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Spectroscopic Identification of the Binary Dinitrogen Complexes of Chromium in Low-Temperature Matrices[1]

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The products of the cocondensation of Cr atoms with N_2 at 10 K have been investigated using infrared and uv–visible spectroscopy and the products of the cocondensation of Cr atoms with N_2/Ar mixtures have been investigated using infrared spectroscopy. From the behavior of each species upon annealing and upon changing the concentration of N_2 in the matrix, the binary dinitrogen complexes $Cr(N_2)_n$, where $n = 1–6$, have been identified. Tentative structures have been determined for each complex from the analysis of the spectrum. In addition, the electronic spectrum of $Cr(N_2)_6$, obtained in a nitrogen matrix, has been analyzed. The observed Δ value for this octahedral complex was found to be 28 800 cm^{-1}, which clearly establishes that N_2 is a strong-field ligand.

Introduction

Since the calculated orbital energies of CO and N_2 are surprisingly similar,[2] it is of theoretical interest to compare binary complexes with these isoelectronic molecules as ligands. Several new binary dinitrogen complexes with from one to four N_2 molecules have been synthesized in low-temperature matrices including those of Cr,[3a] Cu,[3a] Ni,[3] Pd,[3b] Pt,[3a,4,5] and Rh.[6] Both experimental evidence[7] and empirical calculations[8] indicate that these complexes are generally structurally similar to the corresponding carbonyl complexes. However, to date, the only known binary dinitrogen analogue to the well-studied six-coordinated octahedral complexes found for the carbonyls of the 5A and 6A metals,[9] the rare earth metals,[10] and uranium[11] is $V(N_2)_6$.[12] By parameterizing the three- and four-center integrals, Caulton et al.[13] have performed an ab initio SCF-like molecular orbital calculation for $Cr(N_2)_6$. This calculation indicates $Cr(N_2)_6$ should also be stable, at least at low temperatures where entropy effects are small. However, a previous investigation of the chromium–dinitrogen system failed to produce evidence of any complex with more than one coordinated dinitrogen molecule per metal atom. While this result appeared to be inconsistent with the results of the similar experiments using different metals, there was no a priori reason to question the validity of the study. Since molecules like CrN_2 have potential astronomical interest, the original purpose of this study was to examine the electronic spectrum of this three-atom "complex". However, no bands were found in the visible absorption spectrum. Since most small transition metal compounds contain at least one visible absorption band, the observed electronic spectrum seemed to be incompatible with the assumption of but one coordinated dinitrogen per metal atom. Consequently, the chromium–dinitrogen system has been reexamined and the binary chromium–dinitrogen complexes $Cr(N_2)_{1-6}$ have tentatively been identified from their infrared spectra. In addition the electronic spectrum of $Cr(N_2)_6$ has been analyzed.

Experimental Section

The apparatus used in this work has been described previously[10] so only a brief resume of the experimental conditions will be given. Chromium metal 99.995% pure was vaporized using a resistively heated tungsten wire basket purchased from Ladd Research Industries, Inc. The furnace temperature was adjusted to give metal atom vapor pressures ranging from 0.005 to 0.05 Torr. Even using the heaviest deposition conditions only atomic chromium bands could be observed in the electronic spectrum of chromium isolated in argon matrices containing no N_2, indicating that negligible amounts of polymeric chromium were produced during the deposition process. The metal atoms were codeposited on a CsI window at 8–12 K with N_2 or with N_2/Ar mixtures ranging from 1 to 15 mol % N_2. The rate of deposition of matrix gas was typically 0.3 mmol of mixture/min for 25 min.

Research grade argon from Matheson, Inc., nitrogen from Air Products, and 95% enriched nitrogen-15 from Merck and Co. were used in this study. All spectra were obtained at 8 K using a Beckman IR-7 instrument in the infrared region and a Cary 14 recording spectrometer in the uv–visible region. The continuum for the Cary 14 instrument was provided by a high-intensity tungsten lamp in the visible region and by a hydrogen discharge lamp in the ultraviolet region. The band positions in the infrared region were calibrated using atmospheric H_2O and CO_2 bands and are estimated to be accurate to ±2 cm^{-1}. The uv–visible band positions were calibrated from matrix-isolated iron bands and are estimated to be accurate to ±0.3 nm for the sharper bands.

