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Metal Atom Synthesis of Binary Carbon Disulfide–Nickel Complexes, $Ni(CS_2)_n$ (Where $n = 1–3$)

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Matrix reactions of Ni atoms with CS_2 are investigated at 10–12 K by infrared and UV–visible spectroscopy. Metal and ligand concentration studies and matrix warm-up experiments demonstrate that *three* mononuclear compounds can be generated under these conditions, their spectral data being best rationalized in terms of a binary $Ni(CS_2)_n$ formulation. By employing $^{12}CS_2/^{13}CS_2/Ar$ isotopic substitution techniques, the lowest stoichiometry product was established to be $Ni(CS_2)$. The remaining two complexes are deduced to be $Ni(CS_2)_2$ and $Ni(CS_2)_3$. The problem of providing a satisfactory structural and bonding picture for the interaction of the CS_2 moiety with the Ni atom even in the simplest complex $Ni(CS_2)$ proved to be a perplexing one, in that the available spectroscopic data could be rationalized in terms of any one of four different yet reasonable models.

Introduction

The interaction of CS_2 and transition metals is now a well-established phenomenon and many complexes have now been discovered which contain one or two coordinated CS_2 moieties.[1–3] Of chemical interest is the observation that CS_2 can be inserted into M–H, M–C, M–N, M–O, M–S, and M–halogen bonds[4,5] yielding a variety of interesting new products. These aspects of CS_2 chemistry have been recently reviewed.[5] In addition, the adsorption of CS_2 onto several transition metal surfaces has been explored,[6,7] although infrared spectroscopic data for the chemisorbed surface molecules is not overwhelmingly abundant. However, the adsorption of CS_2 onto Ni films has produced optical evidence for chemisorption.[8] Despite the extensive study, no binary complexes of CS_2 and a transition metal have yet been synthesized, and in fact there are few examples containing more than a single CS_2 ligand.[5]

Recently we have demonstrated the usefulness of the metal atom technique for synthesizing binary metal–olefin complexes of the form $M(C_2H_4)_n$ (where M = Ni,[9] Pd,[10] Cu,[11] $n = 1–3$; M = Ag,[12] Au,[12] $n = 1$). This fact, coupled with the scarcity of Ni complexes with CS_2, tends to make the attempted synthesis of binary $Ni(CS_2)_n$ complexes most attractive. The uniqueness of Ni among the nickel triad with respect to its CS_2 chemistry makes this study particularly interesting; for example, while $M(PPh_3)_2(CS_2)$ (M = Pd or Pt) are both known[13] and have quite similar structural characteristics,[14,15] the analogous Ni complex does not exist; instead, in solution a dimeric sulfur-bridged species is obtained, with the formula $[Ni(PPh_3)(CS_2)]_2$.[13]

In this paper, we wish to report the matrix synthesis and properties of *three* new binary nickel–carbon disulfide complexes of the form $Ni(CS_2)_n$ (where $n = 1–3$).

Experimental Section

Monoatomic Ni vapor was generated by directly heating a 0.010-in. ribbon filament of the metal with a.c. in a furnace which has been described previously.[16] The nickel metal (99.99%) was supplied by McKay Inc., New York, N.Y. Research grade carbon disulfide (99.99%) was supplied by Anachemia, Montreal, and was doubly distilled before use, using standard vacuum-line techniques. Isotopically enriched $^{13}CS_2$ (95%) was supplied by Prochem, Summit, N.J. The rate of metal atom deposition was continuously followed and controlled using a quartz crystal microbalance.[17] The metal concentration could be set anywhere in the range Ni/matrix $\simeq 1/10^6$ to 1/10 by simply varying the metal and matrix gas deposition rates. Matrix gas flows, controlled by a calibrated micrometer needle valve, were maintained in the range 0.1–2.0 mmol/h. In the infrared experiments the matrices were deposited on a CsI optical window cooled to 10–12 K by means of an Air Products Displex closed-cycle helium refrigerator. IR spectra were recorded using a Perkin-Elmer 180 spectrophotometer. UV–visible spectra were recorded on a Varian Techtron spectrophotometer, the sample being deposited onto a NaCl optical window.

