

## The Synthesis and Characterization of Mono- and Dinuclear Cobaloxime–Selenocyanate Complexes\*

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Complexes of the type  $\text{trans}[\text{Co}(\text{dmgH})_2(\text{L})\text{SeCN}]$  and  $\text{trans}[(\text{L})\text{Co}(\text{dmgH})_2\text{SeCN}-\text{Co}(\text{dmgH})_2\text{SeCN}]$  have been synthesized, by the reaction between  $\text{trans}[\text{Co}(\text{dmgH})_2(\text{L})\text{Cl}]$  and  $\text{SeCN}^-$  in a variety of solvents ( $\text{dmgH}^-$  = monoanion of dimethylglyoxime and  $\text{L} = 4\text{-acetylpyridine}$ , triphenylphosphine, tri-*n*-butylphosphine, methyl-diphenylphosphine, *n*-butyldiphenylphosphine, triphenylphosphite, tri-*n*-butylphosphite, tri-*i*-propylphosphite, trimethylphosphite). The formation of dinuclear complexes resulted from reactions carried out in solvents having low dielectric constants, while predominately mononuclear complexes resulted in solvents of high dielectric. All of the terminal  $\text{SeCN}^-$  groups exhibit coordination via the selenium atom, regardless of the nature of  $\text{L}$ , both in the solid state and in solution. A possible mechanism for the formation of the dinuclear complexes is presented. These results demonstrate symbiotic electronic control of the selenocyanate's bonding mode by the other ligands present in the coordination sphere, and are consistent with the considerable  $\pi$ -donor capability of the Se-bound selenocyanate, as reflected in its low position in the spectrochemical series.

### Introduction

Pearson's Hard–Soft Acid–Base Principle [1] has proved to be quite useful in the prediction of relative stabilities of combinations of various Lewis acids and bases. Subsequently, Jørgensen [2] proposed the principle of symbiosis as being operative in octahedral complexes of class 'a' (hard) metals, wherein similar ligands (with respect to their relative hardness or softness) tend to flock together. Pearson [3] later proposed the principle of antisymbiosis and the *trans* effect in order to explain experimental

observations that class 'b' (soft) metal complexes, especially those which are square planar, are most stable with hard ligands *trans* to soft, strongly *trans*-directing ligands.

The use of the thiocyanate anion to study the factors which govern symbiosis and antisymbiosis in metal complexes has been rather extensive [4–6]. Marzilli, *et al.* [7], have studied the bonding mode of the thiocyanate group in a series of  $\text{trans}[\text{Co}(\text{dmgH})_2\text{L}(\text{CNS})]$  complexes ( $\text{L} =$  series of substituted pyridines, phosphines and phosphites,  $\text{CNS}$  represents thiocyanate without specification of bonding mode). They found that the  $\text{Co}-\text{NCS}/\text{Co}-\text{SCN}$  ratio was sensitive to the nature of the  $\text{L}$  ligand, increasing as the  $\text{pK}_a$  of the substituted pyridines increased and as the effective electronegativity of the substituent groups in the phosphine and phosphite series decreased. In studying the  $\text{trans}[\text{Co}(\text{dmgH})_2(\text{t-butylpyridine})\text{CNS}]$  complex, Marzilli [8] also found that the  $\text{Co}-\text{NCS}/\text{Co}-\text{SCN}$  ratio was sensitive to the dielectric constant of the solvent, increasing as solvent dielectric increased.

The selenocyanate anion has yielded fewer examples of linkage isomerism. Burmeister, *et al.* [9], found that the  $\text{Pd}-\text{NCX}/\text{Pd}-\text{XCN}$  ratios ( $\text{X} = \text{S}, \text{Se}$ ) for square planar palladium(II) complexes decreased as solvent dielectric increased and observed antisymbiotic behavior in square planar rhodium(I) and iridium(I) thiocyanate and selenocyanate complexes [10]. Studies carried out with a series of  $\text{trans}[\text{Co}(\text{dmgH})_2(\text{L})(\text{SeCN})]$  complexes [11] (where  $\text{L}$  is a series of substituted pyridines) showed that only  $\text{Co}-\text{SeCN}$  bonding occurs, regardless of the  $\text{pK}_a$  of the *trans* ligand and the dielectric of the solvent used.

