39394-81-5; [Co(P[-Pf]$_3$)(CO)][B(C_6H_5)$_4$], 41777-22-4; [Co(Pf-Pf-Pf-Pf)(CO)][B(C_6H_5)$_4$], 41777-23-5; [Co(Asf-Pf)$_2$(CO)][B(C_6H_5)$_4$], 41777-24-6; $Co_2(CO)_8$, 10210-68-1.

Contribution from the Todd Wehr Chemistry Building,
Marquette University, Milwaukee, Wisconsin 53233

Infrared Spectrum of Matrix-Isolated Nickel Carbonyl

Alan D. Cormier, J. David Brown, and Kazuo Nakamoto*

Received April 5, 1973

The infrared and Raman spectra and normal-coordinate analysis of $Ni(CO)_4$ have been reported by many investigators.[1] However, its matrix-isolated spectrum has not been previously reported. Although DeKock[2] obtained the infrared spectra of the $Ni(CO)_{1-4}$ series in an Ar matrix, his measurements were limited to the CO stretching region. No information has been available on matrix-isolation spectra of $Ni(CO)_4$ and other metal carbonyls in the low-frequency region. This paper reports the matrix-isolation and gaseous-phase infrared spectra of $Ni(CO)_4$ in the CO stretching (2300-2000 cm^{-1}) and Ni-C-O bending and Ni-C stretching (500-400 cm^{-1}) regions.

Experimental Section

$Ni(CO)_4$ was purchased from Strem Chemical Co., Danvers, Mass., and purified by vacuum distillation. A mixture of $Ni(CO)_4$ with argon at *ca.* a 1/1000 ratio was deposited on a CsI window at *ca.* 14 K which was cooled by a Cryogenic Technology Model 20 closed-cycle refrigerator. The matrix-isolated spectra were measured on a Beckman IR-12 infrared spectrophotometer with an expanded frequency scale. The spectrum of $Ni(CO)_4$ in the gaseous phase was obtained by using a 10-cm gas cell with CsBr windows. Calibration of the frequency reading was made by measuring the spectra of water vapor and carbon dioxide. The accuracy of the frequency reading was ±0.2 cm^{-1}.

Results and Discussion

The gaseous infrared spectrum of $Ni(CO)_4$ has been reported by Jones.[3] It exhibits four fundamentals at 2057 (ν_5), 459 (ν_6), 422 (ν_7), and 79 cm^{-1} (ν_8). Our frequencies shown in Tables I and II are in good agreement with those of Jones. ν_5 and ν_8 are definitely due to the CO stretching and C-Ni-C bending modes, respectively. However, the nature of the remaining two bands was not certain.[3] As is seen in Figure 1, ν_6 is weaker than ν_7. In general, the M-C-O bending mode is stronger than the M-C stretching mode in the infrared spectrum (for example, compare $Fe(CO)_5$[4] and $Mo(CO)_6$[5]). This tends to suggest that the stronger band (ν_7) is the Ni-C-O bending and the weaker band (ν_6) is the Ni-C stretching. On the other hand, the M-C-O bending frequency is generally higher than the M-C stretching frequency.[4,5] According to this trend, the 459-cm^{-1} band (ν_6) is the Ni-C-O bending and the 422-cm^{-1} band (ν_7) is the Ni-C stretching. Furthermore, the fact that these two bands are close in frequency suggests a possibility of vibrational coupling between these two modes in the F_2 species. The latter assignment was supported by recent normal-coordinate analyses[6,7] combined with the ^{13}C and/or ^{18}O substitutions. However, the preparation of these isotopically pure compounds involves technical inconveniences as well as financial burdens.

Table I. Infrared Spectra of $Ni(CO)_4$ in the 500-400-cm^{-1} Region

Gas	Ar matrix	Assignment[a]
	469.0	δ(NiCO)
458.5	464.0	
	454.4	
	433.4	$\nu(^{58}Ni-C)$
422.0	430.5	$\nu(^{60}Ni-C)$
	428.3	$\nu(^{62}Ni-C)$
	425.0	$\nu(^{64}Ni-C)$

[a] Key: ν, stretching; δ, bending.

