

Electronic and Solvent Effects on the Bonding Mode of the Selenocyanate Ion in *trans*-Selenocyanatobis(dimethylglyoximato)(substituted pyridine)cobalt(III) Complexes*

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Complexes of the general formula *trans*-[Co(dm_g)₂L(SeCN)] have been synthesized (dm_g = monoanion of dimethylglyoxime; L = pyridine, 4-*t*-butylpyridine, 4-cyanopyridine, 4-aminopyridine). Unlike the corresponding [Co(NH₃)₅NCSe]²⁺ complex, the selenocyanate group is bound through the selenium atom in all of the dm_g complexes (solid state), thereby demonstrating symbiotic electronic control of the selenocyanate's bonding mode by the other ligands present in the coordination sphere. Se-bonding also prevails in CH₂Cl₂ solution, in marked contrast to the results of Marzilli, *et al.*, who found that the Co–NCS/Co–SCN ratio for the corresponding thiocyanate complex was quite sensitive to the nature of L, increasing as the pK_a of L increased. The bonding mode of the [Co(dm_g)₂(*t*-bupy)SeCN] complex was found to be insensitive to changes in the dielectric constant of the solvent, again contrasting with the behavior of the corresponding thiocyanate complex. Marzilli has reported that the Co–NCS/Co–SCN ratio for the latter increases as the dielectric constant of the solvent is increased. All of these results are consistent with a greater π-donor capability on the part of the Se-bound selenocyanate, in accord with its very low position in the spectrochemical series.

Introduction

Two diametrically opposed bonding patterns have come to light during the decade following Pearson's initial publication¹ of the HSAB principle. The principle of symbiosis, first proposed by Jørgensen², is apparently operative in octahedral complexes of class (a) metals, wherein like ligands (with respect to their relative hardness or softness) tend to flock together. More recently, Pearson³ has proposed the principle

of anti-symbiosis and the *trans* effect to account for the fact that, in complexes of class (b) metals, especially those which are square planar, the most stable arrangement is to have relatively hard ligands *trans* to ligands which are both soft and strongly *trans*-directing.

The ambidentate thiocyanate ion has been used to good advantage as a test ligand in both situations⁴. One of the most definitive examples of symbiosis involving the thiocyanate ion has been reported by Marzilli, *et al.*⁵. They found that the Co–NCS/Co–SCN ratio for a series of *trans*-[Co(dm_g)₂L(thiocyanate)] complexes (dm_g = monoanion of dimethylglyoxime; L = series of substituted pyridines, phosphines and phosphites) was markedly sensitive to the nature of the L ligand, increasing as the pK_a of the substituted pyridines increased and the effective electronegativity of the substituent groups in the phosphine and phosphite series decreased. Marzilli⁶ also found that the Co–NCS/Co–SCN ratio for the *trans*-[Co(dm_g)₂(*t*-butylpyridine)thiocyanate] complex tended to increase as the dielectric constant of the solvent in which it was dissolved was increased, in direct opposition to the trend previously reported by Burmeister, *et al.*⁷ for square planar thiocyanate-containing palladium(II) and platinum(II) complexes. Since the Pd–NCSe/Pd–SeCN ratio was also found⁷ to decrease as the solvent dielectric was increased, and the selenocyanate group had been previously shown⁸ to be subject to anti-symbiosis in the square planar complex *trans*-[Rh(PPh₃)₂(CO)NCSe], the investigation of possible symbiotic and solvent effects on the selenocyanate's bonding mode in *trans*-[Co(dm_g)₂(substituted pyridine)selenocyanate] complexes was of considerable interest.

