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Detection of Neodymium and Ytterbium Carbonyls Using Matrix Isolation

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The first rare earth carbonyls have been prepared by codeposition of neodymium and ytterbium atoms with carbon monoxide in argon matrices. The new rare earth carbonyls were detected by infrared spectroscopy. The final product of the neodymium reaction was assigned to $Nd(CO)_6$ and infrared absorptions were assigned for the lower carbonyls $Nd(CO)_{1-5}$. No assignment of the ytterbium data was made.

Introduction

The infrared spectra of metal carbonyls have been widely studied because of the qualitative insight they provide about the metal-carbon bonding. Matrix isolation greatly increases the number of molecules that are accessable to investigation. A number of metal carbonyls have been synthesized by this technique, either by the *in situ* photolysis of a more highly substituted compound resulting in the expulsion of one or more molecules of CO or by the codeposition of the metal vapor with CO-argon mixtures followed by controlled annealing of the matrix.

Stoltz and coworkers[1] presented infrared evidence for $M(CO)_5$ (M = Cr, Mo, W) prepared by photolysis of the corresponding hexacarbonyls in hydrocarbon glasses at 77°K. Turner and coworkers[2] have expanded this work and have observed the intermediate metal carbonyls $M(CO)_{2-5}$ (M = Cr, Mo, W) in argon matrices prepared by irradiation of the corresponding metal hexacarbonyls. Other metal carbonyls, *e.g.*, $Ni(CO)_4$,[3] $HMn(CO)_5$,[4] and $Fe_2(CO)_9$,[5] also have been shown to lose CO upon irradiation to form intermediate carbonyls.

The codeposition technique has been used by Slater, *et al.*,[6] to prepare $U(CO)_{1-6}$ and in other studies to prepare unstable carbonyls that have been assigned to $Ni(CO)_{1-3}$,[7] $Pd(CO)_4$,[8] $Pt(CO)_4$,[9] $Cu(CO)_x$,[10] $Ag(CO)_x$,[10] $Al_x(CO)_2$,[11] $Ge(CO)_x$,[12] and $Sn(CO)_x$.[12] It is probably safe to say that the codeposition matrix-isolation technique is a general method for the synthesis of metal carbonyls.

In the present work, the codeposition method is used to prepare the carbonyls of the rare earths Nd and Yb. The former was chosen as a typical lanthanide, and the latter as an atypical lanthanide.[13] Typical lanthanides exhibit an oxidation state of +3 and possess the characteristic physical properties associated with rare earth metals. The atypical lanthanides, Yb and Eu, exhibit an oxidation state of +2 and have physical properties more nearly like Ca, Sr, and Ba. These different properties occur in Yb and Eu because of the presence of the half-filled and filled 4f orbitals in these rare earths.

Experimental Section

Two liquid helium cryostat systems were used in this work. The first was a variable-temperature Andonian dewar which has been described previously,[14] and the second was a standard fixed-temperature liquid helium dewar constructed in the laboratory.[15] The metals were vaporized from a tungsten container using resistance heating and were cocondensed on a CsI window at 8–12°K with a mixture of CO and Ar ranging in concentration from 0.1 to 10 mol % depending upon the experiment. The furnace temperature was selected so that the vapor pressure of the metal was about 10^{-5} Torr. This corresponds to 1590 and 740°K for Nd and Yb, respectively, and ensures that only metal atoms were deposited in the matrix. In some experiments the metals were deposited in pure CO. The deposition rate was typically 0.3 mmol of mixture/min, deposited for about 50 min. The neodymium and ytterbium were obtained from the Ames Laboratory and had purities of 99.94 and 99.96%, respectively. The argon and CO were research grade obtained from Matheson Inc. Enriched ^{13}CO (90% ^{13}C) was obtained from Monsanto Research Corp. All spectra were recorded at 10°K on a Beckman IR-7. The band positions are estimated to be accurate to ±2 cm^{-1}.