Table II. Infrared Spectra of $Ni(CO)_4$ in the 2200-2000-cm^{-1} Region

Gas	Hexane soln[a]	Ar matrix	Assignment
		2150.0	
		2139.0	Free ^{12}CO
2121.0	2117.8	2125.0	A_1, $Ni(^{13}CO)(^{12}CO)_3$
2059.0	2045.7	2052.7	F_2, $Ni(^{12}CO)_4$
	2045.7	2048.2	E, $Ni(^{13}CO)(^{12}CO)_3$
		2045.7	
		2041.0	
2018.6	2007.5	2013.0	A_1, $Ni(^{13}CO)(^{12}CO)_3$
		2011.8	
		2007.0	

[a] Reference 8.

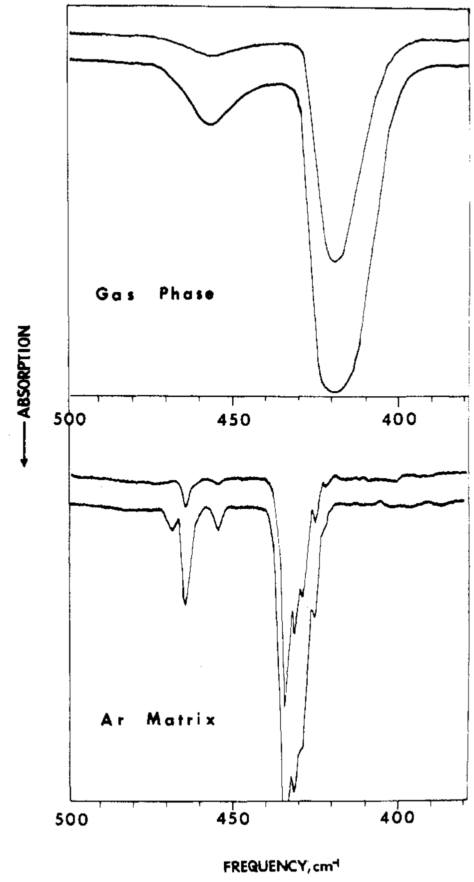


Figure 1. Infrared spectra of $Ni(CO)_4$ in the 500-400-cm^{-1} region.

---

(1) For example, see K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," 2nd ed, Wiley, New York, N. Y., 1970.

(2) R. L. DeKock, *Inorg. Chem.*, 10, 1205 (1971).

(3) L. H. Jones, *J. Chem. Phys.*, 28, 1215 (1958).

(4) W. F. Edgell, W. E. Wilson, and R. Summit, *Spectrochim. Acta*, 19, 863 (1963).

(5) L. H. Jones, *Spectrochim. Acta*, 19, 329 (1963); *J. Chem. Phys.*, 36, 2375 (1962).

(6) G. Bouquet and M. Bigorgne, *Spectrochim. Acta, Part A*, 27, 139 (1971).

(7) L. H. Jones, R. S. McDowell, and M. Goldblatt, *J. Chem. Phys.*, 48, 2663 (1968).

Figure 1 shows that the band corresponding to the 422 cm^{-1} of Ni(CO)$_4$ in the gaseous phase splits into at least four bands in an Ar matrix at 14 K. Table I lists the frequencies of these peaks. In rare gas matrices, metal-halide stretching bands of simple salts such as NiF$_2$ and ZnF$_2$ exhibit isotopic splitting patterns characteristic of each metal involved.[8] In the present case, these peaks are reasonably assigned to the Ni isotopes in natural abundance. In fact, the abundance of Ni isotopes is as follows: ^{58}Ni, 67.8%; ^{60}Ni, 26.2%; ^{61}Ni, 1.2%; ^{62}Ni, 3.7%; ^{64}Ni, 1.1%. Although the ^{61}Ni peak could not be separated from the neighboring band, the relative peak intensity of the four bands observed is close to that expected from the percentage natural abundance of each Ni isotope.

