

Transition Metal Atom Inorganic Synthesis in Matrices

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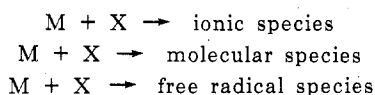
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The general techniques of matrix isolation have been well documented since the pioneering work of Whittle, Dows, and Pimentel.¹ Briefly, the matrix isolation technique may be described as a method for studying molecules or molecular fragments (radicals or ions) which, although possibly unstable at room temperature, are stabilized at cryogenic (4.2–20 K) temperatures in solid matrices. These matrices may be inert or reactive with respect to the molecule or fragment in question.

The species under study may be produced prior to condensation by high-temperature vaporization, by microwave or electrical discharge techniques, or *in situ* by photolysis studies. Conventional forms of optical spectroscopy as well as electron spin resonance and Mössbauer methods are then employed to study the trapped or "matrix-isolated" species. The reader is referred to recent reviews^{2–9} and a book¹⁰ for detailed descriptions of the matrix-isolation technique.

Although most of the elements of the periodic table can be produced in a monatomic form and have been at some time the subject of study by vapor equilibrium, uv-visible, and mass spectrometric techniques, only very recently has this wealth of physical data been utilized in a practical sense by the synthetic chemist.

Gaseous metal atoms characteristically have small activation energies for reactions with each other in interatomic collisions, the effects of which can be minimized by using high-vacuum conditions. The cocondensation of metal atoms with other compounds in an inert matrix, onto a surface cooled to cryogenic temperatures, can result in reactions of the type



Transition metal atoms tend to undergo reactions of the second type—*i.e.*, formation of binary species—

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and it is these with which this Account will be primarily concerned.

Cocondensation reactions of this type are currently being examined by matrix infrared and Raman spectroscopy.^{11–14} Although matrix uv-visible,^{15,16} electron spin resonance, and Mössbauer¹⁷ spectroscopy are potentially useful, they are playing only a minor role in these studies. Whenever possible, the experiments are supplemented by variable concentration studies, isotopic substitutions, observations of spectral changes when diffusion is allowed to occur at higher temperatures, and matrix Raman depolarization measurements.¹⁸

With these methods, it is proving feasible to synthesize entirely new compounds which would be difficult, if not impossible, to prepare and stabilize by other methods, to control and monitor the courses of chemical reactions, and to study their reactive intermediates. The results of many of these studies involving transition metal atoms have important implications in the fields of chemisorption, homogeneous and heterogeneous catalysis, nitrogen fixation, and synthetic and naturally occurring oxygen carriers.

Binary Transition Metal Complexes, M(XY)

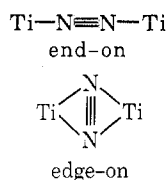
Using high-dilution experimental conditions, a number of carbonyl (M(CO)), dinitrogen (M(N₂)), and dioxygen (M(O₂)) complexes have recently been isolated and identified in rare gas matrices.

- (1) E. Whittle, D. A. Dows, and G. C. Pimentel, *J. Chem. Phys.*, **22**, 1943 (1954).
- (2) W. Weltner, Jr., *Advan. High Temp. Chem.*, **2**, 85 (1969).
- (3) H. E. Hallam, *Annu. Rep. Progr. Chem.*, **A**, **67**, 117 (1970).
- (4) A. J. Barnes and H. E. Hallam, *Quart. Rev., Chem. Soc.*, **23**, 392 (1969).
- (5) J. W. Hastie, R. H. Hague and J. L. Margrave, *Spectrosc. Inorg. Chem.*, **1**, 58 (1970).
- (6) D. E. Milligan and M. E. Jacox, *Advan. High Temp. Chem.*, **4**, 1 (1971).
- (7) G. A. Ozin, *Spex Speaker*, **16** (4) (1971).
- (8) J. S. Ogden and J. J. Turner, *Chem. Brit.*, **7**, 186 (1971).
- (9) L. Andrews, *Annu. Rev. Phys. Chem.*, **22**, 109 (1972).
- (10) B. Meyer, "Low Temperature Spectroscopy," Elsevier, New York, N. Y., 1971.
- (11) E. P. Kündig, M. Moskovits, and G. A. Ozin, *J. Mol. Struct.*, **14**, 137 (1972).
- (12) G. A. Ozin and A. Vander Voet, *J. Chem. Phys.*, **56**, 4768 (1972).
- (13) See, for example: (a) L. Andrews, *J. Chem. Phys.*, **50**, 4288 (1969); (b) R. R. Smardzewski and L. Andrews, *ibid.*, **57**, 1327 (1972); (c) R. C. Spiker, L. Andrews, and C. Trindle, *J. Amer. Chem. Soc.*, **94**, 2401 (1972).
- (14) See, for example: (a) J. S. Anderson, A. Bos, and J. S. Ogden, *J. Chem. Soc. D*, 1381 (1971); (b) A. J. Hinchcliffe, J. S. Ogden, and D. D. Oswald, *J. Chem. Soc., Chem. Commun.*, 338 (1972).
- (15) R. L. DeKock, *Inorg. Chem.*, **10**, 1205 (1971).
- (16) L. Andrews and G. C. Pimentel, *J. Chem. Phys.*, **47**, 2905 (1967).
- (17) A. Bos, A. T. Howe, D. W. Dale, and L. W. Becker, *J. Chem. Soc., Chem. Commun.*, 730 (1972).
- (18) (a) J. W. Nibler and D. A. Coe, *J. Chem. Phys.*, **55**, 5133 (1971); (b) H. Huber, G. A. Ozin, and A. Vander Voet, *Nature (London), Phys. Sci.*, **232**, 166 (1971).

