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## Rates and Mechanisms of Substitution Reactions of Palladium(II) Thiocyanate and Selenocyanate Linkage Isomers<sup>1</sup>

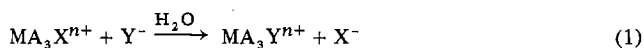
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The kinetics of the linkage isomerization and bromide ion substitution reactions of  $[\text{Pd}(\text{Et}_4\text{dien})\text{XCN}] [\text{B}(\text{C}_6\text{H}_5)_4]$  ( $\text{Et}_4\text{dien} = 1,1,7,7\text{-tetraethyl-diethylenetriamine}$ ;  $\text{X} = \text{S}, \text{Se}$ ) in DMF solution are presented in detail. Rate constants and activation parameters are reported for these reactions as well as for the  $\text{Br}^-$  substitution reactions of the  $[\text{Pd}(\text{Et}_4\text{dien})\text{NCX}] [\text{B}(\text{C}_6\text{H}_5)_4]$  isomers. As a result of the steric hindrance created by the four ethyl groups, the  $\text{PdSCN}^+$ ,  $\text{PdNCS}^+$ , and  $\text{PdNCSe}^+$  complexes react at rates which are independent of  $\text{Br}^-$  concentration, the  $\text{PdSCN}^+$  complex undergoing concurrent isomerization and substitution. The reactions of the  $\text{PdSeCN}^+$  complex with  $\text{Br}^-$ , as well as with  $\text{I}^-$ ,  $\text{N}_3^-$ , and  $\text{CN}^-$ , follow a two-term rate law:  $\text{rate} = k_1[\text{PdSeCN}^+] + k_2[\text{PdSeCN}^+][\text{Br}^-]$  where  $k_1 \cong k_{\text{isom}}$ . This represents a unique case where the mechanism of a Pd(II) substitution reaction is dependent upon the nature of the *outgoing* group. The rate of the  $\text{PdSeCN}^+ + \text{Br}^-$  reaction was studied as a function of ionic strength.  $\log k_2$  was found to decrease with increasing  $\mu^{1/2}$ , as would be expected for species having opposite unit charges. A mechanism is proposed in which steric interaction caused by the *outgoing* group is responsible for the reagent-dependent path.

### Introduction

The substitution reactions of square planar complexes have generally been found<sup>2</sup> to follow a two-path reaction mechanism characterized by a two-term rate law



$$\text{rate} = k_1[\text{MA}_3\text{X}^{n+}] + k_2[\text{MA}_3\text{X}^{n+}][\text{Y}^-] \quad (2)$$

The first term is presumably due to the slow displacement of  $\text{X}^-$  by the solvent, which is then rapidly replaced by  $\text{Y}^-$ . A direct nucleophilic displacement of  $\text{X}^-$  by  $\text{Y}^-$  is thought to be responsible for the second term.

Utilization of the bulky ligand 1,1,7,7-tetraethyl-diethylenetriamine ( $\text{Et}_4\text{dien}$ ) has been found<sup>3</sup> to result in drastic changes in the reaction chemistry of square-planar complexes. The steric hindrance created by the four ethyl groups of the  $\text{Et}_4\text{dien}$ , which effectively fill the space above and below the square plane, generally<sup>3</sup> serves to depress the reagent-dependent path ( $k_2$ ) to the point where it is not observed in the substitution reactions of  $[\text{Pd}(\text{Et}_4\text{dien})\text{X}]^+$  complexes in solvents of high dielectric constant, e.g., water and methanol. Two noteworthy exceptions have been observed. The rate dependence on the concentration of the hydroxide ion has been attributed by Baddley and Basolo<sup>3</sup> to an  $\text{SN}1_{\text{cb}}$  mechanism, while that due to the concentration of the thiosulfate ion<sup>4</sup> is presumably due, according to Goddard and Basolo, to its very large nucleophilic reactivity constant.<sup>5</sup> Moreover, the  $k_2$  path also appears when acetonitrile is used as solvent,<sup>6</sup> due to a combination of better solvation of the ethyl groups and poorer solvation of the reagent ions.

