tion and reduction waves of the Cu(III) and Cu(II) compounds, respectively, are practically identical. This fact, as well as the observed linearity of the log $[i/(i_d - i)]$ *vs.* E plot, reveals that both compounds can be interconverted by a reversible one-electron step $(i_d$ = diffusion current). This reversibility strongly suggests that both complexes have very similar structures, *viz.*, planar four-coordination as illustrated in Figure 2.

The data of the electronic spectra of KCu(bi)$_2$ and KCu(oxam)$_2$, together with those of the isoelectronic Ni(II) species, are given in Table V. This similarity in these spectra give support to the idea of the structural similarity of these compounds. Regarding the structure of the Ni(III) complexes, however, no more evidence is available at the moment.

From a structural point of view these compounds are thus much like the series of MN$_4{}^n$ complexes reported by Balch and Holm.[9] The ligand in these series (where n can vary from 2− to 2+) is o-C$_6$H$_4$-(NH)$_2$, which can exist in two forms of different oxidation state, *viz.*, as the dianion of o-phenylenediamine and as o-benzoquinonediimine. This fact is strongly related to the characteristic properties of these series of metal complexes. Since different oxidation forms

(9) A. L. Balch and R. H. Holm, *J. Amer. Chem. Soc.*, **88**, 5201 (1966).

of the dianions of biuret and oxamide are obviously not possible, we think them to be representatives of a different class of ligands.

The structure of the interesting compounds KM-(3-Rbi)$_2$(1-RbiH$_2$)$_2$ is not definitely established. Nmr data (see Table IV) and ir spectra show that the 1-propylbiuret is not deprotonated and not coordinated to the metal. The identical uv spectra and magnetic properties of KCu(3-Rbi)$_2$·2H$_2$O and KCu(3-Rbi)$_2$-(1-RbiH$_2$)$_2$ indicate also that there is no coordination of 1-Rbi or H$_2$O to the Cu. Extensive H bridging is a characteristic feature of the chemistry of the biurets so we think that the two 1-propylbiuret molecules are H bonded to the biuretato ligands, probably *via* the 3-NH groups, because when these places are blocked by substituting an alkyl group, no extra biurets are found to be bonded to the complexes. The two H$_2$O molecules in KCu(3-Rbi)$_2$·2H$_2$O are probably bonded in the same way.

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Preparation and Identification of Intermediate Carbonyls of Nickel and Tantalum by Matrix Isolation[1]

By R. L. DeKOCK[2]

All four carbonyls of nickel, Ni(CO)$_{1-4}$, and possibly six carbonyls of tantalum, Ta(CO)$_{1-6}$, have been identified *via* infrared spectra in argon matrices at 4.2°K. The carbonyls are prepared by the vaporization of the metal atoms and condensation into a CO–argon mixture. C^{18}O was also used in the identification. Careful warming of the matrix results in the growth and disappearance of ν_{oo} bands in the 2000-cm^{-1} region. In the nickel experiments these bands appear at 2052, 2017, 1967, and 1996 cm^{-1} and are assigned to Ni(CO)$_4$, Ni(CO)$_3$, Ni(CO)$_2$, and NiCO, respectively. Specific assignments for tantalum carbonyls are more difficult, but five or six molecules are definitely formed during the diffusion experiments. For the tantalum carbonyls also, the general trend is that the stretching frequencies increase with increasing coordination number, a fact which is predicted on the basis of simple bonding theory. In the electronic spectra broad absorptions at 3000 and 2725 Å are attributed to Ni(CO)$_4$ and Ta(CO)$_6$, respectively.

Introduction

The matrix isolation technique is ideally suited for the study of unstable species. Such species can include radicals such as HNO[3] or transition metal oxides such as WO and WO$_2$.[4] It is also possible to prepare molecules within the matrix that may be quite stable under ambient conditions; for example, KrF$_2$ is prepared by the photolysis of fluorine in a krypton matrix.[5] Another example of the preparation of unique

(1) Support from the National Science Foundation under Grant No. GP-9316 is gratefully acknowledged.
(2) Address correspondence to the author at the Chemistry Department, Birmingham University, Birmingham 15, England.
(3) H. W. Brown and G. C. Pimentel, *J. Chem. Phys.*, **29**, 883 (1958).
(4) W. Weltner, Jr., and D. McLeod, Jr., *J. Mol. Spectrosc.*, **17**, 276 (1965).
(5) J. J. Turner and G. C. Pimentel, *Science*, **140**, 974 (1963).

species is the identification of (SiO)$_2$ and (SiO)$_3$ formed by annealing matrices containing SiO.[6] Recently, Timms[7] has presented an approach to the preparation of macro quantities of compounds by allowing the "matrix" material to be a reactant. One of the reactions carried out is the cocondensation of nickel atoms with a solid layer of PF$_3$ at 77°K to form Ni-(PF$_3$)$_4$.

Carbon monoxide has been found to be a particularly reactive molecular species at low temperature. For example, CCO has been prepared by the photolysis of N$_3$CN in an Ar–CO matrix,[8] while HCO can be

(6) J. W. Hastie, R. H. Hauge, and J. L. Margrave, *Inorg. Chim. Acta*, **3**, 601 (1969).
(7) P. L. Timms, *Chem. Commun.*, 1033 (1969).
(8) M. E. Jacox, D. E. Milligan, N. G. Moll, and W. E. Thompson, *J. Chem. Phys.*, **43**, 3734 (1965).

prepared similarly by the photolysis of HI.[9] Carbon monoxide itself has been used as a matrix to prepare HCO,[10,11] FCO,[12] and ClCO,[13] by generating the appropriate atomic precursor through photolysis.