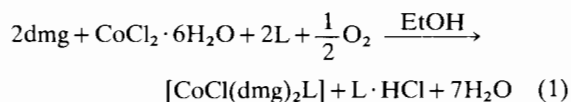
Experimental

Preparation of Complexes

trans-[CoCl(dm_g)₂L], where L = pyridine (py)⁹, 4-tertiarybutylpyridine (tbupy), 4-cyanopyridine (NCpy), and 4-aminopyridine (NH₂py)

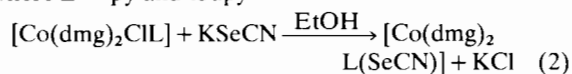
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To a hot solution of 2.732 g dmg (~22 mmol) and 2.506 g $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (~11 mmol) in 95% ethanol was added, with stirring, 22 mmol of the ligand, L. For L = py and tbupy, the ligand was added directly. For L = NCpy and NH_2py , it was first dissolved in ethanol and was then added to the hot solution. The solution was allowed to cool to room temperature. A stream of air was bubbled through the solution for 30 minutes. The solution was allowed to stand for an hour while a solid precipitated, which was then filtered out of the solution. The precipitate, which was the desired $[\text{Co}(\text{dmg})_2\text{CIL}]$ complex, was washed with distilled water, ethanol, and anhydrous diethyl ether. See Table I for the colors, yields, and melting points of these complexes.

trans- $[\text{Co}(\text{dmg})_2\text{L}(\text{SeCN})]$,
where L = py and tbupy



About 2 mmol (0.285 g) of KSeCN was dissolved in 25 ml of 95% ethanol. Two mmol of insoluble *trans*- $[\text{CoCl}(\text{dmg})_2\text{L}]$ was suspended in 75 ml of ethanol, and the 2 solutions were combined with heating and stirring. The $[\text{CoCl}(\text{dmg})_2\text{L}]$ disappeared rapidly. On cooling in ice, a white precipitate (probably KCl) appeared and was removed by filtration. The volume of the filtrate was reduced and a dark solid, *trans*- $[\text{Co}(\text{dmg})_2\text{L}(\text{SeCN})]$, appeared. The solid was filtered out and washed with distilled water to remove any remaining KCl.

trans- $[\text{Co}(\text{dmg})_2\text{NCpy}(\text{SeCN})]$

To a hot solution of 0.857 g of *trans*- $[\text{CoCl}(\text{dmg})_2\text{NCpy}]$ (~2 mmol) in 200 ml of 95% ethanol was added 0.285 g KSeCN (~2 mmol), dissolved in 35 ml of ethanol. The solution turned brown in color. On cooling in ice, a brown precipitate appeared, which was collected by filtration and washed with distilled water to remove

the KCl by-product. The filtrate was reduced in volume until a precipitate again appeared. This second solid was collected by filtration and washed with distilled water to remove KCl. The first solid's infrared spectrum matched that of the starting material, $[\text{Co}(\text{dmg})_2\text{CIL}]$. The second solid proved to be the desired product.

trans- $[\text{Co}(\text{dmg})_2\text{NH}_2\text{py}(\text{SeCN})]$

To 50 ml of a 50% distilled water/ethanol solution containing 0.417 g *trans*- $[\text{CoCl}(\text{dmg})_2\text{NH}_2\text{py}]$ (~1 mmol) was added 0.148 g KSeCN (~1 mmol), dissolved in the 50% ethanol solution. The mixture was heated and stirred for ten minutes until the solution cleared and darkened. The solution was then cooled on an ice bath and a red-brown precipitate, *trans*- $[\text{Co}(\text{dmg})_2\text{NH}_2\text{py}(\text{SeCN})]$, appeared. The solution was filtered and the solid thus obtained was washed with distilled water to remove KCl. See Table II for the properties and analyses of the selenocyanate complexes.

Bridged Species

To a hot solution of 5.186 g of the insoluble *trans*- $[\text{CoCl}(\text{dmg})_2\text{tbupy}]$ (~11.3 mmol) in 95% ethanol was added 1.635 g KSeCN (>11.3 mmol), dissolved in ethanol. On heating and increasing the volume to about 900 ml, the solid dissolved and the solution became a dark clear liquid. The solution was cooled in an ice bath. A grey precipitate formed and was collected by filtration. The filtrate was reduced in volume and allowed to stand for two days, whereupon a dark precipitate was isolated by filtration. The precipitate was a medium brown powder which gave an analysis corresponding to $[(\text{tbupy})(\text{dmg})_2\text{Co}-\text{SeCN}-\text{Co}(\text{dmg})_2(\text{SeCN})]$. *Anal.* Calcd: C, 35.11; H, 4.48; N, 16.69. Found: C, 34.96; H, 4.35; N, 16.76. This complex, whose decomposition range is 246–253°C, is less soluble in most solvents than its parent, *trans*- $[\text{Co}(\text{dmg})_2\text{tbupy}(\text{SeCN})]$.