Table I. Infrared Spectra and Assignments for $Ni(CS_2)_n$ (Where $n = 1–3$)

Complex[a]	$\nu(C{=}S)$, cm^{-1}	Matrix
$Ni(CS_2)$[a]	1276, 1210	Ar
	1273, 1204	Kr
$Ni(CS_2)_2$[b]	1382, 1314	Ar
	1327, 1306	Kr
$Ni(CS_2)_3$[c]	1344, 1286	Ar
	1338, 1297, 1288, 1276	CS_2

[a] Low-frequency modes assigned on the basis of CS_2 concentration experiments were observed as follows: $Ni(CS_2)$, 626 cm^{-1}; $Ni(CS_2)_2$, 594 cm^{-1}; $Ni(CS_2)_3$, 614–610 cm^{-1}.

Results and Discussion

Infrared Experiments. When Ni atoms are cocondensed at 10–12 K with $CS_2/Ar \simeq 1/100$ mixtures using low Ni concentrations to minimize complications due to cluster formation,[18] aside from the absorptions belonging to free carbon disulfide isolated in the Ar matrix ($^{12}CS_2$, 1535 cm^{-1}; $^{13}CS_2$—natural abundance, 1475 cm^{-1}), a number of new bands were observed in the "high-frequency" $\nu(C{=}S)$ stretching region which are clearly associated with CS_2 coordinated to Ni (Figure 1). An intense doublet was observed at 1276 and 1210 cm^{-1}, together with a much weaker doublet at 1328 and 1314 cm^{-1}. On warming of the matrix in the range 10–40 K, both of these doublets gradually diminished in intensity, but at noticeably different rates. However, under these high matrix dilution conditions, no new absorptions were observed to grow in.

Particularly noteworthy is the result of the corresponding experiment in $CS_2/Kr \simeq 1/100$ matrices, which shows essentially the same lines (with small matrix-induced frequency shifts) at 1273, 1204 cm^{-1} (species I) and 1327, 1306 cm^{-1} (species II), showing behavior parallel to the Ar data during warm-up. These results are summarized in Table I. Further dilution to $CS_2/Ar \simeq 1/1000$ to 1/10 000 mixtures resulted solely in the observation of the 1276, 1210 cm^{-1} doublet absorption, confirming that the species denoted I is best ascribed to the lowest stoichiometry mononuclear complex in the $Ni/CS_2/Ar$ system. It should be noted that the presence of the two bands (1276, 1210 cm^{-1}) in identical intensity ratios under a wide variety of deposition and warm-up conditions effectively precludes our assigning them to a matrix-split absorbance, a point important to the discussion of the mode of bonding (see later).

Matrix experiments were performed in which the $\nu(C{=}S)$ bands of species I were arranged to be fully absorbing. Under these conditions a low-frequency absorption associated with I was observed at 626 cm^{-1} (see later). Note that the *absence* of an infrared absorption at 536 cm^{-1}, ascribable to matrix-isolated NiS monomer,[19] eliminates the possibility of