The observed splitting cannot be attributed to the lowering of T_d symmetry in an Ar matrix for three reasons. First, the space group[9] of solid argon is $O_h{}^5$ which provides sites such as O_h, T_d, V_h, etc. The presence of O_h and T_d sites allows the preservation of T_d symmetry of Ni(CO)$_4$. Second, the splitting due to lowering of symmetry should be much larger than that observed. Third, the observed intensity pattern is difficult to explain on the basis of lowering of symmetry. We, therefore, conclude that this mode involves the substantial motion of the Ni atom during the vibration and should be assigned to the Ni-C stretching.

On the other hand, the band corresponding to the 459-cm^{-1} band of the gaseous phase does not show any indication of isotopic splitting under the same condition. In general, the isotopic shifts of the bending modes by metal isotope substitution (2-0 cm^{-1}) are much smaller than those of the stretching modes (10-2 cm^{-1}).[10] Thus, it is most reasonable to assign the 459-cm^{-1} band to the Ni-C-O bending mode in which the carbon and oxygen atoms are displaced. The present result also agrees with the result of normal-coordinate analysis[7] which revealed that there is almost no vibrational coupling between the Ni-C stretching and Ni-C-O bending modes.

The present result demonstrates that matrix-isolation spectra serve as a valuable tool in assigning the metal-ligand vibrations of coordination compounds. We have shown previously[10] that the metal isotope technique provides definitive band assignments of metal-ligand vibrations. However, this technique is difficult to apply to gaseous or liquid compounds since they are difficult to prepare on a milligram scale. Interestingly, these compounds are rather ideal for matrix-isolation studies because of their volatility. Needless to say, metal isotope frequencies such as listed in Table I are indispensable for the refinement of M-C stretching and related force constants in normal-coordinate analysis. At present, the origin of two weak bands at 469.0 and 454.4 cm^{-1} is not clear.

The CO stretching region exhibits many bands in an Ar matrix, some of which have been assigned previously.[2] In the gaseous-phase spectrum, a very intense band is centered at 2059 cm^{-1} with a half width of about 20 cm^{-1}. Clearly, this band is due to the F$_2$ CO stretching fundamental of Ni(^{12}CO)$_4$. In an Ar matrix, this band is shifted to 2052.7 cm^{-1} with a half-width of 1.5 cm^{-1} (Figure 2). Bor[11] observed this same vibration at 2045.7 cm^{-1} in a hexane solution.

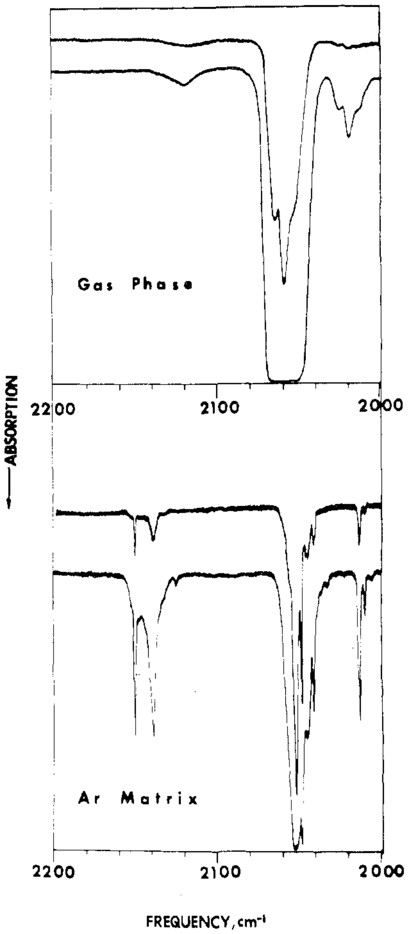


Figure 2. Infrared spectra of Ni(CO)$_4$ in the 2200-2000-cm^{-1} region.