The steric hindrance created by the  $\text{Et}_4\text{dien}$  ligand also

causes the ambidentate thiocyanate<sup>7,8</sup> and selenocyanate<sup>9</sup> ions to switch from their normal nonlinear



linkages, expected for a soft metal ion such as Pd(II), to linear Pd-NCX linkages in solution. We now wish to report in detail the results of a study of the isomerization and substitution reactions of the linkage isomers  $[\text{Pd}(\text{Et}_4\text{dien})(\text{XCN}/\text{NCX})]^+$  ( $\text{X} = \text{S}, \text{Se}$ ). This has provided a unique example of mechanistic control by the nature of the *outgoing* group in a substitution reaction.<sup>10</sup>

### Experimental Section

The tetraphenylborate salts<sup>9</sup> of the four linkage isomers provided the kinetic substrates. Unless otherwise specified, *N,N*-dimethylformamide reaction solutions were prepared at 20° for the kinetics measurements. Ionic strength was maintained with sodium perchlorate monohydrate.

The visible and ultraviolet spectra of the reaction mixtures were measured with a Cary Model 14 spectrophotometer, using matched 1-cm quartz cells in thermostated sample and reference compartments. The reaction temperatures were held within a range of  $\pm 0.1^\circ$ . The rates of the reactions at different temperatures were measured by following the changes in optical density with time near the wavelength of the lowest energy absorption maximum in the visible-uv spectra of the substrates. Each rate constant is the slope of a least-squares line which was determined with a Fortran IV program written for the Burroughs 5500 computer. All of the rate constants are accurate within 10%. A plotting program used with a Wang 700A programmable calculator fitted with a Model 702 plotting output writer provided a visual record of the data.

When the reagent strength of the reaction mixture exceeded 0.1 *M*, the rate of reaction was accelerated to the point that a fast method of mixing the substrate and reagent was required. The procedure used for these reactions involved preparation of a reagent solution at the exact concentration and ionic strength desired for the reaction. An aliquot of the reagent solution at the reaction temperature was then added to the quantity of solid substrate needed to provide the desired molarity in a volume the same size as that of the aliquot. This procedure ignored any volume change that occurred upon dissolution of the substrate. Once mixing had been effected in a bath at the reaction temperature, a reaction sample was transferred by syringe to the spectrophotometer compartment through a small opening in the lid. The whole procedure required less than 1 min and did not alter the compartment temperature. For additional

(1) Presented, in part, at the XIIIth International Conference on Coordination Chemistry, Zakopane, Poland, Sept 14-22, 1970 (see Proceedings, p 284), and at the 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March 29-April 1, 1971 (see Abstracts, No. INOR 63).

(2) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, p 377.

(3) W. H. Baddley and F. Basolo, *J. Amer. Chem. Soc.*, **88**, 2944 (1966).

(4) J. B. Goddard and F. Basolo, *Inorg. Chem.*, **7**, 936 (1968).

(5) R. G. Pearson, H. Sobel, and J. Songstad, *J. Amer. Chem. Soc.*, **90**, 319 (1968).

(6) J. B. Goddard and F. Basolo, *Inorg. Chem.*, **7**, 2456 (1968).

(7) F. Basolo, W. H. Baddley, and J. L. Burmeister, *Inorg. Chem.*, **3**, 1202 (1964).

(8) F. Basolo, W. H. Baddley, and K. J. Weidenbaum, *J. Amer. Chem. Soc.*, **88**, 1576 (1966).

(9) J. L. Burmeister, H. J. Gysling, and J. C. Lim, *J. Amer. Chem. Soc.*, **91**, 44 (1969).

(10) J. L. Burmeister and J. C. Lim, *Chem. Commun.*, 1154 (1969).

Table I. Kinetic Data for the Reactions of Thiocyanate Linkage Isomers

Temp, °C	$10^4 k_{\text{obsd}}, \text{sec}^{-1}$	Temp, °C	$10^4 k_{\text{obsd}}, \text{sec}^{-1}$
Pd-SCN → Pd-NCS <sup>a-c</sup>		Pd-SCN → Pd-Br, early <sup>a-e</sup>	
20	0.62	20	1.49
25	1.12	25	2.9
30	1.93	30	5.0
35	3.39	35	8.9
40	5.9	40	14.6
45	9.7		
Pd-NCS → Pd-Br <sup>b,d,f,g</sup>		Pd-SCN → Pd-Br, late <sup>b,d,f,h</sup>	
20	0.34	20	0.36
25	0.63	30	1.01
30	1.05	40	2.70
35	1.80		
40	2.86		

<sup>a</sup> Concentration of substrate  $2 \times 10^{-3} M$ . <sup>b</sup> Ionic strength 0.1 M. <sup>c</sup> Wavelength 405 nm. <sup>d</sup> Concentration of bromide  $1 \times 10^{-2} M$ . <sup>e</sup> Early stage of reaction (see text). <sup>f</sup> Concentration of substrate  $1 \times 10^{-3} M$ . <sup>g</sup> Wavelength 334 nm. <sup>h</sup> Late stage of reaction (see text).

accuracy, a close correspondence between room temperature and reaction temperature was maintained.

