Inorganic Linkage Isomerism of the Selenocyanate Ion

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Abstract: Utilization of the steric hindrance created by the ligand 1,1,7,7-tetraethyldiethylenetriamine, Et_4dien, when complexed with palladium(II), has resulted in the first synthesis of inorganic linkage isomers of the selenocyanate ion. The formulation of $[Pd(Et_4dien)SeCN][B(C_6H_5)_4]$, isolated at low temperatures, as an Se-bonded complex is supported by the integrated absorption intensity of its C–N stretching band and characteristic shifts, relative to those of the free ligand, of its C–Se stretching and NCSe bending vibrations. Dissolution in a variety of solvents yields the corresponding N isomer, the first-order rate of isomerization decreasing as the dielectric constant of the solvent is decreased, thereby supporting a dissociative process. The isomerization produces characteristic band shifts in both the infrared and visible-ultraviolet spectra of the complex. The corresponding diethylenetriamine complex, $[Pd(dien)SeCN][B(C_6H_5)_4]$, has been found to be stable with respect to isomerization. Surprisingly, the N-bonded isomer of the Et_4dien complex, once isolated, ***reisomerizes*** to the Se-bonded form at room temperature in the solid state. The tetraphenylborate salt of $[Pd(Et_4dien)NCS]^+$ behaves in an analogous manner, but the thiocyanate salt is stable with respect to isomerization, both in solution and in the solid state. This represents the first observation of the dependence of the bonding mode of an ambidentate ligand on the nature of a *noncoordinated* group.

Although the phenomenon of linkage isomerization in coordination complexes was first discovered more than a century ago[1] and was included by Werner in his sevenfold complex classification,[2] virtually all of the known examples have been reported during this decade. Only three examples, all involving nitrito-nitro isomers of cobalt(III) complexes, were known prior to 1960; as of today, at least 31 examples, involving six[3] ambidentate ligands (NO_2^-, NCS^-, $S_2O_3^{2-}$, CN^-, 3-formylacetylacetonate, $NCSe^-$), have been reported.[4] The majority of the syntheses have been accomplished by design, rather than by chance, utilizing mechanistic, electronic, and steric considerations.

The bonding mode of the thiocyanate ion has been found to be particularly sensitive to changes in its environment. Whether a bond is formed to the nitrogen or sulfur atoms, or both, in its complexes depends upon the nature of the metal atom (*e.g.*, $[Zn(NCS)_4]^{2-}$ *vs.* $[Hg(SCN)_4]^{2-}$ [5]), the electronic and steric character of other ligands in the coordination sphere (*e.g.*, $[Pd\text{-}1,10\text{-phenanthroline})(SCN)_2]$ *vs.* $[Pd(5\text{-nitro-}1,10\text{-phenanthroline})(NCS)_2]$[6] and $[Pd(diethylenetriamine)SCN]^+$ *vs.* $[Pd(1,1,7,7\text{-tetraethyldiethylenetriamine})NCS]^+$ [7]), and/or the nature of the physical state of the complex (*e.g.*, $[Mn(CO)_5SCN]$ is S-bonded in the solid state but N-bonded in acetonitrile solution;[8] $[Pd(As(n\text{-}C_4H_9)_3)_2(SCN)_2]$ is S-bonded in the solid state but undergoes partial isomerization when molten[6]).

Owing to its electronic similarity to the thiocyanate ion, the selenocyanate ion was expected to exhibit much the same sensitivity. This has not proved to be the case. Although both ions follow a $M_{(\text{class a})}$–NCX, $M_{(\text{class b})}$–XCN bonding pattern in complexes wherein they are the only ligands present,[9] the bonding mode of the selenocyanate ion, unlike that of the thiocyanate ion, has not yet been found to be affected by changes in the electronic character of other ligands in the coordination sphere.[10] It does, however, display a steric sensitivity, and utilization of this property has made possible the first synthesis of linkage isomers of the selenocyanate ion.[11] We now wish to report in detail on their synthesis and characterization, the kinetics of the isomerization, and our discovery of the first examples of the dependence of the bonding mode of an ambidentate ligand on the nature of the *noncoordinated* counterion.

