

## Synthesis of Inorganic Linkage Isomers of the Selenocyanate Ion

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THE first example of linkage isomerism in metal complexes, that involving the nitrite ion, was reported by Jørgensen.<sup>1</sup> Subsequently, first syntheses of linkage isomers of the thiocyanate and cyanide ions were reported by, respectively, Burmeister and Basolo<sup>2</sup> and Shriver, *et al.*<sup>3</sup> We now report the synthesis of the linkage isomeric forms of  $[\text{Pd}(\text{Et}_4\text{dien})\text{X}]\text{B}(\text{C}_6\text{H}_5)_4$ , where  $\text{Et}_4\text{dien} = \text{NNN}'\text{N}'\text{-tetraethyl-diethylenetriamine}$  and  $\text{X} = \cdot\text{SeCN}, \cdot\text{NCS}$ .

The procedure was suggested by that employed by Basolo, *et al.*,<sup>4</sup> to prepare the analogous thiocyanate complexes, and utilizes the greater steric requirements of *Se*-bonded selenocyanate as the driving force behind the isomerization. Tetra-selenocyanatopalladate(II) was prepared *in situ* by stirring palladium dichloride (1 mmole) and potassium selenocyanate (4 mmoles) in methanol for 0.5 hr. The solution was filtered and the filtrate cooled to  $-78^\circ$  in a Dry Ice-acetone bath. To the filtrate was added *NNN}'\text{N}'\text{-tetraethyl-diethylenetriamine}*. A heavy brown precipitate {presumably  $[\text{Pd}(\text{Et}_4\text{dien})(\text{SeCN})_2]$ , in which the amine is functioning as a bidentate ligand} formed in about 1 min. The solution was stirred at  $-78^\circ$  for 10 min., then removed from the bath and stirred for 5 min., after which time most of the precipitate had re-dissolved. The solution was filtered to remove a small amount of black decomposition product and the filtrate cooled in an ice-salt bath. The addition of sodium tetraphenylborate (1 mmole) resulted in the slow precipitation of the bright yellow *Se*-bonded isomer, which was isolated by filtration, washed with cold water, ethanol, and ether and dried *in vacuo* over calcium chloride (yield: 78% of theory).

Support for the formulation of the product as  $[\text{Pd}(\text{C}_{12}\text{H}_{29}\text{N}_3)\text{SeCN}]\text{BPh}_4$  is found in the micro-analytical results, molar conductivity ( $64.8 \text{ ohm}^{-1}$

$\text{cm.}^{-2} \text{ mole}^{-1}$ ,  $10^{-3}\text{M}$  in dimethylformamide at  $25^\circ$ ), and infrared spectrum (Nujol mull: sharp C-N stretching band at  $2123 \text{ cm.}^{-1}$ , C-Se stretching band at  $532 \text{ cm.}^{-1}$ ;  $5 \times 10^{-3}\text{M}$ -acetone solution: C-N stretch at  $2125 \text{ cm.}^{-1}$ , integrated absorption intensity =  $0.77 \times 10^4 \text{ mole}^{-1} \text{ cm.}^{-2}$ ). The infrared data are in agreement with the general trends observed<sup>5,6</sup> for *Se*-bonded selenocyanate complexes.

Dissolution of the *Se*-bonded isomer in dimethylformamide at room temperature results in its complete isomerization to the *N*-bonded form over a period of *ca.* 5 hr. The latter was precipitated from the solution as a pale yellow powder by the addition of ether. The observed spectral changes are in accord with the suggested isomerization. In the infrared region, the C-N stretching band at  $2125 \text{ cm.}^{-1}$  decreases in intensity and eventually disappears, coincident with the appearance and increase in intensity of a broad C-N band at  $2090 \text{ cm.}^{-1}$  (integrated absorption intensity =  $8.60 \times 10^4 \text{ mole}^{-1} \text{ cm.}^{-2}$ ). The C-Se stretching band at  $532 \text{ cm.}^{-1}$  disappears, concurrent with the pronounced broadening of a tetraphenylborate absorption band at  $618 \text{ cm.}^{-1}$ . In the visible-ultraviolet region, the longest-wavelength absorption maximum, at  $410 \text{ m}\mu$  (shoulder), shifts to  $337 \text{ m}\mu$ , with well defined isobestic points at  $395$  and  $328 \text{ m}\mu$ , the presence of the latter indicating that no side-reactions are taking place. Qualitatively, the rate of isomerization was observed to decrease as the dielectric constant of the solvent was decreased (*e.g.*, dimethylformamide : acetonitrile : methanol). No isomerization was observed to take place in the solid state at room temperature, and heating a sample of the complex over benzene resulted only in its decomposition. All the preceding observations are analogous to those reported by Basolo, *et al.*,<sup>4</sup> for the corresponding  $\text{Pd-SCN} \rightarrow \text{Pd-NCS}$

isomerization, for which they suggested a dissociative, intermolecular process to be operative. Quantitative rate studies are now in progress, and will be reported presently.

This research was supported by the University of Delaware Research Foundation.

(Received, April 27th, 1967; Com. 399.)

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