In determining the rate constants for the various reactions, it was implicitly assumed that the concentrations of only two absorbing species were changing (those of the substrate and the product). Since this assumption was reasonable but not assured, each system was tested using the graphical method of Coleman, Varga, and Mastin.<sup>11</sup> An absorbance matrix for each system was set up, the rows of the matrix corresponding to absorbance at different wavelengths and the columns designating the time into the reaction. For two absorbing species, the necessary requirement of a zero value for any  $3 \times 3$  determinant was met by all but one system. A departure from the rule indicated a third absorbing species in the bromide substitution of  $[\text{Pd}(\text{Et}_4\text{dien})\text{SCN}]^+$ .

In every case the product of the reaction was prepared so that the final spectrum of the product could be compared with that of a known sample. For each reaction, it was confirmed that the substrate was totally converted to the expected product.

## Results

The kinetic data for the reactions of the two thiocyanate linkage isomers  $[\text{Pd}(\text{Et}_4\text{dien})\text{SCN}]^+$  and  $[\text{Pd}(\text{Et}_4\text{dien})\text{NCS}]^+$  are recorded in Table I. These results complement an earlier study by Basolo, Baddley, and Weidenbaum.<sup>8</sup>

A related set of data for the selenocyanate complexes is included in Table II. An obvious relationship exists between the  $\text{Br}^-$  concentration and the rate of substitution of  $[\text{Pd}(\text{Et}_4\text{dien})\text{SeCN}]^+$ .

A plot of  $k_{\text{obsd}}$  vs. reagent concentration at a given temperature yields a straight line, the slope of which is reported as  $k_2$ . The first numeral of the intercept of each line is given as an approximate value of  $k_1$ . The observation of a bromide ion dependency raises the question of whether pseudo-first-order kinetics with respect to  $\text{Br}^-$  might be induced at high concentration. Unfortunately, the level of  $\text{Br}^-$  concentration is limited by its solubility in DMF. At near-maximum concentration, 0.78 M, no leveling in the rate of substitution was observed. Rate constants for various high levels of  $\text{Br}^-$  concentration are reported in Table III. These rate constants are also shown graphically in Figure 1. They exhibit a striking dependence on the ionic strength of the medium. For each given ionic strength, a value of  $k_2$  was determined and also appears in Table III. It was noted that the presence of water in the reaction mixture retards the rate of substitution. For example, at a bromide ion concentration of 0.4 M (ionic strength the same), the value of

$k_{\text{obsd}}$  drops from 0.00311 to 0.00026  $\text{sec}^{-1}$  in going from pure DMF as the solvent to a 3:1 DMF- $\text{H}_2\text{O}$  mixture.

The exact nature of the relationship between the rates of substitution and the ionic strength of the medium was elucidated by plotting  $\log k_2$  vs. the square root of the ionic strength of the medium (Figure 2).

The activation parameters for the isomerization and substitution reactions appear in Table IV. The rate data for the substitution of  $[\text{Pd}(\text{Et}_4\text{dien})\text{SeCN}]^+$  by some additional reagents are shown in Table V.

## Discussion

A consideration of the data reveals that the selenocyanate complex isomerizes faster than the thiocyanate complex. Greater relief of steric strain in the case of the larger selenocyanate would facilitate the dissociation of the substrate and the concomitant formation of a solvento intermediate. The small, negative activation entropies for both isomerizations (Table IV) are consistent with separation of charge and increased solvent orientation in the transition state of a dissociative process. Roulet and Gray<sup>12</sup> have shown that the halide ion substitution reactions of  $[\text{Pd}(\text{Et}_4\text{dien})\text{X}]^+$  ( $\text{X}^- = \text{Cl}^-, \text{Br}^-, \text{I}^-$ ) complexes most probably proceed *via* a dissociative mechanism with leaving group solvation in aprotic solvents such as DMF and DMSO. In these cases, the solvent molecules are apparently too large to permit their activating the substitution process by associating with the palladium(II). Conversely, the reactions in protic solvents having more accessible donor atoms are thought to proceed *via* an associative solvolysis pathway, in accord with their more negative activation entropies.<sup>12</sup> The larger (negatively) activation entropies shown in Table IV for the  $[\text{Pd}(\text{Et}_4\text{dien})\text{NCS}]^+ + \text{Br}^-$  reactions could result from more extensive solvation of the nitrogen end of the ion by DMF molecules as the thiocyanate group is released from the complex.