$[\text{Co}(\text{dmg})_2\text{P}(\text{C}_6\text{H}_5)_3]$

The cobalt(II) complex was synthesized using the method of Schrauzer and Lee¹⁰. *Anal.* Calcd.: C, 56.63; H, 5.30; N, 10.16. Found: C, 56.88; H, 5.25; N, 9.95.

TABLE I. Properties of *trans*- $[\text{Co}(\text{dmg})_2\text{LCl}]$ Complexes.

L	Color	Yield ^a	Melting Point (°C) ^b
py	light brown	73%	235–243
tbupy	medium brown	59%	221–228
NCpy	medium red-brown	93%	216–223
NH_2py	light yellow-brown	67%	258–264

^a Yield based on $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$. ^b Melting points are actually decompositions in all cases; the beginning of the range is the temperature at which the solid began to darken.

Physical Measurements

Solid state infrared spectra were recorded on a Perkin–Elmer 337 spectrophotometer, which has a range of 4000–400 cm^{-1} . The spectra were of powdered solid samples mixed thoroughly with Nujol oil. These general survey spectra were used for identification of products. Solution spectra were recorded on a Perkin–Elmer 180 spectrophotometer with expandable abscissa. The cells used were a) polyethylene cells, approximately matched; b) sodium chloride cells, 1.00 mm; and c) calcium fluoride cells, 1.1 mm. Solution spectra

TABLE II. Properties of *trans*-[Co(dmg)₂L(SeCN)] Complexes.

L	Color	Yield	Melting Point (°C) ^a	Analyses		
				Element	Calc., %	Found, %
py	dark red-brown	59% ^b	265–268	C	35.53	35.32
				H	4.06	4.22
				N	17.76	17.52
tbupy	golden-brown	93% ^c	203–215	C	40.84	40.66
				H	5.15	5.40
				N	15.88	15.60
NCpy	dark red-brown	47% ^b	195–200	C	36.16	36.92
				H	3.64	3.72
				N	19.68	19.40
NH ₂ py	medium red-brown	68% ^c	247–251	C	34.44	34.22
				H	4.13	4.03
				N	20.09	19.89

^a Melting points are actually decompositions in all cases; the beginning of the range is the temperature at which the solid began to darken. ^b Yield based on KSeCN. ^c Yield based on CoCl₂ · 6H₂O.

were used to determine the integrated absorption intensities of the ν_{CN} bands of the complexes, using Ramsey's equation¹¹ for direct integration.

Conductance measurements were made at 25°C with an Industrial Instruments, Inc. Model RC-16B2 conductivity bridge, using 10⁻³M solutions. Proton NMR spectra were recorded on a Perkin-Elmer R-12 spectrometer, using TMS as an internal standard. Melting points were measured on a Thomas Hoover capillary melting point apparatus, and are uncorrected. Microanalyses were carried out by M-H-W Laboratories, Garden City, Michigan 48135 and Micro-Analysis, Inc., Wilmington, Delaware 19808.

Results

The proton nuclear magnetic resonance spectra of the complexes showed no splitting of the methyl protons or the hydroxy protons of the dimethylglyoxime monoanions. Since the environments of the protons in the two dimethylglyoximates are identical only in the *trans* isomer, it may be concluded that the complexes are geometrically *trans*.