Monodinitrogen Complexes, $M(N_2)$. With the increasing number of reports of stable and matrix-isolated transition metal compounds containing coordinated dinitrogen molecules, there has also arisen considerable interest in the mode of bonding and nature of the interaction between the metal and the ligands. Although X-ray crystallography serves to determine unambiguously the type of bonding (end-on or sideways) in stable species, in such cases where diffraction studies are not possible (*i.e.*, matrix-isolation systems), vibrational spectroscopic investigations using mixed isotopically substituted ligands, $^{14}N^{15}N$, are able to distinguish between the bonding types (see later).

X-Ray crystallography has shown that the dinitrogen ligand in transition metal-dinitrogen complexes studied to date is always bonded in an "end-on" linear or near-linear $M-N\equiv N$ skeleton.

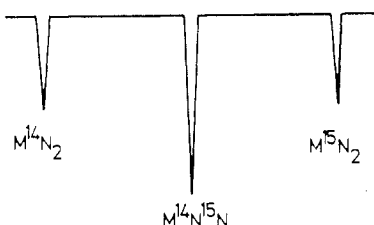
Direct evidence for the existence of a compound containing the dinitrogen molecule bonded in a "sideways fashion" has not previously been reported in the literature. It was, however, postulated¹⁹ as a transition state in the intramolecular $^{14}N^{15}N$ exchange of the cations $[Ru(NH_3)_5(^{14}N^{15}N)]^{2+}$ – $[Ru(NH_3)_5(^{15}N^{14}N)]^{2+}$ as evidenced in the time-dependent intensity changes in the $Ru-N_2$ stretching region. It is noteworthy that Brintzinger's dinitrogen-bridged binuclear titanocene complex $(C_5H_5)_2TiN_2Ti(C_5H_5)_2$ shows no absorption in the infrared attributable to the NN stretching mode. Of the two suggested dinitrogen-bridged centrosymmetric structures, *i.e.*



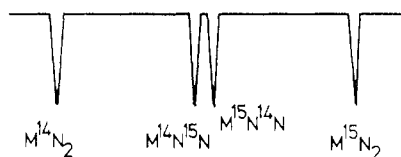
the latter was favored on the basis of chemical intuition.²⁰

Using statistical mixtures of nitrogen isotopes $^{14}N_2$ – $^{14}N^{15}N$ – $^{15}N_2 = 1:2:1$ diluted in Ar, the expected patterns (see Chart I) of NN absorptions are iden-

Chart I
SIDE-ON BONDED DINITROGEN



END-ON BONDED DINITROGEN



(19) J. N. Armor and H. Taube, *J. Amer. Chem. Soc.*, **92**, 2560 (1970).

(20) J. E. Bercaw, R. H. Marvich, L. G. Bell, and H. H. Brintzinger, *J. Amer. Chem. Soc.*, **94**, 1219 (1972).

ally: (a) "side-on" bonded dinitrogen—*three* equally spaced lines with absorption intensities in the ratio 1:2:1; (b) "end-on" bonded dinitrogen—*four* lines, with a closely spaced central *doublet*, where the absorption intensities of the four lines are 1:1:1:1. The reason for the four-line pattern with a central doublet for "end-on" bonded N_2 as opposed to a 1:2:1 triplet for the "side-on" bonded is related to the non-equivalence of the mixed isotopic species $M^{14}N\equiv^{15}N$ and $M^{15}N\equiv^{14}N$ and the absence of such isotopic effects in the case of



In the case of "end-on" bonded N_2 , it is worth noting that the magnitude of the splitting of the central doublet (3.8 cm^{-1} in $Ni^{14}N\equiv^{15}N/Ni^{15}N\equiv^{14}N$,^{21,22} 1.7 cm^{-1} in $Rh^{14}N\equiv^{15}N/Rh^{15}N\equiv^{14}N$,²³ and 4.0 cm^{-1} in $[Ru(NH_3)_5(^{14}N^{15}N)]^{2+}/[Ru(NH_3)_5(^{15}N^{14}N)]^{2+}$ ²⁴) can be used to estimate the bond stretching force constant of the metal-nitrogen bond. This has been done for NiN_2 and has considerable relevance to chemisorption studies of gaseous N_2 on nickel (see, for example, the work of Eischens²⁵).