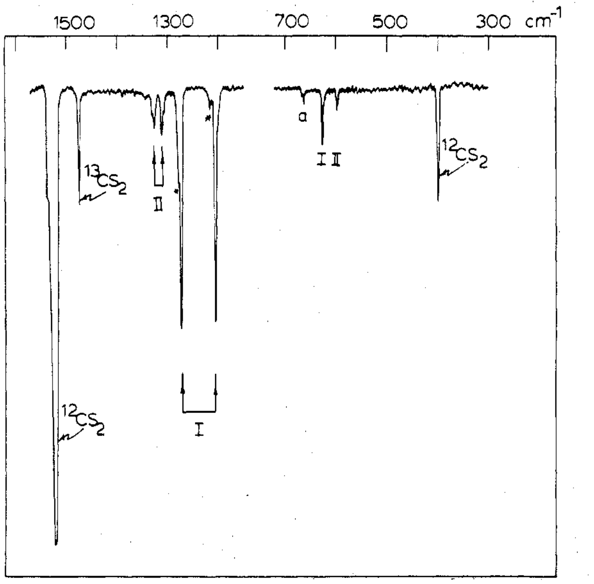


Figure 1. Infrared spectrum obtained on cocondensing Ni atoms with $^{12}CS_2/Ar \simeq 1/100$ matrices at 10–12 K and Ni/Ar $\simeq 1/10^4$. "a" refers to a trace of CO_2 while the asterisks indicate small, multiple trapping site effects of species I. I, II, and III refer to $Ni(CS_2)$, $Ni(CS_2)_2$, and $Ni(CS_2)_3$ respectively. Lines due to natural abundance $^{13}CS_2$ are also indicated.

Table II. Calculated and Observed Frequencies for $Ni(^{12}CS_2)$ and $Ni(^{13}CS_2)$

Freq, cm^{-1}		
Obsd	Calcd[a,d]	Assignment[a]
1279	1276	$(B_1)\ \nu(^{12}CS)$
1214	1208	$(A_1)\ \nu(^{12}CS)$[b]
626	626	$(A_1)\ \nu(Ni^{12}C)$[b]
c	170	$(A_1)\ \delta(S^{12}CS)$
c	150	$(B_1)\ \delta(Ni^{12}CS)$
1242	1238	$(B_1)\ \nu(^{13}CS)$
1178	1172	$(A_1)\ \nu(^{13}CS)$

[a] Carbene structure. [b] The calculated potential energy distribution matrix shows that these two modes are highly coupled. [c] Not observed. [d] Best fit force constants were calculated to be $k_{CS} = 6.38$, $k_{NiC} = 7.79$, $k_{CS-CS} = 0.39$, $k_{NiC-CS} = 1.32$, $k_{NiCS} = 0.3$, and $k_{SCS} = 0.3$ mdyn/Å. All other force constants were constrained to zero.

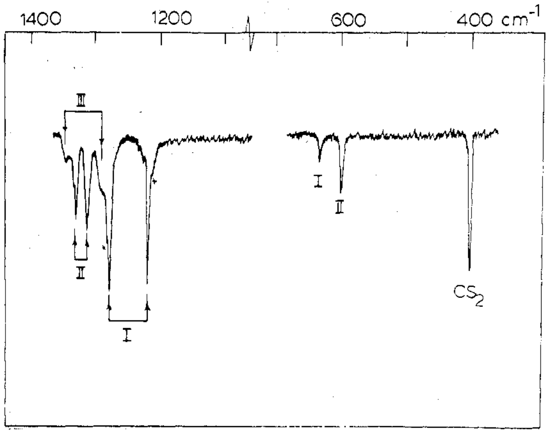


Figure 2. Same as Figure 1 except $^{12}CS_2/Ar \simeq 1/40$ matrices were used instead.

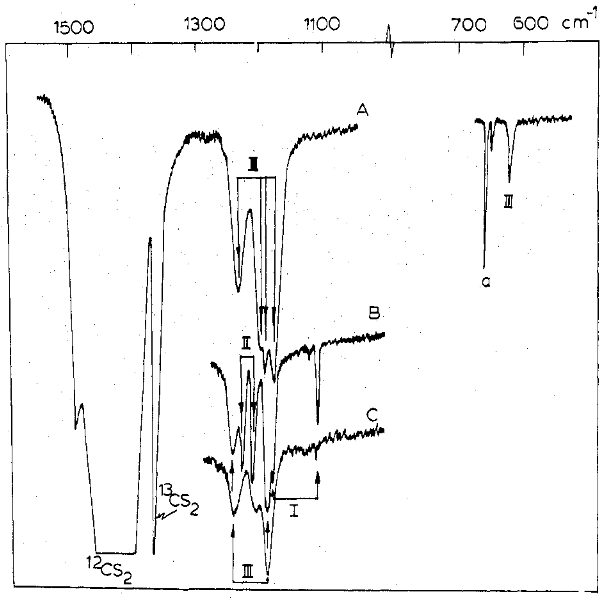


Figure 3. Same as Figure 1 except that A is pure CS_2, B is $^{12}CS_2/Ar \simeq 1/10$ at 10–12 K, C is the same as B but after warm-up to 35–40 K.

