Table IV. ^{13}C NMR Carbonyl Chemical Shifts and Stretching Frequencies in Transition Metal Carbonyl Compounds

Compd	δ, ppm	Ref	$\nu_{C=O}$, cm^{-1}	Ref
CO	181.5	17	2143	22
$Cu(CO)^+$	169.0		2160	*a*
$Cu(CO)_3^+$	169.2		2177	*b*
$Cu(CO)_4^+$	169.5		2185	*a*
$Ag(CO)_2^+$	173.4		2193	*a*
$Ni(CO)_4$	191.1	18	2057	23
$Co_2(CO)_8$	203.8	19	2070, 2043, 2025	24
$Fe(CO)_5$	211.9	20	2045, 2027	25
$Cr(CO)_6$	212.3	21	2100, 2020	26
$V(CO)^-$	225.7	16	1850	27
$V_2(CO)_{12}$			1980	28

[a] This work–data in $BF_3 \cdot H_2O$. [b] This work–data in 1.0:0.3 H_2SO_4–FSO_3H.

The comparison of ^{13}C NMR chemical shifts and ir stretching frequencies in transition metal carbonyl compounds is shown in Table IV. The $\nu_{C=O}$ in 1B metal carbonyl compounds is larger than in free CO or other metal carbonyl compounds. The ^{13}C NMR chemical shifts of 1B metal carbonyl compounds are observed at higher field than in other carbonyl compounds. This may be due to the shortening of C—O bond caused by the C→M dative bond.

Bodner et al. have observed a correlation between ^{13}C NMR carbonyl chemical shifts and the stretching frequencies for a series of (π-arene)tricarbonylchromium complexes and suggested that the ^{13}C chemical shift is deshielded with increasing π back-donation.[16] From Table IV, the decrease of π back-donation in the order $V(CO)_6^- > Cu(CO)_4^+$ is suggested from the increase in $\nu_{C=O}$ and in the shielding of the ^{13}C NMR chemical shift. A linear relationship is found between ^{13}C NMR chemical shift and the carbonyl stretching frequency.

Registry No. $Cu(CO)^+$, 28410-99-3; $Cu(CO)_3^+$, 28990-05-8; $Cu(CO)_4^+$, 41697-87-4; $Ag(CO)_2^+$, 49694-96-4.

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(29) The half-bandwidths of $Cu(CO)^+$ were 38, 33, 8, 10, and 10 Hz in H_2SO_4, CF_3SO_3H, FSO_3H, $BF_3 \cdot H_2O$, and HCl solutions, respectively. On the other hand, the half-bandwidths of $Ag(CO)_2^+$ were 6 Hz in all of the above solutions.
(30) The half-bandwidths of $Cu(CO)_4^+$ in FSO_3H solution were 52 Hz at −30 °C and 133 Hz at −60 °C. In $BF_3 \cdot H_2O$ solution the values were 15 Hz at −30 °C and 37 Hz at −45 °C.

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Niobium–Dinitrogen Complexes Studied by Infrared Matrix Isolation Spectroscopy[1a]

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Nitrogen had long been thought to have no affinity for transition metals on the basis of the inertness of gaseous nitrogen itself. This view has changed drastically in the last few years which have seen the preparation of a large number of transition metal complexes containing molecular nitrogen[2] following the initial synthesis[3] of $[Ru(NH_3)_5(N_2)]^{2+}$. More recently binary metal–dinitrogen complexes including those of Li,[4] Ni and Pd,[5] Cr and Cu,[6] Pt,[7] Co,[8] and Rh[9] have been synthesized in noble gas matrices at low temperatures. It is the purpose of this Note to present some results of experiments in which Nb atoms were cocondensed with N_2 in Ar matrices at 14 K.

Experimental Section

Metal atoms were produced by a sputtering source[10] with a Nb metal (Research Organic/Inorganic Chemical Corp.) cathode using Ar as the sputtering gas as well as the matrix gas. Experimental procedures were similar to those described previously in the study of Pt–N_2 complexes.[7a] The estimated Ar:Nb ratio was 10^4:1 in the matrix. Due to the breadth of most of the observed peaks, the frequency accuracy is ±1 cm^{-1} above 2000 cm^{-1} and ±0.5 cm^{-1} below 2000 cm^{-1}.