The data collected so far (as shown in Table I)

Table I

Fe— $N\equiv N$, 2020 cm^{-1} 23c	Co— $\begin{array}{c} N \\ \parallel \\ N \end{array}$, 2100 cm^{-1} 26	Ni— $N\equiv N$, 2090 cm^{-1} 21,22
	Rh— $N\equiv N$, 2155– 2158 cm^{-1} 23c	Pd— $N\equiv N$, 2211– 2215 cm^{-1} 21
		Pt— $N\equiv N$, 2166– 2170 cm^{-1} 27

yield the surprising result that both modes of bonding occur. These data for cobalt provide the only "direct" observation indicating that dinitrogen can be bonded to a transition metal in a "sideways" fashion. It is important to note that all of these monodinitrogen compounds were synthesized under virtually identical matrix conditions and that the observed structural variations from end-on to side-on bonded N_2 must reflect properties characteristic of the metal atoms.

At this early stage in the experiments it is not possible to offer a rationale for this remarkable set of data, although it is worth commenting on the extended Hückel MO calculations that have been performed on both end-on and side-on FeN_2 and that predict that the end-on configuration will be favored from an energy point of view.²⁸ The n_σ and n_π orbi-

(21) H. Huber, E. P. Kündig, M. Moskovits, and G. A. Ozin, *J. Amer. Chem. Soc.*, **95**, 332 (1973).

(22) M. Moskovits and G. A. Ozin, *J. Chem. Phys.*, **55**, 1251 (1973).

(23) Unpublished work done at the University of Toronto (1972): (a) H. Huber, E. P. Kündig, M. Moskovits, and G. A. Ozin; (b) E. P. Kündig and G. A. Ozin; (c) G. A. Ozin and A. Vander Voet.

(24) Yu. J. Borodko, A. K. Shilova, and A. E. Shilov, *Russ. J. Phys. Chem.*, **44**, 349 (1970).

(25) R. P. Eischens, *Accounts Chem. Res.*, **5**, 75 (1972).

(26) G. A. Ozin and A. Vander Voet, *Can. J. Chem.*, **51**, 637 (1973).

(27) G. A. Ozin, M. Moskovits and E. P. Kündig, *Can. J. Chem.*, in press.

(28) K. B. Yatsimirskii and Yu. A. Kraglyak, *Dok. Akad. Nauk SSSR*, **186**, 885 (1969).

tal populations for N-N and N-Fe bonds in FeN₂ suggest that the NN stretching frequency of side-on N₂ should lie at a considerably lower frequency than end-on N₂. In actual fact the NN stretching frequency of CoN₂ lies about 80 cm⁻¹ above FeN₂ and 10 cm⁻¹ above NiN₂.

Monodioxygen Complexes, M(O₂). Using techniques similar to those described for M(N₂), Ni, Pd, and Pt atoms have been cocondensed with dilute ¹⁶O₂, ¹⁶O₂-¹⁸O₂, and ¹⁶O₂-¹⁶O¹⁸O-¹⁸O₂ in Ar.²⁹ In all cases matrix infrared spectra were obtained characteristic of complexes containing a single molecule of dioxygen having oxygen atoms in equivalent environments; that is



(i.e., in each case using ¹⁶O₂-¹⁶O¹⁸O-¹⁸O₂-Ar = 1:2:1:800, a 1:2:1 triplet of O-O stretching modes was observed). As found for M(O₂) and (O₂)M(O₂) (see later) and many synthetic dioxygen carriers, the "side-on" mode of bonding appears to be the more common form, which is not unexpected for transition metals in relatively low oxidation states.³⁰ The O-O stretching frequencies corresponding to the three isotopic molecules M(¹⁶O₂), M(¹⁶O¹⁸O), and M(¹⁸O₂) are shown in Table II.