After the initial deposition, further reaction was accomplished by controlled annealing of the matrix. By using this procedure, it was possible to observe the growth and disappearance of the various absorption bands, which aided in the assignment of the spectra.

Results and Discussion

Figure 1 contains the infrared spectra observed for chromium isolated in N_2 matrices. If the matrix was deposited slowly, minimizing the surface diffusion and maximizing the probability of good isolation, the infrared spectrum contained one band at 2136 cm^{-1} (spectrum 1a). Since this band was not observed in N_2 matrices containing no Cr, it is believed to arise from a chromium–dinitrogen complex. After prolonged exposure to the hydrogen and tungsten lamps used to obtain the electronic spectrum, a new band was observed in the infrared spectrum at 2112 cm^{-1} (spectrum 1b). If the matrix was deposited at a faster rate, allowing more surface diffusion to occur, the 2112-cm^{-1} band could also be obtained prior to the exposure to the lamps. Spectrum 1c is an example of a spectrum obtained using these conditions. In addition, this spectrum contained three additional bands at 2028, 2072, and 2195 cm^{-1}.

The ultraviolet spectrum of a Cr-containing N_2 matrix, containing only the 2112-cm^{-1} infrared band, is shown in Figure 2. Spectrum 2a is the uncorrected spectrum actually observed and spectrum 2b is the same spectrum corrected for baseline drift and resolved into component Gaussians. The two bands marked with asterisks are "window bands" which were observed in blank N_2 matrices. The spectrum resolves into four bands: two weak bands centered at 367.2 and 340.8 nm, a medium-intensity band centered at 311.5 nm, and a weak to medium-intensity band centered at 297.2 nm. In addition, there is a very strong band centered at ~230 nm, which is not shown.

Qualitatively, this spectrum is similar to the electronic spectrum reported by Beach and Gray[14] for $Cr(CO)_6$. Consequently, the species giving rise to the infrared band at 2112 cm^{-1} in N_2 matrices is assigned as $Cr(N_2)_6$. As shown in Table I, the observed electronic transitions can readily be assigned by analogy with the observed electronic spectrum of $Cr(CO)_6$. Approximate ligand field parameters were calculated for $Cr(N_2)_6$ and they are compared to the ligand field parameters calculated for $Cr(CO)_6$ and $Cr(CN)_6{}^{3-}$ in Table II. The magnitude of the d–d splitting parameter (Δ) clearly

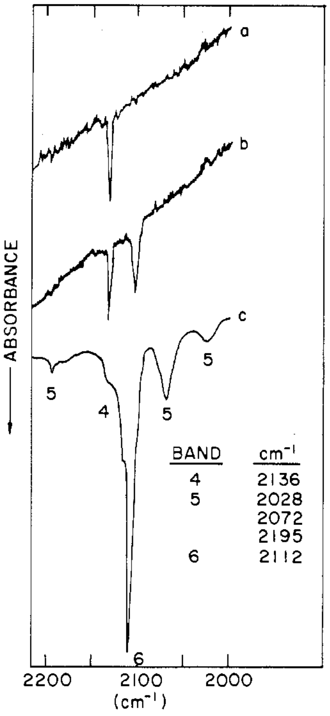

Figure 1. Infrared spectra of $Cr(N_2)_n$, $n = 4-6$, in N_2 matrices during photolysis.

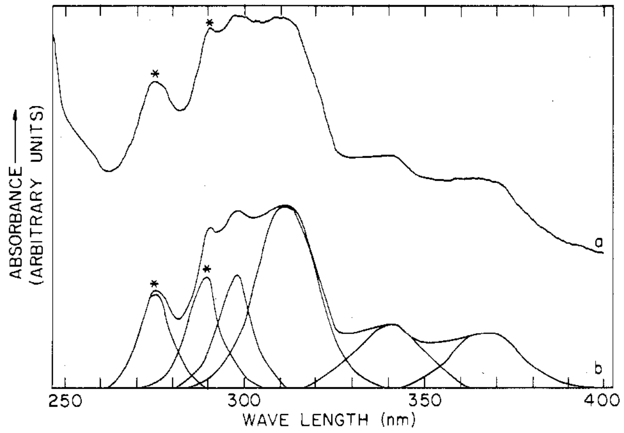

Figure 2. Uv spectrum of $Cr(N_2)_6$ in an N_2 matrix. Trace a is the observed spectrum; trace b shows the spectrum resolved into Gaussians.