Results

Compared to the corresponding spectra obtained[7a] by cocondensing Pt and N_2, the spectra obtained by cocondensing Nb and N_2 are strikingly different in two ways. First, the number of absorption peaks observed is much greater in the case of Nb + N_2 which suggests that a larger number of complexes are formed. Second, the frequency range of these peaks (1850–2200 cm^{-1}) extends to considerably lower frequency in the case of Nb + N_2. This suggests the Nb–N_2 interaction is stronger than that of Pt–N_2 (or any other reported metal–dinitrogen complex with the possible exception of Li, for which the assigned[4] N–N stretch of LiN_2 is 1800 cm^{-1}) if one interprets the difference between the frequency of gaseous N_2 and that of the complex as a measure of the strength of interaction.

In order to determine the nature of the absorbers responsible for these peaks, several experiments were performed. The spectrum of Nb in an Ar matrix, taken in the absence of N_2, demonstrated that no major absorption peak in the frequency range of interest was due to an impurity in the Nb, in the Ar, or in the background gas. A study of the products of the condensation of Nb with CO in Ar matrices[11] has specifically shown that none of the major absorptions can be attributed to $Nb(CO)_x$ or $Nb(CO)_x(N_2)_y$ complexes. Further evidence that all of the peaks can be assigned to the N–N stretches of various Nb–N_2 complexes is contained in Table I which compares the frequencies observed in different experiments using $^{14}N_2$ to their counterparts when $^{15}N_2$ was used. When the Cotton–Kraihanzel force-field approximation[12] is applied to metal–dinitrogen complexes, it is predicted that at least one N–N stretching mode of a $M(^{15}N_2)_x$ complex should show

Table I. Comparison of the Observed N–N Stretching Frequencies of $^{14}N_2$ Complexes with $^{15}N_2$ Complexes in an Ar Matrix ($\rho_{calcd} = 0.9662^a$)

$\bar{\nu}(^{14}N_2)$, cm^{-1}	$\bar{\nu}(^{15}N_2)$, cm^{-1}	$\rho_{obsd}{}^b$	$\bar{\nu}(^{14}N_2)$, cm^{-1}	$\bar{\nu}(^{15}N_2)$, cm^{-1}	$\rho_{obsd}{}^b$
1601	1548.6	0.967	1993.9	1928.0	0.9669
1649	1594.8	0.967	2011.6	1944.2	0.9665
1700	1646.0	0.968	2038.1	1971.0	0.9671
1719	1662.8	0.967	2042.9	1976.0	0.9673
1728	1670.7	0.967	2049.9	1981.6	0.9667
1736	1676.2	0.966	2065.9	1998.6	0.9674
1767	1709.5	0.967	2073.6	2004.2	0.9665
1836.2	1775.8	0.9671	2079.8	2010.7	0.9668
1854.9	1792.1	0.9661	2090.1	2021.2	0.9670
1865.1	1803.3	0.9669	2093.5	2024.3	0.9669
1875.9	1814.0	0.9670	2098.7	2030.3	0.9674
1900.4	1837.0	0.9666	2103.6	2035.0	0.9674
1906.4	1843.0	0.9667	2120.7	2050.4	0.9669
1916.4	1853.4	0.9671	2136.3	2064.1	0.9662
1925.0	1861.3	0.9669	2146.4	2075.2	0.9668
1930.6	1866.5	0.9668	2164.5	2093.5	0.9672
1942.8	1879.1	0.9672	2172.1	2098.9	0.9663
1949.7	1884.9	0.9668	2190.7	2118.1	0.9669
1960.6	1894.4	0.9662	2200.7	2125.7	0.9659
1967.2	1901.2	0.9664			

[a] $\rho_{calcd} = [\mu(^{14}N_2)/\mu(^{15}N_2)]^{1/2}$. [b] $\rho_{obsd} = \bar{\nu}(^{15}N_2)/\bar{\nu}(^{14}N_2)$.