Table II

Molecule	Frequencies, cm ⁻¹		
	Ni	Pd	Pt
M(¹⁶ O ₂)	966.2	1024.0	926.6
M(¹⁶ O ¹⁸ O)	940.1	995.5	901.4
M(¹⁸ O ₂)	913.6	967.0	875.0

The bonding of O₂ to Ni, Pd, and Pt in these cocondensation reactions can be discussed on the basis of the π bonding scheme of Chatt and Dewar.^{31,32} A delocalized three-center molecular orbital scheme involving the symmetry-allowed metal orbitals and an in-plane π* of O₂ describes the situation more satisfactorily than a localized model in terms of O₂²⁻ or O₂⁻. The degree of back-bonding which occurs will depend upon the relative energies and the amount of overlap between the orbitals.

We now try briefly to relate Ibers'³³ rationale for the factors affecting reversible oxygen uptake in synthetic dioxygen carriers to our data for binary dioxygen complexes. Ibers proposes that increased electron density at the metal, upon changing the metal in a complex, for example Ir > Rh > Co in the series in Table III, will assure increasing O₂ uptake properties. This would appear to be borne out by the above crystallographic data and is in fact also reflected in the "anomalous" order of the O-O stretching frequencies for Ni(O₂), Pd(O₂), and Pt(O₂) which

Table III

	O-O, Å	M-O, Å	Chemical properties
[Co(O ₂)(2=phos) ₂]BF ₄	1.42	1.902 1.871	Irreversible ³⁴
[Rh(O ₂)(diphos) ₂]PF ₆	1.418	2.026 2.025	Reversible ³⁵
[Ir(O ₂)(diphos) ₂]PF ₆	1.625	1.961 1.990	Irreversible ³⁵

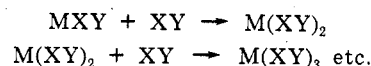
parallel (in an inverse fashion) the order of O-O bond lengths in the Co, Rh, and Ir complexes given in Table III, that is

$$r(\text{O-O}), \text{Å} \quad \text{Rh} < \text{Co} < \text{Ir}$$

$$\nu(\text{O-O}), \text{cm}^{-1} \quad \text{Pd} > \text{Ni} > \text{Pt}$$

1:2 Binary Transition Metal Complexes, M(XY)₂

The cocondensation of transition metal atoms with more concentrated matrices than those previously described often leads to higher stoichiometry complexes. In addition, diffusion-controlled warm-up experiments of MXY in the presence of excess XY may lead to stepwise reactions of the type



In the case of Ni, Pd, and Pt, dicarbonyl (M(CO)₂)^{15,36}, bisdinitrogen (M(N₂)₂)²¹, and bisdioxygen (M(O₂)₂)²⁹ complexes have been synthesized by one or either of the above routes and have been characterized in some detail using isotopic substitution. For example, the bisdioxygen complexes of Ni, Pd, and Pt are formed when the metal atoms are cocondensed with either pure O₂ at 4.2-10 K or with dilute O₂-Ar matrices which have been annealed to 30 K.²⁹ All three molecules contain sideways-bonded O₂ in which the two dioxygen molecules as well as the oxygen atoms are equivalent. For example, in ¹⁶O₂-Ar matrices the single line at 1115.5 cm⁻² assigned to (¹⁶O₂)Pd(¹⁶O₂) splits into a "six"-line spectrum in ¹⁶O₂-¹⁶O¹⁸O-¹⁸O₂-Ar matrices (Figure 1) which corresponds to all the possible combinations of the ¹⁶O-¹⁸O isotopes (Table IV) with an intensity distribution tending to favor a D_{2d} tetrahedral "spiro"

Table IV

Molecule	$\nu_{\text{obsd.}}^{27}$ cm ⁻¹	$\nu_{\text{calcd.}}^{27}$ cm ⁻¹	Assignment
(¹⁶ O ₂)Pd(¹⁶ O ₂)	1115.5	1110.9	ν_{OO}
(¹⁶ O ₂)Pd(¹⁶ O ¹⁸ O)	1092.2	1094.2	ν_{OO}
(¹⁶ O ¹⁸ O)Pd(¹⁶ O ¹⁸ O)	1080.5	1079.9	ν_{OO}
(¹⁶ O ₂)Pd(¹⁸ O ₂)	1067.2	1074.4	ν_{OO}
(¹⁶ O ¹⁸ O)Pd(¹⁸ O ₂)	1060.5	1062.5	ν_{OO}
(¹⁸ O ₂)Pd(¹⁸ O ₂)	1048.5	1047.7	ν_{OO}
(¹⁶ O ₂)Pd(¹⁸ O ₂)	504.0	504.8	ν_{PdO}

(29) H. Huber and G. A. Ozin, *Can. J. Chem.*, **50**, 3746 (1972).

(30) R. Mason, *Nature (London)*, **217**, 543 (1968).

(31) J. Chatt, *J. Chem. Soc.*, 2939 (1953).