S-atom abstraction processes and hence thiocarbonyl complex formation under these experimental conditions.

Supporting evidence for the proposed 1:1 stoichiometry of I originated from $^{12}CS_2/^{13}CS_2/Ar \simeq 1/1/100$ isotopic substitution experiments. In essence, the original 1276, 1210 cm^{-1} doublet assigned to I in $^{12}CS_2/Ar \simeq 1/100$ matrices now appears as a "doublet-of-doublets" isotope pattern at 1276, 1210 cm^{-1} and 1240, 1186 cm^{-1} in the corresponding $^{12}CS_2/^{13}CS_2/Ar = 1/1/100$ experiment (Table II) and can be confidently assigned to $Ni(^{12}CS_2)$ and $Ni(^{13}CS_2)$, respectively.

In more concentrated $CS_2/Ar \simeq 1/40$ matrices, the absorptions of I still appear with highest intensity but with the bands at 1328, 1310 cm^{-1} (II) now being roughly half as large (Figure 2). Particularly noteworthy in this run are the additional very weak absorptions at 1344 and 1286 cm^{-1}. On warming of the matrix to 25–35 K, the absorptions associated with I tend to decrease with respect to the others. In concentrated $CS_2/Ar \simeq 1/10$ mixtures, no new absorptions are observed; however, the shoulder at approximately 1286 cm^{-1} on the 1276-cm^{-1} band of $Ni(CS_2)$ (I) is now prominent and has grown in roughly in proportion to the absorption at 1344 cm^{-1}. On warming of this matrix to 25–35 K, the $Ni(CS_2)$ (I) absorptions essentially disappear, but at a rate different from the two absorptions at 1328, 1314 cm^{-1} (II). Concomitant with these band intensity changes, one observes a *growth* in the absorbances of the two bands at 1344, 1286 cm^{-1} at roughly the same rate, indicating that they are associated with a single absorbing species (III). After 35-K annealing, species III predominates. An a priori assignment of species II and III in view of the mono(carbon disulfide) nature of I is therefore II = $Ni(CS_2)_2$ and III = $Ni(CS_2)_3$.

Evidence that the tris complex III is the highest stoichiometry species in the system stems from Ni atom depositions into *pure* CS_2 matrices at 10–12 K. A typical trace is shown in Figure 3. Aside from small splittings of the major absorptions, this spectrum is essentially identical with that of III in Ar. The spectroscopic absence of species I and II in this experiment is noteworthy. Furthermore, the infrared spectrum of III in pure CS_2 matrices remains unchanged over a wide range of deposition conditions and warm-up experiments, implying that the observed "triplet" splitting 1297, 1288, 1276 cm^{-1} most probably originates in a site symmetry or multiple trapping site splitting of the original (yet broad) absorption of species III at 1286 cm^{-1} in Ar matrices.