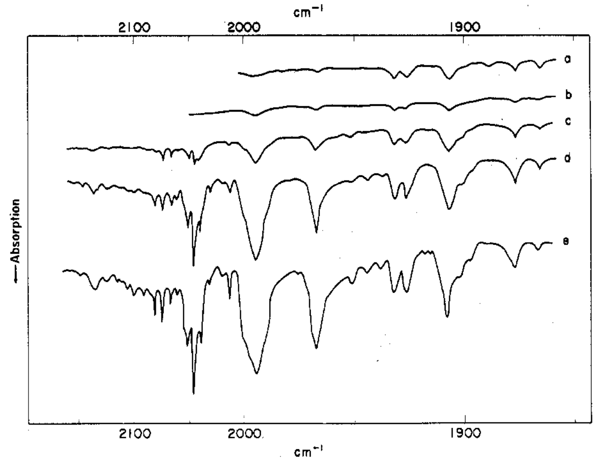

Figure 1. Infrared absorption spectra obtained by deposition of Nb atoms into an Ar matrix containing small amounts of $^{14}N_2$. Spectrum a was obtained from a 2-h deposition in a matrix containing 0.01% N_2 after annealing to 45 K; spectra b–e were obtained from a 2.5-h deposition in a matrix containing 0.1% N_2 after annealing to 17, 30, 36, and 40 K, respectively.

an isotope shift relative to the corresponding $^{14}N_2$ complex which is independent of x. Furthermore, the shift can be calculated from the reduced masses of $^{14}N_2$ and $^{15}N_2$. On this basis, all of the 39 measured frequencies of Table I can be assigned to the N–N stretching modes of binary Nb–N_2 complexes.

In order to assign peaks to particular stoichiometries and geometries of the $Nb(N_2)_x$ complexes, information from three types of experiments was correlated: the behavior of the peaks upon annealing, the dependence of the absorbance upon the N_2:Ar ratio, and the frequencies of mixed isotope peaks. Figure 1 shows several of the spectra obtained in these studies.[13]

The observations of the studies may be summarized as follows.

(1) The spectrum obtained by annealing a matrix containing small amounts of N_2 (~0.1%) is similar to that obtained initially in a matrix containing larger amounts of N_2 (~6%). Thus, the annealing behavior of all observed peaks can be explained by reactions of the type

$$Nb(N_2)_x + N_2 \rightarrow Nb(N_2)_{x+1} \qquad (1)$$

Table II. Observed Frequencies in an Ar Matrix Containing Nb, 0.5% $^{14}N_2$, and 0.5% $^{15}N_2$ Compared to the N–N Stretching Frequencies Calculated for the Isotopic Complexes $Nb(N_2)_4$ with a Square-Planar (D_{4h}) Geometry

$\bar{\nu}$, cm^{-1}		
Obsd	Calcd^a	N–N str mode (complex^b)
2003.9	2003.2	E_u (I) + B_2 (II) + B_{2u} (III)
2019.6	2019.9	B_2 (IV)
c	2023.0	A_1 (II)
2024.3	2024.5	A_1 (V)
2028.7	2029.0	A_1 (IV)
2073.0	2073.3	E_u (VI) + B_2 (V) + B_{1u} (III)
c, d	2074.5	A_1 (II)
2106	2107.0	B_2 (IV)
d	2113.8	A_1 (V)
d	2163.2	A_1 (II)
d	2179.6	A_1 (IV)
d	2195.5	A_1 (V)

[a] Calculated from $f = 18.55$, f_i(cis) = 0.371, and f_i'(trans) = 0.815 mdyn/Å. [b] I represents the Nb Complex with four $^{15}N_2$ ligands; II, three $^{15}N_2$ ligands and one $^{14}N_2$ ligand; III, two $^{15}N_2$ and two $^{14}N_2$ ligands in a trans configuration; IV, two $^{15}N_2$ and two $^{14}N_2$ ligands in a cis configuration; V, one $^{15}N_2$ ligand and three $^{14}N_2$ ligands; VI, four $^{14}N_2$ ligands. [c] Not observed. May be masked by nearby peaks. [d] Not observed. Should be a very weak absorption.

