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Synthesis and Characterization of Linkage Isomers of Dithiocyanato(5-nitro-1, 10-phenanthroline)palladium(II); Observation of an Unusual N- to S-bonded Linkage Isomerization in the Solid State*

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Since the first examples of inorganic linkage isomers of the thiocyanate ion were isolated in 1963 [1], the number of known thiocyanate linkage isomeric pairs has increased at an impressive rate (14 in 1968 [2], 61 in 1976 [3]). Virtually all of the linkage isomerizations that have been studied in the solid state have been observed to involve S- to N-bonded rearrangements [4]. Notable exceptions include the N- to S-bonded linkage isomerization reactions of *mer*-$[Rh(P(CH_3)_2C_6H_5)_3Cl_2(NCS)]$ [5] and [Pd(N,N′-tetraethyldiethylenetriamine) NCS] $B(C_6H_5)_4$ [6]. We now wish to report the synthesis and characterization of linkage isomers of [Pd(5-nitro-1,10-phenanthroline)(thiocyanate)$_2$], including the observation of a rate N- to S-bonded isomerization reaction in the solid state.

Experimental

Diisothiocyanato(5-nitro-1,10-phenanthroline)palladium(II), [Pd(5-nitrophen)(NCS)$_2$]

The preparation of this complex has been reported by Bertini and Sabatini [7]. After several unsuccessful attempts to prepare the pure linkage isomer by their method, the following preparative technique was elucidated and used successfully. $K_2[Pd(SCN)_4]$ (0.9311 g, 2.233 mmol) and 5-nitro-1, 10-phenanthroline (0.5029 g, 2.233 mmol) were dissolved separately in 30 ml and 45 ml of N,N-dimethylformamide, respectively. The solution containing the ligand was added slowly, with stirring, to the metal-containing solution. The resulting red solution was stirred for about one hour at room temperature. This solution was then poured into approximately fifteen times, by volume, as much ice cold ethanol, and stirred for forty-five minutes. The yellow-colored solid was isolated by filtration and washed with small portions of cold ethanol and room temperature diethyl ether. The solid was dried under vacuum. The yield was 60% and the decomposition temperature was 248–250 °C. The infrared spectrum (Nujol mull) exhibited a peak in the ν_{CN} region at 2093 cm^{-1} (s, br) with a weak shoulder at 2120 cm^{-1}. The reported value for the ν_{CN} stretching frequency of this complex is 2090 cm^{-1} (s, br), with a shoulder at 2120 cm^{-1}. *Anal.* Calcd for $PdC_{14}H_7N_5O_2S_2$: Pd, 23.76; C, 37.55; H, 1.58; N, 15.64. Found: Pd, 23.11; C, 37.01; H, 1.53; N, 15.71.

Dithiocyanato(5-nitro-1,10-phenanthroline)palladium(II), [Pd(5-nitrophen)(SCN)$_2$]

The compound was prepared by dissolving $K_2[Pd(SCN)_4]$ (1.0425 g, 2.500 mmol) in 153 ml of 98% ethanol and heating the solution to approximately 60 °C. The ligand (0.5635 g, 2.502 mmol) was dissolved in 100 ml of absolute ethanol and added slowly, dropwise, with stirring to the metal-containing solution. The formation of an orange solid began less than ten minutes after the initial addition of ligand. The orange solid was isolated by filtration, and washed with small portions of water, ethanol and diethyl ether, in that order The complex was air dried, and gave a single band in the ν_{CN} region of the infrared spectrum (Nujol mull) at 2122 cm^{-1} (s, sp). The yield was 96% and the complex decomposed at 248–250 °C. *Anal.* Calcd for $PdC_{14}H_7N_5O_2S_2$: Pd, 23.76; C, 37.55; H, 1.58; S, 14.32. Found: Pd, 23.98; C, 37.78; H, 1.58; S, 14.18.

Physical Measurements

Infrared spectra were measured using a Perkin-Elmer 180 spectrophotometer. Nitrogen-14 nuclear quadrupole resonance data were obtained at the University of Illinois using the adiabatic demagnetization in the laboratory frame double resonance level crossing technique described previously [8, 9].

