Direct Synthesis with Vanadium Atoms. II. Synthesis and Characterization of Vanadium Hexadinitrogen, $V(N_2)_6$, in Low-Temperature Matrices

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Abstract: The compounds $V(N_2)_6$ and $V_2(N_2)_n$ (where n is probably 12) are synthesized by cocondensing vanadium atoms with pure N_2. The two above-mentioned dinitrogen complexes were investigated by infrared and uv-visible spectroscopy. The stoichiometry with respect to the metal was established from vanadium concentration experiments. A comparison of the optical spectra of matrix-isolated $V(N_2)_6$ and $V(CO)_6$ suggests that these molecules have very similar electronic properties and are probably isostructural. The data clearly establish that dinitrogen is a strong field ligand in its bonding properties. Finally, the intriguing observation that atomic V can be isolated in N_2 matrices from 8 to 12 K codepositions, yet $V(N_2)_6$ is preferentially formed at 20-25 K, is discussed in terms of the subtle temperature dependence of product yield when performing direct syntheses with metal atoms.

In part I of this study we demonstrated that the V/CO cocondensation reaction at high V concentrations provides not only a direct route to $V(CO)_6$ but also the elusive dimer $V_2(CO)_{12}$.[1] These experiments stimulated a search for the analogous $V(N_2)_6$ and $V_2(N_2)_{12}$ dinitrogen complexes, which by comparison with previous M/N_2 reactions[2] would be the anticipated products of the V/N_2 reaction. This proved to be the case in practice and provides the only known synthetic pathway to a complex containing *six* dinitrogen ligands coordinated to a single metal atom. Moreover, $V(N_2)_6$ provides an interesting opportunity to determine the ligand field character of N_2 compared to the strong field ligand CO.

Experimental Section

Monatomic V was generated by directly heating a thin vanadium filament (0.025 in). The vanadium metal (99.99%) was supplied by A. D. McKay, New York, N.Y. Research grade $^{14}N_2$ (99.99%) was supplied by Matheson of Canada. The furnace used for the evaporation of the metals has been described previously.[3] The rate of metal atom deposition was continuously monitored using a quartz crystal microbalance.[3] To obtain quantitative data for V/N_2 cocondensations, it was necessary to calibrate carefully the rate of deposition of both metal and gas onto the sample window as described previously.[4] In the infrared experiments, matrices were deposited on a CsI plate cooled to 10-12 K by means of an Air Products Displex closed-cycle helium refrigerator or to 6 K by a liquid helium transfer system. Infrared spectra were recorded on a Perkin-Elmer 180 or 621 spectrophotometer. Uv-visible spectra were recorded on a standard Unicam S.P. 8000 instrument in the range 190-700 nm, the sample being deposited onto a LiF or NaCl optical plate cooled to 6-12 K.

Results

Vanadium Atom-Dinitrogen Cocondensation Reactions. Synthesis and Characterization of Vanadium Hexadinitrogen, $V(N_2)_6$ and $V_2(N_2)_n$ (where n is probably 12). In view of our successes with V/V_2 mixtures in Ar[5] and $V(CO)_6/V_2(CO)_{12}$ mixtures in pure CO,[1] we undertook a vanadium concentration study in pure N_2 matrices. Using $V/N_2 \simeq 1/10^4$, the infrared spectrum shown in Figure 1 was obtained, showing an intense NN stretching mode at 2100 cm^{-1} with *three* other weaker bands at 2176, 2080, and 2056/2048 cm^{-1} (qualitatively very similar to the V/CO reaction[1]). When the V concentration was progressively increased in the reaction, the three weaker lines continued to grow in, with absorbances relative to the 2100-cm^{-1} line which were proportional to $[V_0]$ (Figure 2). Two other weaker bands at 2216 and 2140 cm^{-1} appear in the higher concentration runs but were too weak for meaningful absorbance measurements (Table I).

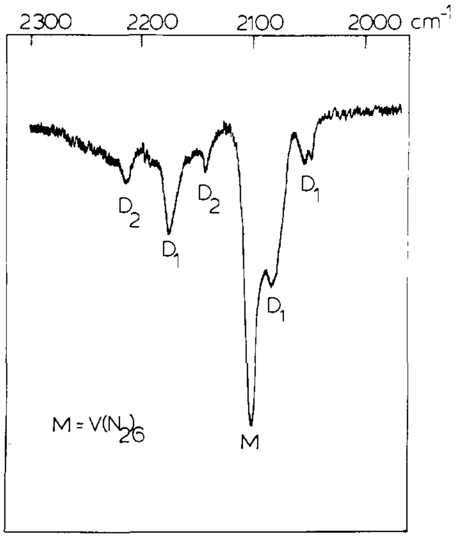

Figure 1. The infrared spectrum of the products of the cocondensation reaction of V atoms with pure N_2 matrices at 6-12 K where $M = V(N_2)_6$ and D_1 is probably $V_2(N_2)_{12}$.