Marzilli did not observe [7, 8] the formation of any bridging thiocyanate complexes, *i.e.*, complexes of the type  $\text{trans}[(\text{L})\text{Co}(\text{dmgH})_2(\text{CNS})\text{Co}(\text{dmgH})_2(\text{CNS})]$  (where  $\text{L}$  is any of the substituted pyridines, phosphines or phosphites), whereas Allison and Burmeister [11] reported the formation of the  $\text{trans}[(\text{t-butylpyridine})\text{Co}(\text{dmgH})_2\text{SeCN}-\text{Co}(\text{dmgH})_2\text{SeCN}]$  complex. The investigation of possible symbiotic and solvent effects on the selenocyanate's bonding

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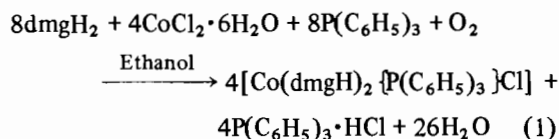
mode in *trans*-[Co(dmgH)<sub>2</sub>(substituted phosphine or phosphite)(CNSe)] and also *trans*-[(substituted phosphine or phosphite) Co(dmgH)<sub>2</sub>(CNSe)-Co(dmgH)<sub>2</sub>(CNSe)] complexes, as well as the elucidation of a method of selective synthesis for both mononuclear and dinuclear complexes, served as the twin goals of this study.

## Experimental

### Preparation of Complexes

*trans*-[Co(dmgH)<sub>2</sub>(P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)Cl] [12]

The reaction scheme for the above complex was as follows:



A solution of 10.149 g (~42.6 mmol) of CoCl<sub>2</sub>·6H<sub>2</sub>O and 11.151 g (~92.0 mmol) of dimethylglyoxime in 300 ml of 95% ethanol was heated and stirred until a green solid formed ([Co(dmgH)<sub>2</sub>(Cl)<sub>2</sub>]). A solution of 22.437 g (~86.0 mmol) of P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> in 80 ml of hot 95% ethanol was added in bulk to the green cobalt(II) complex solution, causing the formation of a brown complex ([Co(dmgH)(dmgH<sub>2</sub>)(P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)Cl]). This solution was allowed to stir for 0.5 hr and reach room temperature. A stream of air was bubbled through the solution for 1 hr and the solution was allowed to stir for an additional hour. Filtration yielded the brown product complex, which was washed with distilled water, ethanol and anhydrous diethyl ether.

*trans*-[Co(dmgH)<sub>2</sub>(4-*acpy*)Cl]

The synthesis of this complex was similar to that of the corresponding triphenylphosphine complex. A solution of 2.506 g (~10.5 mmol) of CoCl<sub>2</sub>·6H<sub>2</sub>O and 2.732 g (~23.5 mmol) of dimethylglyoxime in 75 ml of 95% ethanol was heated and stirred. To this solution, 2.662 g (~21.9 mmol) of 4-acetylpyridine was added dropwise while stirring and reaching room temperature. After aeration for 20 min, the mixture was allowed to stir for 1.5 hr. Filtration yielded a greenish beige solid which was washed with distilled water, ethanol and anhydrous diethyl ether.

*trans*-[Co(dmgH)(dmgH<sub>2</sub>)Cl<sub>2</sub>] [13]

To a solution of 11.866 g (~50 mmol) of CoCl<sub>2</sub>·6H<sub>2</sub>O in 200 ml of warm acetone was added 12.686 g (~110 mmol) of dimethylglyoxime. The solution was stirred until all of the solid had dissolved, followed by removal of heat. The solution was then allowed to stir overnight at room temperature. Filtration yielded a green solid. No aeration was necessary.

*trans*-[Co(dmgH)<sub>2</sub>(P(OC<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)Cl] [14]

A solution of 9.985 g (~27.7 mmol) of [Co(dmgH)(dmgH<sub>2</sub>)Cl<sub>2</sub>] and 5.184 g (~27.9 mmol) of tri-*n*-butylamine in 400 ml of CHCl<sub>3</sub> was stirred at room temperature. To this solution, 10.815 g (~34.9 mmol) of P(OC<sub>6</sub>H<sub>5</sub>)<sub>3</sub> was added, resulting in the formation of a dark brown solution. The solution was allowed to stir for 1 hr and then filtered to remove any undissolved materials. The filtrate was extracted with five 100-ml portions of distilled water. The CHCl<sub>3</sub> solution was then reduced on a Roto-Vap to an oily residue. The residue was dissolved in 150 ml of CH<sub>2</sub>Cl<sub>2</sub> and filtered. To this filtrate was added 150 ml of toluene and the resulting solution was reduced on a Roto-Vap to ~125 ml. Filtration yielded an orange solid which was washed with acetone and anhydrous diethyl ether.