This is in contrast with the case of Pt + N_2 where reactions of the type

$$Pt(N_2)_x + Pt \rightarrow Pt_2(N_2)_x \qquad (2)$$

were required to explain the annealing data.

(2) There are distinct differences in the behavior of major peaks upon annealing which allow their classification into three groups. Peaks due to species which contain a small number of N_2 ligands decrease absorbance as reaction 1 occurs (1865, 1876, 1906, 1915, 1925, and 1931 cm^{-1}). Peaks due to species which contain an intermediate number of N_2 ligands first grow upon annealing, due to their production from complexes with a smaller number of N_2 ligands, and then decrease as further diffusion produces complexes with a larger number of N_2 ligands (1967, 1995, and 2045 cm^{-1}). A third group of peaks may be assigned to complexes with a large number of N_2 ligands. These peaks are present initially in matrices containing 6% N_2 in Ar and they grow in strongly upon annealing matrices with less than 1% N_2 (2073, 2136 cm^{-1}).

(3) Experiments conducted with 50% enriched N_2 were largely inconclusive due to the presence of an extensive number of peaks and overlap among them. However, several peaks could be clearly identified as originating from species containing both $^{14}N_2$ and $^{15}N_2$ ligands. Of these peaks, a good fit could be made to a square-planar $Nb(N_2)_4$ complex (D_{4h}) as shown in Table II. The observed frequency pattern is well fit by a D_{4h} complex and the observed intensity pattern is in good qualitative correspondence. Nevertheless, the assignment of a D_{4h} $Nb(N_2)_4$ entity should be considered tentative due to the complexity of the spectrum and the overlap of peaks observed whenever both $^{14}N_2$ and $^{15}N_2$ were present.

(4) The pair of peaks at 1926 and 1931 cm^{-1} are most probably due to $Nb(N_2)$ from their annealing behavior and concentration dependence. In particular, these peaks are the only ones with measurable absorbance that are initially present in a matrix containing 0.1% N_2 in Ar.

Discussion

The large number of peaks observed upon cocondensation of Nb and N_2 is unprecedented (see ref 4–9) and was unexpected. Several explanations should be considered. (1) More than one geometry exists for the higher stoichiometry complexes, for example, both the C_{3v} and D_{3h} geometries of $Nb(N_2)_3$. (2) Both "sideways" and "end-on" bondings of N_2

to Nb result in more than one absorption peak for even the lower stoichiometry species such as NbN_2. (3) There is an unusually strong interaction between the complexes and the matrix environment resulting in multiple sites in the matrix, each site giving rise to a distinct absorption peak for each complex. (4) Some of the complexes contain more than one Nb. (5) Some of the complexes contain a ligand in addition to N_2.

The possibility that a ligand other than N_2 is involved seems unlikely in view of the negative results of our experiments designed to detect impurities. The possibility that more than one Nb atom is involved also seems unlikely because careful studies of the visible and uv spectra of Nb atoms in Ar were conducted[14] and no polymeric species were observed except after annealing. Furthermore, the concentration of Nb_2 and other polymers would need to be about the same as that of isolated Nb in order to explain the many strong peaks observed. There is precedent for multiple matrix sites. In short, we have been unable to account for the unexpected and rich spectrum in an unambiguous manner despite extensive variation of the experimental parameters. Tentative assignments of NbN_2 and D_{4h} $Nb(N_2)_4$ complexes can be made but the majority of the peaks can only be classified roughly as to the number of N_2 ligands attached to Nb.

Registry No. Nb, 7440-03-1; $^{14}N_2$, 7727-37-9; $^{15}N_2$, 29817-79-6.