Collecting together the available infrared spectroscopic data from a wide variety of Ni and CS_2 concentration and warm-up

Table III. UV-Visible Spectra for the Binary Complexes $Ni(CS_2)_n$ (Where $n = 1$-3)

	Ni atoms cocondensed with		
Free CS_2 in Ar	CS_2/Ar[b] $\simeq 1/10$	CS_2/Ar[b,c] $\simeq 1/40$	Tentative assignment
	402 w, br		$Ni(CS_2)_3$
		388-398 w, br	$Ni(CS_2)_{1,2}$
324 318 312 w[a] 307 302			CS_2
		242 s	$Ni(CS_2)_2$
	237 s		$Ni(CS_2)_3$
		230 s, sh	$Ni(CS_2)$
220 s			CS_2

[a] Vibrational progression with average spacing of 561 cm^{-1}. [b] Presence of free Ni atoms indicated by weak lines at about 287 nm; implies overlap between the 320-nm absorption of free CS_2 and other Ni atom absorptions at 302, 317, and 330 nm.[20] [c] On warming of the system to 30-40 K the 230-nm band first decreases in intensity and the 398-nm band shifts to 388 nm.

experiments in Ar, Kr, and CS_2 matrices, together with the isotopic confirmation of species I as $Ni(CS_2)$, it would appear that species II and III are indeed most reasonably associated with $Ni(CS_2)_2$ and $Ni(CS_2)_3$, respectively, with band assignments as listed in Table I.

Observation of Low-Frequency Infrared Modes. As mentioned earlier, experiments were performed in $CS_2/Ar \simeq 1/100$ and $1/40$ matrices where species I is the major absorbing species in the presence of smaller amounts of II. Under these conditions, *two* low-frequency absorptions were observed at 626 and 594 cm^{-1} which, from their concentration and warm-up behavior, can be associated with species I and II, respectively. In concentrated $CS_2/Ar \simeq 1/10$ matrices in which species III predominates, with minor quantities of II, the low-frequency infrared spectrum displays *two* absorptions at 614 and 594 cm^{-1}, of which the 594-cm^{-1} band parallels the warm-up behavior of species II while the 614-cm^{-1} band parallels that of III. Confirmation that the 614-cm^{-1} band can be assigned to III stems from experiments in pure CS_2 matrices in which a *single* absorption is observed at 610 cm^{-1}, having undergone a small (4 cm^{-1}), matrix-induced frequency shift from that of III in $CS_2/Ar \simeq 1/10$ mixtures. A summary of the assignments of the low-frequency modes of $Ni(CS_2)_{1,2,3}$ is listed in Table I.

UV-Visible Experiments. Obtaining complete UV-visible data for the $Ni(CS_2)_n$ complexes was problematical on account of band overlap. In brief, absorptions of free CS_2 in the matrix occurred in the regions 302-324 and 215-225 nm and tended to overlap with the known absorptions of matrix-isolated atomic nickel (some of which is always present in CS_2/Ar matrices) in the regions 280-330 and 210-225 nm.[20] Therefore, in order to establish the regions in which the $Ni(CS_2)_n$ complexes absorb, careful CS_2/Ar concentration experiments were performed in 1/10 to 1/100 matrices. Typical 1/10 and 1/40 traces are displayed in Figure 4, from which one can establish the regions 388-402 and 230-245 nm to be characteristic of complexation. Tentative assignments of the observed absorptions in these regions to the individual $Ni(CS_2)_n$ ($n = 1$-3) species are listed in Table III.

Discussion of Results. From the experimental results it is evident that *three* new mononuclear, binary nickel-carbon disulfide complexes have been synthesized. With the prior knowledge that CS_2 can coordinate to transition metals either (i) through one of the S atoms, e.g.