The  $\text{Br}^-$  substitution of  $[\text{Pd}(\text{Et}_4\text{dien})\text{SCN}]^+$  proceeds at a rate that is independent of  $\text{Br}^-$  concentration. A comparison between the first-order substitution rate constants and the appropriate rates of isomerization (see Table I) might lead to the supposition of a discrepancy in substrate reactivity. Actually, supplementary evidence supports the view that two concurrent processes are involved in the reaction labeled as the  $\text{Br}^-$  substitution of  $[\text{Pd}(\text{Et}_4\text{dien})\text{SCN}]^+$ . Near the end of the reaction, slight curvature in the plot of  $\log(A_t - A_\infty)$  vs. time requires an explanation, as does the failure of later absorbance values to correspond to an isosbestic point established early in the reaction at 330 nm. As mentioned earlier, a graphical method<sup>11</sup> showed that there were more than two absorbing species in the reaction mixture. It is proposed that the three absorbing species involved in this reaction are S-bonded substrate, N-bonded isomer, and bromo-substituted product. In the early part of the reaction, the conversion of  $[\text{Pd}(\text{Et}_4\text{dien})\text{SCN}]^+$  to its N-bonded isomer most likely predominates. Late in the reaction, when the S-bonded isomer has been depleted,  $\text{Br}^-$  substitution of  $[\text{Pd}(\text{Et}_4\text{dien})\text{NCS}]^+$  prevails. The absorptivity of  $[\text{Pd}(\text{Et}_4\text{dien})\text{NCS}]^+$  is roughly half that of  $[\text{Pd}(\text{Et}_4\text{dien})\text{Br}]^+$  at the wavelength of observation. The isomerization of substrate therefore causes a disproportionate change in absorbance relative to the final absorbance of the bromide-substituted product, since the  $A_\infty$  value used in the calculations is that of the latter. The *apparent* rate constants reported in Table I for the early stage of the bromide ion substitution reaction with  $[\text{Pd}(\text{Et}_4\text{dien})\text{SCN}]^+$  are correspondingly larger

(11) J. S. Coleman, L. P. Varga, and S. H. Mastin, *Inorg. Chem.*, **9**, 1015 (1970).

(12) R. Roulet and H. B. Gray, *Inorg. Chem.*, **11**, 2101 (1972).

Table II. Kinetic Data for the Reactions of Selenocyanate Linkage Isomers

Pd-SeCN $\rightarrow$ Pd-NCSe <sup>a-c</sup>			Pd-NCSe $\rightarrow$ Pd-Br <sup>b,d-f</sup>		
Temp, °C	$10^4 k_{\text{obsd}}, \text{sec}^{-1}$		Temp, °C	$10^4 k_{\text{obsd}}, \text{sec}^{-1}$	
20	0.93		20	1.88	
25	1.7		30	4.7	
30	3.1				
35	5.5		40	13.8	
40	9.8				

Pd-SeCN $\rightarrow$ Pd-Br <sup>a-c</sup>					
20°		30°		40°	
[Br <sup>-</sup> ], M	$10^4 k_{\text{obsd}}, \text{sec}^{-1}$	[Br <sup>-</sup> ], M	$10^4 k_{\text{obsd}}, \text{sec}^{-1}$	[Br <sup>-</sup> ], M	$10^4 k_{\text{obsd}}, \text{sec}^{-1}$
0.002	1.25	0.005	6.3	0.005	19
0.01	3.4	0.01	10.7	0.01	29
0.03	6.4	0.02	17.0	0.02	44
0.04	8.0	0.04	26.8	0.04	71
0.05	8.5	0.1	63		

<sup>a</sup> Concentration of substrate  $2 \times 10^{-3} M$ . <sup>b</sup> Ionic strength 0.1 M. <sup>c</sup> Wavelength 425 nm. <sup>d</sup> Concentration of substrate  $1 \times 10^{-3} M$ . <sup>e</sup> Concentration of bromide  $1 \times 10^{-2} M$ . <sup>f</sup> Wavelength 327 nm.