After the initial deposition, further reaction between the metal atoms and CO was accomplished by controlled annealing of the matrices. In the variable-temperature dewar this was achieved simply by reducing the flow rate of liquid He. In the fixed-temperature dewar annealing of the matrix was achieved by focusing an infrared heat lamp on the matrix and window mount for a short period of time. Separate experiments showed that similar results were obtained by the two methods. The reaction of the metal atoms with CO was halted when the matrix was recooled to low temperatures. By carrying out this procedure carefully it was possible to observe the growth and disappearance of certain features which aided in the assignment of the observed spectra. Enhancement of certain features was also obtained by varying the concentration of CO in the matrix.

Results and Discussion

Neodymium Carbonyls. The infrared spectra taken at four stages of annealing of Nd atoms in a 10% CO–Ar matrix are shown in Figure 1. Strong bands at 2138 and 2092 cm^{-1}, due to CO, are present in all spectra but are omitted from the figures. Spectrum 1a, taken prior to annealing, shows six absorptions in the metal-carbonyl stretching region. Spectrum 1b shows the same region after the first annealing. The 1840-cm^{-1} absorption has disappeared and the 1861-cm^{-1} feature has lost much of its original intensity. On the other hand, the 1990-cm^{-1} band has increased so much in intensity that the bands at 2003 and 1965 cm^{-1} are overlapped. Spectra 1c and 1d, taken after additional annealing, show only one strong band at 1990 cm^{-1}.

The infrared spectra of Nd atoms in a 3.3% CO–Ar matrix is shown in Figure 2. Prior to annealing (trace 2a), the lower frequency bands at 1840 and 1861 cm^{-1} are much

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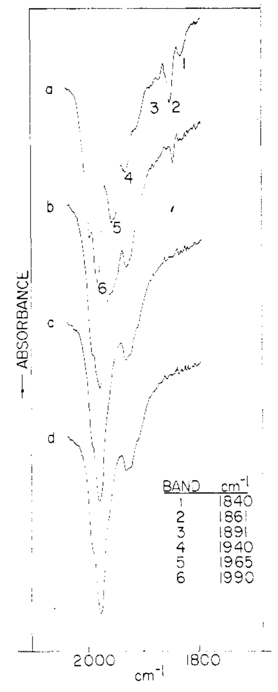

Figure 1. The infrared spectra of Nd in an argon matrix doped with 10% CO at 10°K: trace a, prior to annealing; traces b-d, after warming the matrix to about 35°K.