Experimental Section

Preparation of Complexes. $\mathbf{[Pd(Et_4dien)SeCN][B(C_6H_5)_4]}$. Sodium selenocyanate (42.5 mmoles) was added to a suspension of 10.3 mmoles of palladium(II) chloride in 600 ml of reagent grade methanol. After stirring for 1 hr, the resulting blood red solution was filtered to remove all residual solids (primarily sodium chloride), and the filtrate was cooled for 1 hr in a Dry Ice–acetone bath. 1,1,7,7-Tetraethyldiethylenetriamine (6 ml) was added and the stirring continued for an additional hour. The solution was then allowed to gradually warm up to *ca.* −25°, whereupon it was filtered, the filtrate passing into an ice–salt bath cooled solution containing 10.0 mmoles of sodium tetraphenylborate dissolved in a minimum volume of methanol. Within 30 sec, a yellow, flocculent precipitate formed. It was isolated by filtration, and a second crop was obtained by allowing the filtrate to pass into ice water. The combined precipitates were air-dried for 30 min and redissolved in a minimum volume of acetone at 2°. Reprecipitation was accomplished by pouring the acetone solution into 1 l. of ice water. The solid was removed by filtration, washed with two 20-ml portions of anhydrous ethyl ether, and dried *in vacuo* for 3 hr. A canary yellow

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(1) W. Gibbs and F. A. Genth, *Am. J. Sci.*, **24**, 86 (1857).

(2) A. Werner, *Ber.*, **40**, 765 (1907).

(3) D. R. Stranks has been incorrectly quoted (R. T. M. Fraser, "Linkage Isomerism," in "Werner Centennial," Advances in Chemistry Series, No. 62, American Chemical Society, Washington, 1967, p 296) as having prepared the unstable pink O-bonded sulfito complex, $[Co(NH_3)_5OSO_2]^+$, by the addition of sulfur dioxide or sodium sulfite to solutions of $[Co(NH_3)_5OH_2]^{3+}$ at low temperatures and low pH. In point of fact, it has not been isolated, nor has any physical evidence been presented which would support its existence in solution. Only the stable yellow-brown S-bonded complex is known [E. H. Riesenfeld, *Z. Anorg. Allgem. Chem.*, **132**, 99 (1923)]; D. R. Stranks, private communication.

(4) J. L. Burmeister, *Coord. Chem. Rev.*, **3**, 225 (1968), and references contained therein.

(5) J. Lewis, R. S. Nyholm, and P. W. Smith, *J. Chem. Soc.*, 4590 (1961).

(6) A. Sabatini and I. Bertini, *Inorg. Chem.*, **4**, 1665 (1965).

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

(8) M. F. Farona and A. Wojcicki, *ibid.*, **4**, 857 (1965).

(9) See, for example, J. L. Burmeister and L. E. Williams, *ibid.*, **5**, 1113 (1966).

(10) J. L. Burmeister and H. J. Gysling, *Inorg. Chim. Acta*, **1**, 100 (1967).

(11) J. L. Burmeister and H. J. Gysling, *Chem. Commun.*, 543 (1967).

powder was obtained in 97% yield. A crystalline sample can be obtained by dissolving the powder in a minimum volume of acetone–water (9:1 v/v) with slight warming and subsequent chilling in an ice bath.

Anal. Calcd for $BC_{37}H_{49}N_4PdSe$: C, 59.49; H, 6.63; N, 7.52. Found: C, 59.39; H, 6.72; N, 7.36.

[Pd(Et$_4$dien)NCSe][B(C$_6$H$_5$)$_4$]. A 7.00 × 10^{-3} *M* solution (36 ml) of freshly reprecipitated Se-bonded isomer dissolved in N,N-dimethylformamide–water (4:1 v/v) was stirred for 4 hr at 25°. The solution was then triple filtered through a fine sintered glass funnel to remove a slight amount of decomposition product, the filtrate passing into 500 ml of water. Filtration of the mixture yielded a yellow solid, which was washed with anhydrous ethyl ether and dried *in vacuo* for 3 hr, yield 77%.

Anal. Found: C, 59.52; H, 6.55.