Clearly the lines assigned to species D_1 in Table I belong to a binuclear dinitrogen complex (see for example ref 6) which by analogy with $V_2(CO)_{12}$[1] is probably best assigned to $V_2(N_2)_n$ (where n is most probably 12).

The corresponding optical studies of the V/N_2 reaction proved to be quite revealing in terms of the nature of the products and the optimum conditions for complexation. For example, using V atom concentrations which minimized the formation of D_1, we obtained at 6-12 K a uv-visible spectrum of atomic vanadium superimposed on a broad molecular spectrum centered at about 30 000 cm^{-1} (Figure 3A). On annealing the matrix at 25-30 K, the atomic spectrum gradually decreased in intensity and the molecular spectrum became more prominent (Figure 3B). Eventually a molecular spectrum was left behind (cf. Figure 4B).

When the cocondensation was performed at 20 K, the same molecular spectrum was obtained but with the noticeable absence of atomic vanadium (Figure 4B). For the purposes of comparison, the corresponding data for the V/CO reaction are displayed in Figure 4A. Note that in this reaction, the product is entirely $V(CO)_6$ at 6-12 K. The optical data for the dinitrogen complex, as well as $V(CO)_6$, are summarized in Table II.

Table I. Infrared Spectra of the Products of the V/N_2 Cocondensation Reaction

cm^{-1}	Assignment^a	cm^{-1}	Assignment^a
2216	D_2	2100	M
2176	D_1	2080	D_1
2140	D_2	2056/2048	D_1

[a] M is assigned to $V(N_2)_6$, D_1 to $V_2(N_2)_n$, where n is probably 12, and D_2 to an isomer of D_1 or possibly a binuclear carbonyl complex, $V_2(N_2)_n$, where $n < 12$ (see text).

Table II. Optical Data for Matrix Isolated $V(CO)_6$ and $V(N_2)_6$

$V(CO)_6$ (cm^{-1})	$V(N_2)_6$ (cm^{-1})	Δ^b (cm^{-1})	Tentative^a assignment
25840 vw	19455 w	6385	$^2B_{1g} \leftarrow {}^2B_{2g}$
30478 vw	23585 vvw	6893	$^2B_{1g} \leftarrow {}^2E_g$ or $^2A_{1g} \leftarrow {}^2E_g$
32154 wsh	26740 msh	5414	C.T.
33784 mwsh	29155 s	4629	C.T.
37453 s	31646 s	5807	C.T.
40650 msh	33557 mssh	7093	C.T.
44248 w	35461 mwsh	8787	C.T.

[a] Assuming approximately D_{4h} symmetry. C.T. = charge transfer transition. [b] Δ represents the frequency shift on passing from $V(CO)_6$ to $V(N_2)_6$.

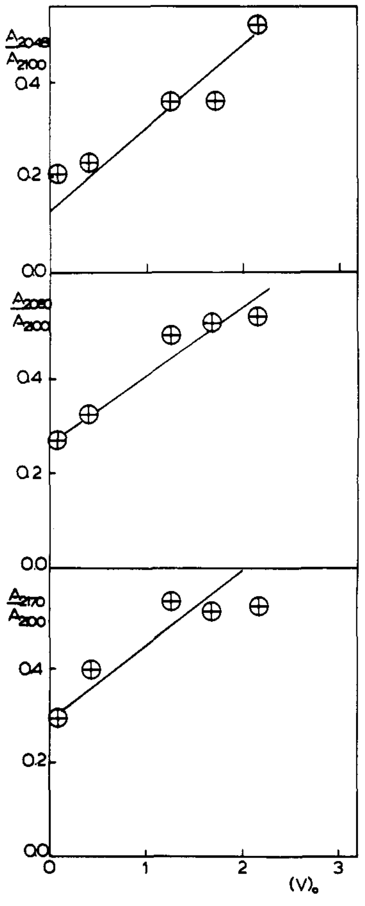

Figure 2. Plots of the absorbances of the lines attributed to $V_2(N_2)_{12}$ to that of $V(N_2)_6$ as a function of the V metal concentration at constant N_2 deposition rate.

