The Electron Paramagnetic Resonance and Optical Spectra of Vanadium Hexacarbonyl

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Abstract: Electron paramagnetic resonance spectra of vanadium hexacarbonyl in frozen glasses have been observed with the hyperfine structure clearly seen. The spectra in cyclohexane glasses were fitted with $g_{\parallel} = 1.988_5$, $g_{\perp} = 2.075$, $A_{\parallel} = 4.5 \times 10^{-4}$ cm^{-1}, and $A_{\perp} = 50.5 \times 10^{-4}$ cm^{-1}. Evidence is seen for molecular association in solution at low temperatures. Quantitative optical spectra were obtained for the material in solution and the solid. Evaluation of the bonding is discussed.

Since its initial preparation,[2-4] vanadium hexacarbonyl has been a source of discussion: whether it exists as a monomer or dimer,[4-6] what form and extent of distortion results from the expected Jahn–Teller effect,[7,8] and what is the nature of its electronic structure.[2,9] In these investigations, the methods used include magnetic susceptibility measurements,[2,4,6,10,11] electron paramagnetic resonance (EPR),[5,7,12] optical,[8] infrared,[5,8,10] and photoelectron[9] spectroscopies, as well as x-ray[2] and electron diffraction methods.[13] Nevertheless, substantial questions remain on this basic carbonyl on almost all points. With this in mind, we have reinvestigated the compound using EPR and optical spectroscopies and subsequently can more clearly describe the electronic structure of the molecule and some aspects of chemical interest.

Experimental Section

$V(CO)_6$ was prepared by a modified method of Silvestri et al.[14] reacting the diglyme stabilized sodium salt of $V(CO)_6^-$ (Strem Chemicals, Danvers, Mass.) with 4:1 weight-to-weight H_3PO_4:P_2O_5 at ambient temperature. All samples used were purified by fractional sublimation. Cyclohexane (spectroscopic grade) was dried and distilled from sodium metal. Toluene was fractionally distilled off CaH_2. It was found to be less than 7 ppm (70 μM) benzene by gas chromatography. Other solvents used were dried over sodium and degassed by at least three freeze–pump–thaw cycles immediately prior to addition of solute.

The X-band EPR spectra were obtained on an extensively modified Varian V4500 system with a 6-in. magnet. The microwave bridge consists of a Varian V-265 reflex klystron operating at about 800 mW; an isolator; a Flann 16/15B, -10db coupler to the bias arm; a Flann 16/11 rotary attenuator; a Microwave Associates 8K212 three-port circulator; Varian TE102 cavity, -20dB isolator to the detector arm; Marconi Saunders 6029/2 20dB coupler to the bias arm; Hewlett Packard Model X485B detector mount; and Microwave Associates MA40075 Shottkey barrier diode. The bias arm consists of a Hewlett Packard X532B frequency meter, Caswell Electronics X-206-A variable attenuator, and Flann 16/6 phase shifter. The output stage of the V4560, 100-KHz detection system, was replaced with an operational amplifier as a voltage follower. The field was detected with a Hall effect magnetic field monitor of our own design. The field is plotted with ±1 G accuracy relative to a standard and greater than 0.1% linearity. Pitch (Varian 904450-01) with $g = 2.0029$ was used as a standard.

The optical spectra were obtained on either a Pye Unicam SP1800, or SP700A, or a Cary 14M-50 modified with the monochromater placed between the light source and sample compartment. The solution samples were prepared in an apparatus designed to be able to weigh the sample and measure solvent volume as well as obtain the spectra in vacuo. It was found that borosilicate glass catalyzed the decomposition of the carbonyl, and so all parts of the apparatus not made from fused silica were siliconized with "Repelcote" (Hopkin and Williams, Ltd, Chadwell Heath), a 2% solution of dimethyldichlorosilane in CCl_4. The low temperature optical spectra were obtained in transmission from a sample of $V(CO)_6$ evaporated onto a silica plate fused onto the bottom of a silica cold finger containing liquid nitrogen. This was enclosed in a glass vacuum jacket with silica optical windows. The spectrum baseline was identical before depositing the solid and after warming and subliming the sample off indicating that little or no decomposition occurred from possible photolysis in the light beam.