[Pd(dien)SeCN][B(C$_6$H$_5$)$_4$]. A solution of 2.07 mmoles of silver nitrate in 5 ml of water was added, with vigorous stirring, to a suspension of 1.00 mmole of [Pd(dien)I]I, prepared according to the method of Basolo, *et al.*,[12] in 50 ml of water. A pale yellow precipitate formed immediately. The solution was maintained at a temperature of 50° for 45 min, with continued stirring, whereupon it was cooled to 0° and filtered. A solution of 1.08 mmoles of sodium selenocyanate in 5 ml of water at 0° was added to the straw yellow filtrate, resulting in the formation of an orange precipitate (most probably [Pd(dien)(SeCN)$_2$], wherein the diethylenetriamine is functioning as a bidentate ligand). The mixture was stirred for 30 min and then filtered into a solution of 1.00 mmole of sodium tetraphenylborate in 10 ml of water at 0°. A very heavy cream-colored precipitate formed immediately. The mixture was stirred for 1 hr, during which time the precipitate became more flocculent. The light yellow solid was isolated by filtration, washed with two 10-ml portions of water and 10 ml of ethyl ether, and dried *in vacuo* over P_4O_{10}, yield 71%.

Anal. Calcd for $BC_{29}H_{33}N_4PdSe$: C, 54.95; H, 5.25; N, 8.87. Found: C, 54.74; H, 5.38; N, 8.78.

[Pd(Et$_4$dien)Cl][B(C$_6$H$_5$)$_4$]. 1,1,7,7-Tetraethyldiethylenetriamine (2 ml) was added to a solution of 4.99 mmoles of $Na_2[PdCl_4]$ in 30 ml of water. The solution was warmed to 40°, cooled to room temperature, and then added to a solution of 5.00 mmoles of sodium tetraphenylborate in 20 ml of acetone. No precipitation took place. A light yellow solid formed upon the addition of water. It was isolated by filtration and recrystallized from a minimum volume of acetone–water (9:1 v/v). Light yellow needles were obtained in 84% yield.

Anal. Calcd for $BC_{36}ClH_{49}N_3Pd$: C, 63.94; H, 7.31; N, 6.22. Found: C, 64.08; H, 7.24; N, 6.09.

[Pd(Et$_4$dien)SCN][B(C$_6$H$_5$)$_4$]. Sodium thiocyanate (4.08 mmoles) was added to a suspension of 1.01 mmoles of palladium(II) chloride in 100 ml of acetone. A clear, blood red solution formed, with stirring, over a period of 2 hr, accompanied by the precipitation of sodium chloride. The mixture was filtered and the filtrate cooled to −10° in an ice–salt bath. As the filtrate was being stirred rapidly, 0.6 ml of 1,1,7,7-tetraethyldiethylenetriamine was added dropwise. The color of the solution changed to straw yellow within a few minutes, coincident with the appearance of a light precipitate, presumably sodium thiocyanate. The solution was filtered after being stirred for an additional 30 min, and to the filtrate was added a solution of 1.05 mmoles of sodium tetraphenylborate in acetone at −10°, resulting only in the further precipitation of sodium thiocyanate. After another 30-min stirring period, the mixture was filtered into 400 ml of ice water, yielding a light yellow precipitate. It was isolated by filtration, washed with two 15-ml portions each of water and anhydrous ethyl ether, and dried *in vacuo* over P_4O_{10}, yield 94%. The complex exhibits a strong, sharp C–N stretching band at 2113 cm^{-1}.

Anal. Calcd for $BC_{37}H_{49}N_4PdS$: C, 63.48; H, 7.07; N, 8.04. Found: C, 63.44; H, 6.94; N, 7.86.

[Pd(Et$_4$dien)NCS][B(C$_6$H$_5$)$_4$]. A 3.5 × 10^{-4} *M* solution (10 ml) of the S-bonded isomer in DMF was stirred for 3 hr at 25°. It was then filtered into 400 ml of ice water, yielding a heavy cream-colored precipitate. After the mixture was stirred for 10 min, the solid was isolated by filtration, washed with two 20-ml portions of anhydrous ethyl ether, and dried *in vacuo* over P_4O_{10}, yield 74%. The complex exhibits a more intense, broad C–N stretching band at 2088 cm^{-1}.

Anal. Found: C, 63.52; H, 7.11; N, 7.62.