Table III. Kinetic Data for the Bromide Substitution of  $2 \times 10^{-3} M$  [Pd(Et<sub>4</sub>dien)SeCN]<sup>+</sup> in DMF at 20° (Wavelength 425 nm)

$\mu, M$	[Br <sup>-</sup> ], M										
	0.05	0.075	0.1	0.15	0.2	0.3	0.4	0.5	0.6	0.78	
	$10^4 k_{\text{obsd}}, \text{sec}^{-1}$									$10^4 k_2, M^{-1} \text{sec}^{-1}$	
0.1	~8	~11	15.7								~150
0.2			12.8	17.5	23.2						104
0.3			10.6		19.3	27.3					84
0.4			9.1		16.4	23.7	31.1				73
0.5			7.9		14.5	20.8	27.2	33.4			64
0.6			6.9		12.2	17.8	23.6	30.1	36.1		59
0.78			5.6		9.9	14.6	19.3	24.3	28.2	36.2	45

Table IV. Kinetic Data and Activation Parameters for the Isomerization and Substitution Reactions in DMF at 30°

Reaction	$10^4 k_1, \text{sec}^{-1}$	$10^4 k_2, M^{-1} \text{sec}^{-1}$	$\Delta G^*, \text{kcal mol}^{-1}$	$\Delta H^*, \text{kcal mol}^{-1}$	$\Delta S^*, \text{eu}$
Pd-SCN $\rightarrow$ Pd-NCS	1.93	0	22.9	19.8	-10
Pd-SeCN $\rightarrow$ Pd-NCSe	3.1	0	22.6	21.0	-5
Pd-SCN					
↙ ↘					
Pd-NCS $\rightarrow$ Pd-Br (late)	1.01	0	23.3	17.8	-18
Pd-SeCN $\rightarrow$ Pd-Br	~4	580	~22 ( $k_1$ )	~20 ( $k_1$ )	~-7 ( $k_1$ )
			19.5 ( $k_2$ )	20.0 ( $k_2$ )	+2 ( $k_2$ )
Pd-NCS $\rightarrow$ Pd-Br	1.05	0	23.3	18.1	-17
Pd-NCSe $\rightarrow$ Pd-Br	4.7	0	22.4	17.6	-16

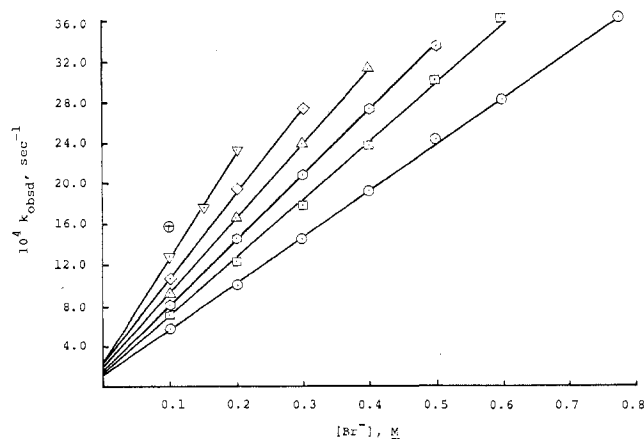


Figure 1. Analytical plot of  $k_{\text{obsd}}$  vs. bromide ion concentrations for the substitution reaction of [Pd(Et<sub>4</sub>dien)SeCN]<sup>+</sup> in DMF at various ionic strengths:  $\ominus$ ,  $\mu = 0.1$ ;  $\nabla$ ,  $\mu = 0.2$ ;  $\diamond$ ,  $\mu = 0.3$ ;  $\Delta$ ,  $\mu = 0.4$ ;  $\odot$ ,  $\mu = 0.5$ ;  $\square$ ,  $\mu = 0.6$ ;  $\odot$ ,  $\mu = 0.78$ .

than the rate constants determined for the linkage isomerization.<sup>13</sup>

The data for the Br<sup>-</sup> substitution of [Pd(Et<sub>4</sub>dien)SeCN]<sup>+</sup> establish the complex as an exception to the usual behavior

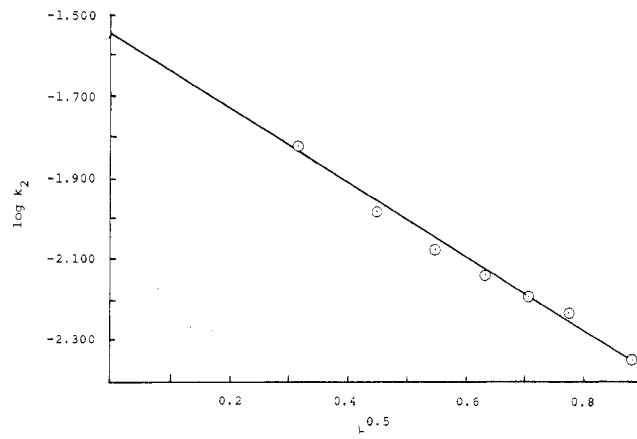
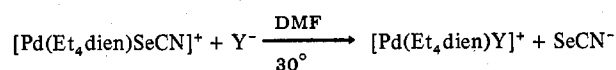