Optical spectra shown in the text were corrected for baseline and converted to wavenumber plots from the original spectra linear in wavelength. Tentative spectral bands in the solution spectrum were fitted with a DuPont 310 curve resolver using information from preliminary matrix-isolation experiments.

Results and Discussion

Figure 1 shows the experimental and best-fit curves of $V(CO)_6$ in a frozen cyclohexane glass. The spectrum is axial with a strongly temperature dependent line width leading to undetectability above 130 K even in a magnetically dilute glass as seen in Figure 2. No solution spectra were obtainable.

Where β is the Bohr magneton, H refers to the external magnetic field, S to the electron spin, and I to the nuclear spin, the spectrum was simulated using the Hamiltonian for an $S = \frac{1}{2}$, $I = \frac{7}{2}$ system:

$$\mathcal{H} = g_{\parallel}\beta H_z S_z + g_{\perp}\beta(H_x S_x + H_y S_y) + A'_{\parallel} S_z I_z + A'_{\perp}(S_x I_x + S_y I_y)$$

calculating the energies to second order. This was done using a computer program written by P. D. W. Boyd (personal communication). The values of the parameters used are given in Table I.

Since a solution spectrum was not obtainable, the relative signs of the anisotropic hyperfine coupling constants are not determined. Although the spectrum in toluene could not be simulated with the accuracy obtained in the cyclohexane case, the g and A values are seen to be similar. The toluene values are not accurate enough to consider in detail. Note that the line shape changes from Gaussian to Lorentzian indicating faster relaxation in toluene. We believe that the species observed is $V(CO)_6$ since the material has been shown to be stable in hydrocarbons and toluene under the conditions encountered.[2]

In addition to the main paramagnetic species, there was usually an air-stable, paramagnetic impurity in the cyclohexane solution. It has a spectrum in frozen solution which appears nearly isotropic having $g = 1.984 \pm 0.002$, and at 88 K has a peak to peak width about 80 G. No hyperfine structure is evident. While in benzene no spectrum was observed, the EPR spectra at 90 K of $V(CO)_6$ in glasses made from pentane, hexane, hexadecane, diglyme, and diethyl ether gave unresolved spectra similar to those seen by Pratt.[7,12]

The appearance of spectra in all solvents depends on the history of the sample. A paramagnetic spectrum is observed when the solution, bright yellow at room temperature, is quenched rapidly in liquid nitrogen. However, as the sample warms, the melting is accompained by a color change to blue or blue-green and, upon refreezing, no EPR spectrum is observable. When reheated to room temperature, the cycle can

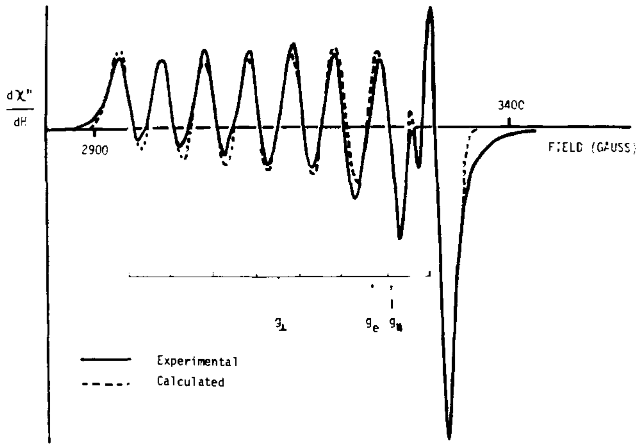

Figure 1. EPR spectrum of $V(CO)_6$ in frozen cyclohexane solution: temperature 88 K, frequency 9.067 GHz. All spectra were obtained under nonsaturating conditions with field modulation below a level which would influence the line shape.