*trans*-[Co(dmgH)<sub>2</sub>(L)Cl] [14] (L = P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>(*n*-C<sub>4</sub>H<sub>9</sub>), P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>CH<sub>3</sub>, P(*O*-*n*-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>, P(*O*-*i*-C<sub>3</sub>H<sub>7</sub>)<sub>3</sub>, and P(OCH<sub>3</sub>)<sub>3</sub>)

The preparation of these complexes involved the displacement of the labile P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> from [Co(dmgH)<sub>2</sub>(P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)Cl] by L. A 4.000 g (~6.8 mmol) portion of [Co(dmgH)<sub>2</sub>(P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)Cl] was dissolved in 35 ml of CH<sub>2</sub>Cl<sub>2</sub> at room temperature. For L = P(*O*-*n*-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>, P(*O*-*i*-C<sub>3</sub>H<sub>7</sub>)<sub>3</sub> and P(OCH<sub>3</sub>)<sub>3</sub>, ~8.0 mmol of L was added dropwise, whereas only ~6.8 mmol was added dropwise for L = P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>(*n*-C<sub>4</sub>H<sub>9</sub>) and P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>CH<sub>3</sub>. The latter additions were carried out in an N<sub>2</sub> atmosphere. All solutions were allowed to stir for 15 min, then filtered to remove any undissolved material. Solids were obtained upon the addition of 100–200 ml of anhydrous diethyl ether for all of the complexes, except for L = P(*O*-*n*-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>, which involved the addition of 150 ml of cyclohexane. All products were isolated and washed with anhydrous diethyl ether or cyclohexane, followed by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/ether or cyclohexane.

*trans*-[Co(dmgH)<sub>2</sub>(P(*n*-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>)Cl] [13]

A solution of 2.935 g (~5.0 mmol) of [Co(dmgH)<sub>2</sub>(P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)Cl] in 25 ml of CHCl<sub>3</sub> was stirred with slight warming while 1.025 g (~5.0 mmol) of P(*n*-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub> was added dropwise. After stirring for 15 min, 200 ml of anhydrous diethyl ether was added to the solution, which was then stirred overnight. Filtration yielded a brown solid which was washed with anhydrous diethyl ether.

The properties of the chloro complexes are shown in Table I. KSeCN was prepared from KCN and Se metal [15]. The preparation of complexes of the type *trans*-[Co(dmgH)<sub>2</sub>L(SeCN)] and *trans*-[LCo(dmgH)<sub>2</sub>-SeCN-Co(dmgH)<sub>2</sub>SeCN] differed depending upon the nature of L. For *dinuclear complexes*, the synthetic route was as follows:

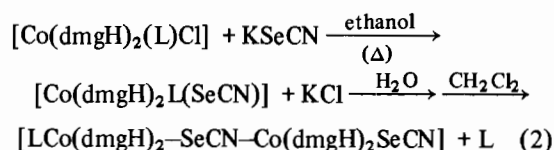
TABLE I. Properties of *trans*-[Co(dmgH)<sub>2</sub>(L)Cl] Complexes.

L	Color	Yield <sup>a</sup>	Melting Point (°C)
P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	Med. Brown	79% <sup>b</sup>	191–192
P(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> ( <i>n</i> -C <sub>4</sub> H <sub>9</sub> )	Gold	95%	217–219
P(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CH <sub>3</sub>	Beige	85%	242–244
P( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub>	Yellow Brown	72%	188–193 <sup>c</sup>
P(OC <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	Orange	75% <sup>d</sup>	180–181
P(O- <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub>	Reddish Orange	88%	134–136
P(O- <i>i</i> -C <sub>3</sub> H <sub>7</sub> ) <sub>3</sub>	Orange	91%	158–160
P(OCH <sub>3</sub> ) <sub>3</sub>	Yellow	76%	210–212 <sup>c</sup>
4-acpy	Greenish Beige	43% <sup>b</sup>	184–187 <sup>c</sup>

<sup>a</sup>Yield based on amount of *trans*-[Co(dmgH)<sub>2</sub>(P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)Cl] employed. <sup>b</sup>Yield based on CoCl<sub>2</sub>·6H<sub>2</sub>O. <sup>c</sup>Melting points are actually decomposition temperatures. <sup>d</sup>Yield based on [Co(dmgH)(dmgH<sub>2</sub>)Cl<sub>2</sub>].

TABLE II. Preparative Variables for *trans*-[LCo(dmgH)<sub>2</sub>–SeCN–Co(dmgH)<sub>2</sub>SeCN] Complexes.