(32) M. J. S. Dewar, *Bull. Soc. Chim. Fr.*, **18**, C71 (1951).

(33) J. A. McGinnity, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 2247 (1967).

(34) N. W. Terry, E. L. Amma, and L. Vaska, *J. Amer. Chem. Soc.*, **94**, 653 (1972).

(35) J. A. McGinnity, N. C. Payne, and J. A. Ibers, *J. Amer. Chem. Soc.*, **91**, 6301 (1969).

(36) E. P. Kündig, M. Moskovits, and G. A. Ozin, *Can. J. Chem.*, **50**, 3587 (1972).

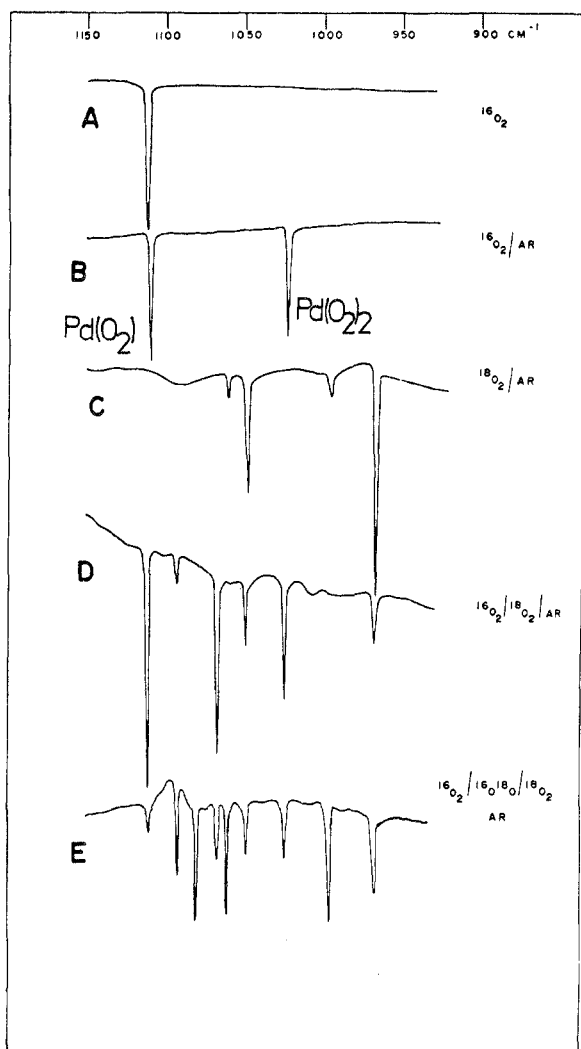


Figure 1. Observed infrared spectra of products of cocondensation of Pd atoms with (A) $^{16}\text{O}_2$; (B) $^{16}\text{O}_2$ -Ar (1:200); (C) $^{18}\text{O}_2$ -Ar (1:200); (D) $^{16}\text{O}_2$ - $^{18}\text{O}_2$ -Ar (1:1:400); (E) $^{16}\text{O}_2$ - $^{16}\text{O}^{18}\text{O}$ - $^{18}\text{O}_2$ -Ar (1:2:1:800), showing the presence of $\text{Pd}(\text{O}_2)$ and $(\text{O}_2)\text{Pd}(\text{O}_2)$. (Note that the $^{18}\text{O}_2$ contains 7% of $^{16}\text{O}^{18}\text{O}$ and is most apparent in spectra C and D.)

structure. The nonobservation of a splitting for cis-trans possibilities of the $(^{16}\text{O}^{18}\text{O})\text{M}(^{16}\text{O}^{18}\text{O})$ molecule also supports the D_{2d} assignment (see Chart II). This model would also be favored on a Dewar-Chartt π -bonded scheme^{32,33} from maximum π -bonding overlap considerations illustrated schematically above.

1:3 Binary Transition Metal Complexes, $\text{M}(\text{XY})_3$

The 1:3 complexes $\text{M}(\text{XY})_3$ have been characterized only in the case of CO and N_2 .^{15,21,27,36} In the case of the tricarbonyl species the structure conforms to that expected on the basis of Gillespie's electron-pair repulsion model³⁷ and Kettle's overlap arguments,³⁸ that is, D_{3h} triangular planar. A similar situation appears to exist for $\text{Ni}(\text{N}_2)_3$, $\text{Pd}(\text{N}_2)_3$, and $\text{Pt}(\text{N}_2)_3$.