References and Notes

(1) (a) Work performed under the auspices of the U.S. Energy Research and Development Administration. (b) Honors Research participant from Bethany Nazarene College, Bethany, Okla., Spring 1973.
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(13) Several experiments were performed using $^{14}N_2$ and $^{15}N_2$ concentrations from 100% to 0.01% in Ar. Annealing experiments on each of these matrices generated large quantities of data on the behavior of the absorption peaks in Table I. In addition other peaks could be identified as species containing both $^{14}N_2$ and $^{15}N_2$. Due to the limitations of brevity imposed by this Note, these data are not presented.
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Phosphorus-31 Chemical Shift Variations with Countercation and Ionic Strength for the Various Ethyl Phosphates

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Observations in our laboratories have shown ^{31}P nuclear magnetic resonance (NMR) chemical shifts of a number of biological phosphorus compounds (studied by the Fourier-transform method in aqueous and nonaqueous solvents, as well as in intact living cells) to be differently affected by various simple, singly charged cations.[1-6] In order to provide a foundation for the understanding of such studies, we have carried out ^{31}P shift determinations on some simple orthophosphate compounds (and a phosphonate), as reported herein.

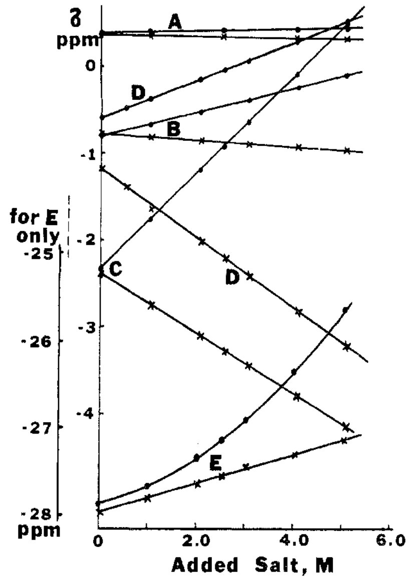

Figure 1. ^{31}P chemical shifts, δ, of 0.010 M aqueous solutions at pH 7.00 as a function of added salt concentration for (A) triethyl orthophosphate, (B) the diethyl orthophosphate anion, (C) the monoethyl orthophosphate anion, (D) the inorganic orthophosphate anion, and (E) the ethylphosphonate anion. The upper curves of each set (with data points denoted by black circles) correspond to the added salt being tetramethylammonium chloride with the counterion to the phosphorus acids being the tetramethylammonium ion. The lower lines of each set (with data points denoted by crosses) correspond to the added salt being sodium chloride with the counterion to the phosphorus acids being the sodium ion.

Experimental Section

Field frequency stability of the Bruker HFX-5 spectrometer[2,4] (^{31}P field 36.43 MHz) was provided by the protons of tetramethylsilane contained in a capillary coaxially mounted in the 13-mm spinning sample tube. As is customary,[7] the NMR chemical shifts are reported relative[8] to "external" 85% H_3PO_4,[9] with positive shifts being upfield. The salts of the phosphorus oxy acids were prepared in the chosen solvent by previously published procedures.[10] All of the reported data correspond to the phosphorus concentrations being held at 0.010 M and the pH at 7.00 at a temperature of 25.0 ± 0.2 °C. The pH was adjusted without use of a buffer so that foreign ions were not introduced.

Results and Discussion

The variations with added tetramethylammonium chloride or sodium chloride of the ^{31}P chemical shifts at pH 7.00 of dilute, aqueous solutions of triethyl orthophosphate, $(C_2H_5O)_3PO$, the diethyl orthophosphate anion, $(C_2H_5O)_2PO_2^-$, the monoethyl orthophosphate anion, $(C_2H_5O)PO_3H_{1.3}{}^{0.7-}$, and the unesterified orthophospate anion, $PO_4H_{1.6}{}^{1.4-}$, are shown in Figure 1, along with the same information for the ethylphosphonate ion, $C_2H_5PO_3H_{1.5}{}^{0.5-}$. If tetramethylammonium bromide or sodium bromide are employed in place of the respective chloride, exactly the same curves as shown in Figure 1 are obtained. Although less work was done with the perchlorate or sulfate salts, it also appeared that the results were essentially the same. In other words, the role of the anion in causing these chemical shift changes is unimportant. At

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