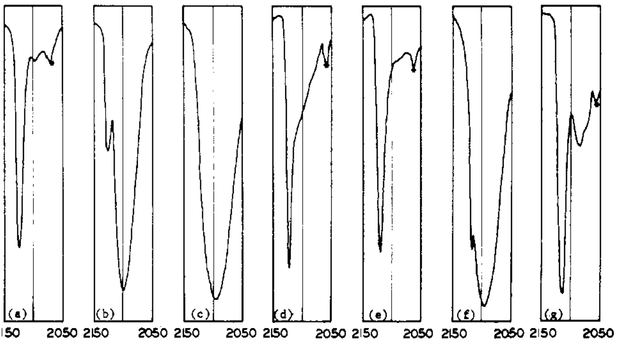

Figure 1. C–N stretching bands of (a) 8.00 × 10^{-2} *M* DMF solution, at 25°, of freshly prepared [Pd(Et$_4$dien)SeCN][B(C$_6$H$_5$)$_4$]; (b) same solution, 2 hr later; (c) solid [Pd(Et$_4$dien)NCSe][B(C$_6$H$_5$)$_4$], freshly isolated; (d) same sample, after 7 days at 40°; (e) solid [Pd(Et$_4$dien)SCN][B(C$_6$H$_5$)$_4$]; (f) solid [Pd(Et$_4$dien)NCS][B(C$_6$H$_5$)$_4$], freshly prepared (containing a small amount of the S-bonded isomer); (g) same sample, after 14 days at 40°. The vertical scale in spectra b, c, and f has been compressed in order to show the more intense N-bonded C–N stretching bands in their entirety. The weak peaks marked with an asterisk are due to small amounts of ionic XCN$^-$.

Analyses. Carbon, hydrogen, and nitrogen microanalyses were performed by the Alfred Bernhardt Microanalytical Laboratory, Mülheim, Germany, and Micro-Analysis, Inc., Wilmington, Del.

Melting Point and Conductance Measurements. Melting points (corrected) were determined by means of a Fisher-Johns melting point apparatus. Molar conductances, at 25°, of 10^{-3} *M* solutions of the complexes in N,N-dimethylformamide were measured with an Industrial Instruments, Inc. Model RC-16B2 conductivity bridge and a cell with platinized electrodes. The data obtained for the complexes are shown in Table I.

Table I. Melting Point and Conductivity Data for the Complexes

Complex	Mp, °C dec	Molar conductance, ohm^{-1} cm^2 mole^{-1}
[Pd(Et$_4$dien)SeCN][B(C$_6$H$_5$)$_4$]	120[a]	47.7
[Pd(Et$_4$dien)NCSe][B(C$_6$H$_5$)$_4$]	105	42.5
[Pd(dien)SeCN][B(C$_6$H$_5$)$_4$]	144	42.6
[Pd(Et$_4$dien)Cl][B(C$_6$H$_5$)$_4$]	163	43.2
[Pd(dien)I]I	235	72.5

[a] Darkening of sample noted at 86°.

Infrared Spectra. Infrared spectra, in the 4000–400-cm^{-1} range, of complexes held in Nujol or Fluorolube suspension between KBr plates were measured on a Perkin-Elmer Model 337 spectrophotometer. Low-frequency (700–200 cm^{-1}) spectra of Nujol mulls using KRS-5 plates were scanned on a Hitachi spectrophotometer. A Perkin-Elmer Model 421 spectrophotometer was used to record high-resolution solid state and solution spectra in the selenocyanate C–N stretching range (2200–2000 cm^{-1}). Matched 0.1-mm sodium chloride cells were employed for the solution measurements. The integrated absorption intensities, *A* (M^{-1} cm^{-2}), of the C–N stretching bands were determined by Ramsay's method of direct integration.[13] The infrared data for the selenocyanate complexes are given in Table II. Changes occurring in the C–N stretching bands of the isomers with time, both in solution and in the solid state, are shown in Figure 1. Band assignments were made by comparing the spectra of the selenocyanate complexes with each other and with those of the analogous halogeno complexes.[14]

Visible and Ultraviolet Spectra. Spectra in the visible and ultraviolet region were measured on a Cary Model 14 spectrophotometer

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(12) F. Basolo, H. B. Gray, and R. G. Pearson, *J. Am. Chem. Soc.*, **82**, 4200 (1960).