For the complexes [CoCl(dmg)₂NCpy] and [CoCl(dmg)₂NH₂py], there are two different nitrogen atoms in each of the pyridine ligands which can bond to the cobalt(III) center. For the cyanopyridine complex, the infrared spectra indicate that the bonding is via the pyridine nitrogen. The ν_{CN} of the free cyanopyridine is slightly higher than the ν_{CN} of the complex. In general, coordinated nitriles exhibit ν_{CN} frequencies which are considerably higher than those of the free ligands¹². Only in the cases of ruthenium(II) nitrile complexes¹³ and an isolated example of a cobalt(I) nitrile complex¹⁴ have significant red shifts been ob-

served for ν_{CN} frequencies of the complexed nitriles. It should be noted that both ruthenium(II) and cobalt (I) are exceptionally strong π -donors, as evidenced by the fact that they coordinate molecular nitrogen. Since the ν_{CN} frequency of the complexed NCpy decreases only slightly, relative to the free ligand, it may safely be concluded that the nitrile nitrogen is not bonding to the cobalt(III).

Barnes¹⁵ has observed that 3-aminopyridine is dibasic and 2- and 4-aminopyridine are monobasic, showing basic character at the pyridine nitrogen. Only in highly acidic solutions does the second nitrogen react with a proton. According to Barnes, in any reactions of the aminopyridines with reagents having positive centers, the same principles apply: the 3-aminopyridine is dibasic and the 2- and 4-amino-pyridines are monobasic. Therefore, the cobalt(III) center should bond to the monobasic 4-aminopyridine through the pyridine nitrogen.

Conductivity studies were carried out on samples of *trans*-[Co(dmg)₂tbupy(SeCN)] and the bridged species to determine if the complexes would dissociate in solution and if [Co(dmg)₂tbupy(SeCN)] might really be [Co(dmg)₂(tbupy)₂][Co(dmg)₂(SeCN)₂]. The results are shown in Table III. By comparing the calculated molar conductances, Λ_m , with those for known electrolytic types, Table III, the ionic characters of the original complexes can be evaluated. [Co(dmg)₂tbupy(SeCN)] and the bridged species conduct to a small extent, probably due to some dissociation of the SeCN⁻, but cannot be classed as 1:1 electrolytes.

The integrated absorption intensities of the coordinated selenocyanate's ν_{CN} bands were determined using three different concentrations, ranging from 0.01 M to 0.02 M, of the complexes *trans*-[Co(dmg)₂L(SeCN)], where L = py, tbupy, and NCpy, and the

TABLE III. Conductivity Data for *trans*-[Co(dmg)₂tbupy (SeCN)] and the Bridged Species.

Solvent	Λ_m^a (ohm ⁻¹ cm ² mol ⁻¹)	Λ_m^a Range for 1:1 Electro- lytes ¹⁶ (ohm ⁻¹ cm ² mol ⁻¹)
	<i>trans</i> -[Co(dmg) ₂ tbupy (SeCN)]	
Acetonitrile	57	120–160
DMF	28	65–90
Ethanol	14	35–45
Nitromethane	36	75– 95
Acetone	47	100–140
	Bridged Species	
Acetonitrile	49	120–160
DMF	28	65– 90
Nitromethane	28	75– 95

^a10⁻³ M, 25° C.

bridged species in solvents containing 2% BrCCl₃ (the 4-aminopyridine complex was insoluble in these solvents). The integrated absorption intensity values, compiled in Table IV, are well within the range for selenium bound selenocyanates¹⁷, showing that all of the complexes are selenium bound in the solid state (the basis for this conclusion is discussed below).

Absorbance values were calculated for the three concentrations of the complexes so that their Beer's Law plots and molar extinction coefficients could be determined. The slopes of the Beer's Law plots were determined by using the method of least squares. The molar extinction coefficients were calculated by dividing the path length, 0.1 cm, into the slopes. See Table IV for the results.