$$Ni{-}S{=}C{=}S$$

A

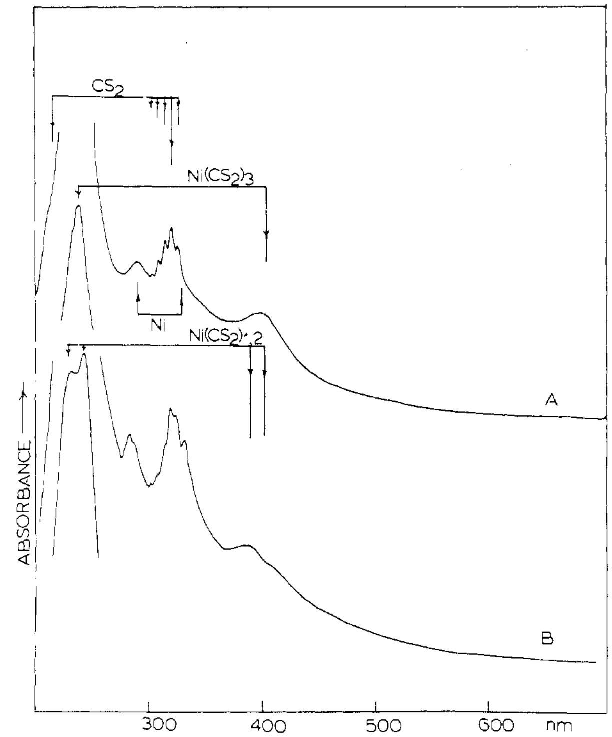
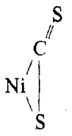


Figure 4. UV-visible spectra obtained on cocondensing Ni atoms with $^{12}CS_2/Ar$ = (A) 1/10 and (B) 1/40 matrices at 10-12 K and $Ni/Ar \simeq 1/10^4$.

in which case the CS_2 moiety may be considered as a neutral donor ligand, or (ii) by oxidative addition to the metal, e.g.



B

where the bond orders of the two CS bonds would be considerably different and the metal is formally in oxidation state II, let us consider which models, if any, are most consistent with the observed data.

To begin with, recall that $Ni(CS_2)$ displays *two* high-frequency $\nu(C{=}S)$ stretching modes at 1276, 1210 cm^{-1} and a low-frequency mode at 626 cm^{-1} under a wide variety of reaction conditions. Moreover, $Ni(CS_2)$ shows UV-visible absorptions around 242 and 398 nm, with no evidence for strong visible absorptions in the range 450-700 nm, characteristic of low-coordination Ni(II). This latter point, however, is of minimal importance in our subsequent assignments in view of the fact that structure **B** only formally carries a charge of 2+ on the nickel atom. Initial consideration of model **B** would lead one to expect a *single* high-frequency infrared $\nu(C{=}S)$ mode and a *single* low-frequency $\nu(C{-}S)$ mode[5] which is in contradistinction to our spectral observations. However, a more careful examination of our high-frequency doublet shows that the average frequency (1243 cm^{-1}) is approximately that value expected for the *first overtone* of the low-frequency band at 626 cm^{-1}. Noting that both the low-frequency $\nu(C{-}S)$ and high-frequency $\nu(C{=}S)$ modes for model **B** are both totally symmetric (A′) under C_s symmetry, one must be alert to the fact that Fermi resonance could be the cause of the observed high-frequency 1276, 1210 cm^{-1} doublet. In view of this complication, we cannot eliminate model **B** as a possible formulation for $Ni(CS_2)$. However, we do note that low-energy visible transitions are absent in $Ni(CS_2)$ and it would seem that oxidative addition of a carbon disulfide ligand to nickel(0) to give nickel(II) can be precluded, especially as one or two more CS_2 ligands are unlikely to add simultaneously and oxidatively to $Ni(CS_2)$ to yield Ni(IV) and Ni(VI) in $Ni(CS_2)_2$ and $Ni(CS_2)_3$, respectively.

Sulfur-bonded CS_2 (model A) would be an acceptable form of coordination for low-valent $Ni(CS_2)$ except that this type of compound (although only one of its type is known) is reported to have ν(C=S) stretching modes in the range 1500–1520 cm^{-1}, which are higher by 200 cm^{-1} than those observed in our complexes.[5] While a normal-coordinate analysis for a model Ni—S=C=S compound, using a MVFF approximation (this study), leads one to expect an infrared spectrum displaying a *single high*-frequency, out-of-phase ν(C=S) stretching mode (~1500–1200 cm^{-1}) and a *single low*-frequency in-phase ν(C=S) stretching mode (700–600 cm^{-1}) rather than *two* closely spaced, high-frequency ν(C=S) absorptions, it is difficult to completely discount this model as a formulation for $Ni(CS_2)$ in view of the Fermi resonance complication alluded to earlier.