The natural abundance of ^{13}C is 1.1%. In the Ni(CO)$_4$ molecule there are four equivalent positions that a ^{13}C can occupy. Thus, the effective percentage of the mono-^{13}C species in a sample of Ni(CO)$_4$ would be about 4% which is sufficient to observe the bands arising from this species. Bor[11] in his work involving the ^{13}C enrichment of Ni(CO)$_4$ in hexane solution observed two weak bands at 2007.5 and 2117.8 cm^{-1} which are due to the ^{13}CO and ^{12}CO stretching modes of Ni(^{13}CO)(^{12}CO)$_3$ (both A$_1$ species), respectively. The E ^{12}CO stretching mode was hidden by the strong band at 2045.7 cm^{-1} of Ni(^{12}CO)$_4$. Jones[3] observed a band at 2018 cm^{-1} in the gaseous-phase spectrum and assigned it to the ^{13}CO stretching mode. In an Ar matrix, this band is observed at 2013.0 cm^{-1} and the less intense ^{12}CO stretching (A$_1$) band is at 2125.0 cm^{-1}. The E ^{12}CO stretching mode appears at 2048.2 cm^{-1}, only 4.5 cm^{-1} lower than the F$_2$ mode of Ni(^{12}CO)$_4$ at 2052.7 cm^{-1}. This may indicate that there is weak interaction between the A$_1$ and E CO stretching modes of the mono-^{13}CO species due to nonrigid behavior[12] or coupling with the E Ni^{13}CO bending mode.

The 2048.2-cm^{-1} band is 2-3 times as intense as the 2013.0-cm^{-1} band and is not due to impurities since the ratio of its intensity to that of the main peak at 2052.7 cm^{-1} remained constant regardless of the method of purification used. Fermi resonance of the F$_2$ mode with some combination band must also be excluded since the frequency separation of 4.5 cm^{-1} is much too small.

---

(8) D. E. Milligan, M. E. Jacox, and J. D. McKinley, *J. Chem. Phys.*, 42, 902 (1965); J. W. Hastie, R. H. Hauge, and J. L. Margrave, *High Temp. Sci.*, 1, 76 (1969).

(9) B. I. Swanson, L. H. Jones, and R. R. Ryan, *J. Mol. Spectrosc.*, 45, 324 (1973).

(10) K. Nakamoto, *Angew. Chem., Int. Ed. Engl.*, 11, 666 (1972).

(11) G. Bor, *J. Organometal. Chem.*, 10, 343 (1967).

(12) H. C. Longuet-Higgins, *Mol. Phys.*, 6, 445 (1963); J. W. Fleming and C. N. Banwell, *J. Mol. Spectrosc.*, 31, 378 (1969).

The origin of the remaining five bands at 2150.0, 2045.7, 2041.0, 2011.8, and 2007.0 cm^{-1} is not clear. Unambiguous assignments of these bands must await a rigorous normal-coordinate analysis. The peak observed at 2139.0 cm^{-1} is due to the free ^{12}CO.

Acknowledgment. The authors are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research.

Registry No. $Ni(CO)_4$, 13463-39-3.

Contribution from the Department of Chemistry, State University of New York, Stony Brook, New York 11790

Adjacent Attack in the Redox Reaction between Pentacyanocobaltate(II) and Thiocyanatopentaamminecobalt(III)[1]

Christopher J. Shea[2] and Albert Haim*

Received April 20, 1973

It was reported previously[3] that the reduction of thiocyanatopentaamminecobalt(III) by chromium(II) proceeds *via* parallel adjacent and remote attack mechanisms. Since on the basis of thermodynamic[3,4] and steric[3] considerations a negligible contribution of the adjacent attack pathway would have been anticipated, the occurrence of such a pathway was interpreted as a manifestation of the high electron mediating ability of thiocyanate sulfur in inner-sphere redox reactions.[3] Another example of high redox reactivity when sulfur is bound to cobalt(III) was discovered earlier[5] in the mercaptoacetatobis(ethylenediamine)cobalt(III)-chromium(II) reaction. Since the two cases of sulfur-mediated electron transfer involved chromium(II) as the reductant, it was decided to investigate the reduction of $Co(NH_3)_5SCN^{2+}$ by $Co(CN)_5{}^{3-}$. This reductant was chosen because examination of the cyanocobalt(III) products can provide direct evidence about the position of attack on the bridging ligand and for comparison with the analogous $Co(NH_3)_5NCS^{2+}$-$Co(CN)_5{}^{3-}$ reaction which is known to proceed by remote attack.[6,7]

