_2NH_2]_3[Co(CN)_5SCN]$ and $[CH_3NH_3]_3[Co(CN)_5SCN]$

One gram of $K_3[Co(CN)_5SCN]$ was dissolved in 10 ml of H_2O and passed over a cation-exchange column (Dowex 50-8X). The solution was titrated to pH 7 with an ethanolic solution of dimethylamine or methylamine. It was then taken to dryness under a vacuum. The resulting solid was dissolved in 50 ml of methanol and the product was precipitated by the addition of 100 ml of anhydrous diethyl ether, isolated by filtration, washed with anhydrous diethyl ether and dried *in vacuo*.

$[(CH_3)_2NH_2]_3[Co(CN)_5NCS]$

This complex was prepared by the same method as $[(CH_3)_2NH_2]_3[Co(CN)_5SCN]$ using $[(n\text{-}C_4H_9)_4N]_3[Co(CN)_5NCS]$ instead of $K_3[Co(CN)_5SCN]$.

$[CH_3NH_3]_3[Co(CN)_5NCS]$

A solution containing 0.975 g of $[(n\text{-}C_4H_9)_4N]_3[Co(CN)_5NCS]$ in 10 ml of H_2O was passed over a cation-exchange column (Dowex 50-8X). The acid was titrated to pH 7 with aqueous methylamine. The volume was reduced to dryness. The resulting solid was dissolved in 25 ml of methanol containing 3 ml of H_2O. After filtering the solution, 200 ml of ethanol followed by 500 ml of anhydrous diethyl ether was added to precipitate the product. The complex was isolated by filtration, washed with anhydrous diethyl ether and dried *in vacuo*.

$[Co(NH_3)_5NCSe]Br_2$

The method of Duffy and Kosel[11] was used, except that $[Co(NH_3)_5NO_3](ClO_4)_2$ and $[Co(NH_3)_5OP(OC_2H_5)_3](ClO_4)_3$[12] were used instead of $[Co(NH_3)_5OH_2](ClO_4)_3$. There was also no need for the molecular sieves. The $[Co(NH_3)_5NO_3](ClO_4)_2$ was prepared by adding excess $NaClO_4$ and 100 ml of 72% perchloric acid to one liter of a solution containing 5.0 g of $[Co(NH_3)_5NO_3](NO_3)_2$[13]. After cooling the mixture to 0°C, the product was isolated by filtration, washed with ethanol and anhydrous diethyl ether and air dried.

$[Co(NH_3)_5NCSe](ClO_4)_2$

Crude $[Co(NH_3)_5NCSe]Br_2$ was dissolved in a minimum amount of $10^{-3}M$ HBr. After filtering the solution, excess solid $NaClO_4$ was added and the solution was placed in a refrigerator overnight. The orange product was isolated by filtration, washed with methanol and then anhydrous diethyl ether, and air dried.

$K_3[Co(CN)_5SeCN]$

A modification of the method of Burmeister and Al-Janabi[6] was used. $Co(NCSe)_4Hg$ (20.38 g) was slurried in a mixture of 20 ml of H_2O and 30 ml of ethanol. The color changed immediately upon the addition of 9.77 g of KCN. A black solid, thought to be $Hg_2(SeCN)_2$, was removed by filtration. The filtrate was passed directly into 250 ml of ethanol. The volume was increased to 500 ml with ethanol to precipitate more of the brown product. After stirring for 3 hours, the complex was isolated by filtration, washed with ethanol followed by anhydrous diethyl ether and dried *in vacuo*.

$[(n\text{-}C_4H_9)_4N]_3[Co(CN)_5SeCN]$

The inner sphere redox reaction was carried out in deoxygenated water under a blanket of nitrogen. One-half gram of $[Co(NH_3)_5NCSe]Br_2$ was slurried in 15 ml of H_2O. A catalytic amount of $Co(CH_3CO_2)_2 \cdot 4H_2O$ was added, followed by 0.400 g of KCN. The reaction was complete in less than one min. The insolubles were removed by filtration and the filtrate was allowed to pass directly into 200 ml of ethanol to precipitate the brown product. This was isolated by filtration, washed with ethanol and dried *in vacuo*. The product was converted to the $[(n\text{-}C_4H_9)_4N]^+$ salt as described by Gutterman and Gray[5].

Analyses

The yields and analyses for the complexes prepared are given in Table I. Microanalyses were performed by the Alfred Bernhardt Microanalytical Laboratory, Elbach-über-Engelskirchen, West Germany, M–H–W Laboratories, Garden City, Michigan and Micro-Analysis, Inc., Wilmington, Delaware.

Physical Measurements

Solid state infrared spectra were recorded as Nujol mulls on a Perkin–Elmer 337 spectrophotometer using KBr plates. A Perkin–Elmer 180 spectrophotometer was used for high resolution solid state Nujol mull and solution infrared spectra in the νCN region and in the far infrared to 180 cm^{-1}. When the solvent used was either dichloromethane or benzene, matched 1.00 mm NaCl solution cells were used. For all other solvents, matched 0.5 mm polyethylene cells were used. These are transparent in the regions, 2170–2040 cm^{-1} and 570–180 cm^{-1}, in which they were used. They were used to remove the possibility of chloride, from NaCl windows, substituting for thiocyanate[14]. The cells were constructed from 0.027 inch thick sheets of polyethylene, purchased from Barnes Engineering Co., Stamford, Connecticut, cut to fit Perkin–Elmer sealed liquid absorption cell mounts. The windows were separated

TABLE I. Analytical Data for the Complexes.

Complex	% Yield	Analyses: Calcd. (Found). %				
		C	H	N	Co	S or Se
$K_3[Co(CN)_5SCN]$	90	19.77	0.00	23.06		
		(20.31)	(0.15)	(22.66)		
$[(n{-}C_4H_9)_4N]_3[Co(CN)_5)NCS]$	83	66.54	11.19	12.94	6.05	3.29
		(66.30)	(10.91)	(13.25)	(6.43)	(3.11)[a]
$[Co(NH_3)_6][Co(CN)_5SCN]$	94	17.65	4.45	41.18	28.51	7.85
		(17.54)	(4.62)	(40.94)	(28.87)	(8.03)[a]
$[Co(NH_3)_6][Co(CN)_5NCS]$	95	(17.69)	(4.62)	(40.92)		
$Cs_3[Co(CN)_5SCN]$	81	11.16	0.00	13.02		
		(11.26)	(0.20)	(13.46)		
$Cs_3[Co(CN)_5NCS]$	87	(11.25)	(0.12)	(12.91)		
$[(CH_3)_4N]_3[Co(CN)_5NCS]$	68	46.03	7.74	26.85	12.55	6.83
		(45.91)	(7.74)	(26.71)	(12.62)	(7.02)[a]
$[(CH_3)_3NH]_3[Co(CN)_5SCN]$	71	42.14	7.09	29.49	13.78	7.50
		(42.25)	(7.12)	(29.68)	(13.89)	(7.06)[a]
$[(CH_3)_3NH]_3]Co(CN)_5NCS]$	71	(42.01)	(6.91)	(29.39)		
$[(CH_3)_2NH_2]_3[Co(CN)_5SCN]$	84	37.39	6.29	32.71	15.29	8.32
		(37.22)	(6.33)	(32.65)	(15.38)	(8.24)[a]
$[(CH_3)_2NH_2]_3[Co(CN)_5NCS]$	83	(37.37)	(6.37)	(32.57)		
$[CH_3NH_3]_3[Co(CN)_5NCS]$	97	31.49	5.28	36.72		
		(31.24)	(5.12)	(36.78)		
$[Co(NH_3)_5NO_3](ClO_4)_2$	88	0.00	3.75	20.75		
		(0.19)	(3.88)	(20.73)		
$[Co(NH_3)_5NCSe]Br_2$		2.94	3.70	20.56	14.42	
	43[b]	(3.15)[b]	(3.89)[b]	(20.61)[b]	(14.90)[b]	
	40[c]	(2.96)[c]	(3.91)[c]	(20.70)[c]	(14.09)[c]	
$[Co(NH_3)_5NCSe](ClO_4)_2$	27	2.68	3.38	18.78		
		(2.62)	(3.30)	(18.50)		
$K_3[Co(CN)_5SeCN]$	90	17.52	0.00	20.43		
		(18.13)	(0.05)	(20.45)		
$[(n{-}C_4H_9)_4N]_3[Co(CN)_5SeCN]$	d	63.49	10.68	12.34	5.77	7.73
		(63.69)	(10.76)			
$[(n{-}C_4H_9)_4N]_3[Co(CN)_5NCSe]$	d	(63.32)	(10.56)	(12.36)	(6.13)	(7.63)[a]
$[(CH_3)_4N]_3[Co(CN)_5SeCN]$	75	41.86	7.03	24.41	11.41	15.29
		(41.84)	(7.00)	(23.97)	(11.34)	(15.85)[a]
$Cs_3[Co(CN)_5SeCN]$	90	10.40	0.00	12.13		
		(10.47)	(0.09)	(12.43)		
$[Co(NH_3)_6][Co(CN)_5SeCN]$	88	15.23	4.27	35.53		
		(15.60)	(4.51)	(35.55)		

