Mass Spectroscopic Detection of $Ni(CS)_4$

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Summary I.r. evidence is presented for the production of a nickel thiocarbonyl species in argon matrices; the species volatilizes in the mass spectrometer to yield a parent ion consistent with the formation of $Ni(CS)_4$.

Although the synthesis and properties of several transition-metal thiocarbonyl complexes have been reported[1,2] all of them contain other ligands in the co-ordination sphere. Evidence is presented here for the formation of $Ni(CS)_4$.

Nickel metal, vaporized from a resistance heated tungsten wire basket, and a mixture of CS and argon were codeposited on a CsI window at 10 K. The CS was prepared by passing a 0·5—8 vol % mixture of CS_2 and argon through a microwave discharge just prior to deposition. Following deposition times of 1—16 h, i.r. absorptions were observed that were attributable to matrix isolated CS_2, SO_2, CS, H_2O, and CO_2. In addition there was a sharp absorption at 1305 cm^{-1} which appeared only when Ni and CS were codeposited but not when either was deposited by itself. This band lies within the range reported for other thiocarbonyls (1263—1381 cm^{-1})[1a,2] and it strongly suggests the presence of a nickel thiocarbonyl species. As in most other thiocarbonyls, this feature lies to higher frequencies than the stretching frequency of diatomic CS. This contrasts with the shift of the CO stretching vibration to lower frequencies observed in metal carbonyls. Attempts to enhance the intensity of the 1305 cm^{-1} band by controlled diffusion of the matrix were prevented by the fact that the energetic reactions of the matrix isolated species invariably resulted in loss of the matrix. Immediately upon warming the matrix, the band at 1305 cm^{-1} rapidly decreased in intensity and an intense, broad absorption extending between 1200 and 500 cm^{-1} appeared. This process resulted in the formation of a black, amorphous, polymeric residue. In some cases visible emissions were observed during the diffusion and in one instance the polymerization produced an explosion which destroyed the outer optical windows.

The black residue remaining after warming yielded no soluble products when extracted with organic solvents of varying polarity. On the other hand, a mass spectrum of this substance showed two overlapping peaks at m/e 234 and 236, corresponding to those of the parent ion of $Ni(CS)_4$. Although the m.s. resolution did not afford quantitative intensities, the ratio of the two mass peaks was about 3 to 1 as expected from the natural abundance of ^{58}Ni and ^{60}Ni. These mass peaks were not present in the mass spectrum of the residue of either Ni or CS deposited alone. The mass spectrum was obtained only when the source temperature was above 200 °C. Subjecting the residue to vacuum sublimation at temperatures exceeding 200 °C produced no visible sublimate, however. One explanation of these results is that only small quantities of $Ni(CS)_4$ are formed which are thus detectable only by such sensitive techniques as mass and i.r. spectroscopy. The high mass spectrometer temperature necessary to detect $Ni(CS)_4$, however, suggests an unexpectedly low volatility and/or strong affinity of the product for the CS polymer. A more plausible possibility is *that the* nickel carbon monosulphide initially formed polymerizes on warming the matrix and is subsequently pyrolysed to $Ni(CS)_4$ in the mass spectrometer.

J.G.V. thanks the National Science Foundation for a grant in support of this work.

(*Received, 19th June* 1973; *Com.* 876.)

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