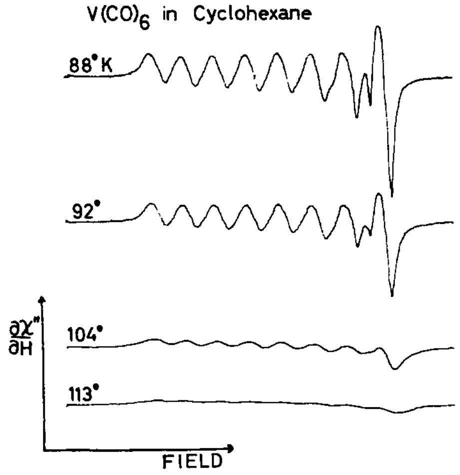

Figure 2. EPR spectra of $V(CO)_6$ in frozen cyclohexane solution. Excepting the temperature variation as noted, all conditions are identical throughout.

Table I

	Cyclohexane glass 88 K	Toluene glass 90 K[d]
$g_\parallel$	$1.988_5 \pm 0.002$	1.99 ± 0.01
$g_\perp$	2.075 ± 0.002	2.064 ± 0.002
g_{av}	2.046	
$A'_\parallel$[a]	4.5×10^{-4} cm^{-1} (4.8 G)	$(5 \pm 5) \times 10^{-4}$ cm^{-1}
$A'_\perp$[a]	50.5×10^{-4} cm^{-1} (52.1 G)	$(51 \pm 1) \times 10^{-4}$ cm^{-1}
A_{av}[e]	35.2×10^{-4} cm^{-1} (~36 G)	
$W_\parallel$	6.0 G[b]	4 ± 2 G[c]
$W_\perp$	13.5 G[b]	12 ± 1 G[c]
Line shape	Gaussian	Lorentzian

[a] The prime means that this is in the same axis system as the g values. [b] This is the half-width at half-height for the Gaussian line shape used. [c] This is the half-width (= 0.58 σ) at half-height for the Lorentzian line shape used. [d] Error limits are where significant deviations from the estimated best fit simulation are seen. [e] The signs of $A'_\parallel$ and $A'_\perp$ are assumed to be the same.

be started again. The dark color which arises may be from impurities in the sample and not from the main product since it appeared to increase with the number of cycles.

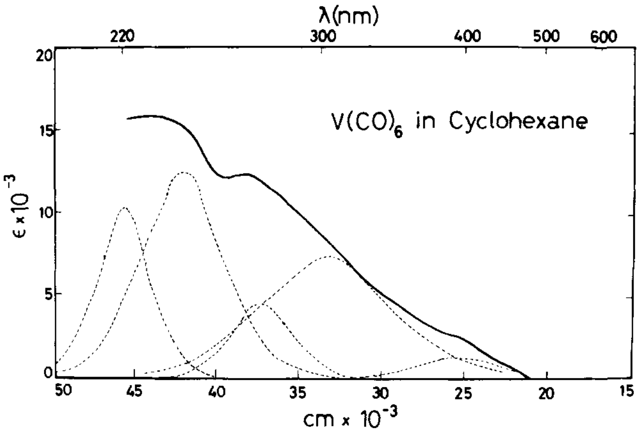

Figure 3. Ultraviolet-visible spectrum of $V(CO)_6$ in cyclohexane at ambient temperature. The fitting curves are tentative; parameters of these are listed in Table II. ϵ is the molar extinction coefficient.

Table II. Peaks Fitting the $V(CO)_6$ Optical Spectrum in Cyclohexane

Peak position (kK)[a]	Half-width (kK)[a]	Approx $\epsilon_{molar} \times 10^{-3}$ [b]
25.4	0.30	1.4
33.2	0.47	7.5
37.4	0.31	4.5
41.8	0.28	12.5
45.4	0.18	10.2

[a] kK = 10^3 cm^{-1}. [b] Error limits of the experimental spectrum extinction coefficients are +0, −20%.

An intermolecular interaction is indicated which, if weak, will shorten the relaxation time until the spectrum cannot be observed at liquid nitrogen temperature. A strong interaction will manifest itself as a ferromagnetic or antiferromagnetic coupling. Measurements of the temperature dependence of the magnetic susceptibility of frozen solutions might resolve this point.