(13) D. A. Ramsay, *ibid.*, **74**, 72 (1952).

(14) Complete spectra (4000–400 cm^{-1}) of Nujol and Fluorolube mulls of both isomers have been deposited with the Documentation of Molecular Spectroscopy Index, London W.C.2, England.

Table II. Infrared Data for the Selenocyanate Complexes[i]

Complex	$[Pd(Et_4dien)SeCN]$-$[B(C_6H_5)_4]$	$[Pd(Et_4dien)NCSe]$-$[B(C_6H_5)_4]$	$[Pd(dien)SeCN]$-$[B(C_6H_5)_4]$
Pd–Se stretch, cm^{-1} [a]	282 w	. . .	. . .[b]
C–Se stretch, ν_1 (SeCN), cm^{-1} [a]	533 w	618[c]	538 w
NCSe bend, ν_2 (SeCN), cm^{-1} [a]	404 w	. . .[d]	. . .[b]
C–N stretch, ν_3 (SeCN), cm^{-1}	2121[a] s, sp 2125[e]	2085[a] s, br 2089[e]	2118[a] s, sp 2127[e]
Integrated intensity of ν_3, $A \times 10^{-4}$, M^{-1} cm^{-2} [e]	0.63[f]	6.6[g]	0.85[h]

[a] Nujol mull. [b] Not determined. [c] Assigned on the basis of a very pronounced broadening and intensification of one of the three tetraphenylborate bands in the 630–600-cm^{-1} region as the Se→N-bonded isomerization proceeds. [d] Obscured by amine or tetraphenylborate bands. [e] Acetone solutions. [f] 8.03×10^{-2} *M*. [g] 4.22×10^{-2} *M*. [h] 8.24×10^{-2} *M*. [i] Abbreviations: w, weak; s, strong; sp, sharp; br, broad.

Table III. Kinetic Data for the Isomerization of $[Pd(Et_4dien)SeCN]^+$ in Various Solvents at 20°

Solvent	10^4k, sec^{-1}
DMF-water (4:1)	1.1
DMF	1.0
Acetonitrile	0.76
Acetone	0.32

using 1-cm quartz cells. Thermostated sample and reference compartments were employed for the kinetic measurements. The rates of isomerization were determined by following the changes in optical density at 23.5 kK of solutions initially containing the Se-bonded isomer. The changes which occur in the absorption spectrum of a DMF-water solution of the Se-bonded isomer with time are shown in Figure 2. First-order kinetic plots for the linkage isomerizations in various solvents are shown in Figure 3. The corresponding rate constants are given in Table III.

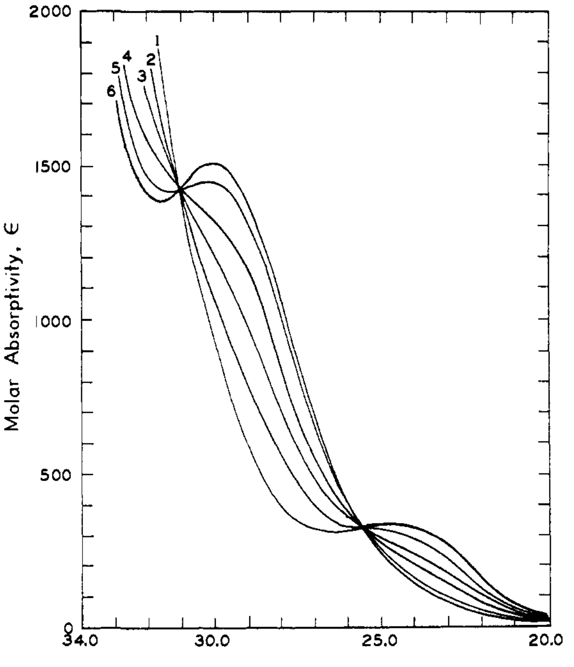
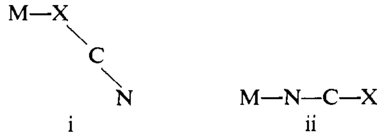


Figure 2. Changes in the absorption spectrum of a 4.00×10^{-4} *M* DMF-water (4:1) solution of $[Pd(Et_4dien)SeCN][B(C_6H_5)_4]$ at 25°: (1) after 2.5 min; (2) 32 min; (3) 1.2 hr; (4) 2 hr; (5) 3.7 hr; (6) 11.5 hr (isomerization to N-bonded isomer complete).