Figure 2. Variation in rates as a function of ionic strength for the bimolecular process in the reaction of  $2 \times 10^{-3} M$  [Pd(Et<sub>4</sub>dien)SeCN]<sup>+</sup> with bromide ion.

exhibited by Et<sub>4</sub>dien pseudooctahedral<sup>3</sup> complexes. The reactivity of the substrate is consistent with the two-path mechanism followed by unhindered square-planar complexes. A comparison of the approximate  $k_1$  values with the isomerization rate constants (Table II) provides evidence

Table V. Kinetic Data for the Reaction<sup>a</sup>

Y <sup>-</sup>	10 <sup>4</sup> k <sub>1</sub> , sec <sup>-1</sup>	10 <sup>4</sup> k <sub>2</sub> , M <sup>-1</sup> sec <sup>-1</sup>	n <sup>b</sup> (Pt)
Br <sup>-</sup>	~4	580	4.18
I <sup>-</sup>	~2	185	5.42
N <sub>3</sub> <sup>-</sup>	<i>d</i>	<i>d</i>	3.58
CN <sup>-</sup>	<i>d</i>	<i>d</i>	7.14
SeCN <sup>-</sup> <sup>c</sup>	4.9 (0.002)		7.11
	5.1 (0.0035)		
	5.3 (0.005)		
	6.3 (0.01)		
	6.2 (0.02)		
	6.0 (0.04)		

<sup>a</sup> Concentration of substrate  $2 \times 10^{-3} M$ ; concentration of Y<sup>-</sup> varied from  $5 \times 10^{-3}$  to  $1 \times 10^{-1} M$ ; ionic strength 0.1 M.

<sup>b</sup> Nucleophilic reactivity constant. <sup>c</sup> Concentration (M) of SeCN<sup>-</sup> in parentheses. <sup>d</sup> Very fast.

of a shared mechanism for the  $k_1$  path. An explanation of the Br<sup>-</sup>-dependent  $k_2$  path is offered below.

Two results regarding the  $k_2$  path lend themselves to immediate interpretation. The activation entropy for the bimolecular process is positive (Table IV). This result is consistent with the decrease in solvent orientation that would accompany the neutralization of charge created by the formation of the activated complex. Furthermore, the negative slope resulting from a plot of  $\log k_2$  vs.  $\mu^{1/2}$  (Figure 2) supports the observation that the charges of the two ions forming the activated complex have different signs.<sup>14</sup> Our conclusion, at this point, may be simply stated. Direct reagent attack by the bromide ion upon the substrate [Pd-(Et<sub>4</sub>dien)SeCN]<sup>+</sup> with resulting charge neutralization leads to the formation of substituted product. Since charge has been demonstrated to be an important factor in the reaction, a solvent effect is expected. Increasing the dielectric constant of the solvent medium by the addition of water insulates the charges of the reactants from each other and lowers the rate of reaction.

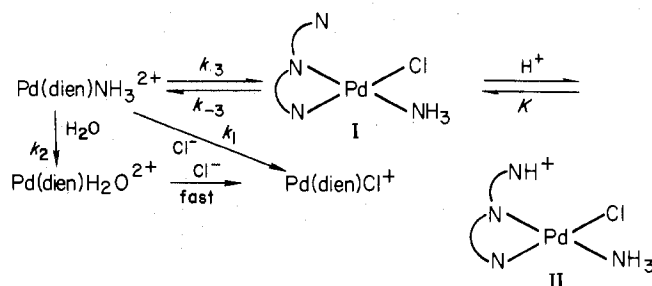
The question remains as to how the reagent finds its way into the coordination sphere. Two mechanistic interpretations will be considered. The opening and closing of one of the chelate rings, a process that would alleviate steric strain created by the large selenium atom and the angular SeCN linkage, is a possibility.<sup>10</sup> The results of the only other kinetic study of a tridentate amine-palladium(II) complex in which ring opening has been considered as a reaction possibility are germane to this point. Coe and Lyons<sup>15</sup> have reported Scheme I for the reaction of [Pd(dien)NH<sub>3</sub>]<sup>2+</sup> with Cl<sup>-</sup>. Strong support for the opening of the chelate ring was obtained from the observation of an inverse dependence of the reaction rate on hydrogen ion concentration. There is, however, no evidence that intermediate I proceeds

(13) The hypothesis that isomerization as well as substitution occurs is supported by several experimental observations. A temporary absorption maximum was observed at 327 nm, a wavelength at which [Pd(Et<sub>4</sub>dien)NCS]<sup>+</sup> exhibits an absorption maximum. When a reaction solution was poured into water 90 min after the initiation of the reaction (at a time when the graphical method<sup>11</sup> showed that the two original absorbing species had been joined by a significant concentration of a third), the infrared spectrum of the solid which immediately precipitated exhibited two CN stretching bands. One was characteristic of the S-bonded isomer,<sup>9</sup> the other, characteristic of the N-bonded isomer.<sup>9</sup> Finally, monitoring absorbance changes at 334 nm near the end of the reaction yielded rate constants (Table I) which were identical with those for the bromide ion substitution of [Pd(Et<sub>4</sub>dien)NCS]<sup>+</sup>.