A third possible model (C) (weak π-bonding model) can

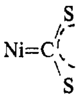
C

be proposed which differs from model B in the actual "bend-back" angle of the ligand on coordination. In crystal structures of $M(PPh_3)_2(CS_2)$[13–15] where M = Pd and Pt, the SCS angle is 139.7 and 136.2°, respectively; however, in view of the four-coordinate square-planar arrangements about the central metal atom, these species are best viewed as having M in oxidation state II. We considered this "weak form" of π complex C with an approximately linear, side-on coordination to Ni(0) and computed the vibrational spectrum expected in the ν(CS), ν(NiC), and ν(NiS) stretching regions.

Once more, the predicted spectrum required a *single* (out-of-phase) *high* frequency ν(C=S) stretching mode and a *single* (in-phase) *low* frequency ν(C=S) stretching mode. However, the possibility of a Fermi resonance complication in the high-frequency region makes it difficult once again to exclude model C as a formulation for $Ni(CS_2)$.

To summarize up to this point, we have considered three reasonable bonding models for $Ni(CS_2)$ all of which are in qualitative agreement with our observed spectra, *providing the assumption is made that a Fermi resonance is responsible for the observed doublet at 1276, 1210 cm*$^{-1}$. If no resonance complication had occurred, then models A to C could have been eliminated on the basis of one too many high-frequency modes. We therefore find ourselves in a somewhat paradoxical situation in that no clear-cut assignment of structure is possible with the available spectral data even for the simplest complex $Ni(CS_2)$.

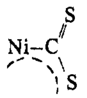
For the sake of completeness, we examined a "carbene" type of carbon disulfide coordination as illustrated in model D

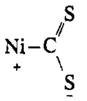


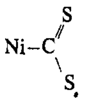
D

where the SCS angle is less than 180°. Although the vibrational data are not sufficiently complete to precisely define the angle in question, one can easily fit the observed spectra for $Ni(^{12}CS_2)$ and $Ni(^{13}CS_2)$ for an assumed angle of 120° and an intuitively reasonable MVFF (Table II) *without* the need to invoke the action of Fermi resonance to explain the presence of the two high-frequency modes (1276, 1210 cm^{-1}).

We fully realize that the bonding representation for the "carbene"–carbon disulfide complex $Ni(CS_2)$ illustrated above is a naive description of the actual electron distribution within this type of complex and that other forms, such as







certainly could contribute to the overall bonding picture of the molecule.

Conclusion

The cocondensation of Ni atoms with CS_2 and CS_2/inert gas mixtures at 10–12 K has resulted in the formation of *three* complexes which are identified as $Ni(CS_2)_n$, where $n = 1$–3. For the case of $Ni(CS_2)$ the definition of stoichiometry is strongly supported by $^{12}CS_2/^{13}CS_2/Ar$ mixed isotopic substitution data and Ni concentration experiments. Despite comparison with the available infrared data for known carbon disulfide complexes, together with normal-coordinate calculations for the various models proposed for $Ni(CS_2)$, it is not possible to make a definitive statement concerning the structure of the 1:1 complex. Similar difficulties exist for the 1:2 and 1:3 species. Further studies are currently under way involving the interaction of CS_2 with Pd and Pt atoms. It is possible at this time to state that the complex $Pd(CS_2)$[21] does *not* display the same high-frequency ν(C=S) doublet observed for $Ni(CS_2)$; rather it shows a single ν(C=S) bond, perhaps eliminating the "carbene" carbon disulfide structure as a possible formulation for $M(CS_2)$.

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Registry No. I, 63133-60-8; II, 63133-57-3; III, 63133-58-4; $Ni(^{13}CS_2)$, 63133-59-5; CS_2, 75-15-0; $^{13}CS_2$, 30860-31-2.

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