[a] By difference. [b] Prepared from $[Co(NH_3)_5NO_3](ClO_4)_2$. [c] Prepared from $[Co(NH_3)_5OP(OC_2H_5)_3](ClO_4)_3$.
[d] Not determined.

with 0.5 mm lead spacers. Since the cell was so thin, three 1/16 inch thick aluminium spacers were made and placed below the cell to allow it to be held in the mount. A set was matched by the addition of 0.015 and 0.025 mm spacers to the thinnest cell until the base line was as flat as possible in the $\nu C{\equiv}N$ stretching region when DMF was used as the solvent. The cells leaked badly in the IR beam with solvents having low boiling points. Since spectra in the far infrared region took longer to record than those in the $\nu C{\equiv}N$ stretching region, dibromomethane (b.p. 97 °C) was the solvent used for solution spectra recorded in this region. CsI plates were used when Nujol mull spectra were recorded in the far infrared region. All of the aprotic solvents except DMF and DMSO were distilled, nitrobenzene being distilled over P_2O_5, prior to use. All solvents expect dichloromethane were stored over Linde 4A molecular sieves. Electronic absorption spectra were recorded on a Cary 14 spectrophotometer using matched 1 cm quartz cells.

Results and Discussion

Synthesis of $[Co(CN)_5SeCN]^{3-}$

Burmeister and Al-Janabi's initial synthesis[6] of $K_3[Co(CN)_5CNSe]$ utilized the following reaction:

$$[Hg(SeCN)_4]^{2-} + [Co(CN)_5]^{3-} \rightarrow [Co(CN)_5CNSe]^{3-} + {}^1/_2 Hg_2(SeCN)_2 + 2SeCN^- \tag{2}$$

The selenocyanate group was assigned[6] an N-bonded mode in the $K_3[Co(CN)_5CNSe]$ product, based on the observation of a weak absorption band in the infrared spectrum of the complex at 664 cm^{-1}, which was thought to be the νCSe band. Although the formation of $K_3[Co(CN)_5NCSe]$ was easily rationalized on kinetic grounds (the reaction was expected to proceed *via* the formation of an $[(NCSe)_3Hg–SeCN–Co(CN)_5]^{5-}$ bridged complex), the apparent stability of the N-bonded isomer was totally unexpected, given the known[1] stability of the corresponding S-bonded $K_3[Co(CN)_5SCN]$ complex.

Gutterman and Gray[5] repeated the synthesis of the $K_3[Co(CN)_5CNSe]$ complex and also converted it to the $[(n\text{-}C_4H_9)_4N]^+$ salt. They did not observe the 664 cm^{-1} peak in the infrared spectrum of the K^+ salt; furthermore, as in the case[3,5] of thiocyanate in the $[Co(CN)_5CNS]^{3-}$ complex, the selenocyanate's bonding mode in the $[Co(CN)_5CNSe]^{3-}$ complex was dependent upon which counterion was employed. The results of electronic spectral studies[5] (see Table II) indicated that the K^+ salt contained a significant amount of the Se-bonded isomer, whereas the $[(n\text{-}C_4H_9)_4N]^+$ salt was completely N-bonded.

The complex $K_3[Co(CN)_5SCN]$ was initially prepared[1] by an inner-sphere redox reaction between $[Co(NH_3)_5NCS]^{2+}$ and $[Co(CN)_5]^{3-}$. The synthesis of $[Co(NH_3)_5NCSe]Br_2$ by Duffy and Kosel[11] enabled us to use an analogous reaction to prepare an isomerically pure sample of $[Co(CN)_5SeCN]^{3-}$ for the first time:

$$[Co(NH_3)_5NCSe]^{2+} + [Co(CN)_5]^{3-} + 6H_2O \rightarrow [Co(CN)_5SeCN]^{3-} + [Co(OH_2)_6]^{2+} + 5NH_3 \tag{3}$$

Remote attack by the $[Co(CN)_5]^{3-}$ to form an $[(H_3N)_5Co–NCSe–Co(CN)_5]^-$ bridged complex would certainly be expected to predominate, yielding an Se-bonded $[Co(CN)_5SeCN]^{3-}$ product complex. It should be noted that the spectra of the filtered solution of the product prior to isolation and that of the redissolved potassium salt after isolation were found to be the same, within experimental error. Furthermore, the energies of the lowest energy *d–d* transitions (see Table II) for the various linkage isomers follow the generally accepted spectrochemical series for these ligands: $-NCSe^-$ (28.0kK) $\geqslant$ $-NCS^-$ (27.6kK) > $-SCN^-$ (26.4kK) > $-SeCN^-$ (23.3kK).

The complex $K_3[Co(CN)_5SeCN]$ was also prepared, in the present study, by employing a variation of reaction (2) wherein both the Hg(II) and the Co(II) were incorporated in the same complex:

$$Co(NCSe)_4Hg + 5KCN \rightarrow K_3[Co(CN)_5SeCN] + 2KSeCN + {}^1/_2 Hg_2(SeCN)_2 \tag{4}$$

The electronic spectral data (see Table II) for the product isolated from this reaction are virtually identical to the data obtained for the product of reaction (3).

At first glance, the presence of two absorption bands (at 429 and 363 nm) which could be attributed to *d–d* transitions in the electronic spectra of the products of reactions (3) and (4) would seem to indicate that they contain some of the N-bonded isomer, since its *d–d* transition at 358 nm is very similar in energy to the 363 nm band. However, while only one *d–d* transition (at 378 nm) is listed for the corresponding

TABLE II. Electronic Absorption Spectra of Complexes.