Table I. Comparison of the Observed Electronic Transitions for $Cr(N_2)_6$ and $Cr(CO)_6$

	$Cr(N_2)_6$			$Cr(CO)_6$[a]		
Assignment	λ, nm	$\bar{\nu}$, cm^{-1}	$\Delta G'_{1/2}$	λ, nm	$\bar{\nu}$, cm^{-1}	$\Delta G'_{1/2}$
$^1T_{1g} \leftarrow {}^1A_{1g}$	367.2	27 218	2254	344.8	29 000	2550
	339.3	29 472		317.0	31 550	
$^1T_{1u} \leftarrow {}^1A_{1g}$	311.5	32 103		279.3	35 800	
$^1T_{2g} \leftarrow {}^1A_{1g}$	297.2	33 647		256.8	38 970	
$^1T_{1u} \leftarrow {}^1A_{1g}$	~230	43 478		226.2	44 200	

[a] From ref 13.

shows N_2 to be a strong-field ligand, with field strength similar in magnitude to those of the isoelectronic ligands CO and CN^-.

Table II. Ligand Field Parameters for $Cr(CO)_6$, $Cr(N_2)_6$, and $Cr(CN)_6{}^{2-}$

Parameter	$Cr(CO)_6$[a]	$Cr(N_2)_6$	$Cr(CN)_6{}^{3-}$[b]
Δ, cm^{-1}	32 200	28 800	26 600
B, cm^{-1}	520	400	
C, cm^{-1}	1700[c]	1600[c]	
$\beta = B_{exptl}/B_{free}$[d]	0.66	0.51	

[a] From ref 13. [b] From H. B. Gray and N. A. Beach, *J. Am. Chem. Soc.*, **85**, 2922 (1963). [c] Estimated value. [d] B_{free} = 790 cm^{-1}.

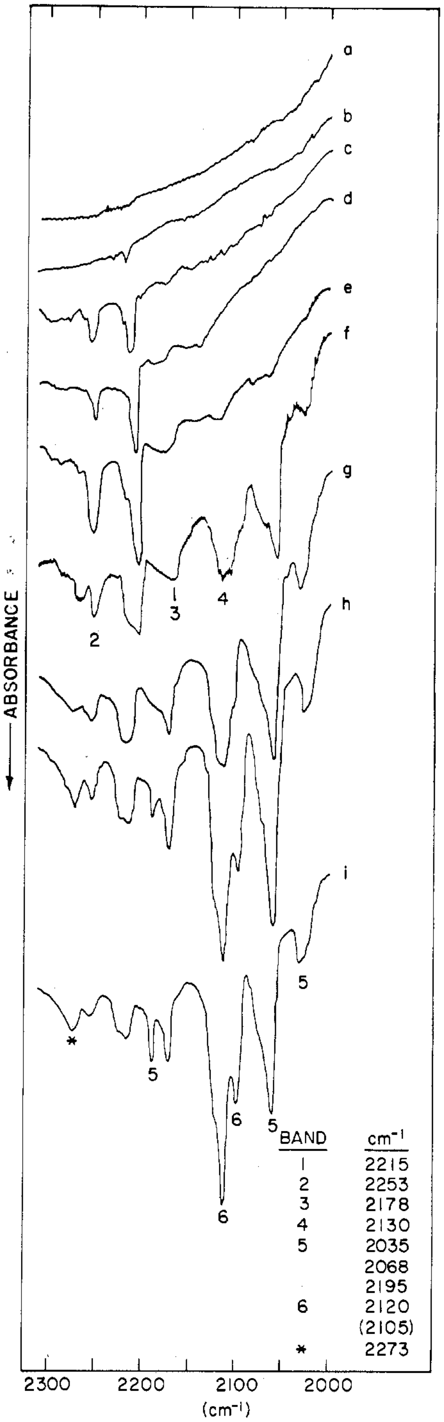

Figure 3. Infrared spectra of the chromium-dinitrogen complexes with increasing N_2 concentrations and/or annealing.