Examination of the data reveals a remarkable correlation between all of the lines of $V(CO)_6$ and those of the dinitrogen complex. Compared to the dinitrogen complex, all of the absorptions of $V(CO)_6$ have undergone a "red" shift of between 4500 and 8800 cm^{-1}. The similarity between the two sets of optical data and the infrared data is striking and strongly suggests that the mononuclear dinitrogen complex M is indeed $V(N_2)_6$.

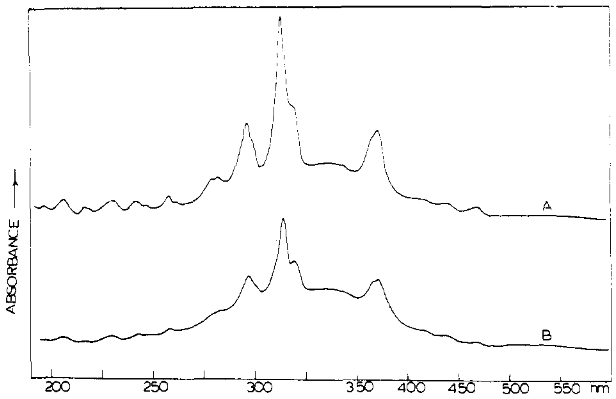

Figure 3. The optical spectrum of the products of the V/N_2 reaction formed (A) on deposition at 6-12 K and (B) after matrix annealing at 25-30 K.

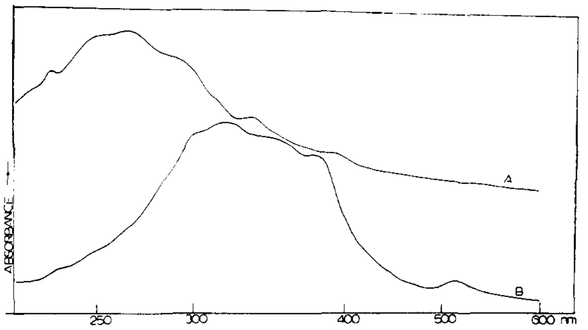

Figure 4. The optical spectrum of (A) $V(CO)_6$ in CO and (B) $V(N_2)_6$ in N_2 formed from V/CO and V/N_2 cocondensation reactions at 6-10 K and approximately 20 K, respectively.

Assuming the $V(CO)_6$ molecule undergoes a small tetragonal distortion and making use of the available ESR estimates for the ligand field parameters of $V(CO)_6$[7]

$$\Delta_1 = E(b_{1g}) - E(b_{2g}) = 36\,200\ \text{cm}^{-1}$$

and

$$\Delta_2 = E(b_{2g}) - E(e_g) = 1880\ \text{cm}^{-1}$$

it seems most likely that the weak absorptions in the 25 480-30 478 cm^{-1} region for $V(CO)_6$ are d → d transitions, whereas the stronger, high-energy transitions are probably charge transfer in origin. By analogy, the weak lines in the region 19 455-23 585 cm^{-1} for $V(N_2)_6$ are probably best assigned to d → d transitions, the remaining intense high-energy absorptions being charge transfer in origin. Qualitatively, the optical spectrum of $V(CO)_6$ closely resembles that of $V(N_2)_6$ as well as $Cr(CO)_6$.[8] The ligand field parameter Δ_1 for $V(CO)_6$ is approximately equal to 10*Dq* (25 000-30 000 cm^{-1}) which is in good agreement with 10*Dq* (34 150 cm^{-1}) for $Cr(CO)_6$, a low-spin, strong field complex. The implication is, therefore, that 10*Dq* for $V(N_2)_6$ is approximately 22 000 cm^{-1} and clearly shows that N_2 is a strong field ligand with a field strength comparable to CO.