Our work with nickel and tantalum carbonyls was prompted by accident and reason. First, in experiments in which CO was present in the matrix several infrared bands were observed to appear which could only be due to the tantalum cell material. Since no binary monomeric tantalum carbonyls had yet been reported, we were inclined to examine the situation further. Second, the recent work by Rest and Turner[14] indicating the existence of Ni(CO)$_3$ formed by photolysis of Ni(CO)$_4$ brought about a desire to prepare NiCO and Ni(CO)$_2$ also. The existence of Ni(CO)$_3$ and Ni(CO)$_2$ had been reported in the interpretation of the flash photolysis results of Ni(CO)$_4$.[15]

Experimental Section

The furnace and dewar arrangement used in the matrix isolation work have been described previously.[16] The dewar was constructed so that annealing experiments could be carried out by shutting off the flow of liquid helium to the copper block surrounding the CsI window. The relative temperature was monitored with a chromel—Au-0.02 at. % Fe thermocouple. After reaching the desired annealing temperature the matrix was quenched immediately.

The tantalum cells were 0.5 in. long and 0.25 in. in o.d. with 0.010-in. walls. The metallic nickel was obtained from Spex Industries, Inc., with a purity of 99.99%. The nickel was vaporized from graphite cells (spectroscopic grade) with dimensions 0.75 in. long, 0.030-in. walls, and 0.25-in. o.d. with an 0.080-in. orifice.

Both the graphite and the tantalum cells were resistively heated by passing several hundred amperes of current through them at about 6 V.[17] Typical temperatures employed are 2800°K for the tantalum experiments and 1700°K for the nickel experiments.

The infrared spectra were recorded from 4000 to 200 cm^{-1} on a Perkin-Elmer 621 grating infrared spectrophotometer with an accuracy of ±1 cm^{-1}. A Jarrell-Ash 0.5-m Ebert scanning spectrometer was used for the electronic spectra.

The argon gas and the C^{16}O were Airco research grade. The C^{18}O was obtained from Miles Laboratories, Inc., and is enriched to 92.95%. Ar:CO dilution ratios were 200:1 and 500:1.

The gas mixture flow rate was maintained at 0.5 l. atm/hr and precooled with liquid nitrogen immediately before entering the dewar. All trapping was done at liquid helium temperature, 4°K. Each of the samples was outgassed for at least 30 min at or near the final operating temperature prior to the experiment. The average deposition time employed was 30 min.

Results and Discussion

A. Nickel Carbonyls.—The basis of the matrix isolation approach is that high dilution ratios exist between the argon lattice and guest molecules, so that there are no interactions between molecular species within the lattice. We also assume that activation energies will be low enough so that the formation of the intermediate metal carbonyls will be controlled by diffusion processes within the matrix. In order to facilitate the interpretation of the infrared spectra,

the number of active modes for each possible species is presented first, followed by the observations.

Infrared-Active Modes of Nickel Carbonyls.—The number of infrared-active bands corresponding to C–O stretching motion is listed in Table I for each of

TABLE I
INFRARED-ACTIVE STRETCHING MODES FOR M(CO)$_n$

Molecule	Molecular symmetry	Ir-active C–O^a str vib
MCO	$C_{\infty v}$ (linear)	1 Σ^+
M(CO)$_2$	$D_{\infty h}$ (linear)	1 Σ_u^+
M(CO)$_2$	C_{2v} (angular)	1 A$_1$ + 1 B$_1$
M(CO)$_3$	D_{3h} (trigonal plane)	1 E'
M(CO)$_3$	C_{3v} (trigonal pyramid)	1 A$_1$ + 1 E
M(CO)$_4$	T_d (tetrahedral)	1 T$_2$
M(CO)$_4$	D_{4h} (tetragonal plane)	1 E$_u$
M(CO)$_5$	C_{4v} (tetragonal pyramid)	2 A$_1$ + E
M(CO)$_5$	D_{3h} (trigonal bipyramid)	1 A$_2''$ + E'
M(CO)$_6$	O_h (octahedral)	1 T$_{1u}$

^{a} The number of allowed M–C stretches is the same as the C–O stretches since they belong to the same representations.

the possible symmetries. Coordination numbers up to 6 are included since Table I will also be used in the discussion of the tantalum carbonyls.

For C–O (or M–C) stretching modes, only one band is predicted for NiCO; one is predicted for linear Ni(CO)$_2$, and two are predicted for bent Ni(CO)$_2$. For planar Ni(CO)$_3$, only one band is ir active; trigonal Ni(CO)$_3$ has two allowed bands. Finally, the known tetrahedral structure of Ni(CO)$_4$ has only one allowed infrared band. Thus, one might expect between four and six bands in the 2000-cm^{-1} region attributable to Ni(CO)$_{1-4}$.

Infrared Spectrum of Nickel Carbonyls.—The infrared spectra for the nickel carbonyl experiments are presented in Figure 1. The spectra indicate that initially a band is present at 1996 cm^{-1}. In experiments in which the 1996-cm^{-1} band is quite strong, a weak band at 1967 cm^{-1} is also present. As annealing progresses, these bands grow and two new bands appear successively at 2017 and 2052 cm^{-1}. A band at 2035 cm^{-1} appears at about the same time as the 2052-cm^{-1} band or perhaps slightly later. Further annealing results in a large increase in the band at 2052 cm^{-1} and a lesser increase in the band at 2035 cm^{-1}. These two bands grow at the expense of the bands at 1996, 1967, and 2017 cm^{-1}.