Figure 3 is a composite of several experiments showing the observed changes in the dinitrogen stretching region of the infrared spectrum upon increasing the amount of N_2 in the matrix and/or annealing. Spectrum 3a is the spectrum of Cr in 1% N_2/Ar prior to annealing. After annealing, a band was observed at 2215 cm^{-1}. In addition to the 2215-cm^{-1} band, a second band was observed at 2253 cm^{-1} in 3.5% N_2 matrices prior to annealing (spectrum 3c). Increasing the N_2 concentration to 10% N_2 (spectrum 3d) produced two new bands at 2130 and 2178 cm^{-1}. As shown in spectrum 3e, both bands increase in intensity upon annealing. Further annealing or increasing the concentration of N_2 in the matrix to 15% prior to annealing produced three new bands at 2035, 2068, and

Table III. Assignments for $Cr(N_2)_n$, n = 1-6

	ν_{N_2}, cm^{-1}		
Species	*a*	*b*	*c*
$Cr(N_2)$	2215		2142
$Cr(N_2)_2$	2253		2178
$Cr(N_2)_3$	2178		2108
$Cr(N_2)_4$	2130	2136	2060
$Cr(N_2)_5$	2035	2028	1966
	2068	2072	2000
	2195	2195	
$Cr(N_2)_6$	2120 (2105)[d]	2112	2042

[a] Argon matrix. [b] Nitrogen matrix. [c] $^{15}N_2$ in argon matrix. [d] Matrix splitting.

2273 cm^{-1} (spectrum 3f). Annealing the 15% matrix caused a marked increase in the 2034- and 2068-cm^{-1} bands, and three new bands at 2105, 2120, and 2195 cm^{-1} appear. With further annealing these five bands increasingly dominate the spectrum (spectrum 3h), and with still more annealing the bands at 2035, 2068, and 2195 cm^{-1} decrease in intensity with the bands at 2120 and 2105 cm^{-1} finally dominating the spectrum. Since the observed ir spectra were found to be insensitive to the amount or rate of chromium deposition, each species is thought to arise from N_2 molecules coordinated to a single metal atom. Mixed-isotope experiments were attempted to help establish the number of N_2 molecules coordinated to each metal atom. Two bands at 2142 and 2215 cm^{-1} were observed in the spectrum obtained from the codeposition of Cr atoms with 3:3:100 $^{14}N_2$:$^{15}N_2$:Ar, which indicated that this species contained one coordinated N_2 molecule. Upon annealing, four new bands at 2145, 2178, 2253, and 2275 cm^{-1} were observed. The behavior of the relative intensities of these bands during annealing strongly indicated that they all arose from the same species, indicating that this species must contain two coordinated N_2 molecules. Attempts to establish unequivocably the stoichiometry of the higher coordinated species were thwarted by low intensities, highly overlapping bands, and the general inability to isolate single species in the mixed N_2/Ar matrices.

While the spectrum of Cr atoms isolated in 1:1 $^{14}N_2$/$^{15}N_2$ matrices was not examined in this study, it had been reported by Burdett et al.,[3a] who interpreted it as arising from the presence of a matrix-split mono(dinitrogen) complex. However, this spectrum is qualitatively similar to the spectrum which they reported for Ni atoms isolated in 1:1 $^{14}N_2$/$^{15}N_2$ matrices. Since then, Huber et al.[3b] have shown that $Ni(N_2)_4$ is formed in N_2 matrices. The qualitative similarity between the Ni/$^{14}N_2$/$^{15}N_2$ and the Cr/$^{14}N_2$/$^{15}N_2$ spectra suggests that $Cr(N_2)_4$ was formed during the careful deposition of Cr atoms in N_2 matrices. The assignments which have been made based upon all of the experimental data are given in Table III.