Discussion

Se→N-Bonded Isomerization. The synthesis of the selenocyanate linkage isomers was prompted by an analogous synthesis of thiocyanate linkage isomers.[15] Although no X-ray structural data are available, it was assumed that the steric requirements of the selenocyanate ion would parallel those known[5] to be exhibited by the thiocyanate ion, *i.e.*, nonlinear (i) *vs.* linear (ii) (or nearly so) linkages. The larger size of the selenium atom was expected to enhance the tendency for M–NCSe bond formation in sterically crowded environments. Molecular models (Fisher–Hirschfelder–Taylor) clearly show that a Pd–NCSe linkage is sterically favored for the remaining selenocyanate group (even if the Pd–SeCN linkage were linear) when 1,1,7,7-tetraethyldiethylenetriamine is substituted into the coordination sphere of $[Pd(SeCN)_4]^{2-}$. Conversely, no steric hindrance to a Pd–SeCN bond is observed when diethylenetriamine is used.



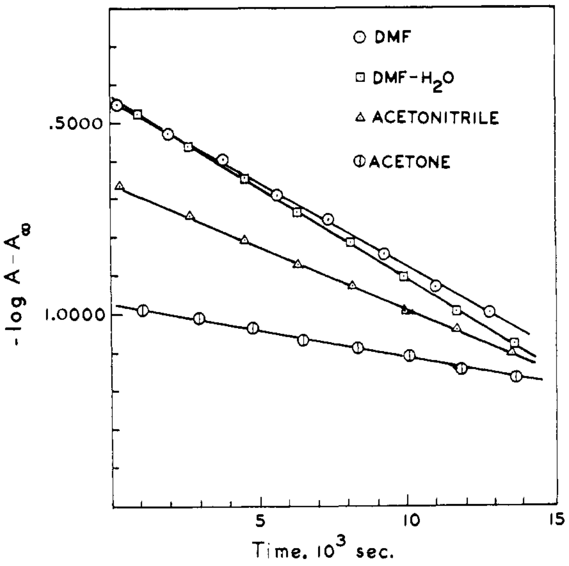


Figure 3. First-order kinetic plots for the linkage isomerization of $[Pd(Et_4dien)SeCN][B(C_6H_5)_4]$ in various solvents at 20°. (The DMF-water ratio was 4:1 by volume.)

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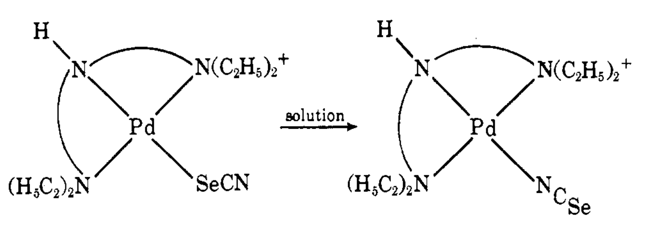
(15) F. Basolo, W. H. Baddley, and K. J. Weidenbaum, *J. Am. Chem. Soc.*, **88**, 1576 (1966).

In agreement with these predictions, the initial kinetic product of the reaction, at low temperatures, between Et_4dien and $[Pd(SeCN)_4]^{2-}$ exhibits an infrared spectrum (Table II) which is characteristic[9] of a complex containing an Se-bonded selenocyanate group (decreased C–Se and NCSe bending frequencies and an increased C–N stretching frequency of lower intensity, all relative to the corresponding bands in the spectrum of an ionic selenocyanate). When the Se-bonded isomer is dissolved in a variety of solvents (DMF–water, DMF, acetonitrile, acetone), the C–N stretching band at 2125 cm^{-1} gradually decreases in intensity, coincident (Figure 1b) with the growth of a new band at 2089 cm^{-1}. The new band eventually exhibits an integrated absorption intensity which is an order of magnitude larger than that of the C–N stretching band of the Se-bonded isomer. Likewise, the spectrum of the solid exhibits a new C–Se stretching frequency (Table II) which is higher than that of the free ion (558 cm^{-1}), the band at 533 cm^{-1} having disappeared. The infrared spectral changes are completely in accord[9] with what would be anticipated for an Se→N-bonded linkage isomerization.