(14) W. J. Moore, "Physical Chemistry," Prentice-Hall, Englewood Cliffs, N. J., 1962, p 368.

(15) J. S. Coe and J. R. Lyons, *J. Chem. Soc. A*, 2669 (1969).

Scheme I



directly to the product; in fact, the experimental results would discount such a possibility.

Any alternative mechanism for the direct substitution of [Pd(Et<sub>4</sub>dien)SeCN]<sup>+</sup> by reagent ion must be derived from the steric destabilization of the substrate by the selenocyanate group. It is probable that the bulky Se atom and the angular Pd-SeCN linkage prevent the two cis tertiary amines from bonding to palladium to the extent that is possible when -SCN (or -NCS or -NCSe) is the fourth group in the coordination sphere. Lengthening of the bonds and a distortion in the orbital overlap angle would relieve steric strain. This alteration in geometry, with concomitant spreading of the ethyl groups, would permit direct reagent attack.

This alternative finds support in several observations. First, the complex Co(Et<sub>4</sub>dien)Cl<sub>2</sub><sup>16</sup> demonstrates that a fifth group can be accommodated in the coordination sphere of metal-Et<sub>4</sub>dien complexes. There is also room for direct reagent attack<sup>4</sup> in the reaction of [Pd(Et<sub>4</sub>dien)Br]<sup>+</sup> with S<sub>2</sub>O<sub>3</sub><sup>2-</sup>. It is therefore reasonable that even more space would be available in the selenocyanate complex. The greater tendency of the Pd-SeCN linkage to distort the Pd-amine bonds follows from the larger size of the selenium atom, coupled with the inherently greater strength of the Pd-Se bond,<sup>17,18</sup> relative to Pd-S. Despite their greater basicity, N-alkyl multidentate amines form less stable complexes than the corresponding N-hydrogen amines, due to steric hindrance.<sup>19,20</sup> The existence of a significant concentration of a ring-opened intermediate is not compatible with the observed maintenance of an isosbestic point throughout the reaction, nor was its presence indicated by the graphical method.

Finally, the results of substitution reactions with a variety of nucleophiles show that the rate-determining factor is the size of the reagent. The rate constants in Table V show that Br<sup>-</sup> substitutes at a faster rate *via* the  $k_2$  step than I<sup>-</sup>, a result contrary to the greater nucleophilicity of I<sup>-</sup>. Azide ion, for which the nucleophilic reactivity constant is less than for either of the other two reagents, substitutes fastest of all. Despite their nearly identical nucleophilic reactivity constants, the cyanide and selenocyanate ions exhibit extreme differences in behavior, the former substituting at an immeasurably (using nonflow techniques) rapid rate and the latter, presumably because of its bulk, coupled with its angular bonding requirement, hardly affecting the rate at all. Free attack on a ring-opened intermediate by the highly nucleophilic Se atom of the selenocyanate would be expected to retard the rate of isomerization. The relatively small

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amount of N-bonded product arising from nitrogen attack would account for the slight rate increase actually observed, or it could simply be due to a salt effect. In summary, a dependence upon the size of the reagent is consistent with the second mechanism but should not be a factor in the ring-opening mechanism.<sup>21</sup>

(21) A referee suggested that the strain on the bent SeCN<sup>-</sup> group by the tridentate amine, without distortion of the Pd-amine bonds, is a more probable explanation of its special position among leaving groups; *i.e.*, a relatively weak interaction of the palladium(II) with a potential entering group might be enough to remove a strained -SeCN<sup>-</sup>. We do not find this explanation to be compelling. Its logical extension suggests that the strained, angular Pd-SCN group should also be susceptible to attack by an incoming group for it, too, is destabilized by the presence of the ethyl groups and isomerizes

**Registry No.** [Pd(Et<sub>4</sub>dien)SCN][B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>], 22143-00-6; [Pd(Et<sub>4</sub>dien)NCS][B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>], 22142-99-0; Br<sup>-</sup>, 24959-67-9; [Pd(Et<sub>4</sub>dien)SeCN][B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>], 19599-79-2; [Pd(Et<sub>4</sub>dien)NCSe][B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>], 18024-40-3; I<sup>-</sup>, 2046-154-5; N<sub>3</sub><sup>-</sup>, 14343-69-2; CN<sup>-</sup>, 57-12-5; SeCN<sup>-</sup>, 5749-48-4.