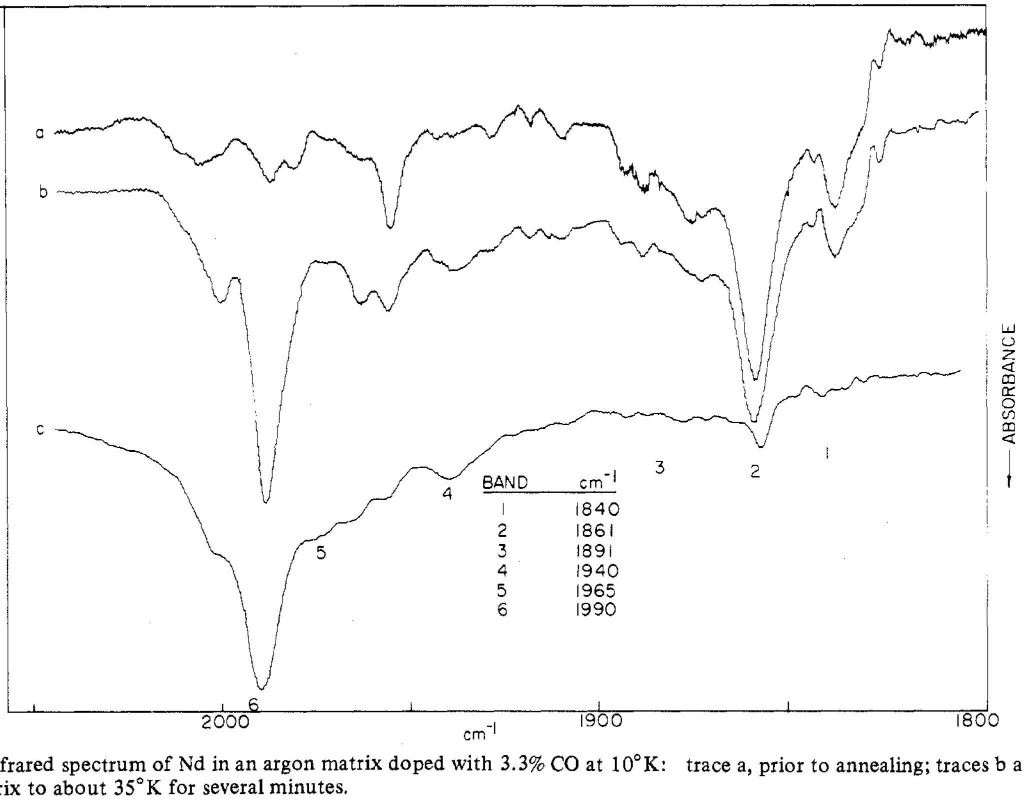

Figure 2. The infrared spectrum of Nd in an argon matrix doped with 3.3% CO at 10°K: trace a, prior to annealing; traces b and c, after warming the matrix to about 35°K for several minutes.

stronger relative to the higher frequency features; *i.e.*, the species giving rise to them are favored by low CO concentrations. After annealing (traces 2b, 2c) the higher frequency features grow in intensity and ultimately the band at 1990 cm^{-1} dominates the spectrum.

Based on the concentration and diffusion dependence of the bands, it is reasonable to conclude that the bands at 1840 and 1861 cm^{-1} are due to partially coordinated neodymium carbonyl species and that the bands at 1940, 1965, and 1990 cm^{-1} originate from more highly coordinated species. Essentially the same spectral results were obtained with isotopically enriched ^{13}CO except, of course, the absorptions were at lower frequency. Unfortunately, because of the similarity in the isotope shifts no information about the coordination number of the absorbing species could be obtained from the isotopic data.

Clearly, several neodymium carbonyls were formed, since only Nd, CO, and Ar were present in the matrix. The presence of a single infrared-active CO vibration in the final diffusion product indicates that this feature arises from a compound with an even number of CO ligands (see Table I). It is also noteworthy that there is an extraordinary similarity between the spectra of the neodymium carbonyls, the carbonyls formed by the d transition metals Cr, Mo, and W, and the carbonyls of U and Ta. This similarity is illustrated in Figure 3. In the upper half of the figure, the CO stretching frequencies of various carbonyl compounds of different coordination ranging from one to six are shown. The correlation can also be expressed by plotting the coordination number for all the carbonyls as a function of vibrational frequency. This illustration of the correlation is shown in the lower half of the figure. The striking similarity of the spectra of the carbonyls of Nd and of Cr, Mo, and W suggests that the maximum coordination of Nd is six.

The hybridization of the Nd atomic orbitals in the octahedral field[16] of six CO molecules would be f^3d^2s since the carbonyls are no doubt covalently bonded to the metal. The T_{1u} f orbitals of the metal would be of the proper symmetry to form the bonding orbitals and the T_{2u} f orbitals have the proper symmetry to provide the traditional back-bonding electrons found in all transition metal carbonyls. For these reasons we tentatively assign the 1990-cm^{-1} band to $Nd(CO)_6$.

The pentacoordinated carbonyl should have two or three

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(16) J. C. Eisenstein, *J. Chem. Phys.*, 25, 142 (1956).

