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1,2-Dithiocyanoethane Complexes of Palladium and Niobium

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In the investigation of the synthesis of metal complexes of organic thiocyanates and their coordinative properties in the context of Pearson's hard/soft acid/base concept, we have prepared decachloro-μ-(1,2-dithiocyanoethane)diniobium(V) and dichloro(1,2-dithiocyanoethane)palladium(II). Organic thiocyanates are ambidentate ligands because they can complex a metal through either their nitrogen or their sulfur atom. The distinction between the nitrogen-bonding and sulfur-bonding modes in these complexes is usually made through ir spectroscopy. For example, it has been found that the CN stretching frequency for N-bonded complexes is at least 20 cm^{-1} greater than for the neat ligand and is nearly unchanged for the S-bonded complexes [1–8]. In this study we examine the ir spectra of the products of the reactions between Nb_2Cl_{10} and $Pd(C_6H_5CN)_2Cl_2$ with $C_2H_4(SCN)_2$ (abbreviated ETC) in an attempt to ascertain the bonding mode and to speculate on the structures of the products.

Experimental

1,2-Dithiocyanoethane was purified by recrystallisation from ethanol. Anhydrous $PdCl_2$ and Nb_2O_5 were used without further purification. Carbon tetrachloride was dried by refluxing over P_2O_5 followed by distillation. A Perkin–Elmer 621 grating spectrophotometer with CsI and NaCl cells was used to record the spectra of Nujol mulls of the products and CsCl pellets of ETC. Elemental analyses were done by Chemalytics, Inc., Tempe, Arizona.

Preparation of Nb_2Cl_{10}

The method of Austin and Tyree was used which consisted in refluxing hexachlorobutadiene-1,3 saturated with chlorine over Nb_2O_5 [9]. The lemon-yellow crystals obtained were washed with CCl_4 in a dry box that contained a dry nitrogen atmosphere (*vide infra*). The yield was 77%.

Preparation of Decachloro-μ-(1,2-dithiocyanoethane)-diniobium(V)

A dry box was used which initially had been purged with dry N_2 for about one hour. The atmosphere inside the dry box was kept dry via a recirculating system in which water and volatile liquids were condensed in traps located outside the dry box cooled by dry ice–acetone mixture. The system is similar to that of Ashby and Schwartz [10]. Niobium (V) chloride (0.50 g) was dissolved in 20 ml of boiling CCl_4. The solution was filtered and the filtrate was heated to redissolve crystallised Nb_2Cl_{10}. To the hot filtrate was added dropwise 10 ml of a hot solution of ETC (0.14 g) in CCl_4. The yellow precipitate that formed was filtered, washed with hot CCl_4, and dried by suction. The yield was 90%. A sample in a sealed capillary tube melted at 181 °C, becoming dark-colored. The product was stored in ampules sealed under nitrogen. Analysis expected for $Nb_2Cl_{10} \cdot C_2H_4(SCN)_2$: 7.02% C, 0.59% H, 4.09% N, 9.37% S, 51.80% Cl. Analysis found: 7.24% C, 0.74% H, 4.19% N, 9.45% S, 51.65% Cl.

Preparation of Trans-$Pd(C_6H_5CN)_2Cl_2$

The method of Kharasch *et al.* was used [11]. A 78% yield of yellow crystals was obtained from the reaction between anhydrous $PdCl_2$ and distilled benzonitrile. The CN stretching frequency for the product (2286 cm^{-1}) and for neat C_6H_5CN (2232 cm^{-1}) indicates N-coordination of the nitrile to the palladium atom in the product. Other workers have reported similar increases in ν(CN) for nitrile complexes [12–14].