Ligand	Initial Reaction Temp., °C	Reaction Time	Length of Exposure to CH <sub>2</sub> Cl <sub>2</sub>	Vol. of Ethanol
P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	~35	Overnight	Overnight	200 ml
P(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> ( <i>n</i> -C <sub>4</sub> H <sub>9</sub> )	~70	4 Hours	Overnight	250 ml
P( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub>	Room temp.	Overnight	Overnight	250 ml
P(OC <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	~50	4 Hours	Overnight	175 ml
P(O- <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub>	Room temp.	Overnight	Overnight	100 ml
P(O- <i>i</i> -C <sub>3</sub> H <sub>7</sub> ) <sub>3</sub>	Room temp.	Overnight	2 Days	250 ml
P(OCH <sub>3</sub> ) <sub>3</sub>	Room temp.	Overnight	Overnight	150 ml



One mmol of *trans*-[Co(dmgH)<sub>2</sub>(L)Cl] was dissolved with stirring and, in some cases, heating, in 95% ethanol. A second solution, containing 0.144 g (~1 mmol) of KSeCN in 15 ml of 95% ethanol was added slowly to the first and allowed to stir at room temperature for a varying amount of time, depending on the ligand. There was always an observable darkening in the color of the solution following the addition of KSeCN. The ethanol solution was then reduced on a vacuum line to a few ml. About 150 ml of distilled water was added to the reduced ethanol solution to dissolve the soluble KCl by-product and the insoluble complex was isolated via filtration, except for L = P(OCH<sub>3</sub>)<sub>3</sub>, which decomposes in water. After washing the solids with distilled water and then anhydrous diethyl ether, the solids were redissolved in ~50 ml of CH<sub>2</sub>Cl<sub>2</sub> and allowed to stir for various periods of time, depending again upon the ligand. The CH<sub>2</sub>Cl<sub>2</sub> solution was then reduced on a vacuum line to a few

ml. Products were isolated by the addition of about 100–150 ml of anhydrous diethyl ether and were also washed with this solvent. Table II shows the variations employed in the preparations.

*Mononuclear complexes* of the type *trans*-[Co(dmgH)<sub>2</sub>L(SeCN)] were synthesized in a similar manner to that of the dinuclear complexes, except that they were not redissolved in CH<sub>2</sub>Cl<sub>2</sub>. One mmol of *trans*-[Co(dmgH)<sub>2</sub>(L)Cl] was dissolved with stirring, and in some cases, heating, in either ethanol, methanol or CH<sub>3</sub>CN, depending on the identity of L. A second solution, containing 0.144 g (~1 mmol) of KSeCN in 10–15 ml of the same solvent, was added slowly to the first and allowed to stir at room temperature for a varying amount of time. The solution tends to darken upon addition of the KSeCN. The solution was reduced on a vacuum line to about 5–10 ml and then added slowly to 150–200 ml of distilled water (except for L = P(OCH<sub>3</sub>)<sub>3</sub>, which decomposes in water) to remove soluble salts. Products were isolated via filtration and dried *in vacuo*. For L = P(OCH<sub>3</sub>)<sub>3</sub>, the solid was isolated upon addition of the reduced reaction solution to 150 ml of benzene. Table III shows the variations employed in the preparations.

TABLE III. Preparative Variables for *trans*-[Co(dmgH)<sub>2</sub>L(SeCN)] Complexes.

Ligand	Solvent	Vol. of Solvent	Reaction Time	Initial Reaction Temp., °C
P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	Methanol	175 ml	3 Hours	~35
P(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> ( <i>n</i> -C <sub>4</sub> H <sub>9</sub> )	Methanol	250 ml	5 Hours	~60
P(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CH <sub>3</sub>	Ethanol	250 ml	24 Hours	Room temp.
P( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub>	Methanol	90 ml	20 Hours	Room temp.
P(OC <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	Ethanol	200 ml	2.5 Hours	~50
P(O- <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub>	CH <sub>3</sub> CN	50 ml	19 Hours	Room temp.
P(O- <i>i</i> -C <sub>3</sub> H <sub>7</sub> ) <sub>3</sub>	Ethanol	175 ml	2.5 Hours	Room Temp.
P(OCH <sub>3</sub> ) <sub>3</sub>	CH <sub>3</sub> CN	75 ml	4 Hours	Room Temp.
4-acpy	Ethanol	300 ml	24 Hours	Room Temp.

[Co(dmgH)<sub>2</sub>P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]

This cobalt(II) complex was synthesized by the method of Schrauzer and Lee [16].