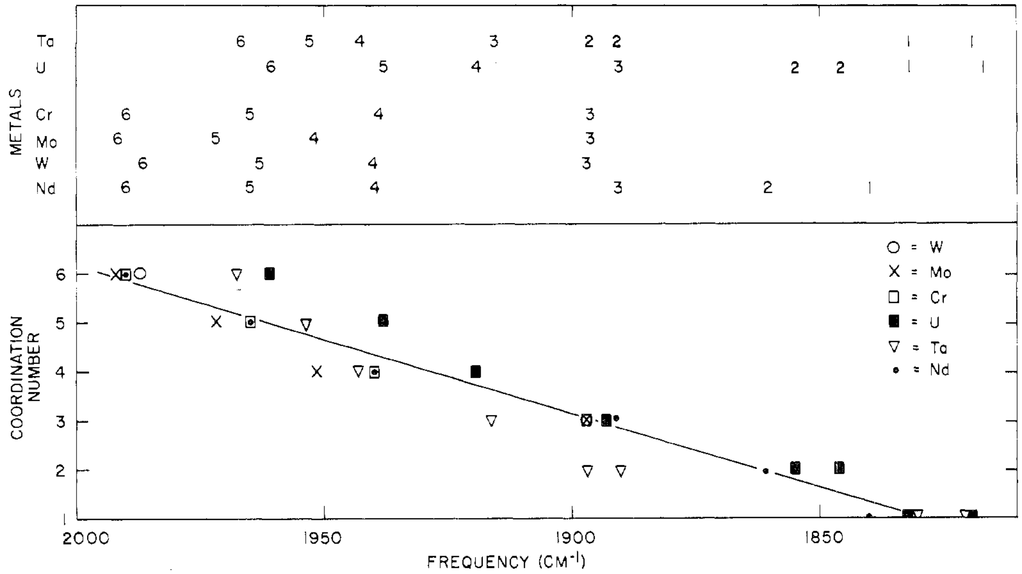

Figure 3. The carbonyl stretching frequencies of several carbonyls whose maximum coordination is six (data taken from ref 6 and citations therein). In the upper part of the figure the value of the stretching frequency for each compound is indicated by the number of CO ligands associated with that absorber. In the lower part of the figure the coordination number is plotted *vs.* frequency for all the compounds.

Table I. Infrared-Active Stretching Modes for M(CO)$_x$

Molecule	Molecular symmetry	Species of ir-active CO str
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 planar)	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 planar)	1 E_u
M(CO)$_5$	C_{4v} (tetragonal pyramid)	2 A_1 + 1 E
M(CO)$_5$	D_{3h} (trigonal bipyramid)	1 A_2'' + 1 E′
M(CO)$_6$	O_h (octahedral)	1 T_{1u}
M(CO)$_7$	D_{5h} (pentagonal bipyramid)	1 E_1' + 1 A_2''
M(CO)$_8$	O_h (octahedral)	1 T_{1u}

Table II. Assignments and Vibrational Frequencies (cm^{-1}) of the CO Stretching Modes of Nd(CO)$_x$, x = 1–6

	^{12}CO	^{13}CO		^{12}CO	^{13}CO
NdCO	1840	1802	Nd(CO)$_4$	1940	1897
Nd(CO)$_2$	1861	1821	Nd(CO)$_5$	1965	1922
Nd(CO)$_3$	1891	1850	Nd(CO)$_6$	1990	1949