Experimental Section

Argon, used in the manipulation of oxygen-sensitive substances, and water were purified as described previously.[8] $[Co(NH_3)_5NCS](ClO_4)_2$ and $[Co(NH_3)_5SCN]Cl_2 \cdot 1.5H_2O$ were synthesized by recorded procedures.[9,10]

Stoichiometric experiments designed to identify the cobalt(III) products of the $Co(NH_3)_5SCN^{2+}$-$Co(CN)_5{}^{3-}$ reaction were conducted in two ways. The first method involved addition of 5-10 mg of $[Co(NH_3)_5SCN]Cl_2 \cdot 1.5H_2O$ to 15 ml of deaerated 5.0×10^{-3} *M* NaCN, 1.0×10^{-3} *M* NaOH, and 0.10 *M* $NaClO_4$. The second method involved anaerobic mixing in the fast-flow apparatus[11] of a solution of $Co(NH_3)_5SCN^{2+}$, Co^{2+}, and $NaClO_4$ with a solution of NaCN, NaOH, and $NaClO_4$. The resulting solutions were collected and their visible and ultraviolet spectra were recorded with a Cary 14 spectrophotometer.

Table I. Identification of the Product of the $Co(NH_3)_5SCN^{2+}$-$Co(CN)_5{}^{3-}$ Reaction[a]

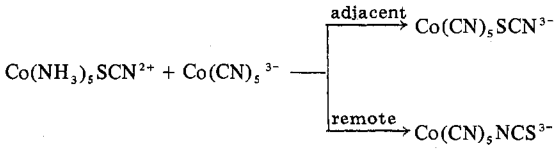
$10^4[Co(NH_3)_5SCN^{2+}]$, *M*	$10^5[Co(CN)_5{}^{3-}]$, *M*	λ,[b] nm	ε,[c] M^{-1} cm^{-1}
14.0	≤0.01[d,e]	377, 263	215, 1.90×10^4
2.93	≤0.01[d,e]	377, 263	201, 1.79×10^4
1.10	≤0.01[d,f]	377, 263	215, 1.74×10^4
0.66	0.40[f]	377, 263	200, 1.83×10^4
1.08	0.40[f]	377, 263	202, 1.85×10^4
0.75[g]	1.0[f]	377, 263	215, 1.78×10^4
		377, 263[h]	196, 1.84×10^4[h]
		378, 264[i]	195, 1.82×10^4[i]
		378, 265[j]	191, 1.71×10^4[j]
		363, 265[k]	500, 2.34×10^3[k]

[a] Measurements at 25°, $[CN^-] = 5.0 \times 10^{-3}$ *M*, $[OH^-] = 1.0 \times 10^{-3}$ *M*, and $[NaClO_4] = 0.10$ *M*. [b] Wavelengths of maximum absorption for product solution. [c] Extinction coefficients at maxima. Calculated on the basis of the initial [Co(III)]. [d] Estimated impurity present in the cobalt(III) preparation. [e] Mixing solid $[Co(NH_3)_5SCN]Cl_2 \cdot 1.5H_2O$ with CN^- solution. See text. [f] Mixed in rapid-flow apparatus. See text. [g] With 0.83×10^{-4} *M* $Co(NH_3)_5NCS^{2+}$ added. [h] Spectrum of $Co(CN)_5SCN^{3-}$ from ref 14. [i] Spectrum of $Co(CN)_5SCN^{3-}$ from S. Nakamura, Ph.D. Dissertation, University of Chicago, 1964. [j] Spectrum of $Co(CN)_5SCN^{3-}$ from ref 15. [k] Spectrum of $Co(CN)_5NCS^{3-}$ from ref 15.