Preparation of Dichloro(1,2-dithiocyanoethane)palladium(II)

ETC (0.10 g) was dissolved in 10 ml of reagent-grade $CHCl_3$ and to this solution 5 ml of $CHCl_3$ containing 0.25 g of $Pd(C_6H_5CN)_2Cl_2$ was added through a glass-fritted funnel. The mixture was stirred for 16 hours. The beige–yellow precipitate was washed with $CHCl_3$ and dried *in vacuo* for one hour (81% yield). The product melted and became dark at 172–178 °C. Analysis expected for $PdCl_2 \cdot C_2H_4(SCN)_2$: 14.94% C, 1.25% H, 8.71% N, 19.95% S, 22.07% Cl, 33.08% Pd. Analysis found: 14.60% C, 1.30% H, 7.78% N, 18.31% S, 23.35% Cl, 32.12% Pd.

Results and Discussion

Significant ir bands for ETC and ETC complexes are listed in Table I. Two aspects of the structures of these complexes must be considered, *viz.*, the bonding mode and the ligand conformation. It is evident from Table I that ETC is attached to the

TABLE I. Significant Infrared Bands (cm^{-1}).

Neat ETC		Solid Complexes		Assignment
Solid (*trans*)[a]	$CHCl_3$ solution (*trans, gauche*)[b]	$PdCl_2 \cdot ETC$[a]	$Nb_2Cl_{10} \cdot ETC$[a]	
2155	2170 (*trans*)	2230	2200	CN stretch
1420	1423 (*trans*)	1417	1423	CH_2 bend
	1419 (*gauche*)			
1220	1215 (*trans*)	1242	1222	CH_2 wag
	1285 (*gauche*)			
1145	1140 (*trans*)	1153	1133	CH_2 twist
	1110 (*gauche*)			
–	918 (*gauche*)	–	–	CH_2 rock
–	845 (*gauche*)	–	–	CH_2 rock
750	–	738	748	CH_2 rock
680	677 (*trans*)			CS stretch
660	660 (*trans*)	664	655	CS stretch

[a] This work. Our values agree closely with those cited in ref. 4. [b] Ref. 4.

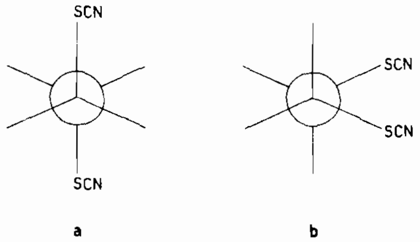

Figure 1. Conformations for $C_2H_4(SCN)_2$. View along C–C bond. (a) *trans*, (b) *gauche*.

palladium and niobium atoms through the nitrogen atom rather than the sulfur atom. The ν(CS) values for the complexes and the neat ligand are similar and ν(CN) is increased by 75 cm^{-1} for the palladium complex and by 45 cm^{-1} for the niobium complex from that for ETC. The N-bonding to niobium is expected on the grounds that $NbCl_5$ is a hard acid and the nitrogen end of the NCS moiety is a hard base. The result for the palladium complex is, however, surprising because $PdCl_2$ is expected to be a soft acid and is therefore considered more likely to bind the sulfur (soft base) end of the NCS moiety. The preference of the palladium for nitrogen may have a kinetic basis since we have also observed a decrease from strong to weak absorption at 2230 cm^{-1} and a concomitant formation of a strong absorption near 2165 cm^{-1} (characteristic of sulfur-bonding to metal) for N-bonded $PdCl_2 \cdot ETC$ that was aged for 40 days at room temperature.

The absence of bands in the 800–1000 cm^{-1} region for both complexes and the correlation of the several CH_2 absorptions (Table I) for the complexes, ETC dissolved in $CHCl_3$, and solid ETC established the conformation of ETC in the complexes to be *trans* instead of *gauche* (Fig. 1).

Finally, we speculate that the *trans* conformer of the ETC molecule connects two $NbCl_5$ units so that both Nb atoms are octahedral and $Nb_2Cl_{10} \cdot ETC$ is a simple molecule. ETC similarly bridges two $PdCl_2$ units so that a polymer with the repeating unit $PdCl_2 \cdot ETC$ is possible. Our observation that $PdCl_2 \cdot$ ETC is insoluble in the common organic solvents (acetone, benzene, chloroform) supports the proposed polymeric nature of the complex.

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