For the study of the electronic effects of the L ligands on the bonding mode of the selenocyanate, high resolution infrared solution spectra were recorded in the region 2230–2030 cm⁻¹, which includes free, bridged, and selenium and nitrogen bound selenocyanates. These

spectra were of *trans*-[Co(dmg)₂L(SeCN)] with L = py, tbupy, and NCpy, and the bridged species in CH₂Cl₂. Two series of solutions were used for each complex. In the first, the complex was dissolved in a solvent containing two volume percent BrCCl₃. BrCCl₃ is an oxidant capable of removing Co(II) impurities, which could catalyze the isomerization of the ambidentate NCSe⁻. Marzilli has definitively shown⁶ that the [Co(dmg)₂L(SCN)] ⇌ [Co(dmg)₂L(NCS)] isomerizations undergo Co(II) catalysis. These spectra show the selenocyanate's bonding mode as it is in the solid state. For the second set of solutions, the complex and 2 to 3 mol percent [Co(dmg)₂P(C₆H₅)₃] (based on moles of Co(III) present) were dissolved in pure solvent. The Co(II) was allowed to interact with the complex for approximately fifteen minutes, and then one drop per ml of solution of BrCCl₃ was added to quench the reaction. These spectra show any tendency which the complexes have to isomerize from selenium to nitrogen bonding. Both series of solutions were monitored for two days to determine if there were any changes with time in the solutions.

The solvent study was based on the same two series of solutions, but the complex was held constant and the solvent was varied. The complex used was *trans*-[Co(dmg)₂tbupy(SeCN)]. The solvents used were benzene, dichloromethane and acetonitrile, which have dielectric constants of 2.27, 8.9 and 37.5, respectively, at 25° C.

The infrared solution spectra taken of the *trans*-[Co(dmg)₂L(SeCN)] complexes (L = py, tbupy, and NCpy) and the bridged species in CH₂Cl₂ show that the selenocyanate's bonding mode is insensitive to the effect of the *trans* ligand, being Se-bonded in all cases. The spectra are virtually identical with and without Co(II) addition and are unchanged with time in solution. For the pyridine and tertiarybutylpyridine complexes, a weak peak, not due to the baseline, appears at 2154 cm⁻¹ on addition of Co(II). With the NCpy complex, a weak peak appears at 2175 cm⁻¹ with Co(II) addition. A weak peak shows up for the bridged species at

TABLE IV. Infrared Data for the Complexes.

Complex	Solvent	ν_{CN} (cm ⁻¹)	$\epsilon \times 10^{-4}$ (cm ² mol ⁻¹)	Integrated Absorption Intensity $\times 10^{-4}$ (M ⁻¹ cm ⁻²)
[Co(dmg) ₂ py(SeCN)]	CH ₂ Cl ₂	2122	20.9	0.8
[Co(dmg) ₂ NCpy(SeCN)]	CH ₂ Cl ₂	2123	14.1	0.6
[Co(dmg) ₂ tbupy(SeCN)]	CH ₂ Cl ₂	2122	28.5	1.0
[Co(dmg) ₂ tbupy(SeCN)]	CH ₃ CN	2122	a	0.8
[Co(dmg) ₂ tbupy(SeCN)]	Benzene	2123	a	0.5
Bridged Species	CH ₂ Cl ₂			
Bridged Peak		2189	15.1	1.5
-SeCN Peak		2120	10.1	0.5

^a Not determined.

2157 cm^{-1} on Co(II) addition. All of these peaks are insignificant when compared to the size of the major ν_{CN} peak.

The infrared solution spectra taken of *trans*-[Co(dmg)₂tbupy(SeCN)] in various solvents show that the bonding mode of the selenocyanate is also insensitive to the dielectric constant of the solvent. The complex's behavior in CH_2Cl_2 is described above. The complex in benzene and acetonitrile shows absolutely no response to Co(II) addition with time.

Discussion

The bonding of the selenocyanate group in the *trans*-[Co(dmg)₂L(SeCN)] complexes in the solid state has been shown to be via selenium, unlike the corresponding nitrogen bound [Co(NH₃)₅(NCS)]²⁺ complex¹⁸. The dimethylglyoxime monoanions and the selenium are quite soft, while the amines and the nitrogen are hard. Thus, symbiotic control about the Co(III) center is evidenced in both cases.