The 1996-cm^{-1} band is assigned to NiCO since it is the first band to appear in the spectra and since it grows very rapidly with the first annealing experiments. The absorption at 1967 cm^{-1} is then assigned to Ni(CO)$_2$ and the 2017- and 2052-cm^{-1} bands are assigned to Ni(CO)$_3$ and Ni(CO)$_4$, respectively. The assignments of Ni(CO)$_3$ and Ni(CO)$_4$ agree with those of Rest and Turner[14] to ±1 cm^{-1}. However, their weak band at 2065 cm^{-1}, which was also assigned to the tricarbonyl, has not been observed here. The assignment of Ni(CO)$_4$ to the 2052-cm^{-1} band in argon compares favorably with the gas-phase infrared band at 2057.8 cm^{-1}.[18]

The band at 2035 cm^{-1} grows in later than any of the other bands and definitely does not correlate in intensity with them. It must be attributed to a species formed by combination of two of the carbonyl mole-

(9) J. F. Ogilvie, *Spectrochim. Acta, Part A*, **23**, 737 (1967).

(10) G. E. Ewing, W. E. Thompson, and G. C. Pimentel, *J. Chem. Phys.*, **32**, 927 (1960).

(11) D. E. Milligan and M. E. Jacox, *ibid.*, **41**, 3032 (1964).

(12) D. E. Milligan, M. E. Jacox, A. M. Bass, J. J. Comeford, and D. E. Mann, *ibid.*, **42**, 3187 (1965).

(13) D. E. Milligan and M. E. Jacox, *ibid.*, **43**, 866 (1965).

(14) A. J. Rest and J. J. Turner, *Chem. Commun.*, 1026 (1969).

(15) A. B. Callear, *Proc. Roy. Soc. Ser. A*, **265**, 71 (1961).

(16) W. Weltner, Jr., in "Advances in High Temperature Chemistry," Vol. 2, L. Eyring, Ed., Academic Press, New York, N. Y., 1969, p 85.

(17) P. H. Kasai, E. B. Whipple, and W. Weltner, Jr., *J. Chem. Phys.*, **44**, 2581 (1966).

(18) L. H. Jones, R. S. McDowell, and M. Goldblatt, *ibid.*, **48**, 2663 (1968).
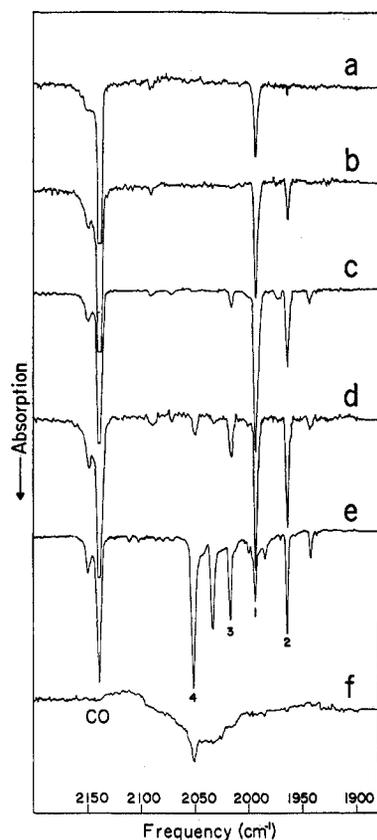
Figure 1.—Infrared spectra of nickel atoms deposited in a 500:1 Ar:CO matrix and subsequent annealing: a, original; b, 17°K; c, 18°K; d, 19°K; e, 26°K; f, 35°K (temperatures are relative). The arabic numerals refer to the relative rate of growth and disappearance of the bands and hence to n in $Ni(CO)_n$.

cules. The other possibility is that this absorption could be a carbonyl of the type

$$
\begin{array}{c}
O \\
\parallel \\
C \\
\diagup \quad \diagdown \\
Ni \qquad Ni
\end{array}
$$
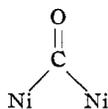
but this is ruled out because such bridging carbonyl groups would be expected to have much lower infrared frequencies.[19] Also, the 2035-cm^{-1} band appears in experiments with light as well as heavy nickel atom concentrations. In several of the experiments a weak band also appears at 1944 cm^{-1} which did not correlate in intensity with any of the other bands. This band is anomalous since its counterpart was never found in the C^{18}O experiments; it remains unaccounted for. The basic conclusion to be obtained from the series of spectra presented in Figure 1 is that each of the intense absorptions belongs to a separate molecular species since each band behaves in a unique manner upon annealing. Since only four bands are observed which can be identified with simple binary nickel carbonyls, we conclude either that $Ni(CO)_3$ is planar and $Ni(CO)_2$ is linear or that the A_1 modes have such a low intensity that they remain unobserved.

A separate experiment was carried out using 200:1 Ar:C^{18}O. The absorption bands are tabulated in Table II for both the C^{16}O and C^{18}O experiments. Since the nickel was vaporized from a graphite cell, a sizable

(19) E. W. Abel, *Quart. Rev., Chem. Soc.*, **17**, 133 (1963).

TABLE II
INFRARED ABSORPTIONS OBSERVED IN NICKEL CARBONYL EXPERIMENTS

Ni–C^{16}O–Ar	Ni–C^{18}O–Ar	Assignment
2138	2138	^{12}C^{16}O
2092		^{13}C^{16}O
	2086	^{12}C^{18}O
2052	2005	$Ni(CO)_4$
	2038	^{13}C^{18}O
	2034	$Ni(C^{18}O)_3$ $(C^{16}O)$
2035	1988	...
2017	1972	$Ni(CO)_3$
1996	1953	$Ni(CO)$
	1939	$Ni(C^{16}O)$ $(C^{18}O)$
1967	1921	$Ni(CO)_2$
1944	...	...
516	504	a
457	450	a
435	428	a

a See text.

amount of C^{16}O was present in the matrix during the C^{18}O experiment so that a band at 1996 cm^{-1} due to NiC^{16}O is observed weakly, and a weak band is observed at 1939 cm^{-1} due to Ni(C^{16}O)(C^{18}O). A band assigned to Ni(C^{18}O)$_3$(C^{16}O) occurs at 2034 cm^{-1}, in good correlation with the corresponding band at 2038 cm^{-1} in the gas phase.[18] No bands due to Ni-(C^{18}O)$_2$(C^{16}O) could be identified because of the presence of bands at 2005, 1996, and 1966 cm^{-1}, all in the region where the mixed isotope might be expected to occur.