Complex	λ_{max}(nm)	$\varepsilon_{max}(M^{-1}cm^{-1})$	Assignment
$K_3[Co(CN)_5SCN]$[a]	378[b]	191[b]	c
	265[b]	17,100[b]	d
$[(n\text{-}C_4H_9)_4N]_3[Co(CN)_5NCS]$[e]	363[b]	500[b]	c
	265[b]	2,340[b]	d
$K_3[Co(CN)_5CNSe]$[a,f]	420 sh[g]	130[g]	h
	362 sh[b]	306[b]	h
	274[b]	17,800[b]	h
$K_3[Co(CN)_5SeCN]$[a,i]	429 sh[j]	121[j]	c
	363 sh[j]	295[j]	h
	273[j]	21,400[j]	d
$K_3[Co(CN)_5SeCN]$[a,k]	429 sh[j]	119[j]	c
	363 sh[j]	290[j]	h
	274[j]	21,200[j]	d
$[(n\text{-}C_4H_9)_4N]_3[Co(CN)_5NCSe]$[e]	358[b]	484[b]	c
	274[b]	6,830[b]	d

[a] Aqueous solution. [b] Data taken from ref. 5. [c] $^1A_1 \rightarrow {}^1E$ ($^1A_2$?) (*d–d* transition). [d] $4e \rightarrow 3a_1$ (charge-transfer). [e] 5 : 5 : 2 ethyl ether : isopentane : ethanol solution. [f] Prepared from reaction between $[Hg(SeCN)_4]^{2-}$ and $[Co(CN)_5]^{3-}$. [g] D. F. Gutterman and H. B. Gray, private communication. [h] Not assigned. [i] Prepared from reaction between $[Co(NH_3)_5NCSe]^{2+}$ and $[Co(CN)_5]^{3-}$. [j] This work. [k] Prepared from reaction between $Co(NCSe)_4Hg$ and CN^-.

S-bonded $[Co(CN)_5SCN]^{3-}$ complex, it actually is a very broad, asymmetric envelope which consists of more than one absorption. The complex $[Co(CN)_5I]^{3-}$ also exhibits two absorption bands (500 and 330 nm) in this region[15].

The last piece of evidence that the $K_3[Co(CN)_5SeCN]$ complex isolated from reactions (3) and (4) is the pure Se-bonded isomer is found in a consideration of the νCN stretching region in the infrared. The potassium salt was found to be soluble in only DMF and DMSO, of the aprotic solvents used in this study, while the $[(n\text{-}C_4H_9)_4N]^+$ salt was soluble in all of the aprotic solvents employed except benzene. While Gutterman and Gray[5] found that the $[(n\text{-}C_4H_9)_4N]^+$ salt yields the N-bonded species as the more stable isomer, it was found in this study that the solid state isomerization did not occur immediately. It was then possible to isolate the same isomer (or isomer mixture) of the potassium salt as the $[(n\text{-}C_4H_9)_4N]^+$ salt as long as the latter was used almost immediately after isolation. The solution infrared spectra in the νCN stretching region of this complex, (the potassium salt in DMSO and the freshly isolated $[(n\text{-}C_4H_9)_4N]^+$ salt in dichloromethane, nitrobenzene and acetonitrile) all show no evidence of an absorption in the range 2134–2138 cm^{-1} (see Figure 1). Solution infrared spectra of the $[(n\text{-}C_4H_9)_4N]^+$ salt after the Se → N isomerization has occurred, however, show a strong absorption in the 2134–2138 cm^{-1} region (see Figure 2). If the isolated potassium salt contained an appreciable amount of the N-bonded isomer, this would certainly show up in the infrared. Since it does not, it is concluded that the isolated potassium salt from both reactions (3) and (4), using $[Co(NH_3)_5NCSe]^{2+}$ and Hg(II) as the oxidants, yields the pure Se-bonded isomer. The infrared spectra of both $[Co(CN)_5CNX]^{3-}$ (X = S, Se) complexes will be discussed in greater detail in the following section.

A comparison of the electronic spectral data in Table II shows that the product of reaction (2) obtained by Gutterman and Gray[5] did indeed contain a small amount of the N-bonded isomer. The predomi-

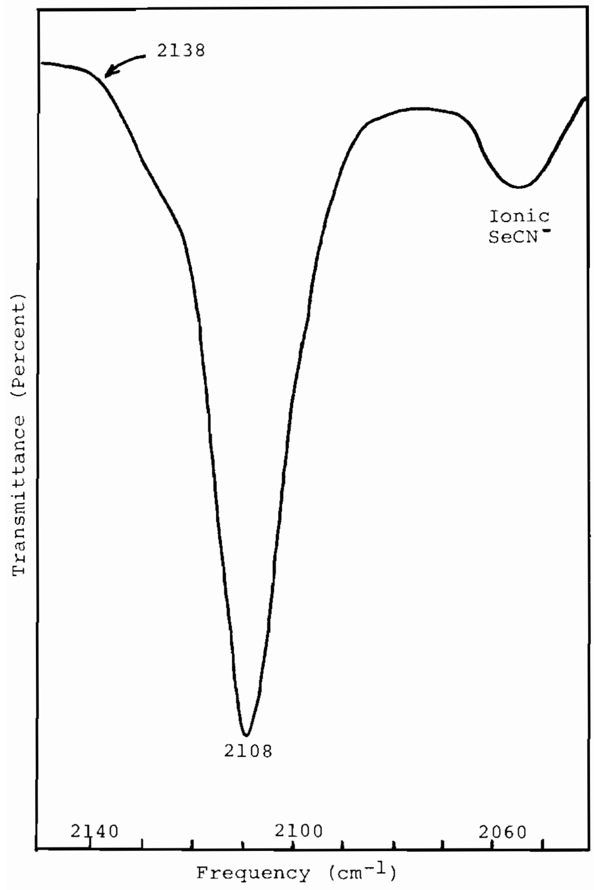


Figure 1. Initial Infrared Spectrum of $[Co(CN)_5SeCN]^{3-}$ ($10^{-2}M$) in DMSO.

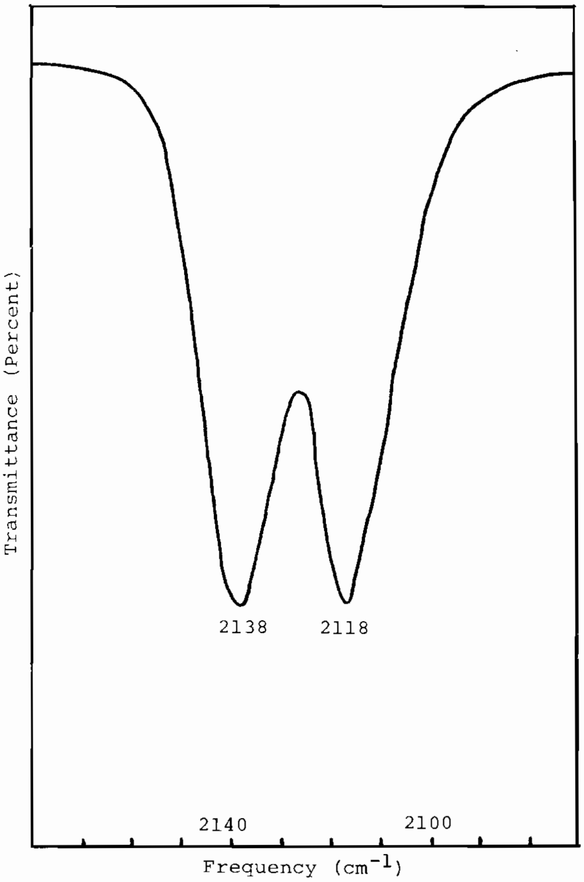


Figure 2. Initial Infrared Spectrum of $[Co(CN)_5NCSe]^{3-}$ ($10^{-2}M$) in DMSO.

nant formation of the Se-bonded isomer in reaction (2) can now be understood as the result of favored *adjacent* attack on the selenium atom, leading to the formation of the bridged complex $[(NCSe)_3Hg{-}Se{-}\begin{array}{c}C\\N\end{array}Co(CN)_5]^{5-}$. In support of this hypothesis, recent studies[16] have shown that the reaction of $[Co(NH_3)_5SCN]^{2+}$ with $[Co(CN)_5]^{3-}$ proceeds *via* adjacent attack on sulfur, and that the rate is considerably faster than the rate of the reaction between $[Co(NH_3)_5NCS]^{2+}$ and $[Co(CN)_5]^{3-}$, which necessitates remote attack on the sulfur. In both cases, $[Co(CN)_5SCN]^{3-}$ is the sole product formed. The mechanism of reaction (4) remains a subject of conjecture.