In the solution spectral studies used for the study of both electronic and solvent effects on the bonding mode of NCS⁻, Co(II) was used in an unsuccessful attempt to catalyze the isomerization reaction. The use of Co(II) is based on a reaction mechanism suggested by Marzilli, *et al.*⁵ for the isomerization equilibration of the corresponding NCS⁻ complex. It was dependent on the presumption that attack on the selenium by the Co(II) center would be kinetically faster than on the nitrogen, irrespective of whether the attack required remote or adjacent attack. This is known to be the case for the corresponding reactions involving the NCS⁻ group⁵.

The effect of changing the coordinated L ligands and solvents on the selenocyanate's bonding mode was found to be minimal, in marked contrast to the results of Marzilli, *et al.*⁵, who found, as noted in the introduction, that the Co-NCS/Co-SCN ratio for the corresponding thiocyanate complexes was quite sensitive to the nature of L and the dielectric constant of the solvent in which they were dissolved.

The unchanging character of the Co(III)-selenium bond in these complexes is consistent with the π -donor capability of selenium, which is believed to be greater than that of sulfur. According to Gutterman and Gray¹⁹, the general class of linear triatomic molecules, including NCS⁻, N₃⁻, and NCSe⁻, have a 2 π level as their highest filled electronic level. It is a non-bonding level and is localized on the end atoms. A molecular orbital calculation, carried out by Di Sipio, *et al.*,²⁰ shows that the 2 π level is largely located on the sulfur in NCS⁻. In these triatomic species the lowest unfilled level is 3 π , which is concentrated on the central atom.²⁰

When compared to cyanide,¹⁹ thiocyanate is seen to have the higher energy, filled level (2 π). Ligand to

metal charge transfer can easily result with the 2 π level of the thiocyanate acting as a π -donor. The empty 3 π level is not as energetically suited to accept π -electron density, as is the π^* level of the cyanide. Therefore, the cyanide will be the more important π -acceptor. Gutterman and Gray concluded that there is no evidence for the participation of π -acceptor orbitals of the triatomic ligands in the metal-ligand bonding in Co(III) complexes.¹⁹

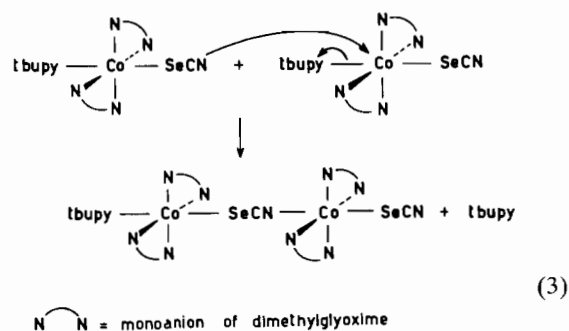
The spectrochemical series supports this assessment of the relative π -donor abilities of -SCN and -SeCN. The observed series for [Co(CN)₅X]³⁻ is:²¹



The low field end of the series includes π -donors. Therefore, the series separates -SCN and -SeCN, π -donors and σ -donors, from -NCS and -NCSe, σ -donors only. Furthermore, -SeCN is found to be lower in the series than -SCN and will tend to be a better π -donor.

The π -electron donating capabilities of both the thiocyanate and the selenocyanate are apparently enhanced by the π -electron withdrawal created by the dimethylglyoximate ions bound to the Co(III). The resulting energy difference between the N- and the S-bound thiocyanate linkage isomers is sufficiently small for the isomeric ratio to be affected by the electronic character of the L ligand and by the nature of the solvent. Sulfur bonding is favored, as would be expected, by the presence of the less basic pyridine derivatives in the *trans* position. However, the resulting energy difference between the N- and Se-bound selenocyanate linkage isomers is evidently too large for such effects to have any noticeable influence on the isomeric ratio.

The proposed bonding mode of the bridging selenocyanate in the bridged species is based on the following reaction scheme:



Ciskowski and Crumbliss²² have recently reported the synthesis of an extensive related series of complexes of the type [BCo(dmg)₂(CNX)-Co(dmg)₂R], where B is an N donor base, X is S or Se, and R is an alkyl group.

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