Table III. Cotton-Kraihanzel Force Constants for Neodymium Carbonyls

	$k - k_t$, mdyn/Å		$k - k_t$, mdyn/Å		$k - k_t$, mdyn/Å
NdCO	13.7	Nd(CO)$_3$	14.4	Nd(CO)$_5$	15.6
Nd(CO)$_2$	14.0	Nd(CO)$_4$	15.2	Nd(CO)$_6$	16.0

infrared-active CO vibrations (see Table I). The strong band at 1965 cm^{-1} is presumably the more intense E or E′ mode for the C_{4v} and D_{3h} point groups, respectively. Unfortunately the assignment for the A_1 or A_2'' vibrations is complicated by the fact that these weaker features may be overlapped by bands due to other species. Although there are some weak features or shoulders that might be attributed to the symmetric modes of the M(CO)$_5$ species, the assignments would be tenuous so we prefer to make no assignments of these vibrations. The tetracoordinated species has only one active CO mode and the band at 1940 cm^{-1} is assigned to that molecule. By analogy to the carbonyls shown in Figure 3, the bands at 1891, 1861, and 1840 cm^{-1} were assigned to the tri-, di-, and monosubstituted neodymium carbonyls. The assignments are summarized in Table II.

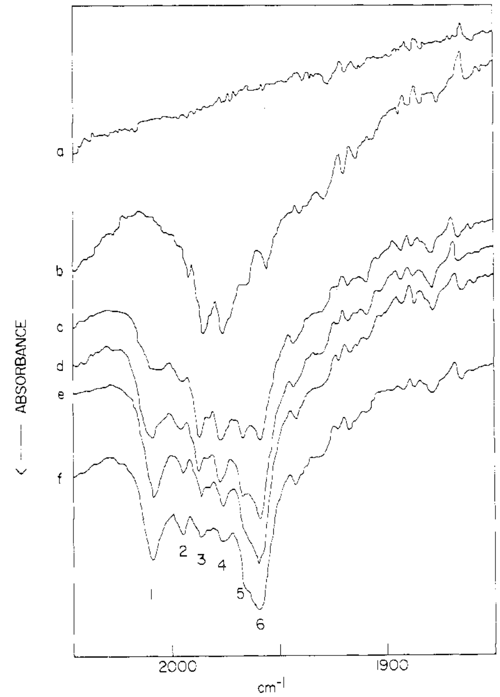

Figure 4. The infrared spectrum of Yb in an argon matrix doped with 1% CO. Traces: a, before annealing; b, 32°K; c, 36°K; d, 39°K (2 min); e, 39°K (35 min); f, 39°K (80 min).

Employing the simplifications introduced by Cotton and Kraihanzel[17] one obtains the approximate CO force constants shown in Table III. Although the absolute value of these force constants is subject to considerable uncertainty, the order of magnitude is correct and the trend is consistent with the prediction that the force constant should increase with increasing CO substitution.

Ytterbium Carbonyls. Ytterbium is noted as one of the atypical rare earths, and the spectra of the carbonyl compounds in argon matrices are no exception to that cognate.

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(17) (a) F. A. Cotton and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, 84, 4432 (1962); (b) C. S. Kraihanzel and F. A. Cotton, *Inorg. Chem.*, 2, 533 (1963); (c) *ibid.*, 3, 702 (1964).

As shown in Figure 4 there are six infrared-active absorptions, two of which dominate in the spectrum after several diffusion cycles (trace d). In a matrix of pure CO, however, the lower of these two absorptions at 1958 cm^{-1} becomes much stronger indicating that the two absorptions do not arise from the same molecular species and that the 1958-cm^{-1} band originates from the most highly coordinated species. The frequencies are tabulated in Table IV. Yb is electronically and chemically similar to the group IIa elements for which there are no known carbonyls. As a result there is no analogy from which to extrapolate even a tentative stoichiometry for the compounds. The annealing pattern is definitely different from that observed in the case of Nd and in previous studies of tetra- and hexacoordinated carbonyls in that the monotonic relation between rate of disappearance of an absorption upon diffusion and the frequency of absorption is no longer found. Without further data on other lanthanide carbonyls from which to draw some analogy, it is futile to conjecture about the stoichiometry of the ytterbium carbonyls. It is possible to conclude that Yb does form several carbonyls, however. The frequencies of the natural and ^{13}C-enriched spectra are shown in Table IV.