The positions of all of these infrared bands near 2000 cm^{-1} and their shifts upon isotopic substitution of C^{18}O indicate that they are basically C–O stretching frequencies. However, as indicated in Table II, three weak absorptions were observed in the 500-cm^{-1} region. By analogy with the infrared spectrum of gas-phase Ni(CO)$_4$,[18] these low-frequency bands must correspond to either M–C stretching or M–C–O bending frequencies, and the former is more likely since in Ni(CO)$_4$, the M–C stretching bands are more intense than the M–C–O bending. None of these bands appear to belong to NiCO since the 1997-cm^{-1} band assigned to NiCO has appeared strongly in several experiments without observation of the bands at 516, 457, and 435 cm^{-1}. Annealing experiments indicate that the 435-cm^{-1} band belongs to a different molecule than the two bands at 516 and 457 cm^{-1}. The 435-cm^{-1} band is assigned to the M–C stretching frequency of Ni(CO)$_4$, a large positive shift compared to the value of 423.1 cm^{-1} found in the gas phase.[18] The absorptions at 516 and 457 cm^{-1} may belong to the Ni(CO)$_2$ and Ni(CO)$_3$ molecules, but they are too weak to be assigned.

Bonding in the Nickel Carbonyls. Hybridization.—

The bonding of the CO ligand to the metal can be discussed in terms of the familiar σ and π orbitals of the ligand and the metal. Not all of the symmetries presented in Table I produce a strict σ and π separation by group theory but it is still possible in practice to make the distinction for purposes of a qualitative discussion. The main orbitals involved are the 3d, 4s, and 4p of the nickel and the carbon atom lone-pair and π orbitals on the CO ligand.

The discussion of the bonding can be approached from the usual two points of view, the molecular orbital or valence bond approach. Kimball[20] has employed

(20) G. E. Kimball, *J. Chem. Phys.*, **8**, 188 (1940).

group theory to determine which orbitals on the metal are available for σ and π bonding for various symmetries of MX_n. Following this approach we find the results given in Table III. For a complete ex-

TABLE III
SUMMARY OF STABLE BOND ARRANGEMENTS
AND MULTIPLE-BOND POSSIBILITIES[a]

Coord no.	Confign	Arrangement	Strong π orbitals	Weak π orbitals	Coord. no./no. of π orbitals[b]
1	s	Linear	p^2d^2	...	0.25
1	p	Linear	p^2d^2	...	0.25
1	d	Linear	p^2d^2	...	0.25
2	sp	Linear	p^2d^2	...	0.50
2	dp	Linear	p^2d^2	...	0.50
2	p^2	Angular	$d(pd)$[c]	$d(sd)$	0.66
2	ds	Angular	$d(pd)$	$p(pd)$	0.66
2	d^2	Angular	$d(pd)$	$p(spd)$	0.66
3	sp^2	Trigonal plane	pd^2	d^2	0.75
3	dp^2	Trigonal plane	pd^2	d^2	0.75
3	d^2s	Trigonal plane	pd^2	p^2	0.75
4	sp^3	Tetrahedron	d^2	d^3	1.14
4	dsp^2	Tetragonal plane	d^3p	...	1.00
4	d^2p^2	Tetragonal plane	d^3p	...	1.00
5	dsp^3	Bipyramid	d^2	d^2	1.66
5	d^2sp^2	Tetragonal pyramid	d	pd^2	2.00
5	d^2p^3	Tetragonal pyramid	d	sd^2	2.00
6	d^2sp^3	Octahedron	d^3	...	2.00

[a] Because of the particular metals discussed here, Ta and Ni, we have excluded from Kimball's table those configurations employing more than two d orbitals and those in which no strong π bonding is available. [b] Calculated assuming a weak π orbital is half a strong π orbital. However, the assumption of equal strength for all π orbitals does not affect the trend. [c] Parentheses indicate that there is a choice of more than one orbital, only one of which can be chosen. The d orbital should normally be chosen for the carbonyl compounds.

planation of this table the reader is referred to the original paper of Kimball. The basic idea is that σ donation takes place from the carbon atom lone-pair orbital of CO to 3d, 4s, or 4p orbitals on the metal. For some configurations the distinction is made between strong and weak π orbitals because for these species there is no strict separation of σ and π symmetries. The d orbitals which belong to σ and π symmetries are assumed to interact stronger in the σ framework, so that their π interaction will be weak.

The relevant portions of Table III for the nickel carbonyls involves only the first possibility under the coordination numbers 1-4. Of these configurations only the metal s and p orbitals can be used for σ donation from CO, since nickel assumes the d^{10} configuration in the field of the carbonyl ligands. Examination of Table III for the four cases mentioned above yields a predicted geometry for each of these species. NiCO and $Ni(CO)_2$ are predicted to be linear while $Ni(CO)_3$ and $Ni(CO)_4$ are expected to be trigonal planar and tetrahedral, respectively. These predictions are in accord with those of the Gillespie-Nyholm[21] theory for a d^{10} system on the basis of lone-pair bond-pair repulsion arguments. Kettle[22] has shown that for $M(CO)_{1-4}$, if the metal-carbonyl bonding interaction is related to the appropriate overlap integrals, the geometry is purely dependent on repulsion arguments.