Solvent Bonding Mode Control and the Mechanisms of Linkage Isomerizations

Gutterman and Gray, in their initial study[3], observed that an S→N-bonded isomerization takes place when $[Co(CN)_5SCN]^{3-}$ is extracted from an aqueous solution into dichloromethane. They also noted that the equilibrium isomer mixture in aqueous solution contains 70% of the S-bonded isomer and 30% of the N-bonded isomer. Since there is a solvent dependence of the bonding mode of the thiocyanate, it was highly desirable to investigate both of the $[Co(CN)_5CNX]^{3-}$ (X = S, Se) systems in a number of solvents of varying dielectric constant in order to determine the extent and direction of this solvent effect[4,17]. Initially, based on the two data points available, it appeared that the $[Co(CN)_5CNS]^{3-}$ species was exhibiting the same sensitivity to the dielectric constant of the solvent as that observed by Burmeister, *et al.*[4] for palladium(II) and platinum(II) thiocyanate complexes, *i.e.*, an increased tendency for S-bonding to occur in solvents of higher dielectric constant.

The infrared νCN stretching region (2200–2000 cm^{-1}) yields completely different spectra for each of the four linkage isomers. Figures 1 and 2 show the infrared spectra in DMSO in this region for the linkage isomers of $[Co(CN)_5CNSe]^{3-}$ and Figures 3 and 4

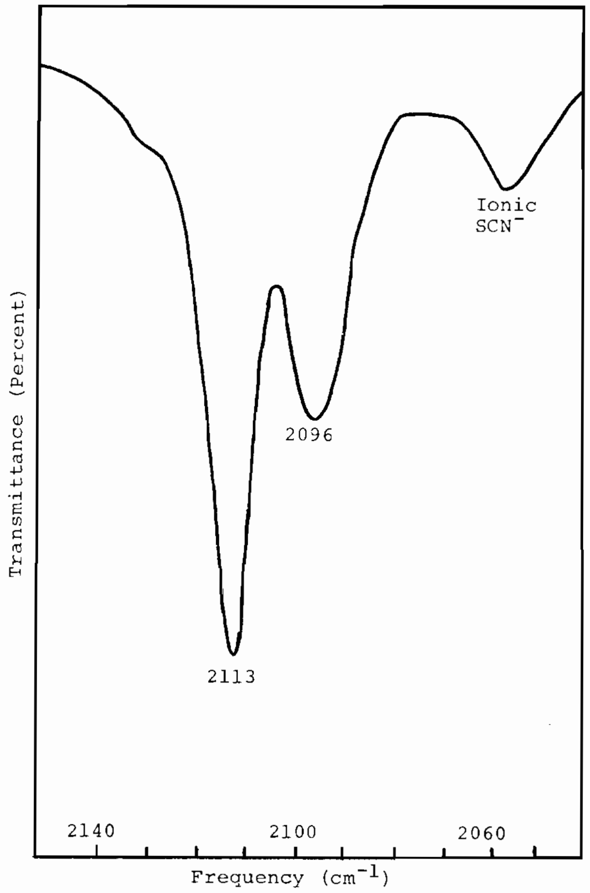


Figure 3. Initial Infrared Spectrum of $[Co(CN)_5SCN]^{3-}$ ($10^{-2}M$) in DMSO.

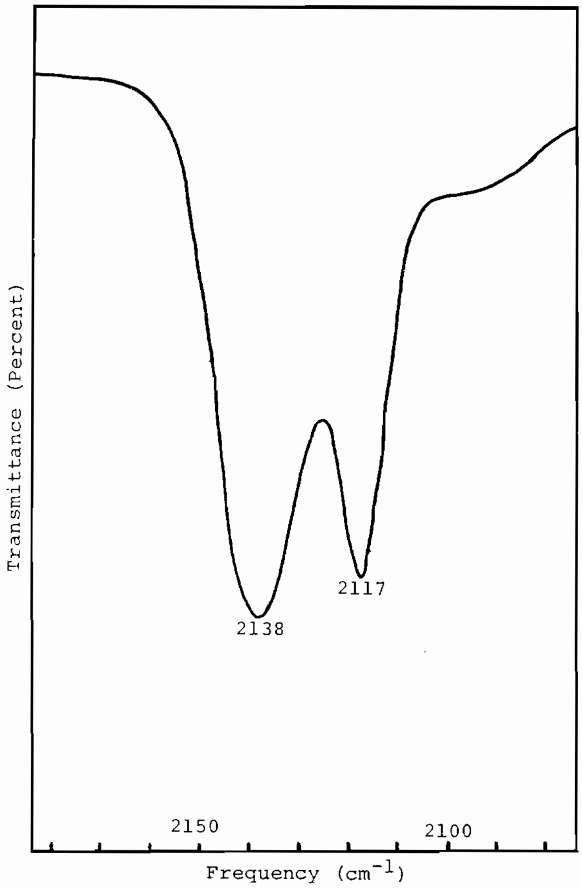


Figure 4. Initial Infrared Spectrum of $[Co(CN)_5NCS]^{3-}$ ($10^{-2}M$) in DMSO.

show the same for $[Co(CN)_5CNS]^{3-}$. Table III shows that the initial νCN absorption bands of each isomer of $[Co(CN)_5CNS]^{3-}$ in a variety of solvents are basically the same as those shown in Figures 3 and 4. The extra absorption (at 2129 cm^{-1}) exhibited by $[Co(CN)_5SCN]^{3-}$ in dichloromethane results from an increase in resolution since this solvent has no appreciable absorption in this region. It is seen as ill defined shoulders in the other solvents. Table IV contains comparable data for $[Co(CN)_5CNSe]^{3-}$. The same relatively weak absorption band is observed in the spectra of $[Co(CN)_5SeCN]^{3-}$ in some of the solvents. The absorption at 2108 cm^{-1} observed in the spectra of $[Co(CN)_5NCSe]^{3-}$ in dichloromethane and acetonitrile will be commented on later. The concentration of the solutions used was $1.0 \times 10^{-2}M \pm 10\%$. This is 2.5 times more concentrated than the solutions used for measuring the electronic absorption spectra and therefore would give less percent dissociation.

It is possible to make relatively certain assignments of the νCN stretching bands. Theoretically, when the symmetry of the $[Co(CN)_5X]^{3-}$ ion is C_{4v} (*e.g.*, when the pseudohalide is N-bonded), there should be five νCN stretches, including that of the pseudohalide. But when the symmetry is C_s (when the pseudohalide is S or Se-bonded, and hence, involves a non-linear Co–X linkage), the number increases to six. Actually, only two (one for $[Co(CN)_5SeCN]^{3-}$) strong νCN stretches are observed for these complexes, as shown in Table V. The νCN stretches exhibited by the chloro and azido complexes are also listed. In both of these complexes, there is only one observable νCN stretch, indicating that all of the theoretical stretches are located under the one envelope and/or are relatively weak. Also, in solvents where the pseudohalides are completely dissociated from the complex (to be discussed later), there is only one observable νCN envelope.