That the effect is caused by an intermolecular interaction is shown by using a saturated solution of $Cr(CO)_6$ to form the glasses; the above mentioned "history" effects are significantly reduced or disappear. This is all consistent with the association of the monomers in hydrocarbons as determined by Calderazzo et al.[4] From the above results, it follows that any magnetic measurements not made on dilute solutions with precautions to prevent association are suspect if used to analyze the monomer.

The optical spectra of $V(CO)_6$ quantitate the observed color changes seen: in dilute solution or in a matrix the system appears yellow, while the pure solid is intense blue-black. Figure 3 shows the spectrum in cyclohexane which is similar to that reported for the gas phase,[8] although the extinction coefficients here are smaller by a factor of three or four. The peaks tentatively used to fit the spectrum are listed in Table II. They are centered at band positions indicated by preliminary MCD experiments (personal communication, A. Thompson). The intensity of the absorption indicates that it is composed of bands which are mainly charge transfer in nature since we do not expect "pure" d-d molar extinction coefficients much greater than about 100. The spectrum is not dissimilar from that of $V(CO)_6^-$.[15] In the solid, new bands arise around 15 kK with extinction coefficients around 500-1000. The peak positions are listed in Table III. The band at 24.8 kK corresponds well to the lowest peak in the solution spectrum. The three peaks around 15 kK are of uncertain origin but are not regular as expected from vibronic structure of a single electronic band. The lowest inflections are probably overtones of vibrational transitions superposed on further electronic transitions.

Theory

We believe the ground state of $V(CO)_6$ is an orbital singlet for two reasons: First, the axial symmetry implies a degenerate

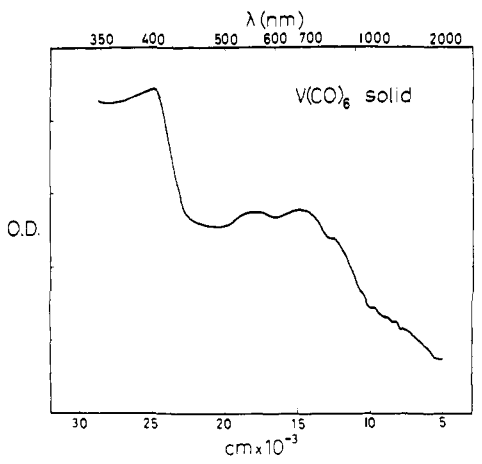

Figure 4. Visible–near-infrared spectrum of $V(CO)_6$ solid at approximately liquid nitrogen temperature. Peak positions and assignments are listed in Table III.

Table III. Peak Positions in Solid State $V(CO)_6$

24.8×10^3 cm^{-1}	monomer band
18.2	"solid state" band
14.9	
12.8	
10.6	
9.9	
8.9	
8.4	
7.8	

upper state in the absence of spin–orbit coupling; and second, the spectrum is observable at relatively high temperatures which would not be the case for a degenerate ground state.[16]

For low spin d^5 systems, because of the complexity of the interactions of the electronic states, two distinct theoretical treatments have emerged in the literature: those for the optical spectra and those for the paramagnetic resonance spectra and other ground state properties. The former take no account of spin (e.g., ref 18), while the latter usually ignore or limit the mathematical interactions of the ground and excited states. For the present, we will consider only the simplest ground state theory because, as shown below, entirely satisfactory fits to the magnetic data are obtained.

