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# Phosphorus, Sulfur, and Silicon and the Related Elements

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# THE CHEMISTRY OF (ECN)<sub>2</sub> (E = S, Se) AND RELATED COMPOUNDS

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# THE CHEMISTRY OF $(ECN)_2$ (E = S, Se)AND RELATED COMPOUNDS

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The psuedohalogens (ECN) $_2$  (E = S, Se) have been prepared by reaction of AgNCS with bromine and AgNCSe with iodine respectively. (SCN) $_2$  spontaneously polymerises to give polythiocyanogen a polymer of unknown structure with empirical formula (SCN) $_x$ . A series of late transition metal complexes bearing the ambidentate psuedohalide ligands (ECN) (E = S, Se) have been synthesised. In addition we have prepared a series of late transition metal complexes of the cyanodithioimidocarbonate ion  $[C_2N_2S_2]^{2-}$  and the first transition metal complexes of the cyanodiselenocarbonate ion  $[C_2N_2Se_2]^{2-}$ .

Keywords: Ambidentate; bidentate; complexes; crystal structure; pseudohalogens

The psuedohalogens are an interesting class of compound, which are rather understudied compared to simple halogen systems. Thiocyanogen (SCN)<sub>2</sub> was first prepared by Soderback in 1919. Thiocyanogen is thermally unstable and spontaneously polymerizes to form the insoluble brick red polythiocyanogen when allowed to warm to room temperature. Very little is known about polythiocyanogen except that it has the empirical formula (SCN)<sub>x</sub>. The selenium analogue selenocyanogen (SeCN)<sub>2</sub> was first synthesized six years later in 1925 by Birckenbach and Kellermann. We report here the synthesis and characterization of (ECN)<sub>2</sub> (E = S, Se) and some related transition metal complexes.

We are grateful to the EPSRC for funding and Johnson Mathey PLC for the loan of precious metals.

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**FIGURE 1** Disulfide bridged structure of (SCN)<sub>2</sub>.

### RESULTS AND DISCUSSION

Thiocyanogen (SCN)<sub>2</sub> was prepared in good yield by the reaction of two equivalents of silver thiocyanate with bromine at  $-20^{\circ}$ C (Scheme 1).

$$2AgSCN + Br_2 \longrightarrow (SCN)_2 + 2AgBr$$

#### **SCHEME 1**

Single peaks were observed in both the <sup>13</sup>C and <sup>14</sup>N NMR specta and the IR and Raman spectra were concurrent with that previously recorded.<sup>3</sup> All of this data agrees with the long time proposed disulfide bridged structure (Figure 1).

On allowing thiocyanogen to warm to room temperature spontaneous polymerization to give polythiocyanogen was noted.

Selenocyanogen was prepared in an analogous fashion to thiocyanogen using silver selenocyanate and iodine (Scheme 2).

$$2AgSeCN + I_2 \longrightarrow (SeCN)_2 + 2AgI$$

#### **SCHEME 2**

Single resonances were observed in the  $^{13}\mathrm{C}$   $^{14}\mathrm{N}$  and  $^{77}\mathrm{Se}$  NMR spectra. The Raman data was very similar to that previously recorded.<sup>4</sup>

A series of transition metal complexes of the type  $[Pt(ECN)(R)(PR_3)_2]$  (E = S, Se and R = Me, Ph) have been prepared as shown in Scheme 3.

$$R_3P$$
  $Pt$  + AgECN  $\longrightarrow$   $R_3P$   $Pt$   $R_3P$   $ECN$ 

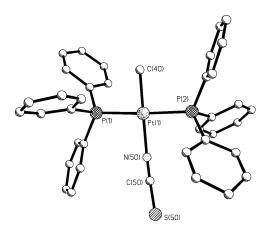
#### **SCHEME 3**

Selected examples were chosen for single crystal diffraction studies (Figure 2).

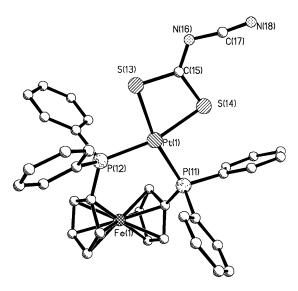
A series of transition metal complexes of the cyanodithioimidocarbonate  $[C_2N_2S_2]^{2-}$  ligand have been prepared by the reaction of the dipotassium salt with transition metal precursors (Scheme 4).

$$R_3P$$
 $Pt$ 
 $+$ 
 $K^+-S$ 
 $N$ 
 $-KCl$ 
 $R_3P$ 
 $Pt$ 
 $N$ 
 $N$ 

## **SCHEME 4**



 $\textbf{FIGURE 2} \quad \text{X-ray crystal structure of } [Pt(NCS)(Me)(PPh_3)_2].$ 



 $\textbf{FIGURE 3} \quad X\text{-ray crystal structure of } [Pt(C_2N_2S_2)(dppf)].$ 

All the complexes were prepared in good yield and fully characterized. Selected examples were chosen for single crystal x-ray diffraction studies (Figure 3).

An analogous series of complexes has been prepared bearing the  $[C_2N_2Se_2]^{2-}$  ligand.

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