The $Co(NH_3)_5SCN^{2+}$-$Co(CN)_5{}^{3-}$ reaction was complete within the dead time (5 msec) of the flow apparatus at 10^{-5} *M* $Co(CN)_5{}^{3-}$. Lower concentrations of $Co(CN)_5{}^{3-}$ could not be used because of its sensitivity to oxygen and because such small concentrations become comparable to the amount of cobalt(II) usually present as an impurity in preparations of cobalt(III) complexes.[12] In fact, it was found that usable, although poorly reproducible, oscillograms could be obtained by mixing $Co(NH_3)_5SCN^{2+}$ and CN^- solutions in the *absence* of added cobalt(II). An estimate of the $Co(CN)_5{}^{3-}$ concentration produced on mixing the above solutions was obtained by "spiking" the $Co(NH_3)_5SCN^{2+}$ solutions with a known amount of $Co(NH_3)_5NCS^{2+}$. When such solutions were mixed with CN^- solutions, two distinct absorbance changes were detected at 263 or 288 nm.[13] The first, rapid change (with half-life $t^f_{1/2}$) corresponded to the disappearance of $Co(NH_3)_5SCN^{2+}$ and formation of $Co(CN)_5SCN^{3-}$ and was followed by the slower (half-life $t^s_{1/2}$) cobalt(II)-catalyzed conversion[6,7] of $Co(NH_3)_5NCS^{2+}$ to $Co(CN)_5SCN^{3-}$. The concentration of $Co(CN)_5{}^{3-}$ during the second reaction was calculated from the measured half-life and the known[7] second-order rate constant ($[Co(CN)_5{}^{3-}] = 0.693/1.1 \times 10^6 \times t^s_{1/2}$) and was *assumed* to be prevalent during the first reaction in order to calculate its second-order rate constant ($k = 0.693/[Co(CN)_5{}^{3-}] \times t^f_{1/2}$). The half-lives for the two reactions were estimated from the corresponding ln ($D_t - D_\infty$) *vs.* time plots. D_t and D_∞ are the absorbances at time *t* and when the reaction under consideration is complete, respectively. The difference in rates between the two reactions was sufficiently large to obtain fairly steady D_∞ values for the first reaction.

Results and Discussion

There are two possible pathways for the inner-sphere redox reaction between $Co(NH_3)_5SCN^{2+}$ and $Co(CN)_5{}^{3-}$



---

[1] This work was supported by the National Science Foundation under Grant GP-9669.

[2] Based on the M.S. thesis of C. J. Shea, State University of New York at Stony Brook, Aug 1971.

[3] C. Shea and A. Haim, *J. Amer. Chem. Soc.*, 93, 3055 (1971).

[4] D. P. Fay and N. Sutin, *Inorg. Chem.*, 9, 1291 (1970).

[5] R. H. Lane and L. E. Bennett, *J. Amer. Chem. Soc.*, 92, 1089 (1970).

[6] J. L. Burmeister, *Inorg. Chem.*, 3, 919 (1964).

[7] J. Candlin, J. Halpern, and S. Nakamura, *J. Amer. Chem. Soc.*, 85, 2517 (1963).

[8] B. Grossman and A. Haim, *J. Amer. Chem. Soc.*, 93, 6490 (1971).

[9] R. L. Carlin and J. O. Edwards, *J. Inorg. Nucl. Chem.*, 6, 217 (1958).

[10] D. A. Buckingham, I. I. Creaser, and A. M. Sargeson, *Inorg. Chem.*, 9, 655 (1970).

[11] G. Dulz and N. Sutin, *Inorg. Chem.*, 2, 917 (1963).

[12] A. W. Adamson, *J. Amer. Chem. Soc.*, 78, 4260 (1956).

[13] Extinction coefficients (in M^{-1} cm^{-1}) at 288 and 263 nm: $Co(NH_3)_5SCN^{2+}$, 15,600 and 5000; $Co(NH_3)_5NCS^{2+}$, 1250 and 512; $Co(CN)_5SCN^{3-}$, 3600 and 18,400.