In common with most others[17-19] we follow the theory for low-spin d^5 complexes as described by Stevens.[20] He shows that for an octahedral d^5 complex with a $^2B_{2g}$ ground state in a strong ligand field, the g values are given by

$$g_\parallel = 2|(1 + k)\cos^2\alpha - \sin^2\alpha|$$

$$g_\perp = 2|\sqrt{2}\,k\cos\alpha\sin\alpha + \sin^2\alpha| \qquad (1)$$

and

$$\tan 2\alpha = \sqrt{2}\,\zeta/\tfrac{1}{2}\zeta - \Delta \qquad (2)$$

where cos α and sin α are coefficients of the three dϵ orbitals used as basis functions, ζ is the one-electron spin–orbit coupling constant, Δ is the axial crystal field splitting between the orbital doublet and the orbital singlet in the $(d\epsilon)^5$ $^2T_{2g}$ state, and k is the "orbital reduction factor"—a measure of covalency and other effects.[21] These expressions are the same for both pure trigonal and pure tetragonal distortions.[22] The calculated electronic properties resulting from a trigonal elongation are the same as from a tetragonal compression and vice versa, within the $t_{2g}{}^5$ basis. The existence of $g_\parallel$ and $g_\perp$ unambiguously show that an axial distortion exists in $V(CO)_6$ in cyclohexane and in toluene at low temperatures, but cannot distinguish between an effective tetragonal compression or trigonal elongation. In principle ^{13}C hyperfine splitting(s) could resolve this point.

The accuracy of the data and fitting is such that it is worthwhile to substitute the factor $g_e = 2.0023$ for 2 in each of the g value expressions, eq 1. The only coefficients which fit the experimentally determined g values are cos $\alpha = 0.0522 \pm 0.002$, sin $\alpha = 0.9986$, and $k = 0.530 \pm 0.015$, for which the calculations give $g_\parallel = 1.9885$ and $g_\perp = 2.075$, and the errors given correspond to that for $\Delta g_\perp = 0.002$ since the calculated $g_\parallel$ is relatively insensitive to parameter change. For a tetragonally distorted system, the unpaired electron is in an almost pure d_{xy} orbital and for a trigonal distortion in its symmetry equivalent. Substituting the value of ($\alpha = 87.0°$) and ($\zeta = 95$ cm^{-1})[23] into eq 2, we find that $\Delta = 1327$ cm^{-1}. The energy levels are then predicted at -888, $+490$, and $+398$ cm^{-1} or alternatively 0, 1377, and 1285 cm^{-1}. It should be stated that in the elaboration of the simple theory by Hill[17] utilizing excited electronic states, the calculated values cannot be made to agree with the data as well as the elementary theory. Excited state energies between 10 and 50kK were considered.

The average ^{51}V hyperfine splitting of approximately 36 G is small compared with that of dibenzenevanadium(0)[25,26] of 63.5 G and tris-2,2′-dipyridylvanadium(0)[27] of 83.5 G. The low value of k, the orbital reduction factor, appears to be reasonably correlated with the low average hyperfine splitting. At this time, use of the coefficients sin α, cos α, and k to calculate the expected hyperfine values appears to be unwise since the many formulas derived to be used for such calculations do not agree with each other.[18,19,24,28,29]

Conclusions

We have observed clean EPR spectra of vanadium hexacarbonyl in frozen glasses and observed the nuclear hyperfine splitting. The symmetry of the spectrum shows that the compound is axially distorted from perfect octahedral symmetry. Clear evidence is seen for molecular association in solution at low temperatures. In addition, quantitative optical spectra were obtained for the material as a solid and in solution. Intriguing from a theoretical viewpoint is a comparison of vanadium hexacarbonyl with its well-characterized, isoelectronic partner, hexacyanoferrate anion, especially the differences that occur with differing formal charge. Because of the problems with the theory alluded to above, such a comparison is beyond the scope of this paper.

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The Heat Capacity, Conductivity, and Crystal Structure of Tetrathiafulvalenium 2,5-Diethyltetracyanoquinodimethane

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Abstract: The single-crystal room temperature structure and measurements of the conductivity and heat capacity in the vicinity of the metal insulator transition have been determined for the pseudo-one-dimensional charge transfer salt tetrathiafulvalenium 2,5-diethyltetracyanoquinodimethane (TTF-DETCNQ). The compound crystallizes in space group $P\bar{1}$ with cell dimensions $a = 13.654$ (4) Å, $b = 3.859$ (1) Å, $c = 10.094$ (3) Å, $\alpha = 97.00$ (2)°, $\beta = 96.25$ (2)°, and $\gamma = 85.91$ (2)°. The perpendicular interplanar distances along the segregated stacks are 3.598 (1) Å for TTF and 3.257 (1) Å for DETCNQ. The metal insulator transition observed in the conductivity measurements in the b-axis direction is sharply defined by a peak in the heat capacity curve at 111 K. Assuming a single band model, we estimate the density of states at the Fermi surface to be 5.7 eV^{-1}. The effect on the transition temperature of changes in the density of states, degree of charge transfer, and stacking distances are discussed.