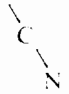


TABLE III. Initial νCN(cm^{-1}) Bands of Pure Isomers of $[Co(CN)_5CNS]^{3-}$ in Solution.[a]

Solvent	S-Bonded Isomer	N-Bonded Isomer
Dichloromethane	2129 mw 2111 s 2096 m	2134 s,br 2117 s
Nitrobenzene	2112 s 2096 m	2133 s 2117 s
Acetone	–	2140 s 2117 s
Acetonitrile	2113 m 2096 mw	2138 s 2118 s
DMF	2115 m 2096 mw	2140 s 2117 ms
Furfural	2112 s 2097 m	2133 s 2119 s
DMSO	2113 ms 2096 mw	2138 ms 2117 ms
Ethylene Glycol	2124 s	2144 sh 2132 s
Formamide	2120 s 2106 sh	2136 sh 2126 s

[a] Abbreviations: vs, very strong; s, strong; m, medium; w, weak; sh, shoulder.

TABLE IV. Initial νCN (cm^{-1}) Bands of Pure Isomers of $[Co(CN)_5CNSe]^{3-}$ in Solution.[a]

Solvent	Se-Bonded Isomer	N-Bonded Isomer
Dichloromethane	2127 mw 2108 vs	2136 s,br 2118 s 2108 m
Nitrobenzene	2128 sh 2107 s	2134 s 2116 s
Acetone	2121 m 2109 m	2140 s 2118 s
Acetonitrile	2117 mw 2109 vs	2138 s 2118 s 2109 m
DMF	–	2142 s 2117 vs
DMSO	2108 s	2138 ms 2116 ms
Ethylene Glycol	2124 s	2132 ms
Formamide	2117 s	2132 sh 2125 ms

[a] Abbreviations: vs, very strong; s, strong; m, medium; w, weak; sh, shoulder.

TABLE V. Assignments of Infrared Absorption Maxima of 10^{-2} *M* Dichloromethane Solutions of $[Co(CN)_5X]^{3-}$ Between 2170 and 2000 cm^{-1}.[a]

X	Absorption	Assignment
$-NCS^-$	2134 s	SC≡N
	2117 s	C≡N
$-NCSe^-$	2136 s	SeC≡N
	2118 s	C≡N
	2108 m	
$-SCN^-$	2129 mw	C≡N
	2111 s	C≡N
	2096 m	SC≡N
$-SeCN^-$	2127 mw	C≡N
	2108 vs	C≡N and SeC≡N
$-Cl^-$	2111 s	C≡N
$-NNN^-$	2111 s	C≡N
	2038 sh	N_3
	2027 s	N_3

[a] Abbreviations: vs, very strong; s, strong; m, medium; w, weak; sh, shoulder.

The absorptions assigned to the cyanides all fall in the range of 2108 to 2122 cm^{-1}. If this holds for the spectra of the pseudohalides, the additional major absorptions must be due to the pseudohalides themselves. The high energy absorptions exhibited by the N-bonded complexes can then be assigned to the νCN stretch of the pseudohalides. The low energy absorption in the $[Co(CN)_5SCN]^{3-}$ spectrum has therefore been assigned to the νCN stretch of the thiocyanate. The single major νCN stretch in the $[Co(CN)_5SeCN]^{3-}$ spectrum is more intense than the corresponding stretch of $[Co(CN)_5SCN]^{3-}$. It has therefore been assumed that the corresponding νCN stretch of the selenocyanate is located under the same envelope as the cyanide stretches. The fact that the pseudohalide νCN stretches of the N-bonded isomers are of higher energy than those of the S and Se-bonded isomers in these hexacoordinated complexes is completely in accord with the results of previous infrared spectral studies of thiocyanate linkage isomers of octahedral complexes[18]. The intensities of these absorptions also follow the expected order[18], *i.e.*, the N-bonded isomers exhibit much more intense νCN absorptions than that observed for the S-bonded thiocyanate in $[Co(CN)_5SCN]^{3-}$.

TABLE VI. νCN Bands (cm^{-1}) of Final Isomerization and Dissociation Products.

Solvent	$[Co(CN)_5CNS]^{3-}$	$[Co(CN)_5CNSe]^{3-}$
Dichloromethane[a]	2134 s,br	2136 s,br
	2117 s	2118 s
	2056 vw	2108 sh
Nitrobenzene[a]	2133 s	2134 s
	2117 ms	2116 s
	2056 w	2064 w
Acetone[a]	2140 s	2140 s
	2117 s	2118 s
	2057 w	2067 w
Acetonitrile[c]	2122 ms	2122 ms
	2057 s	2067 ms
DMF[b]	2140 m	2140 m
	2118 s	2117 s
	2057 s	2066 s
Furfural[a]	2131 s	
	2119 s	
	2055 ms	
DMSO[c]	2121 ms	2121 ms
	2055 s	2064 ms
Ethylene Glycol[d]	2125 ms	2123 s
	2059 mw,br	
Formamide[c]	2121 ms	2121 ms
	2058 mw,br	2068 mw,br

[a] Spectra characteristic of N-bonded isomer, with slight dissociation, at equilibrium. [b] Equilibrium mixture of *ca.* 40% N-bonded and *ca.* 60% dissociated (see text). [c] Essentially completely dissociated at equilibrium. [d] Predominately S- and Se-bonded at equilibrium. Abbreviations: v, very; s, strong; m, medium; w, weak; sh, shoulder.

The results of the solvent study are shown in Table VI in terms of the νCN bands exhibited by the solutions at equilibrium. Both isomers of each complex were placed (individually) in each of the solvents listed. Equilibrium was considered to be reached when the spectrum of each of the linkage isomers in a given pair was identical. The solutions used were stored in volumetric flasks at room temperature and spectra were taken periodically. Since no real control of the temperature of the solutions was attempted, the results are only qualitative in nature. The time required to arrive at equilibrium varied with the solvents from less than one day (acetone) to several months (ethylene glycol). A comparison of these results with the data for the pure isomers (Tables III and IV) shows that in dichloromethane, nitrobenzene, acetone, and furfural, the N-bonded isomers are the more stable. The weak absorptions below 2070 cm^{-1} are due to small amounts of ionic pseudohalide present in the solution. The S- $\rightarrow$ N-bonded and Se- $\rightarrow$ N-bonded isomerizations are relatively slow processes. Figure 5 shows the spectral changes in the νCN region accompanying the S- $\rightarrow$ N-bonded isomerization of $[Co(CN)_5SCN]^{3-}$ and Figure 6 shows the analogous changes caused by the Se- $\rightarrow$ N-bonded isomerization of $[Co(CN)_5SeCN]^{3-}$ with the length of time the complexes were in solution when sampled.

In DMF, the equilibrium point is reached when the complexes are ~ 60% dissociated and ~ 40% N-bonded. These numbers were arrived at by comparing the absorbances calculated from the percent transmittance of the νCN bands of the coordinated N-bonded pseudohalides. They are only intended to be estimates. In the final two aprotic solvents, acetonitrile and DMSO, the dissociation is virtually, if not totally, complete. The time required for the S- and Se-bonded isomers to reach equilibrium in these last three solvents was less than that for the N-bonded isomers.