*Physical Measurements*

Solid state infrared spectra were recorded on a Perkin-Elmer 180 spectrophotometer with expandable abscissa, which has a range of 4000–200 cm<sup>-1</sup>. The spectra were of powdered solid samples mixed with Nujol oil. Solution spectra were recorded on the same instrument. Solid state spectra were measured using potassium bromide plates and solution spectra were measured using matched calcium fluoride cells (1.1 mm). Solution spectra were used to determine the integrated absorption intensities of the ν<sub>CN</sub> bands of the complexes, using Ramsey's method [17] for direct integration. Melting points were measured on a Thomas Hoover Capillary melting point apparatus, and are uncorrected. Microanalyses were carried out by Schwartzkopf Microanalytical Laboratory, Woodside, New York 11377 and Alfred Bernhardt Mikroanalytisches Laboratorium, Fritz-Pregel-Strasse 14 - 16, Elbach-über-Engelskirchen, West Germany.

**Results**

The formation of mono- and dinuclear cobaloxime selenocyanate complexes has been found to be dependent upon the dielectric constant of the solvent in which the complex is dissolved and also upon the nature of the L ligand. Generally, solvents of low dielectric will promote bridging, *i.e.*, the formation of dinuclear complexes, while solvents of high dielectric will not. Table IV shows the dielectric constants of the solvents used in the preparations.

In the case of some ligands (refer to Table III) ethanol had a sufficiently high dielectric to yield mononuclear complexes, while, with other ligands, the use of CH<sub>3</sub>CN was required before a pure mononuclear complex could be isolated. When exposed to

TABLE IV. Solvents and Their Dielectric Constants at 20 °C.

Solvent	ε
CH <sub>2</sub> Cl <sub>2</sub>	9.0
Ethanol	24.3
Methanol	32.6
CH <sub>3</sub> CN	36.0

CH<sub>2</sub>Cl<sub>2</sub>, not all of the complexes could be isolated in a completely dinuclear form, therefore (referring to Table V) relatively little data on yields, melting points, or C, H and N analyses can be reported. Mixtures of mono- and dinuclear complexes can be detected by comparing the intensities of the asymmetrical stretching mode of ν<sub>CN</sub>. For completely dinuclear samples, the bridging peak must be at least as intense, if not more, than the terminal peak. Bridging SeCN ν<sub>CN</sub> bands occur in the general region of 2190–2170 cm<sup>-1</sup>, while terminal SeCN ν<sub>CN</sub> bands occur in the general region of 2125–2110 cm<sup>-1</sup> (see Tables V and VI) [18]. The observed higher energy absorption for bridging SeCN *versus* terminal SeCN agrees well with the expectation that more energy would be required to cause a bridging SeCN to stretch than would be required for a terminal SeCN.

Solution infrared studies of the mononuclear and selected dinuclear complexes were carried out in both a high dielectric (CH<sub>3</sub>CN) and low dielectric (CH<sub>2</sub>Cl<sub>2</sub>) solvent. Two series of solutions (0.01–0.02 M) were used for each complex in each solvent. In the first, the complex was dissolved in solvent containing two volume percent BrCCl<sub>3</sub>. BrCCl<sub>3</sub> is an oxidant capable of removing Co(II) impurities which could possibly catalyze the isomerization of the ambidentate NCSe<sup>-</sup>. Marzilli has shown [8] that the [Co(dmgH)<sub>2</sub>L(SCN)] ⇌ [Co(dmgH)<sub>2</sub>L(NCS)] isomerizations undergo Co(II) catalysis. Infrared spectra of these solutions were recorded at varying intervals during the course of a 15–20 hr period. For the second set

TABLE V. Properties of *trans*-[LCo(dmgH)<sub>2</sub>-SeCN-Co(dmgH)<sub>2</sub>SeCN] Complexes.

L	Color	Yield <sup>a</sup>	Melting Point (°C)	$\nu_{\text{CN}}$ (solid state, $\text{cm}^{-1}$ )		Analysis		
				(Bridged)	(Terminal)	Element	Calc. %	Found %
P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	Light Beige	60%	272–275 <sup>b</sup>	2192	2121	C	41.16	41.36
						H	4.12	4.28
						N	13.33	13.72
P(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> - ( <i>n</i> -C <sub>4</sub> H <sub>9</sub> )	Light Brown	not determined		2190	2117	C	39.62	
						H	4.59	not analyzed
						N	13.59	
P( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub>	Beige	17%	290–292 <sup>b</sup>	2192	2122	C	36.45	34.40
						H	5.40	4.47
						N	14.16	14.28
P(OC <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	Light Brown	32%	135–138	2171	2122	C	39.36	39.15
						H	3.94	3.87
						N	12.75	12.87
P(O- <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub>	Light Brown	12%	238–240 <sup>b</sup>	2190	2123	C	34.69	36.33
						H	5.33	5.35
						N	13.48	15.73
P(O- <i>i</i> -C <sub>3</sub> H <sub>7</sub> ) <sub>3</sub>	Light Orange–Brown	not determined		2187	2118	C	32.54	
						H	4.95	not analyzed
						N	14.05	
P(OCH <sub>3</sub> ) <sub>3</sub>	Light Brown	not determined		2175	2123	C	27.64	
						H	4.08	not analyzed
						N	15.35	