The second feature to note in Table III is that the

ratio of coordination number to metal π orbitals increases with increasing coordination number. This ratio was calculated under the assumption that p_π and d_π orbitals have equivalent π-bonding capacity. On the basis of molecular orbital calculations on $Cr(CO)_6$, $Fe(CO)_5$, and $Ni(CO)_4$[23] it might be argued that a p_π orbital is less effective than a d_π orbital for π bonding. However, even under the assumption that a p_π orbital is half as effective as a d_π orbital the general trend given in the last column of Table III is unchanged.

Bonding in the Nickel Carbonyls. Molecular Orbitals.—In the molecular orbital approach the CO molecule has the configuration $(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2$-$(1\pi)^4(5\sigma)^2(2\pi)^0(6\sigma)^0$. Only the 5σ orbital (mainly the lone pair on the carbon atom) is considered important for σ donation and the 1π and 2π orbitals are important for π interaction with the metal d_π and p_π orbitals. The effect of σ donation is probably to increase the C–O bond strength slightly.[24] However, calculations indicate that changes in σ-bond strength do not appear to be important throughout a series of related molecules.[24-26] From an experimental viewpoint the importance of σ bonding changes is still controversial.[27]

Of the π-bonding orbitals the d_π–1π orbital is completely bonding while the d_π–2π orbital is metal–carbon bonding but carbon–oxygen antibonding. Many experimental data in metal carbonyl chemistry are explained assuming that the d_π–2π interaction ("back-bonding") is the dominant variant.[28] The net result of σ and π bonding is synergistic since an increase in σ donation brings about an increased d_π–2π interaction, both strengthening the metal–carbon bond.

Relating these ideas to the last column in Table III, it is expected that as the coordination number increases, the metal–carbonyl π bond strength will decrease, while the C–O π-bond strength will increase since the d_π–2π interaction is antibonding in the C–O region. The C–O π-bond strength is then expected to follow the order

$$Ni(CO)_4 > Ni(CO)_3 > Ni(CO)_2 > Ni(CO) \qquad (1)$$
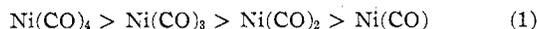
The above arguments have also been employed[29] in the explanation of the mean M–CO dissociation energies as compared to the dissociation energy

$$Ni(CO)_4 \longrightarrow Ni(CO)_3 + CO \qquad (2)$$
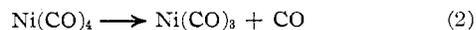
The dissociation energy for eq 2 determined from kinetic studies lies near 13 kcal/mol while the mean M–CO dissociation energy in $Ni(CO)_4$ is much higher, 35.2 kcal/mol. The indication is that removal of successive CO groups from $Ni(CO)_4$ requires increasing energy, a result of the increased amount of π bonding available in the smaller carbonyls.

Bonding and C–O Stretching Frequencies.—The order of the observed C–O stretching frequencies is not the order of the bond strengths expected from the simple theory employed above since the frequency for $Ni(CO)_2$ lies lower than that of $Ni(CO)$. Of

(21) (a) R. J. Gillespie and R. S. Nyholm, *Quart. Rev., Chem. Soc.*, **11**, 339 (1957); (b) R. J. Gillespie, *J. Chem. Educ.*, **47**, 18 (1970).

(22) S. F. A. Kettle, *J. Chem. Soc. A*, 420 (1966).

(23) (a) A. F. Schreiner and T. L. Brown, *J. Amer. Chem. Soc.*, **90**, 3366 (1968); (b) correction: *ibid.*, **90**, 5947 (1968).

(24) K. F. Purcell, *ibid.*, **91**, 3487 (1969).

(25) K. G. Caulton and R. F. Fenske, *Inorg. Chem.*, **7**, 1273 (1968).

(26) W. C. Nieuwpoort, *Philips Res. Rep., Suppl.*, **6** (1965).

(27) D. J. Darensbourg and M. Y. Darensbourg, *Inorg. Chem.*, **9**, 1691 (1970), and references therein.

(28) F. A. Cotton, *ibid.*, **3**, 702 (1964).

(29) F. Basolo and A. Wojcicki, *J. Amer. Chem. Soc.*, **83**, 520 (1961).

TABLE IV
FORCE CONSTANT[a] CALCULATIONS FOR Ni(CO)$_{1-4}$

Molecule	C–K secular equations[b]	Calcn I	Calcn II	Calcn III[c]
NiCO	$\lambda(\Sigma^+) = \mu K_{co}$	$K_{co} = 16.09$	$K_{co} = 16.09$	$K_{co} = 15.57$ $K_{mc} = 3.24$
Ni(CO)$_2$	$\lambda(\Sigma_u^+) = \mu(K_{co} - K_{co,co})$	$K_{co} = 15.63$[d] $K_{co,co} = 0.0$	$K_{co} = 16.63$[e] $K_{co,co} = 1.0$	$K_{co} = 15.53$[f] $K_{mc} = 2.87$
Ni(CO)$_3$	$\lambda(E') = \mu(K_{co} - K_{co,co})$	$K_{co} = 16.43$ $K_{co,co} = 0.0$	$K_{co} = 17.00$ $K_{co,co} = 0.57$[g]	. . .
Ni(CO)$_4$	$\lambda(T_2) = \mu(K_{co} - K_{co,co})$	$K_{co} = 17.01$ $K_{co,co} = 0.0$	$K_{co} = 17.42$[h] $K_{co,co} = 0.32$	$K_{co} = 17.85$[i] $K_{mc} = 2.08$