The results of the infrared spectral studies provide a fairly clear picture of the linkage isomerization mechanisms. Ionic thiocyanate and selenocyanate both have relatively strong absorptions below 2070 cm^{-1} (2056 for SCN$^-$ and 2066 for SeCN$^-$ in DMF), which do not interfere with any of the νCN stretches of the complexes themselves. In all of the solvents, except those where dissociation is complete (acetonitrile and DMSO), an initial increase followed by a decrease in the intensity of the ionic pseudohalide absorption was observed. Figure 5 shows this sequence quite clearly. The isomerization therefore appears to involve a dissociative process.

The analysis of the reaction

$$[Co(CN)_5OH_2]^{2-} + X^- \rightleftarrows [Co(CN)_5X]^{3-} + H_2O \qquad (5)$$

by Haim and Wilmarth[19,20] is considered to be the

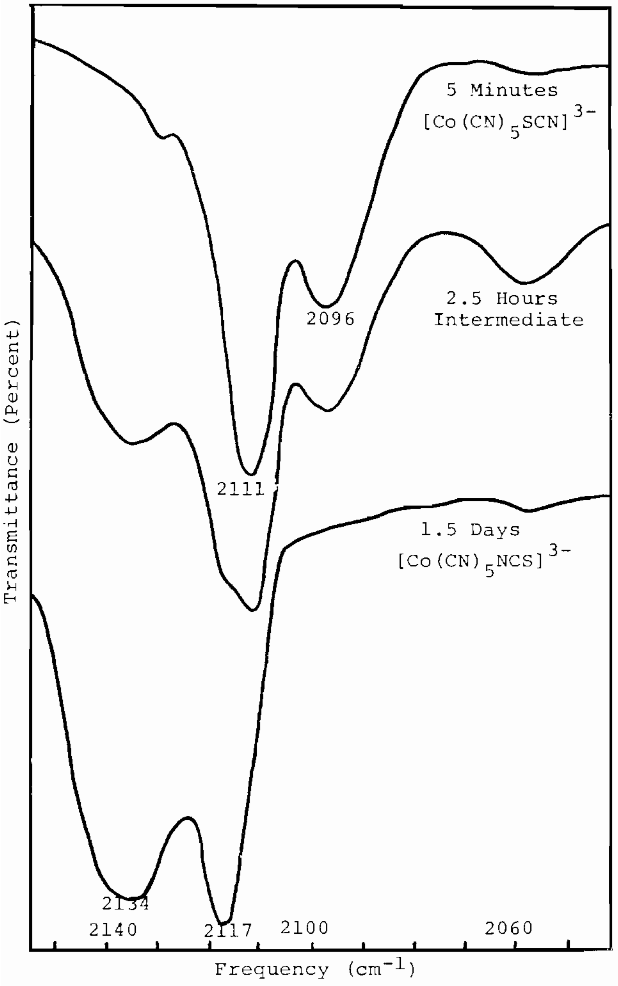


Figure 5. Isomerization of $[Co(CN)_5SCN]^{3-}$ in Dichloromethane ($10^{-2}M$).

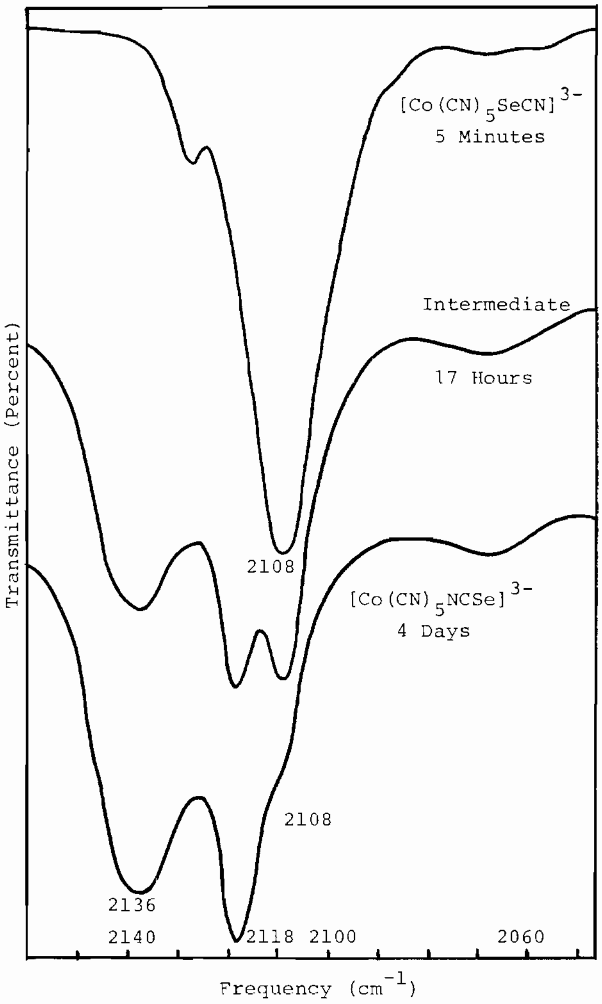


Figure 6. Isomerization of $[Co(CN)_5SeCN]^{3-}$ in Dichloromethane ($10^{-2}M$).

best evidence for a dissociative (S_N1 lim) process. This process can be shown as follows:

$$[Co(CN)_5OH_2]^{2-} \rightleftarrows [Co(CN)_5]^{2-} + H_2O \qquad (6)$$

$$[Co(CN)_5]^{2-} + X^- \rightarrow [Co(CN)_5X]^{3-} \qquad (7)$$

This postulates the existence of a five-coordinate intermediate complex, $[Co(CN)_5]^{2-}$, which then reacts with X^-. There is no direct evidence as to the geometry of the intermediate. It would seem reasonable, though, that the trigonal bipyramidal structure would be less open to attack by solvent water than a square pyramidal one. Since this five-coordinate intermediate occurs in water, it could also occur in other solvents as well. The appearance and subsequent decrease in intensity of the νCN stretch of the free pseudohalides in solvents which would not be expected to coordinate (dichloromethane, acetone, furfural and nitrobenzene) points to this dissociative mechanism, which can be written as follows for the reactions in question:

$$[Co(CN)_5XCN]^{3-} \rightarrow [Co(CN)_5]^{2-} + NCX^- \rightarrow [Co(CN)_5NCX]^{3-} \qquad (8)$$

When the solvent is acetone, the dissociation of selenocyanate in $[Co(CN)_5SeCN]^{3-}$ occurs at such a rate that an absorption band at 2121 cm^{-1} appears and then disappears. This absorption band is thought to be due to the five-coordinate intermediate. The nature of the complexes in solution when the stronger coordinating solvents (DMF, acetonitrile and DMSO) are used is not known. They could be either the five-coordinate intermediate or a solvent substituted complex, $[Co(CN)_5 \text{ solvent}]^{2-}$. $[Co(CN)_5SCN]^{3-}$ dissociated very quickly in DMF, giving an absorption band at 2122 cm^{-1}, which subsequently disappeared. This, like the cyanide νCN stretches observed in DMSO (2121 cm^{-1}) and acetonitrile (2122 cm^{-1}), is due to either a solvent substituted complex or the five-coordinate complex.

Since the N-bonded isomers of both complexes are the more stable in the aprotic solvents used, the unique bonding site in $[\text{Co(CN)}_5\text{X}]^{3-}$ is electronically hard in these solvents, contrary to the results obtained for water and ethylene glycol, wherein the site was found to be soft (S- and Se-bonding predominate). Possible reasons for the difference in behavior will be discussed momentarily.