<sup>a</sup>Yield based on *trans*-[Co(dmgH)<sub>2</sub>(L)Cl]. <sup>b</sup>Melting points are actually decomposition temperatures.

of solutions, the complex and 2 to 3 mol percent [Co(dmgH)<sub>2</sub>P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>] (based on moles of Co(III) present) were dissolved in pure solvent. Infrared spectra of these solutions were also monitored at varying intervals during a 24 hour period, one drop of BrCCl<sub>3</sub> being added per ml of solution to quench any further reaction prior to each measurement.

Measurements of the infrared spectra of the mononuclear complexes in CH<sub>2</sub>Cl<sub>2</sub> were restricted in number by the tendency of most of the complexes to undergo bridging to form the corresponding dinuclear complexes in this low dielectric solvent. The P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>(*n*-C<sub>4</sub>H<sub>9</sub>) and P(O-*i*-C<sub>3</sub>H<sub>7</sub>)<sub>3</sub> mononuclear complexes underwent bridging in CH<sub>2</sub>Cl<sub>2</sub> sufficiently slowly to permit the acquisition of their mononuclear solution infrared data; the P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>CH<sub>3</sub> and 4-*acpy* mononuclear complexes did not exhibit any noticeable bridging in CH<sub>2</sub>Cl<sub>2</sub>.

Conversely, the P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> and P(OC<sub>6</sub>H<sub>5</sub>)<sub>3</sub> dinuclear complexes experienced, as would be expected, decomposition in the high dielectric CH<sub>3</sub>CN solutions, the latter decomposing at a much more rapid rate. Decomposition was evidenced by a decrease in intensity of both the bridging and terminal SeCN  $\nu_{\text{CN}}$

bands (the former experiencing the largest and most rapid decrease) coincident with the appearance, at *ca.* 2140–2145  $\text{cm}^{-1}$ , of a weak  $\nu_{\text{CN}}$  band most probably due to coordinated CN<sup>-</sup>. This would result from a reaction between P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> or P(OC<sub>6</sub>H<sub>5</sub>)<sub>3</sub> with SeCN<sup>-</sup> to form CN<sup>-</sup> and either Se=P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> or Se=P(OC<sub>6</sub>H<sub>5</sub>)<sub>3</sub> [19]. The rate of decomposition was accelerated by the addition of [Co(dmgH)<sub>2</sub>-P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>].

The data shown in Tables VII and VIII are for the initial spectra recorded for the solutions containing BrCCl<sub>3</sub>. However, it should be noted that no significant changes were observed in the spectra of those solutions containing added Co(II), nor were any significant differences observed, with the exceptions noted above, as a function of time (with or without added Co(II)) or change of solvent. The  $\nu_{\text{CN}}$  frequencies and integrated absorption intensities exhibited by the terminal SeCN groups in solution are well within the range normally observed [18] for Se-bonded selenocyanates.

When 0.05 *M* solutions of *trans*-[Co(dmgH)<sub>2</sub>-P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SeCN] and *trans*-[(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>PCo(dmgH)<sub>2</sub>-SeCN-Co(dmgH)<sub>2</sub>SeCN] in DMSO were prepared,

TABLE VI. Properties of *trans*-[Co(dmgh)<sub>2</sub>L(SeCN)] Complexes.

L	Color	Yield <sup>a</sup>	Melting Point (°C)	$\nu_{\text{CN}}$ , cm <sup>-1</sup> (Solid State)	Analysis		
					Element	Calc. %	Found %
P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	Brown	74%	258–262 <sup>b</sup>	2125	C	49.40	49.23
					H	4.45	3.37
					N	10.66	9.58
P(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (n-C <sub>4</sub> H <sub>9</sub> )	Medium Brown	81%	239–242 <sup>b</sup>	2122	C	47.18	48.88
					H	5.22	5.26
					N	11.00	9.83
P(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CH <sub>3</sub>	Light Brown	89%	158–162 <sup>b</sup>	2121	C	44.46	44.34
					H	4.57	4.70
					N	11.78	11.67
P(n-C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub>	Golden Brown	76%	147–148	2119	C	42.29	42.34
					H	6.92	6.78
					N	11.74	11.69
P(OC <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	Light Orange–Brown	82%	218–221 <sup>b</sup>	2121	C	46.06	46.25
					H	4.14	4.38
					N	9.94	10.08
P(O-n-C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub>	Dark Red–Brown	36%	104–105	2118	C	39.14	39.38
					H	6.40	6.17
					N	10.86	10.88
P(O-i-C <sub>3</sub> H <sub>7</sub> ) <sub>3</sub>	Orange–Brown	78%	135–138 <sup>b</sup>	2118	C	35.89	36.01
					H	5.85	5.80
					N	11.62	11.46
P(OCH <sub>3</sub> ) <sub>3</sub>	Orange	not determined		2119	C	27.18	
					H	4.47	not analyzed
					N	13.51	
4-acpy	Light Brown	65%	217–219 <sup>b</sup>	2123	C	36.24	37.38
					H	3.98	4.20
					N	15.85	16.25