[a] Units of mdyn/Å. [b] Reference 30; μ represents the reduced mass of the CO group, 0.1459. $\lambda = (5.891 \times 10^{-7})\nu^2$, where ν is the frequency in cm^{-1}. [c] This calculation employs interaction force constants from ref 18 for Ni(CO)$_4$: $K_{mc,co'} = -0.1$, $K_{mc,mc} = 0.1$, $K_{co,co} = 0.12$, $K_{mc,co} = 0.52$ mdyn/Å. [d] $\nu(16,16) = 1967.1$, $\nu(18,16) = 1967.1$ or 1920.1, $\nu(18,18) = 1920.1$ cm^{-1} where $\nu(16,16)$ refers to the calculated frequency for Ni(C^{16}O)$_2$, etc. [e] $\nu(16,16) = 1967.1$, $\nu(18,16) = 1939.0$, $\nu(18,18) = 1920.1$ cm^{-1}. [f] $\nu(16,16) = 1967.8$, $\nu(18,16) = 1935.1$, $\nu(18,18) = 1924.1$ cm^{-1}. [g] $K_{co,co}$ was estimated since we have no data from which to calculate it; this value falls about midway between that for Ni(CO)$_2$ and Ni(CO)$_4$. [h] Solution for C–K equations obtained from ref 18. [i] Complete solution for Ni(CO)$_4$.[18]

course, a comparison with the force constants of the C–O bonds is really necessary, but it is clear that they cannot be derived accurately from the few observed frequencies.

A usual simplifying assumption is that of Cotton and Kraihanzel,[30] where only C–O stretching and C–O, C–O interaction force constants are retained in the vibrational analysis. In Table IV the C–K equations are listed and the results of several force constant calculations are given. The computed frequencies for each calculation are within ± 1 cm^{-1} of the observed ν_{co} values in Table I, unless indicated otherwise.

Examination of the C–K equations show that in all cases except NiCO the interaction force constant $K_{co,co}$ enters into the solution. It is not surprising then that calculation I in which $K_{co,co} = 0.0$ does not result in the predicted trend of C–O bond strengths (1). In the second set of calculations the mixed-isotope frequency of 1939 cm^{-1} for Ni(C^{16}O)(C^{18}O) is used to calculate $K_{co,co}$ for Ni(CO)$_2$ and a value of 1.0 mdyn/Å is obtained. As seen in Table IV this is sufficient to cause the calculated force constants to follow the trend in (1) if a "reasonable" interaction force constant is chosen for Ni(CO)$_3$. In calculation III presented in Table IV, the M–C force constant is also introduced and this too is seen to cause significant changes in the values of K_{co} needed to fit the observed frequencies.

Although the ordering of force constants in calculation II follows the trend predicted in eq 1, Jones[31] has pointed out that the results should be treated with caution, particularly for species of different symmetry. In any case, the computed force constants in calculations II and III are in reasonable agreement with that predicted on the basis of the π-bonding model.

Examination of metal–carbon overlap populations for Ni(CO)$_4$[28,26] support the ideas presented in Table III. That is, for Ni(CO)$_4$ the 4s and 4p orbitals are heavily involved in σ bonding, while the d$_{z^2}$ and d$_{x^2-y^2}$ orbitals are the "strong" π-bonding orbitals. The d$_{xy}$, d$_{xz}$, and d$_{yz}$ orbitals belong to both σ and π symmetry and as predicted by Kimball, they are less involved in π bonding than d$_{z^2}$ and d$_{x^2-y^2}$. No calculations have been carried out to date on Ni(CO)$_{1-3}$.

B. Tantalum Carbonyls.—Before presenting the spectra of tantalum carbonyls, we will discuss the

possible differences between nickel and tantalum as concerns bonding to carbon monoxide. Nickel has ten valence electrons and is considered a d^{10} system in the nickel carbonyls. Tantalum has only five valence electrons so that all monomeric tantalum carbonyls will be paramagnetic, with only one unpaired electron due to the large spectrochemical splitting of the d orbitals.

The "effective atomic number" rule predicts that no more than six carbonyl ligands can bond to tantalum and that even then there is the possibility of dimerization: $2\text{Ta(CO)}_6 \rightarrow \text{Ta}_2\text{(CO)}_{12}$. In fact, the only binary metal carbonyl of tantalum reported[32] is said to obtain the dimeric structure in the solid state. Thus, we have a possibility in the monomer of six-coordination for tantalum as compared to four-coordination for nickel.

The other difference between nickel and tantalum carbonyls is also produced by the d^5 vs. d^{10} situation mentioned above. In tantalum carbonyls only three of the five 5d orbitals are occupied in the tantalum carbonyl molecules so that the two remaining can be used for σ bonding. Of course, it is just this fact which allows the coordination number to increase to 6. However, this effect also has implications concerning the predicted geometry of the various tantalum carbonyls. For example, examination of Table III indicates that only for TaCO, Ta(CO)$_3$, and Ta(CO)$_6$ can the geometry be predicted, since there is only one arrangement possible—linear for TaCO, trigonal planar for Ta(CO)$_3$, and octahedral for Ta(CO)$_6$. For Ta(CO)$_2$, a linear structure is predicted if σ donation occurs to the hybrid sp or dp metal orbitals. However, a bent structure is predicted for hybridizations p^2, ds, and d^2. The situation is equally complicated for coordination numbers 4 and 5 (see Table III).

Another difference which might be expected to occur in going from nickel to tantalum carbonyls is the occurrence of the Jahn–Teller effect. However, the infrared spectra of V(CO)$_6$[33] and of the hexafluorides of Re, Tc, Os, and Ru[34] do not exhibit extra infrared fundamentals, indicating that the Jahn–Teller effect is dynamic for these molecules.