Another pertinent observation involving these complexes in the aprotic solvents used is that $[\text{Co(CN)}_5\text{SCN}]^{3-}$ always isomerizes or dissociates faster than $[\text{Co(CN)}_5\text{SeCN}]^{3-}$. This would seem to be a rather unexpected result, at first glance. It would seem more likely that, if the site were hard, the softer selenium of selenocyanate would form a weaker bond than the sulfur of thiocyanate. However, the observed order of preference of $\text{N} > \text{Se} > \text{S}$ is not without precedent, *e.g.*, trimethylgallium complexes also exhibit this order[21].

These results exemplify a problem frequently encountered in trying to use Pearson's HSAB[22] principle. Whereas a relatively smooth transition from class (a) to class (b) donor character occurs in going down Group VII, the transition going down Group VI is not nearly so smooth, and a discontinuity occurs at phosphorus in Group V. Phosphorus, not antimony, exhibits the greatest tendency to coordinate to class (b) metals. This illustrates a very important, but frequently neglected point: class (a) is *not necessarily* synonymous with hard nor is class (b) *necessarily* synonymous with soft. The class (a)/(b) classification refers to the relative order of formation constants, K_f, which according to Pearson[22], involves *four* parameters, not just the two hard/soft parameters:

$$\begin{aligned}
\log K_f &= S_A S_B + \sigma_A \sigma_B \\
A &= \text{acid};\ B = \text{base} \qquad\qquad (9)\\
S_A S_B &= \text{Intrinsic strength parameters} \\
\sigma_A \sigma_B &= \text{Hard (soft) parameters}
\end{aligned}$$

In practice, the intrinsic strength parameters are usually ignored, with the primary emphasis being placed on the hard (soft) parameters. While this correctly predicts the greatest tendency for the formation of homogeneous (hard/hard or soft/soft) acid/base adducts, it cannot be used to predict the relative strengths of heterogeneous (hard/soft or soft/hard) acid/base interactions. In these cases, the intrinsic strength parameters assume greater importance. They can no longer be swamped by the hard (soft) parameters. Indeed, the HSAB principle normally cannot be used to predict the relative strengths of like homogeneous interactions, *e.g.*, hard metal/fluoride versus hard metal/oxygen because of the difference in intrinsic strength parameters. Put more simply, the HSAB principle works best when comparing donor atoms in the same group in the periodic table having extreme differences in hard (soft) character with a reference acid. Thus, in the present case, it is not surprising that the observed $\text{N} > \text{Se} > \text{S}$ order is not that of constantly decreasing soft donor atom character, since the Co–Se and Co–S interactions involve heterogeneous hard/soft interactions in the aprotic solvents used.

Even more important is the aforementioned question of why the unique site in $[\text{Co(CN)}_5\text{X}]^{3-}$ is hard in aprotic solvents, but is soft in water and ethylene glycol. The infrared spectra of the complexes in ethylene glycol were poorly resolved because the relatively high absorbance of the solvent required a wide slit width; consequently, it was impossible to determine what percentage of the N-bonded isomers were present. Both complexes dissociate completely in formamide, the other protic solvent employed in this study.

Both water and ethylene glycol are capable of hydrogen bonding. They will strongly solvate hard bases such as F^- and OH^-. The negative hydration heats in water for the halide ions are 61, 74, 85 and 117 kcal/mol for I^-, Br^-, Cl^- and F^-, respectively[23].

Klopman[24] has suggested that the softness parameter $E_n^{\ddagger}$ for a Lewis acid can be calculated as follows:

$$E_n^{\ddagger} = -(\text{orbital energy of lowest unoccupied MO}) + \text{desolvation energy} \qquad (10)$$

The more negative $E_n^{\ddagger}$ values are indicative of greater soft character. Thus, in terms of this equation, the softness parameter of the acid would become more positive (the acid would become harder) as the desolvation energy increases. Therefore, the $[\text{Co(CN)}_5]^{2-}$ moiety should become harder in water than in dichloromethane. Likewise, the softness parameter, $E_m^{\ddagger}$, for Lewis bases can be calculated in a similar fashion:

$$E_m^{\ddagger} = -(\text{orbital energy of the lowest filled MO}) - \text{desolvation energy} \qquad (11)$$

The more positive $E_m^{\ddagger}$ values are indicative of greater soft character. Thus, the softness parameter of the base would become more negative (the base would become harder) as the desolvation energy increases.

These equations predict that the tendence for a hard/hard (Co–NCX) interaction should increase as the desolvation energy increases. The preference for Co–NCX bonding then should be greatest in H_2O. Precisely the opposite result is observed. There is no varying trend observed in the aprotic solvents, which show a preference for the N-bonded complexes only. S-bonding and Se-bonding are favored only in protic solvents where hydrogen bonding is possible. The controlling factor thus appears to be that a stronger hydrogen bond forms with Co–X than with Co–NCX.

The N atoms of the free NCX^- ions would be solvated to a much greater extent *via* H-bonding interactions, making the S and Se atoms more available for coordination. The nitrogen end of the thiocyanate is more apt to be hydrogen bonded to the solvent because it is a first row element. In agreement with this argument, thiocyanic acid exhibits a structure wherein the proton is bonded to the nitrogen[25].

These results place a significant limitation on the concept of inorganic symbiosis[2]. Since symbiotic effects on the bonding modes of NCS^- and $NCSe^-$ in these cobalt(III) complexes in solution are only operable in protic solvents, the question naturally arises as to whether or not the oftquoted example[2] of $[Co(NH_3)_5X]^{2+}{}_{(aq)}$ (most stable halogeno complex for $X = F^-$) *versus* $[Co(CN)_5X]^{3-}{}_{(aq)}$ (most stable halogeno complex for $X = I^-$) is also limited to protic solvents. In any event, the importance of solvation effects in determining coordinate bond strengths is readily apparent.

The infrared spectra of $[Co(CN)_5NCSe]^{3-}$ in acetonitrile and dichloromethane initially exhibit well resolved absorption bands at 2109 and 2108 cm^{-1}, respectively (Table IV). With time, the absorption band at 2108 cm^{-1} decreases in intensity until it becomes a shoulder, as the final spectrum in Figure 6 shows. This decrease in intensity indicates that the solid tetra-n-butylammonium salt contains chiefly, but not totally, the N-bonded isomer. This can partly explain why the molar extinction coefficient of the charge transfer band in $[Co(CN)_5NCSe]^{3-}$ is so much higher (6830)[5] than the same band in $[Co(CN)_5NCS]^{3-}$ (2340)[5]. Gutterman and Gray were not certain[5] if this salt was totally N-bonded or not.

Solution infrared spectra were also measured in the far infrared. Spectra in this region were recorded for some of these complexes as Nujol mulls by Gutterman and Gray[5], but not in solution. Where duplication occurs, the agreement is good. While shown in the published spectra[5], the very strong absorption band at about 400 cm^{-1} was omitted in the tabulation of frequencies. Table VII shows the solution ($10^{-1}M$ in dibromomethane) spectral results. The assignments were made by comparison with the assignments of the vibrational modes in $[Co(CN)_6]^{3-}$[26]. Table VIII shows similar solid state spectra. It was hoped to assign ν_{Se-C} and δ_{NCSe} in the spectra of the two isomers of $[Co(CN)_5CNSe]^{3-}$, but they were not found.

The Raman spectra of this region for $[Co(CN)_5NCSe]^{3-}$ and $[Co(CN)_5NCS]^{3-}$ in CH_2Br_2 both show an additional absorption at 386 cm^{-1} which is the infrared inactive metal-carbon stretch.