The structures predicted by Burdett[15] for low-, intermediate-, and high-spin d^6 ions with from one to six end-bonded coordinated ligands and the number of ir-active bands expected for each structure are given in Table IV. Although some bands may not have been observed because of low intensity and/or the close proximity of other stronger bands, if, as is usually found, all the complexes are assumed to be end-bonded, tentative structures can be determined for each observed dinitrogen complex. Since only one ir band was observed for each molecule, $Cr(N_2)$ and $Cr(N_2)_2$ are linear molecules with $C_{\infty v}$ and $D_{\infty h}$ point group symmetries, respectively. Only one ir band could definitely be assigned to $Cr(N_2)_3$ indicating trigonal-planar (D_{3h}) symmetry. However, two weaker bands which appeared as shoulders at ~2190 and 2225 cm^{-1} seem to be related to the $Cr(N_2)_3$ band. If these bands are truly related, then the molecule may have C_{2v} symmetry. Only one ir band was observed for $Cr(N_2)_4$ in both Ar and N_2 matrices, which suggests either tetrahedral (T_d) or square-planar (D_{4h}) symmetry. Unfortunately it is not possible to distinguish between these structural alternatives. The observation of three ir bands for $Cr(N_2)_5$ indicates this molecule has a tetragonal-pyramidal (C_{4v}) structure. $Cr(N_2)_6$ is expected to have octahedral (O_h) symmetry. Since no splitting was observed for $Cr(N_2)_6$ in N_2 matrices and the ir band of $Cr(CO)_6$ was also observed to be split in argon matrices, the splitting of the $Cr(N_2)_6$ infrared band in argon matrices is probably due to matrix effects.

Table IV. Predicted Structures and the Number of Infrared-Active N-N Stretching Modes for Complexes with Low-, Intermediate-, and High-Spin d^6 Ions

	Low spin		Intermediate spin		High spin	
Species	Symmetry point group	No. of ir-active bands	Symmetry point group	No. of ir-active bands	Symmetry point bands	No. of ir-active bands
M(L)	$C_{\infty v}$	1	$C_{\infty v}$	1	$C_{\infty v}$	1
$M(L)_2$	C_{2v}	2	$D_{\infty h}$	1	$D_{\infty h}$	1
$M(L)_3$	C_{3v}	2	C_{2v}	3	D_{3h}	1
$M(L)_4$	C_{2v}	4	D_{4h}	1	D_{4h}	1
$M(L)_5$	C_{4v}	3	D_{3h}	2	D_{3h}	2
$M(L)_6$	O_h	1	O_h	1	O_h	1

[a] From ref 14.

Although the assignments given in Table III and the structures deduced from the infrared spectra are consistent with all of the experimental observations, several aspects of this study seem to be out of phase with the results of similar studies using different metals. In all of the previous studies, the dinitrogen complex of highest stoichiometry was produced in nitrogen matrices and the partially coordinated species have shown a monotonic increasing frequency–coordination number relationship similar to that observed for the hexacarbonyls. The chromium–dinitrogen system does not. At least two chromium–dinitrogen complexes of different coordination can be produced during the deposition of chromium in nitrogen matrices and the frequencies of the lower coordinated species follow no detectable pattern. This "anomalous behavior" could indicate the presence of polymeric species. However, chromium dimers could not be detected in the uv–visible spectrum of Cr isolated in argon matrices under the conditions used in these experiments. Also, the amount of chromium in the matrix had no effect on the ir spectrum. In addition, the low number of infrared bands observed for each species indicates that a dimeric species would have to have high symmetry and/or contain few coordinated dinitrogen ligands, an occurrence which seems rather unlikely. Thus, the possibility that dimer formation caused the observed anomalies has been discounted.

Impurities, such as CO or O_2 may also be responsible for the anomalous behavior. However, since no spectroscopic evidence of complexes containing these impurities was observed, the possibility that impurities caused the anomalies has also been discounted.

One possible explanation which could not be discounted on the basis of the existing data is that the lower coordinated dinitrogen complexes of chromium, unlike all of the previously reported dinitrogen complexes except possibly CoN_2,[7] are side bonded. [Recent studies suggest that the species previously assigned as side-bonded CoN_2 may in fact arise from Co_2N_2.[12]] In fact, each species which apparently has an anomalously high ir frequency has a side-bonded structure which is consistent with the observed ir spectrum, since only one ir band is expected for side-bonded CrN_2, $Cr(N_2)_2$, $Cr(N_2)_3$, and $Cr(N_2)_4$ with C_{2v}, D_{2h}, D_{3h}, and D_{4h} symmetry, respectively. Since the behavior of the ir frequencies of side-bonded dinitrogen species with increased coordination is unknown, side-bonded complexes could produce the anomalous frequency trend observed for this system.