<sup>a</sup>Yield based on *trans*-[Co(dmgh)<sub>2</sub>(L)Cl]. <sup>b</sup>Melting points are actually decomposition temperatures.

TABLE VII. Solution Infrared Data for *trans*-[Co(dmgh)<sub>2</sub>L(SeCN)] Complexes.

L	CH <sub>3</sub> CN Solution		CH <sub>2</sub> Cl <sub>2</sub> Solution	
	$\nu_{\text{CN}}$ (cm <sup>-1</sup> )	A <sup>a</sup> × 10 <sup>-4</sup> (M <sup>-1</sup> cm <sup>-2</sup> )	$\nu_{\text{CN}}$ (cm <sup>-1</sup> )	A <sup>a</sup> × 10 <sup>-4</sup> (M <sup>-1</sup> cm <sup>-2</sup> )
P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	21 22, 21 26 sh	0.58		not determined
P(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (n-C <sub>4</sub> H <sub>9</sub> )	21 20	0.59	21 21	0.82
P(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CH <sub>3</sub>	21 21	0.56	21 21	0.91
P(n-C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub>	21 19	0.76		not determined
P(OC <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	21 26	0.50		not determined
P(O-n-C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub>	21 21	0.62		not determined
P(O-i-C <sub>3</sub> H <sub>7</sub> ) <sub>3</sub>	21 20	0.89	21 20	0.96
4-acpy	21 26	0.49	21 26	0.67

<sup>a</sup>Integrated absorption intensity of  $\nu_{\text{CN}}$  band.

TABLE VIII. Solution Infrared Data for Selected *trans*-[LCo(dmgh)<sub>2</sub>-SeCN-Co(dmgh)<sub>2</sub>SeCN] Complexes.

L	CH <sub>3</sub> CN Solution <sup>a</sup>				CH <sub>2</sub> Cl <sub>2</sub> Solution			
	$\nu_{\text{CN}}$ (cm <sup>-1</sup> )		$A^b \times 10^{-4}$ (M <sup>-1</sup> cm <sup>-2</sup> )		$\nu_{\text{CN}}$ (cm <sup>-1</sup> )		$A^b \times 10^{-4}$ (M <sup>-1</sup> cm <sup>-2</sup> )	
	(Bridging)	(Terminal)	(Bridging)	(Terminal)	(Bridging)	(Terminal)	(Bridging)	(Terminal)
P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	2193	2123	1.3	0.41	2193	2124	1.8	0.39
P(OC <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	a	2126	a	(1.4)	2176	2124	3.5	0.74

<sup>a</sup>See comments in text concerning decomposition of dinuclear complexes in CH<sub>3</sub>CN. <sup>b</sup>Integrated absorption intensity of  $\nu_{\text{CN}}$  band.

infrared analysis revealed that the selenocyanate bridge in the dinuclear species is broken and that DMSO has coordinated to the metal. Both spectra look very similar, with a strong band at 2124 cm<sup>-1</sup> with a shoulder at 2140 cm<sup>-1</sup> for the mononuclear and a strong band at 2124 cm<sup>-1</sup> with a shoulder at 2140 cm<sup>-1</sup> and also an ionic selenocyanate band at 2162 cm<sup>-1</sup> for the dinuclear complex.

When a 0.05 M solution of *trans*-[(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>PCo(dmgh)<sub>2</sub>-SeCN-Co(dmgh)<sub>2</sub>SeCN] in ethanol contains 2% Co(II), there is no indication of the breakage of the selenocyanate bridge or any rearrangement in the bonding mode of the terminal selenocyanate.