Results and Discussion

The [Pd(5-nitrophen)(NCS)$_2$] complex was first prepared by Bertini and Sabatini [7]. Their conclusion that the thiocyanates were N-bonded was based on the appearance (strong and broad) and frequency (2090 cm^{-1}) of the main thiocyanate ν_{CN} stretching bond. The preference for the di-N-bound isomer in the 5-nitro-1, 10-phenanthroline complex is diametrically opposite to that observed in the correspond-

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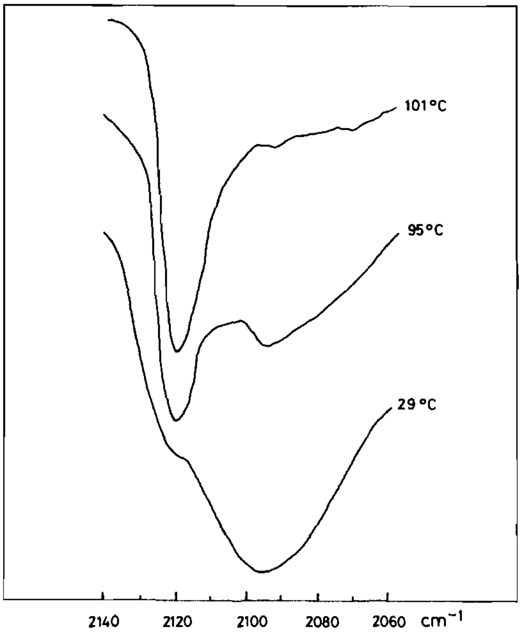

Fig. 1. Changes in the ν_{CN} stretching band accompanying the N- to S-bonded linkage isomerization, upon heating, of [Pd(5-nitrophen)(NCS)$_2$].

ing 1,10-phenanthroline complex, for which only the di-S-bound isomer has been reported [7, 10]. The formation of the di-N-bound isomer was claimed [7] to be due to the inductive and mesomeric effects of the nitro group, which increases the ability of the ligand to form π-bonds with the metal.

In a more recent study, Miezis [11] described the 5-nitrophen complex as containing a mono-S- and a mono-N-bound thiocyanate. He reported the formation of a complex which exhibited very similar ν_{CN} infrared bands [2120 cm^{-1} (sp) and 2090 cm^{-1} (br)] to those reported by Bertini and Sabatini [7], except that the 2120 cm^{-1} band was much stronger in Miezis' spectrum. Miezis prepared samples of [Pd(5-nitrophen)(SCN)(NCS)] at –20 °C and +25 °C and also warmed them to 130 °C with no observable differences in their infrared spectra. He reported the use of varying pressures when preparing KBr disks with no change in the spectra. Miezis also attributed the partial desire for N-bonding to increased π-bond formation.

Upon preparing this complex, results were obtained which differ from those reported earlier. If the complex is prepared in DMF at room temperature and isolated by pouring the DMF solution into cold (~2–3 °C) ethanol, the yellow di-N-bound isomer is formed. This isomer exhibits a single infrared peak in the ν_{CN} region at 2093 cm^{-1} (s, br), with a weak shoulder, due to a trace of the di-S-bound isomer, at 2120 cm^{-1}. If the complex is prepared in ethanol at 60 °C, an orange complex which exhibits a single infrared peak in the ν_{CN} region at 2122 cm^{-1} (s, sp) is isolated. This is believed to be the di-S-bound isomer. This isomer was studied using ^{14}N-nqr and gave a coupling constant (e^{2}Qq/h) of 3224 khz, which, as pointed out in an earlier paper [12], is indicative of S-bonding. The ν_+, ν_-, and ν_o frequencies were observed at 2692, 2144 (by difference), and 548 khz, respectively, and the asymmetry parameter (η) was found to be 0.340. Unfortunately, the di-N-bound isomer did not yield any ^{14}N-nqr data.

The thermal stability of the linkage isomers was determined by slowly heating the two isomers, separately, while in the infrared spectrometer and observing the ν_{CN} region (2300 cm^{-1} to 2000 cm^{-1}) for changes. No change was noted for the S-bound species, even at a temperature of 160 °C. The N-bound complex, however, showed an almost quantitative change from N-bound (ν_{CN} 2093 cm^{-1} s, br) to S-bound (ν_{CN} 2122 cm^{-1} s, sp) at approximately 95–100 °C (see Fig. 1). Upon cooling the sample, the complex retained its ν_{CN} band at 2122 cm^{-1} (s, sp), and, even when cooled in liquid nitrogen, no reisomerization to the N-bonded complex was noted.

The rationale for these observed phenomena is believed to be due to the unusual electronic properties of the 5-nitrophen ligand. The withdrawal of π-electrons from the aromatic nitrogens assumes π-bonding of the nitro group to the ring. If, upon heating the sample, the π-bonding between the ring and the nitro group was destroyed, the preference for N-bonding would also be eliminated. This disruption of the π-bonding ability of the nitro group could occur when heated, if the nitro group began rotating like a propellor. This type of phenomenon has been used by Bertini and Sabatini [7] to explain why the [Pd(4,7-diphenyl-1,10-phenanthroline)(SCN)$_2$] complex contains S-bonded thiocyanates when prepared at room temperature, but contains only N-bonded thiocyanates when prepared at 0 °C. (The authors did not state whether or not either of the two isomers undergoes linkage isomerization when heated.)

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