Binary Tetracarbonyl and Tetradinitrogen Complexes

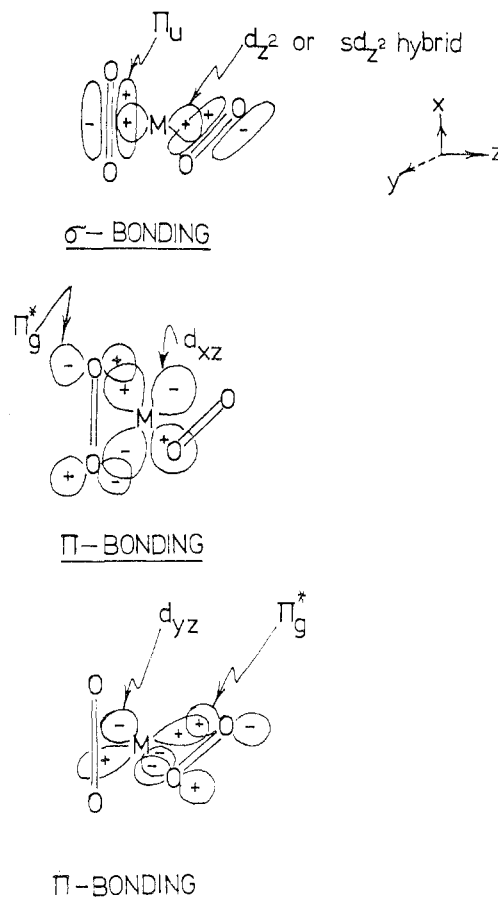
Experience is proving that the cocondensation of

(37) R. J. Gillespie and R. S. Nyholm, *Quart. Rev., Chem. Soc.*, 7, 339 (1957).

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

Chart II

Bonding Scheme for $(\text{O}_2)\text{M}(\text{O}_2)$



metal atoms with pure reactive matrix gases such as CO, N_2 , and O_2 produces the complex with the highest stoichiometry. In the case of pure CO, it proved possible to synthesize the previously unknown tetracarbonyls of Pd and Pt.

Both matrix infrared^{15,39,40} (including mixed $^{12}\text{C}^{16}\text{O}$ - $^{13}\text{C}^{16}\text{O}$ isotopic substitution) and Raman¹¹ (including matrix Raman depolarization measurements) experiments have been reported for the Ni-, Pd-, and Pt-CO cocondensation reactions and define the complexes to be $\text{M}(\text{CO})_4$ with regular T_d symmetry.

When Co atoms were cocondensed with pure CO (Figure 2), the matrix infrared and Raman spectra^{23b} indicated the major product to be the free radical $\text{Co}(\text{CO})_4$. The matrix spectra are consistent with a D_{2d} tetrahedral structure (*i.e.*, a squashed tetrahedron). This distortion is not unexpected for a d^9 Jahn-Teller system.

The only tetradinitrogen species unambiguously identified to date is $\text{Ni}(\text{N}_2)_4$ formed in the cocondensation reaction of Ni atoms with pure N_2 at 4.2-10 K or N_2 -Ar = 1:10 deposited at 30 K.²¹ The infrared and Raman spectral data in argon and the excellent agreement between the calculated and observed NN stretching frequencies and infrared absorption intensities for all isotopic molecules $\text{Ni}(^{14}\text{N}_2)_n(^{15}\text{N}_2)_{4-n}$

(39) J. H. Darling and J. S. Ogden, *Inorg. Chem.*, 11, 666 (1972).

(40) H. Huber, E. P. Kündig, M. Moskovits, and G. A. Ozin, *Nature (London), Phys. Sci.*, 235, 98 (1972).

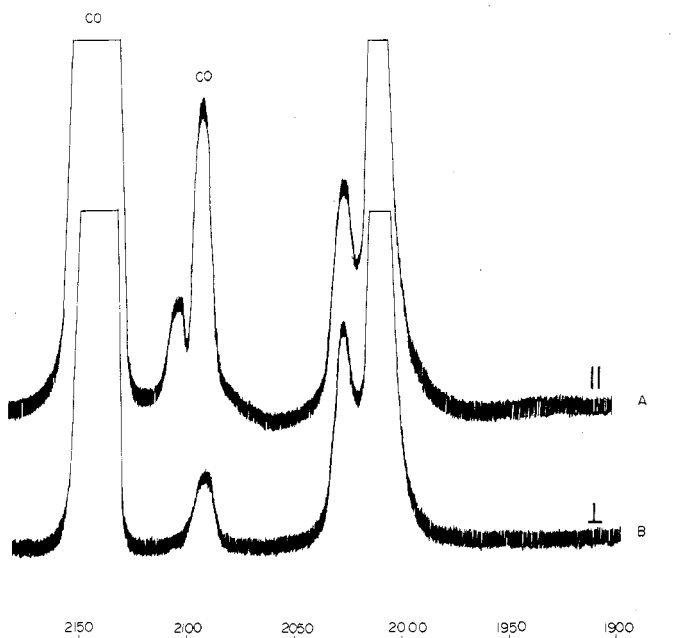


Figure 2. The matrix Raman spectrum of the products of the cocondensation reaction of cobalt atoms and CO at 4.2 K: (A) parallel and (B) crossed polarizations showing the presence of $\text{Co}(\text{CO})_4$.

provided unambiguous evidence for the existence of $\text{Ni}(\text{N}_2)_4$ having regular tetrahedral symmetry and hence "end-on" bonded dinitrogen.