Returning finally to the intriguing observation of atomic V in N_2 matrices deposited at 8-12 K, yet $V(N_2)_6$ at 20 K, this is not an isolated occurrence, as similar effects have been observed in the Cr/N_2 system where atomic Cr is the main reaction product at 8-12 K, whereas $Cr(N_2)_6$ results at 20 K.[9] In fact, the main charge transfer features of $Cr(N_2)_6$ are very similar to those of $V(N_2)_6$, being centered around 30 000 cm^{-1}

and shifted into the red by approximately 5000 cm^{-1} compared with the corresponding transitions of $Cr(CO)_6$.[8]

The isolation of either metal atoms or metal complexes in the V/N_2 and Cr/N_2 cocondensation reactions implies that a very delicate balance between the activation energy for complexation and the thermal energy available at the reaction zone must exist, the latter being intimately related to the temperature at which the deposition is conducted. The fact that the corresponding V/CO and Cr/CO reactions proceed to completion even at 6 K means that complex formation for the carbonyls compared with the respective dinitrogen complexes is a more facile process. Whether this is because of a lower energy of activation or a higher heat of reaction for the carbonyls in the reaction zone, or both, cannot be ascertained. What is clear, however, is the subtle temperature dependence of product yield, an extremely important factor to take into account when performing direct syntheses with metal atoms.

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π-Donor Relaxation in the Oxygen 1s Ionization of Carbonyl Compounds

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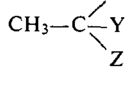
Abstract: Oxygen 1s and carbon 1s binding energies have been measured for a wide variety of compounds containing the carbonyl group. It is concluded that most of the oxygen 1s ionizations include a rather large amount of electronic relaxation corresponding to π electron donation from the groups bonded to the carbonyl groups. The data are analyzed in two different ways to derive π-donor relaxation energies. The two resulting sets of relaxation energies are in fair agreement, and either set may be used to estimate the relative π-donor abilities of substituents.

The oxygen 1s binding energies of compounds containing the keto group, >C=O, do not show a simple correlation with the electronegativities of the substituent groups. For example, the carbonyl oxygen 1s binding energies of methyl carbonate, formaldehyde, and carbonyl fluoride increase in the order $(CH_3O)_2CO < H_2CO < F_2CO$. The present study was carried out to test the hypothesis that this apparently anomalous behavior is due to different electronic relaxation energies in the photoionizations. We have determined the core binding energies of a wide variety of carbonyl compounds to provide sufficient data for systematic analysis. Our experimental results, as well as some from other sources, are presented in Table I. In our analysis of these data we have assumed that, in most of the compounds, core ionization of the carbonyl oxygen atoms involves "extra" relaxation energy due to π electron donation from the substituent groups. Using two different approaches, we have evaluated the relative π donor abilities of the various substituent groups.

The Proximity Effect

The core binding energy of an atom in a molecule changes when other atoms in the molecule are replaced by different atoms or groups. These chemical shifts in binding energy are generally more pronounced the nearer the substituent groups are to the core-ionizing atom. This proximity effect can be seen in the carbon 1s binding energies of compounds of the type



$$CH_3\text{—}C\begin{matrix}X\\Y\\Z\end{matrix}$$

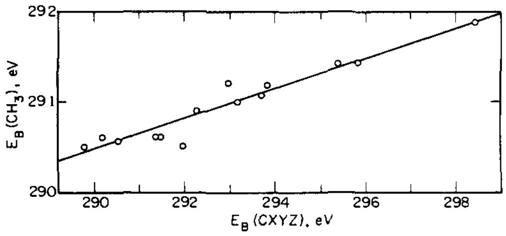


Figure 1. Plot of CH_3 carbon 1s binding energies vs. CXYZ carbon 1s binding energies for compounds of the type CH_3CXYZ. Note that the vertical scale is twice as great as the horizontal scale. The points, in order of increasing $E_B(CXYZ)$, correspond to BEt_3, BEt_2Cl, C_2H_6, Et_3NBH_3, Et_2NBH_2, $B(OEt)_3$, EtOH, $EtO(CO)CF_3$, EtF, CH_3COCH_3, CH_3CHO, CH_3CO_2H, CH_3CHF_2, and CH_3CF_3. For sources of data, see ref 1-5.

As the groups X, Y, and Z are changed, the binding energy of the CH_3 carbon atom changes much less than that of the CXYZ carbon atom. Figure 1 is a plot of the CH_3 binding energies against the CXYZ binding energies for 14 different compounds.[1-5] The data are linearly correlated and may be represented by the relation

$$E_B(CH_3) = 242.57 + 0.165E_B(CXYZ) \qquad (1)$$

This behavior is typical of simple compounds in which the atoms whose binding energies are being compared are joined by single bonds.

An entirely different result is obtained from a comparison of the oxygen and carbon binding energies of carbonyl compounds in Table I. A plot of the oxygen binding energies