One of the methods used in trying to understand the metal insulator transition in the highly conducting charge transfer salt TTF-TCNQ[2] has been the study of chemically modified TTF-TCNQ compounds. The goal of these investigations has been to synthesize new materials with minimal structural changes so that the effects of crystal disorder,[3-5] intra- and interchain coupling,[6] ionization potential, and polarizability on the metal insulator transition and the high temperature conductivity of a series of crystals can be studied.

The TTF-TTF interplanar distances in the one-dimensional systems which have been investigated are 3.47 Å[7] or greater. This spacing is comparable to van der Waals distances associated with nonbonded interactions between organic groups, and it is not surprising that numerous derivatives of TTF[8-11] or TSF[12-15] (the selenium analogue of TTF) are known to form highly conducting complexes with TCNQ. The TCNQ-TCNQ interplanar spacing in TTF-TCNQ is 3.16 Å.[7] This is well below the van der Waals contact for even aromatic carbon atoms (~3.34 Å) so that it can be expected that it will be much more difficult to obtain a closely stacked lattice and metallic behavior with substituted TCNQ. In fact, metallic behavior has not been previously reported for any derivatives of TCNQ, other than the very distantly related TNAP,[16] the 2,6-tetracyquinodimethane derivative of naphthalene.

In this paper, we present the details of the room temperature structure and the specific heat and electrical conductivity in the vicinity of the metal insulator transition of the substituted TCNQ charge transfer salt tetrathiafulvalenium 2,5-diethyltetracyanoquinodimethane (TTF-DETCNQ). A preliminary screening of this and other substituted TCNQ complexes with TTF by Groff[17] of Du Pont Laboratories suggested that a number of these materials are metallic. The fact that one can substitute organic groups on the TCNQ molecule and maintain cooperative behavior greatly expands the potential number of one-dimensional metallic systems which can be made. It also suggests the feasibility of forming conducting materials with TCNQ molecules attached to an organic polymeric backbone or forming donor-acceptor pairs joined together through chemical bonds. Further investigation of the low temperature crystal and molecular structure of TTF-DETCNQ is currently underway and will be reported in a subsequent publication.

Experimental Section

Collection and Reduction of the X-Ray Data. The crystals used in this study were prepared by Drs. R. C. Wheland and E. L. Martin of the Du Pont Central Research Department[18] and graciously supplied to us by Dr. L. J. Guggenberger. The long, black colored crystals appear as bundles of square, cross-sectioned fibers, rather than stacks of thin plates, as in TTF-TCNQ. Weissenberg and precession photographs revealed no systematic extinctions or other indications of symmetry. Therefore, a primitive cell for the triclinic space group $P\bar{1}$ was chosen with the b axis parallel to the needle axis of the crystal. The cell dimensions were refined from the angular diffractometer settings of 20 centered reflections and are $a = 13.654$ (4) Å, $b = 3.859$ (1) Å, $c = 10.094$ (3) Å, $\alpha = 97.00$ (2)°, $\beta = 96.25$ (2)°, $\gamma = 85.91$ (2)°, and $V = 523.8$ Å^3. The assumption of the centrosymmetric space group $P\bar{1}$ is justified by the satisfactory agreement ultimately obtained. With one formula weight of TTF-DETCNQ per unit cell, the calculated density is 1.473 g/cm^3.

Numerous crystals were examined on the diffractometer and found to be twinned or have very large mosaicities. The crystal finally selected for intensity measurements was mounted in a thin-walled glass