Binary Penta- and Hexacarbonyl Complexes

Using metal atom-CO cocondensation reactions DeKock¹⁵ examined the Ta-CO system, Weltner⁴¹ the U-CO system, and Turner⁴² the Cr-CO system. The matrix infrared spectra together with the diffusion-controlled warm-up data, in all three cases, indicated a process in which a monocarbonyl species is initially formed which successively takes on CO ligands to form all of the intermediate binary carbonyls $\text{M}(\text{CO})_n$ up to $n = 6$. Not unexpectedly the spectra were complex, and as a result vibrational assignments were tentative and structural conclusions regarding the intermediates could not be made with any degree of certainty. In this context it is worth noting that a more controlled route to binary penta-carbonyls,⁴² for example, $\text{M}(\text{CO})_5$ where $\text{M} = \text{Cr}$, Mo , and W , is by matrix uv photodetachment of a CO ligand from the parent hexacarbonyl $\text{M}(\text{CO})_6$.

Binary Mixed Carbonyl-Dinitrogen Complexes of Nickel, $\text{Ni}(\text{CO})_n(\text{N}_2)_{4-n}$, $n = 1-3$

A classic example which demonstrates the versatility of metal atom synthesis involves the reaction of nickel atoms with mixed CO- N_2 matrices. Matrix infrared and Raman spectra have been recorded for the products of the above reaction together with $^{12}\text{C}^{18}\text{O}$ and $^{15}\text{N}_2$ isotopic substitution and provide evidence for the formation of all mixed species, $\text{Ni}(\text{CO})_n(\text{N}_2)_{4-n}$, where $n = 1-3$.²⁷ This direct synthesis can be compared with the uv photolysis of $\text{Ni}(\text{CO})_4$

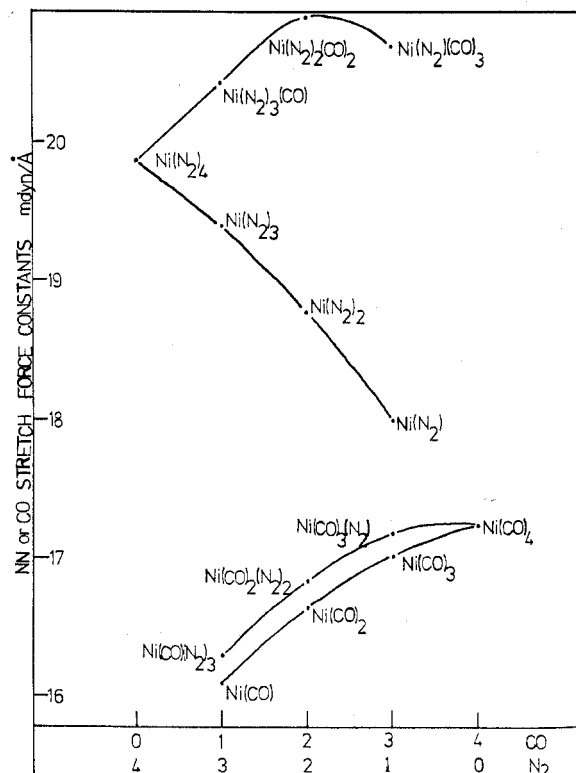


Figure 3. Graphical representation of the variation of the stretching force constants k_{CO} and k_{N_2} for the series of compounds $\text{Ni}(\text{CO})_n(\text{N}_2)_{4-n}$ ($n = 0-4$) indicating the effect of replacement of dinitrogen or carbonyl ligands on tetracoordinated nickel in the matrix.

in N_2 -Ar matrices⁴³ which exclusively yielded $\text{Ni}(\text{CO})_3(\text{N}_2)$.

The vibrational assignments for the ligand stretching modes in $\text{Ni}(\text{CO})_n(\text{N}_2)_{4-n}$ to the individual molecules are relatively clear-cut. A Cotton-Kraihanzel analysis⁴⁴ which can be applied with fair success to pure carbonyl and dinitrogen species has been performed on each molecule, including their $^{12}\text{C}^{18}\text{O}$ and $^{15}\text{N}_2$ isotopically substituted counterparts, in an attempt to examine trends within the various k_{NN} and k_{CO} force constants. The results of these calculations are illustrated graphically in Figure 3.