The complex *trans*-[Co(dmgh)<sub>2</sub>P(OCH<sub>3</sub>)<sub>3</sub>SeCN] undergoes a change from an orange to a red solid upon exposure to moist air and is completely dissolved in water, whereas similar complexes with different ligands are not affected by moist air and do not dissolve in water. Solid state infrared spectrophotometric analysis revealed the orange solid to possess a strong band at 2116 cm<sup>-1</sup> (terminal SeCN) and a weak band at 2070 cm<sup>-1</sup> (ionic SeCN<sup>-</sup>), while the red solid shows a medium band at 2116 cm<sup>-1</sup> (reduced terminal SeCN) and a strong band at 2146 cm<sup>-1</sup>.

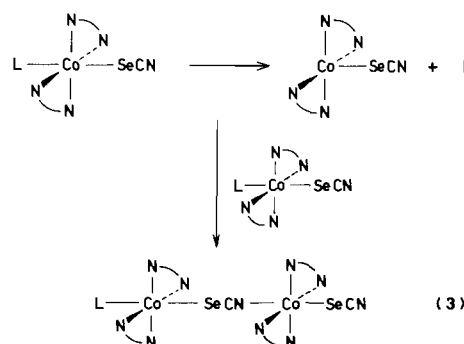
Similarly, when a 0.01 M solution of *trans*-[(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>PCo(dmgh)<sub>2</sub>-SeCN-Co(dmgh)<sub>2</sub>SeCN] in CH<sub>2</sub>Cl<sub>2</sub> with excess P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> added was monitored, a new band at 2142 cm<sup>-1</sup> was observed, along with a slight decrease in the terminal selenocyanate band intensity. As mentioned earlier, the bands at 2146 and 2142 cm<sup>-1</sup> are undoubtedly due to coordinated CN<sup>-</sup>.

## Discussion

The bonding mode of the selenocyanate group in *trans*-[Co(dmgh)<sub>2</sub>L(SeCN)] and also the terminal selenocyanate group in *trans*-[LCo(dmgh)<sub>2</sub>-SeCN-Co(dmgh)<sub>2</sub>SeCN] has been seen to be via selenium, regardless of the nature of L or the solvent employed. This observation serves to underscore the pronounced symbiotic effect of the L ligands and the dimethyl-

glyoximates on the selenocyanate's bonding mode, since the corresponding [Co(NH<sub>3</sub>)<sub>5</sub>NCSe]<sup>2+</sup> complex has only been found to exist in the N-bound form [20]. It is consistent with the considerable  $\pi$ -donor capability of the Se-bound selenocyanate, as reflected in its low position in the spectrochemical series.

The mechanism for the formation of dinuclear complexes can be envisaged to be as follows:



The ability of the nitrogen end of the coordinated selenocyanate to coordinate to a second complex molecule is dependent upon the ability of the solvent to solvate the L ligand and thus weaken the L-Co bond. It has been observed that the lower the dielectric constant of the solvent, the better the capability to cause displacement of the L ligand. This dependence on solvent dielectric varies from ligand to ligand depending on the electron withdrawing effects of the substituents on the phosphine or phosphite.

The results obtained for L = 4-acetylpyridine also correlate with those found previously by Allison and Burmeister [11]. It should be noted that the tendency to form dinuclear complexes is much less pronounced for the pyridine series of complexes.

Once a dinuclear complex has been formed, it is capable of being cleaved in a solvent which has a very high dielectric constant. This phenomenon has been observed in the case of *trans*-[(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>PCo(dmgh)<sub>2</sub>-SeCN-Co(dmgh)<sub>2</sub>SeCN] mentioned earlier in which

the bridging selenocyanate absorption band disappears upon being dissolved in DMSO. DMSO (Dimethylsulphoxide) is a very good coordinating solvent with a dielectric constant of  $\sim 46.6$ . However, the selenocyanate bridge has been observed to remain intact upon exposure to a catalytic amount of Co(II) as mentioned earlier. The bonding mode of the terminal selenocyanate was not altered by the presence of Co(II) as was the thiocyanate bonding mode in similar complexes [8].

The decomposition route of the *trans*-[Co(dmgh)<sub>2</sub>P(OCH<sub>3</sub>)<sub>3</sub>SeCN] complex can be rationalized in the following manner. If ionic selenocyanate is present, it will react with trimethylphosphite forming trimethylphosphite selenide and ionic cyanide. The cyanide is then free to return and coordinate to the cobalt. The appearance of a band at 2146 cm<sup>-1</sup> is consistent with the frequencies of the cyanide  $\nu_{\text{CN}}$  bands reported by Crumbliss and Gaus [21, 22] for monocyanocobaloximes. The band at 2142 cm<sup>-1</sup> exhibited by the *trans*-[(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>PCo(dmgh)<sub>2</sub>-SeCN-Co(dmgh)<sub>2</sub>SeCN] complex, when exposed to excess P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> in solution, is also evidence for this type of decomposition.

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