In summary, carbonyl compounds of Nd and Yb have been synthesized in argon matrices. The most highly coordinated Nd compound has been tentatively identified as $Nd(CO)_6$.

Table IV. Observed Vibrational Frequencies in the CO Stretching Region of Yb in Argon Matrices Doped with CO

Designation	^{12}CO	^{13}CO	Designation	^{12}CO	^{13}CO
1	2008	1964	4	1976	1936
2	1995	1953	5	1966	1923
3	1986	1943	6	1958	1917

Since Nd is a typical lanthanide, the other typical rare earth metals might be expected to form similar carbonyls. The compound(s) formed by Yb, on the other hand, are not analogous and could not be identified by the infrared spectrum.

It would be of interest to try to collect some of the carbonyl compounds at higher temperatures for further characterization; however, this was not feasible with the present apparatus. At temperatures above about 40°K the vapor pressure of the matrix resulted in loss of the insulating vacuum, with concomitant rapid evaporation of the He refrigerant and peeling of the residual matrix from the window.

Registry No. $Nd(CO)_6$, 40299-73-8.

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Further Studies of the Electrochemical Reduction of Sulfur in Aprotic Solvents

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The reduction of sulfur and the solution chemistry of the various polysulfide products have been investigated in dimethyl sulfoxide by cyclic voltammetry, controlled-potential electrolysis, and absorption spectroscopy. At a gold electrode sulfur is reduced by two electrons at a potential of −0.6 V *vs.* sce to produce S_8^{2-} and other polysulfides. These products yield, by a variety of reactions, a blue radical species, S_3^-, with an absorption maximum at 618 nm. Electrolytic reduction of sulfur yields a second process at a potential of −1.29 V with an overall stoichiometry of four electrons per S_8 molecule; the major stable product is the S_4^{2-} species. The dissociation of S_6^{2-} into S_3^- has a pK_d value of 2.11 on the basis of spectrophotometric measurements. Equilibrium constants of other disproportionation and dissociation reactions for the various polysulfides also have been evaluated.

Although the sulfur–polysulfide system in aprotic solvents has been studied extensively, numerous questions remain unresolved. In particular, the nature of the blue species (618 nm) that results from sulfur reduction in aprotic or basic solvents has not been rationalized. In a previous study[1] our group reported that the blue color was due to S_8^-, the one-electron reduction product of elemental sulfur. Subsequent studies have now established that this stoichiometry is in error, probably by an inexplicable consistent misreading of the coulometer; the primary reduction step is a two-electron process. This corrected interpretation of our previous results is consistent with the recent report of Bonnaterre and Cauquis,[2] who proposed that the initial reduction of sulfur in dimethylformamide or dimethyl sulfoxide proceeds by two electrons to produce S_8^{2-} with an absorption maximum at 505 nm. They proposed that S_8^{2-} undergoes a dismutation reaction to give S_6^{2-} as the blue species

$$4S_8^{2-} \rightleftharpoons 4S_6^{2-} + S_8 \qquad (1)$$

Chivers and Drummond[3] agreed with Bonnaterre and Cauquis that the blue species corresponds formally to S_6^{2-} but assigned S_3^- as the species responsible for the 618 nm absorbance.

Giggenbach[4] proposed yet another species, S_2^- (formed by the dissociation of S_4^{2-}), to be responsible for the blue color of reduced sulfur in aprotic solvents. In view of these conflicting reports and the need for a rational explanation of the diverse observations, a further study of the electrochemical reduction of sulfur in aprotic solvents has been undertaken.

Experimental Section

The equipment and procedures for the electrochemical and spectrophotometric measurements were the same as those summarized in the previous paper.[1] Controlled-potential coulometry was carried out in a Dry-Lab glove box with a large gold-foil electrode. Cyclic voltammetry of reduced sulfur was performed in the glove box.

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(2) R. Bonnaterre and G. Cauquis, *J. Chem. Soc., Chem. Commun.*, 293 (1972).
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