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at rates only slightly slower than those of the Pd-SeCN isomer. In point of fact, only the Pd-SeCN isomer exhibits the second-order pathway.

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## Nuclear Magnetic Resonance Studies of the Solution Chemistry of Metal Complexes. VI. Stability Constants of Some Cadmium and Zinc Polyamine and Aminocarboxylate Mixed-Ligand Complexes<sup>1,2</sup>

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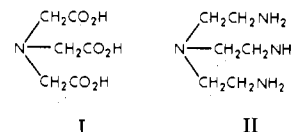
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Stability constants,  $K_{ML}^{MLX}$ , for the complexation reaction  $ML + X \rightleftharpoons MLX$  have been determined from proton magnetic resonance chemical shift measurements for a series of complexes where M is cadmium or zinc, L is nitrilotriacetic acid (nta) or  $\beta$ ,  $\beta'$ ,  $\beta''$ -triaminotriethylamine (tren), and X is ethylenediamine (en), glycine (gly), malonic acid (ma), or iminodiacetic acid (ida). The  $\log K_{ML}^{MLX}$  values are as follows: 5.00, Zn(nta)(en)<sup>-</sup>; 5.05, Cd(nta)(en)<sup>-</sup>; 1.15, Zn(tren)(en)<sup>2+</sup>; 2.83, Cd(tren)(en)<sup>2+</sup>; 3.62, Zn(nta)(gly)<sup>2-</sup>; 2.93, Cd(nta)(gly)<sup>2-</sup>; 1.00, Zn(tren)(gly)<sup>+</sup>; 2.59, Cd(tren)(gly)<sup>+</sup>; 3.61, Zn(nta)(ida)<sup>3-</sup>; 4.01, Cd(nta)(ida)<sup>3-</sup>; 1.34, Zn(nta)(ma)<sup>3-</sup>. The stability constants of the monohydroxy complexes of Zn(nta)<sup>-</sup> and Zn(tren)<sup>2+</sup> were also determined; the  $\log K_{ZnL}^{ZnL(OH)}$  values are 4.01 for Zn(nta)(OH)<sup>2-</sup> and 2.90 for Zn(tren)(OH)<sup>+</sup>. The results indicate the tendency of Zn(tren)<sup>2+</sup> to form mixed complexes with en and gly is significantly less than that of the other complexes studied, suggesting that the structure of Zn(tren)<sup>2+</sup> is different from the structures of the other 1:1 complexes. The structures of the M(nta)(gly)<sup>2-</sup>, M(nta)(ida)<sup>3-</sup>, and M(nta)<sub>2</sub><sup>4-</sup> complexes are discussed on the basis of the formation constants of the ternary complexes.

### Introduction

There has been considerable recent interest in the formation of mixed-ligand complexes in solution, in part due to the use of such complexes as models in studies of metallo-enzyme-substrate interactions.<sup>3-9</sup> In the present work, the stability constants of the mixed-ligand complexes resulting from the addition of glycine (gly) or ethylenediamine (en) to the cadmium and zinc complexes of nitrilotriacetic acid (nta, I) and  $\beta$ ,  $\beta'$ ,  $\beta''$ -triaminotriethylamine (tren, II) have been determined from proton nuclear

magnetic resonance (nmr) chemical shift measurements. The stability constant of the complex formed from Zn(nta)<sup>-</sup> and malonic acid (ma) and the stoichiometry and equilibrium constants for the interaction of hydroxide ions with Zn(nta)<sup>-</sup> and Zn(tren)<sup>2+</sup> have also been determined.



The structures of nta and tren are such that, if M(nta)<sup>-</sup> and M(tren)<sup>2+</sup> complexes are six-coordinate in aqueous solution, the two water molecules which complete the inner coordination shell will be in cis positions. Evidence supporting the cis-octahedral arrangement in Ni(tren)-(H<sub>2</sub>O)<sub>2</sub><sup>2+</sup> has recently been obtained from solvent-exchange studies;<sup>10</sup> however thermochemical data<sup>11</sup> suggest that Zn(tren)<sup>2+</sup> is less hydrated and exists as a four- or five-coordinate complex.

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