Infrared Spectra of Tantalum Carbonyls.—A series of infrared spectra illustrating the course of the annealing experiments is given in Figure 2. As in the case of

(30) F. A. Cotton and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, **84**, 4432 (1962).

(31) L. H. Jones, *Inorg. Chem.*, **6**, 1269 (1967).

(32) J. E. Wyman, *Chem. Abstr.*, **58**, 7639e (1963).

(33) H. Haas and R. K. Sheline, *J. Amer. Chem. Soc.*, **88**, 3219 (1966).

(34) B. Weinstock and G. L. Goodman, *Advan. Chem. Phys.*, **9**, 169 (1965).

the nickel carbonyls the matrix was annealed to the appropriate temperature and then quenched to 4.2°K before recording the spectra. The spectra do not show the CO absorption at 2138 cm⁻¹; its intensity decreases relative to the bands in the 2000–1800-cm⁻¹ region as the annealing progresses.

In the original deposition (Figure 2a) no absorptions
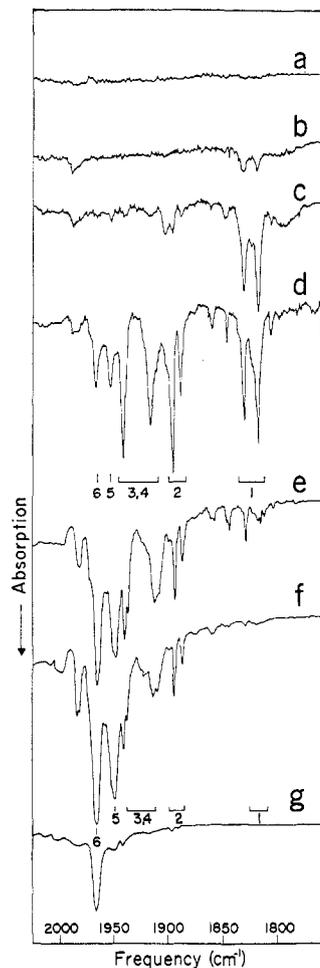
Figure 2.—Infrared spectra of tantalum atoms deposited in a 200:1 Ar:CO matrix and subsequent annealing: a, original; b, 13°K; c, 16°K; d, 18°K; e, 23°K; f, 29°K; g, 35°K (temperatures are relative). The arabic numerals refer to the relative rate of growth and disappearance of the bands.

are present except CO; slight diffusion as in Figure 2b produces a doublet at 1819, 1831 cm⁻¹. Further diffusion (Figure 2c) produces a dramatic increase in this doublet with a new doublet beginning to grow in at 1891, 1897 cm⁻¹. Increasing the temperature of the matrix a few more degrees (Figure 2d) produces a whole new plethora of bands at 1986, 1967, 1953, 1943, 1916, 1862, 1850, and 1808 cm⁻¹. The last three bands and the band at 1986 cm⁻¹ are relatively weak and appear only when the tantalum atom concentration is high in the matrix. Further annealing as presented in Figure 2e illustrates a large increase in the bands at 1967 and 1953 cm⁻¹ at the expense of the doublets at 1897, 1891 and 1831, 1819 cm⁻¹. Meanwhile, proceeding from spectrum e to f results in a further relative decrease of the above doublets and in addition a decrease in the bands at 1943 and 1916 cm⁻¹. Finally, extensive annealing as presented

in spectrum g results in only one significant band remaining at 1967 cm⁻¹.

Infrared Assignments for Tantalum Carbonyls.— The infrared spectra in Figure 2 are considerably more complex than those in Figure 1 for the nickel carbonyls. Not only are there more absorptions but the band widths are broader. However, the observations as presented in Figure 2 and discussed above indicate that the bands at 1967 and 1953 and the doublets at 1897, 1891 and 1831, 1819 cm⁻¹ all belong to individual molecules. The bands at 1943 and 1916 cm⁻¹ may belong to different molecules but this could not be determined from intensity relationships as presented in Figure 2.

The complete listing of bands for both the $C^{16}O$ and $C^{18}O$ experiments is presented in Table V along

TABLE V
INFRARED ABSORPTIONS OBSERVED IN
TANTALUM CARBONYL EXPERIMENTS

Ta–$C^{16}O$–Ar	Ta–$C^{18}O$–Ar	Tentative assignment	Ta–$C^{16}O$–Ar	Ta–$C^{18}O$–Ar	Tentative assignment
1967	1920	$Ta(CO)_6$	1897	1852	$Ta(CO)_2$
1953	1905	$Ta(CO)_5$	1891	1847	$Ta(CO)_2$
1943	1897	$Ta(CO)_4$	1831	1790	TaCO
1916	1872	$Ta(CO)_3$	1819	1778	TaCO

with tentative assignments. These assignments are based on the rate of growth and disappearance of the features presented in Figure 2 and discussed above. First, the assignments are tentative since we do not understand why the bands 1897, 1891 and 1831, 1819 cm⁻¹ assigned to $Ta(CO)_2$ and TaCO are doublets, unless this is caused by matrix sites. Second, the assignment of the bands at 1943 and 1916 cm⁻¹ is uncertain since both absorptions may belong to the same molecule. Their assignment as given in Table V is based upon the fact that, for both nickel and tantalum carbonyls, we find that in general the stretching frequency increases with increasing coordination number. The assignment of the 1967-cm⁻¹ band to Ta-(CO)₆ may be compared to 1986 cm⁻¹ for $V(CO)_6$ in the gas phase.[33] This band could not be due to $Ta_2(CO)_{12}$ since it appears already in Figure 2d, much too early for the formation of such a large molecule. The presence of monomers in the matrix could be confirmed by electron spin resonance measurements.