Countercation Bonding Mode Control

With the discovery[3] that $[Co(CN)_5NCS]^{3-}$ is the more stable isomer when the tetra-n-butylammonium counter-ion is used and the S-bonded isomer is more stable when potassium is the counter-ion, it became of interest to investigate the nature and extent of counter-ion control of the bonding mode of the thiocyanate and selenocyanate ions in these complexes. The degree of isomerization was determined by evaluation of the molar extinction coefficient of the charge transfer band

TABLE VII. Solution Far Infrared Spectra of $[Co(CN)_5X]^{3-}$ Complexes (cm^{-1}).[a]

X	δ_{M-CN}	Unknown	ν_{M-CN}	ν_{M-X}
$-NCS^-$ [b,d]	555 vvw	452 w	423 s 404 vs 371 s	253 m
$-NCSe^-$ [b]	557 vvw 542	459 w	422 sh 403 vs 365 m	196 w,br
$-SCN^-$	556 w 541 mw	454 vw	411 vs 364 m	254 w
$-SeCN^-$	555 vw 539 m	455 vw	412 vs 360 m	196 vvw
N_3^- [b]	557 vvw 538 w	456 vw	416 sh 406 vs 375 m	339 w
Cl^-	555 m 537 vw	c	406 vs 378 m	c

[a] 10^{-1} *M* CH_2Br_2 solutions. [b] Reported by Gutterman and Gray[5] as Nujol mulls. [c] Not observed. [d] δ_{NCS} 474 mw.
Abbreviations: v, very; s, strong; m, medium; w, weak; sh, shoulder.

TABLE VIII. Solid State Far Infrared Spectra of $[Co(CN)_5X]^{3-}$ Complexes (cm^{-1}).[a]

Complex	δ_{M-CN}	Unknown	ν_{M-CN}	ν_{M-X}
$[(n\text{-}C_4H_9)_4N]_3[Co(CN)_5Cl]$	554 mw 536 w	459 w	418 m 402 s 364 m	
$K_3[Co(CN)_5SeCN]$	563 w 545 s	466 w	422 vs,br 398 sh 362 s	
$[(CH_3)_4N]_3[Co(CN)_5NCS]$[a]	558 w 543 w	454 m	426 s 407 vs 378 ms	255 m
$Cs_3[Co(CN)_5SeCN]$	558 vw 542 m	462 w	415 vs,br 392 sh 361 m	

[a] Nujol Mulls on CsI Plates. [b] δ_{NCS}, 478 mw. Abbreviations: v, very; s, strong; m, medium; w, weak; br, broad; sh, shoulder.

in the electronic absorption spectra since it is the most intense absorption. With $[Co(CN)_5CNS]^{3-}$, this band occurs at 265 nm. The ε used for the pure S-bonded isomer was 17,100 and that for the pure N-bonded isomer was 1830. The percent N-bonded isomer was calculated as follows:

$$1830X + 17{,}100(1-X) = \varepsilon \text{ (observed)} \tag{12}$$

where $100X$ = % N-bonded isomer present.

The value of 1830 used for the N-bonded isomer was the lowest value obtained for an analytically pure sample. The results for the thiocyanato complex are shown in Table IX. With the counter-ions $[Co(NH_3)_6]^{3+}$, Cs^+ and $CH_3NH_3^+$, the N-bonded isomers have partially isomerized in the solid state while the S-bonded isomers have not. With these ions and the potassium ion, $[Co(CN)_5SCN]^{3-}$ is the more stable isomer. But, with the dimethylammonium ion, an equilibrium is relatively quickly reached which contains about 23% of the N-bonded isomer. The trimethylammonium ion causes the complex to be rather inert to isomerization. It would been better if the S-bonded isomer had been observed over a longer period of time. When the counter-ion is $(CH_3)_4N^+$, as with $(n\text{-}C_4H_9)_4N^+$ [3], the S-bonded isomer totally isomerizes. There is a trend among the singly charged cations, except for the trimethylammonium ion, in which the tendency toward N-bonding increases with the size of the cation.

TABLE IX. Effect of Counter-ion on the Bonding Mode of Thiocyanate in $[Co(CN)_5CNS]^3$.[a]

Counter-ion	Original Isomer	Time in Solid State	Percent N-Bonded
$[Co(NH_3)_6]^{3+}$	S	2y, 4m	0
	N	2y, 4m	84
Cs^+	S	2y, 5m	0
	N	1y, 9m	72
$CH_3NH_3^+$	S	1m	0
	N	1y, 1m	87
$(CH_3)_2NH_2^+$	S	1.6m	25
	N	5m	23
$(CH_3)_3NH^+$	S	1m	0
	N	1y, 3m	95
$(CH_3)_4N^+$	S	1y	100

[a] Abbreviations: y, year; m, month.

$[Co(CN)_5CNSe]^{3-}$ shows the same trend, but, as in the solvent study, the strength of the Co-Se bond alters the results. The molar extinction coefficients used were 21,400 for the Se-bonded isomer and 6460 for the N-bonded isomer, even though a completely pure sample of the latter has not been prepared, as shown earlier. After 3 years, the Se-bonded isomer reaches an equilibrium which contains 74% of the isoselenocyanato complex when $(CH_3)_4N^+$ is the cation. Also, in agreement with the solvent study is the fact that $[Co(CN)_5SCN]^{3-}$ isomerizes faster than $[Co(CN)_5SeCN]^{3-}$ in the solid state when $(n\text{-}C_4H_9)_4N^+$ is the counter-ion.

This counter-ion effect has been described by Gutterman and Gray[3] in terms of preferential hard/hard or soft/soft interactions between the non-bonded end of NCX^- and the cation. They suggest that the potassium ion can have a more favorable interaction with the hard nitrogen end of the thiocyanate while the soft tetra-n-butylammonium ion will better accommodate the softer sulfur end of the thiocyanate.

An alternative argument can be made on the basis of the size of the cation. In the N-bonded complexes, the thiocyanate and selenocyanate groups protrude out from the complex further than do the cyanides. The smaller counter-ions cannot separate the complexes from each ion in the crystal lattice as well as the larger ones can. The potassium ion is smaller than the sulfur and selenium atoms which protrude from the complex.

The crystal lattice should be more compact when the pseudohalide is S- or Se-bonded since the metal pseudohalide bond angle approaches 90°. The hard/hard nitrogen–counter-ion interactions should also be important. With the larger cations, there is more room in the crystal lattice to accommodate the less spherical N-bonded species. Soft/soft interactions are more covalent in nature. It does not seem probable that there would be a strong enough interaction between the hydrogen atoms of the alkylammonium ions and the sulfur or selenium atoms to cause the pseudohalides to isomerize. Furthermore, the results of our solvent study strongly suggest that, electronically, the unique site is hard. If this is so, then the S- → N-bonded and Se- → N-bonded solid state isomerizations can be said to occur because there is no strong force to prevent them from occurring.

Throughout the history of studies involving ambidentate ligands[27], the primary focus of attention has involved the interaction between the ligand and the metal coordination center. The results of this study vividly illustrate the importance of what might be termed "environmental" effects. They show that the eventual bonding fate of an ambidentate ligand is not solely or, in some cases, even primarily determined by the nature of the direct acid/base interaction between metal and ligand. The nature and extent of interaction of the so-called "free" end with its environment, whether it involves solvent molecules or counter-ions in a crystal lattice can, and does, play an important role in determining the stereochemistry of these ligands.

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