Side bonding can also be used to explain the apparent anomalous behavior observed in nitrogen matrices. It is reasonable to assume that because of steric effects, $Cr(N_2)_4$ is the highest coordinated side-bonded chromium–dinitrogen complex which can be formed and that this complex could be formed in nitrogen matrices using "normal" deposition conditions. However, if this complex is metastable, it could be converted to the thermodynamically more stable end-bonded $Cr(N_2)_6$ by providing sufficient energy to convert side-bonded $Cr(N_2)_4$ to end-bonded $Cr(N_2)_4$, which can then react with free nitrogen in the matrix to form $Cr(N_2)_6$. The lamps used to photolyze the nitrogen matrix provided this energy.

Even if the type of bonding is established, the matrix structures may not be the most stable structures of the free species. There is growing evidence of quasi-stable compounds formed from the interaction between the trapped species and the matrix gas. For example, the electronic spectrum of vanadium atoms trapped in argon matrices[16] was shown to be quite similar to the electronic spectrum expected for the hypothetical molecule $V(Ar)_6$. Thus solvation effects could influence the structures of the intermediate complexes. In fact, Kündig and Ozin[17] have recently suggested the structure of free $Cr(CO)_5$ is trigonal bipyramidal (D_{3h}) rather than the square-pyramidal (C_{4v}) structure reported by Graham et al.[18] They suggested the C_{4v} complex is actually $Cr(CO)_5S$, where S = solvent. From the variation found in the visible absorption spectrum of $Cr(CO)_5$ in mixed rare gas matrices, Perutz and Turner[19] have also concluded that $Cr(CO)_5S$ may be a better representation of the complex. However, they expressed doubt that the solvation effect was strong enough to influence the structure of the complex.

Conclusion

The binary dinitrogen complexes of chromium with from one to six coordinated dinitrogen ligands per metal atom have been identified from their infrared spectra in N_2/Ar mixtures at 10 K. Tentative structures, which are consistent with the infrared spectra, have been determined for each complex. Unfortunately, in several cases, more than one possible structure was found to be consistent with the infrared data.

The uv spectrum of $Cr(N_2)_6$ was observed in a N_2 matrix and found to be qualitatively similar to the previously observed electronic spectrum of $Cr(CO)_6$. Although the magnitude of the d–d splitting parameter in the hexakis(dinitrogen) complex is slightly less than the magnitude of the d–d splitting parameter found for the hexacarbonyl, it clearly establishes that N_2 is a strong-field ligand with a field strength comparable to CN^-.

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Registry No. $Cr(N_2)$, 32376-71-9; $Cr(N_2)_2$, 58815-27-3; $Cr(N_2)_3$, 58815-28-4; $Cr(N_2)_4$, 58815-29-5; $Cr(N_2)_5$, 58815-30-8; $Cr(N_2)_6$, 28042-66-2.

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Synthesis of Dodecacarbonyldivanadium in Low-Temperature Matrices[1]

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The products of the cocondensation of V atoms with CO at 10 K have been investigated using ir and uv spectroscopy. Two vanadium carbonyl complexes, $V(CO)_6$ and $V_2(CO)_{12}$, have been identified and the structure of each complex was determined from the analysis of the ir spectrum. In addition, the electronic spectrum of $V(CO)_6$ has been analyzed.

Introduction

Vanadium hexacarbonyl ($V(CO)_6$) has been investigated by a number of techniques including infrared and ultraviolet spectroscopy,[2a] photoelectron spectroscopy,[2b] electron spin resonance spectroscopy,[3] and magnetic measurements.[4,5] These studies indicate that at room temperature $V(CO)_6$ has one unpaired electron and virtual octahedral geometry producing an effective $^2T_{2g}$ ground state. According to the Jahn–Teller theorem, this structure should undergo some distortion which will remove the orbital degeneracy. In fact, there is strong experimental evidence of a dynamic Jahn–Teller distortion at room temperature.[2a] At ~66 K, both ESR[3] and magnetic measurements[4,5] indicate the dynamic distorted structure is transformed into a statically distorted structure, which is thought to have one unpaired electron and D_{4h} symmetry producing a $^2B_{2g}$ ground state. Since D_{4h} $V(CO)_6$ had not been previously observed spectroscopically, the technique of matrix isolation was used to investigate this molecule spectroscopically.

During this study several additional bands were observed in the infrared spectrum of vanadium isolated in CO matrices. An investigation of these bands indicated that they arose from