The order of k_{NN} bond stretching force constants is found to be: $\text{Ni}(\text{CO})_3(\text{N}_2) < \text{Ni}(\text{CO})_2(\text{N}_2)_2 > \text{Ni}(\text{CO})(\text{N}_2)_3 > \text{Ni}(\text{N}_2)_4$. This is the expected trend when the weaker π acceptor N_2 is successively replaced by the stronger π acceptor CO. A similar but inverse effect is observed for the k_{CO} bond stretching force constants: $\text{Ni}(\text{CO})_4 > \text{Ni}(\text{CO})_3(\text{N}_2) > \text{Ni}(\text{CO})_2(\text{N}_2)_2 > \text{Ni}(\text{CO})(\text{N}_2)_3$ (see ref 27 for a detailed explanation of these force constant trends).

Conclusion

The cocondensation of metal atom vapors in their monatomic form with small gaseous molecules can be effectively studied using matrix isolation spectroscopic techniques. From the magnitudes of the shifts of the stretching frequencies of the coordinated mol-

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ecule XY as compared to those of the free molecule, we know that the products are "real" molecules of definable stoichiometries, with conventional chemical bonding and structures, and not, for example, just weakly interacting van der Waals species. As mentioned in the introduction, the only differences between the "matrix" synthetic method and "normal" syntheses are the choice of a lower temperature and of a rigid inert "solvent."

The advantages of the technique include control of the stoichiometry of the products, the cryogenic stabilization of normally unstable chemical species, the study of chemical reactions under diffusion-controlled conditions, and the synthesis of entirely new compounds. The applications of these studies can be found in any system where the interaction between a metal atom and a gaseous molecule is of importance, *i.e.*, catalysis, chemisorption, and biological-fixation

processes. The future of "matrix" synthesis holds many possibilities as there are yet many interactions to be studied. Perhaps the most exciting chemical possibilities include the chemistry of many of the reactive species formed: hydrogenation (*e.g.*, $M-N_2 + H_2$, $M\text{-olefin} + H_2$), simultaneous cocondensation of two high-temperature species (SiO (monomer) + M (atom)), reactions of metal atoms with free radicals (M (atom) + CH_2), etc. The possibilities are real since, although experimentally unusual, the technique has now been made quite routine.

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Chemical and Biological Applications of Laser Light Scattering

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In a light-scattering experiment, light from a source impinges on a sample and is scattered into a detector placed at a given angle, θ , with respect to the direction of the incident radiation, as depicted in Figure 1. A photon that is scattered by a molecule can either gain or lose energy to translational, rotational, vibrational, and electronic degrees of freedom, thereby suffering frequency shifts. The frequency spectrum of the scattered light will exhibit resonances corresponding to these transitions, and the total light-scattering spectrum is called the *Raman spectrum*.

In order to obtain a resolved Raman spectrum it is necessary, among other things, that the spectral distribution of the incident light have a narrow width compared to the frequency shifts and widths that occur in the Raman process. Before the discovery of the laser, the spectral widths of conventional light sources were such that only electronic, vibrational, and rotational Raman effects with their corresponding large frequency shifts could be studied. With the advent of the laser, it is now not only possible to study the above Raman processes routinely, but it is

also possible to observe the translational Raman process with its much smaller frequency shifts and widths. In fact, frequency shifts as low as 1 Hz can be detected in modern light-scattering laboratories. What makes this all possible is the laser—a light source which delivers very monochromatic light at high intensity.

In the last decade there has been considerable activity in the field of light scattering. Light scattering has been used to probe collective modes¹ in solids, liquids, and gases. It has been particularly useful in the study of critical phenomena and has been used to study the kinetic theory of gases.

In this Account, we shall attempt to outline only a few of the important applications of laser light scattering to problems of a purely chemical and biological interest. In all of these applications intensity-correlation spectroscopy is used. We begin by outlining the techniques involved in these applications.

Methods of Detection

In a light-scattering experiment, a beam of laser light of frequency ω_0 , wave vector \mathbf{k}_1 (the wave vector points in the direction of propagation of the light and has a magnitude $2\pi/\lambda_1$ where λ_1 is the wavelength of the light), and field strength \mathbf{E}_1 first passes through a polarizer, then impinges on a sample from which it is scattered, then passes through an analyzer, and finally enters a detector. The position of the

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(1) See, for example, the review by P. A. Fleury and J. P. Boon, *Advan. Chem. Phys.*, in press.