In the visible–ultraviolet region of the spectrum, the shift (Figure 2) of the lowest energy absorption maximum from 24.5 kK (ϵ 341 M^{-1} cm^{-1}) to 30.1 kK (ϵ 1500 M^{-1} cm^{-1}) is in agreement with the higher ligand field strength exhibited[9] by the selenocyanate ion when it is N-bonded. The presence of the well-defined isosbestic points at 25.5 and 30.9 kK indicates that the isomerization proceeds smoothly, with no side reactions, such as aquation or opening of a chelate ring. The observed decrease of the first-order rate constants for the isomerization as the dielectric constant of the solvent is decreased (Figure 3 and Table III) is in accord with a dissociative process. As predicted by the molecular model, the diethylenetriamine complex contains an Se-bonded selenocyanate group (see Table II) which was found to be stable with respect to isomerization, both in solution and in the solid state. All of the complexes exhibit molar conductances in DMF at 25° (Table I) which are in the range observed[16] for 1:1 electrolytes.

N→Se-Bonded Isomerization. The preceding arguments notwithstanding, the greater stability of the N-bonded $[Pd(Et_4dien)NCSe][B(C_6H_5)_4]$ complex was *not* found to extend to the solid state. The N-bonded isomer, once isolated as a solid, slowly *reisomerizes* (Figures 1c and d) to the Se-bonded form. This unexpected result appeared to be best rationalized in terms of the different crystal-packing requirements of the N- and Se-bonded forms, the steric interaction of the selenium atoms with the tetraphenylborate ions evidently being more important in the solid state than their interaction with the ethyl groups of the amine. Two tests of this hypothesis were apparent: the analogous thiocyanate isomers might be expected to behave in a similar fashion if the counterion used was tetraphenylborate but not if a relatively small counterion was employed.

Accordingly, $[Pd(Et_4dien)NCS][B(C_6H_5)_4]$ was prepared and its solid-state infrared spectrum monitored as a function of time. As shown in Figures 1e–g, the predicted N→S-bonded reisomerization was indeed found to take place, but, as might be expected due to the smaller size of the sulfur atom, at a slower rate. The previously prepared[15] $[Pd(Et_4dien)NCS]SCN$ complex, however, was found to be stable with respect to isomerization in the solid state. Indeed, the "normal" S→N-bonded isomerization takes place both in solution and in the solid.[15] $[Pd(Et_4dien)SCN][PF_6]$ also does not isomerize in the solid state, and it is reasonable to expect that the N-bonded form, once isolated, will reisomerize. This raises the question as to what is the critical size of the counterion necessary to cause reisomerization, a problem which is currently being investigated. We are also exploring the possibility of using counterions to alter the bonding modes of other ambidentate ligands which exhibit steric sensitivity, such as the nitrite ion.[17, 18]

The value of using large counterions of equal but opposite charge to stabilize and isolate metal complex ions has recently been documented.[19] The cases discussed above serve to exemplify a reverse effect and represent the first observations of the dependence of the bonding mode of an ambidentate ligand on the nature of a noncoordinated group. They also serve to reemphasize the danger of assuming that the relative stability of a species in solution infers, *a priori*, that it will exhibit comparable stability in the solid state.

The results of current temperature-dependent kinetic studies of both the solution and solid-state isomerizations and the substitution reactions of the isomers will be reported in due course.

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(16) J. V. Quagliano, J. Fujita, G. Franz, D. J. Phillips, J. A. Walmsley, and S. Y. Tyree, *J. Am. Chem. Soc.*, **83**, 3770 (1961).

(17) D. M. L. Goodgame and M. A. Hitchman, *Inorg. Chem.*, **3**, 1389 (1964); **5**, 1303 (1966).

(18) L. El-Sayed and R. O. Ragsdale, *ibid.*, **6**, 1640 (1967).

(19) F. Basolo, *Coord. Chem. Rev.*, **3**, 213 (1968).