The above assignments were made simply on the basis of annealing experiments, as presented in Figure 2. An assignment in terms of the geometry and infrared-active modes as presented in Table I for each of the tantalum carbonyl molecules is considerably more difficult. For example the doublet at 1897, 1890 cm⁻¹ is assigned to $Ta(CO)_2$. If the molecule is linear, only a single Σ_u^+ C–O stretching mode is active so that one must say that the doublet effect is caused by matrix splitting. On the other hand, $Ta(CO)_2$ could also be bent (Table III) in which case two normal modes are infrared active, $a_1 + b_1$. There is the further complication that even if two or more modes are infrared active, as is the case for bent $Ta(CO)_2$ or tetragonal-pyramidal $Ta(CO)_5$, only the more intense band may achieve enough intensity to be observable. With cognizance of the above effects due to geometry and relative intensities of the bands our assignments are as follows: $M(CO)_3$, E or E′; $M(CO)_4$, T_2 or E_u; $M(CO)_5$, E or E′; $M(CO)_6$, T_{1u}.

Bonding in the Tantalum Carbonyls.—The annealing experiments given in Figure 2 present a basis for assigning the higher frequency infrared bands to molecules with higher coordination numbers. Although application of Table III to the tantalum carbonyls results in more than one geometric possibility for $Ta(CO)_2$, $Ta(CO)_3$, and $Ta(CO)_5$, this does not significantly affect the ratio of coordination number to metal π orbitals. Thus, we find that the general trend is for ν_{co} to increase as this ratio increases. Since the geometries and assignments are not as certain for tantalum carbonyls, force constant calculations were not attempted. Also, no mixed-isotope species were assigned so that $K_{co,co}$ could not be calculated in any case. If ν_{co} can be taken as a rough indication of K_{co}, the general conclusion holds for both the tantalum and nickel carbonyls concerning decreased metal–carbon π bonding with increased coordination number.

C. Electronic Spectra.—The electronic spectra have been recorded from 6200 to 2500 Å for both the nickel and tantalum atoms in a pure argon matrix. The spectra have also been recorded for the 200:1 Ar:CO experiments both before and after annealing. The spectra in Ar–CO before annealing correspond to that obtained in pure argon. The spectra both before and after annealing are presented in Figure 3 for nickel
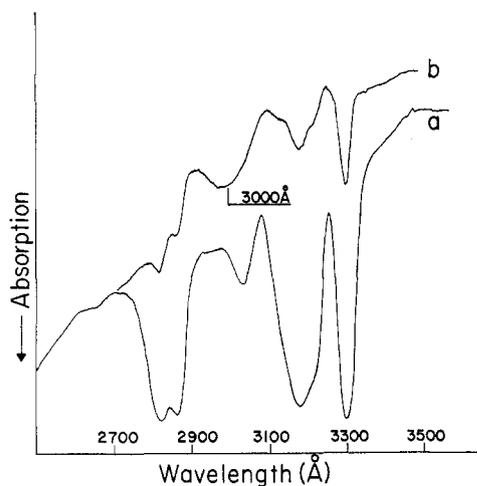
Figure 3.—Electronic spectra of nickel atoms deposited in a 500:1 Ar:CO matrix: a, original; b, annealed to ~30°K.

carbonyl and Figure 4 for tantalum carbonyl. In each case the original atomic bands are found to decrease in intensity with the growth of new features upon annealing.

The nickel carbonyl spectrum shows the growth of a broad feature centered at 3000 Å which is assigned to $Ni(CO)_4$. This band may correspond to the
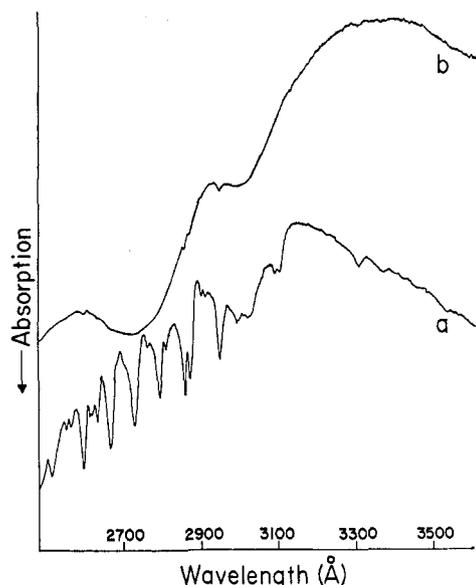
Figure 4.—Electronic spectra of tantalum atoms deposited in a 200:1 Ar:CO matrix: a, original; b, annealed to ~30°K.

broad band observed by Garrett and Thompson[35] at about 3300 Å.

The tantalum carbonyl electronic spectra presented in Figure 4 show the disappearance of tantalum atom bands and the growth of a broad feature at 2725 Å. Since, these bands were recorded after extensive annealing, they are assigned to $Ta(CO)_6$. No electronic absorptions which could be assigned to intermediate tantalum or nickel carbonyls have been assigned.

Summary

Infrared bands in the C–O stretching region have been assigned to the intermediate carbonyls $Ni(CO)_{1-4}$ and $Ta(CO)_{1-6}$ upon annealing Ar–CO matrices containing metal atoms. Since the assignments were based upon the relative growth and disappearance of bands with annealing, the assignments cannot be considered as conclusive evidence for each species, especially in the case of the more complex infrared spectra obtained in the tantalum experiments.

For the nickel carbonyls relative C–O stretching force constants have been calculated from the observed frequencies. For the nickel and tantalum carbonyl, it is found that in general ν_{co} increases with increasing coordination number and that the number of CO ligands per metal π orbitals increases in the same order.

(35) A. P. Garratt and H. W. Thompson, *J. Chem. Soc.*, 524 (1934).