The Electron Spin Resonance Spectrum of Vanadium Hexacarbonyl at Liquid Helium Temperatures

David W. Pratt and Rollie J. Myers

Contribution from the Department of Chemistry, University of California, and the Inorganic Materials Research Division of the Lawrence Radiation Laboratory, Berkeley, California 94720. *Received July 13, 1967*

Abstract: The electron spin resonance spectrum of $V(CO)_6$ has been observed at liquid helium temperatures in samples of the pure solid and in benzene and *n*-pentane glasses. Because of an unusual powder dependence of the spectrum in *n*-pentane, both the isotropic and anisotropic g values have been measured directly. From a comparison of these results with the semiempirical predictions of crystal-field theory, it is concluded that $V(CO)_6$ possesses a small tetragonal distortion at 1.3°K.

The synthesis of vanadium hexacarbonyl was first reported in 1959 by Natta, *et al.*[1] $V(CO)_6$ was found to be a volatile, air-sensitive, blue-green solid at room temperature which is slightly soluble in hydrocarbon solvents. Magnetic susceptibility results on both the pure solid[1] and solutions of $V(CO)_6$ in benzene and toluene[2] have shown that the molecule is paramagnetic with one unpaired electron, thus confirming that $V(CO)_6$ is a low-spin, rather than high-spin, molecule. However, in a series of independent studies, Pruett and Wyman[3] were unable to obtain an esr spectrum of $V(CO)_6$ in solution at room temperature. More recently, Haas and Sheline[4] have studied the infrared and optical spectra of $V(CO)_6$ in the gas phase. From their results, the authors suggested that there was strong evidence for the presence of a Jahn–Teller distortion in this molecule.

In view of the magnetic susceptibility results on this compound, it seemed likely to us that the absence of an esr spectrum of $V(CO)_6$ at normal temperatures was due to a very short electron spin relaxation time of the unpaired electron in this molecule. This would make the esr spectrum very broad and possibly unobservable except at very low temperatures. Consequently, we have investigated the esr spectrum of $V(CO)_6$ at liquid helium temperatures in both the pure solid and in dilute hydrocarbon glasses, and we have found strong esr spectra in both cases at 1.3°K. An unusual power dependence of the spectrum in *n*-pentane has made possible the direct measurement of both the isotropic and anisotropic g values, and they give evidence of a tetragonally distorted complex.

Experimental Section

The $V(CO)_6$ used in these experiments was prepared from bis(diglyme)sodium hexacarbonylvanadate (Alfa Inorganics, Inc.) according to the method of Werner and Podall.[5] Reagent grade benzene and *n*-pentane, which were used as solvents, were dried over sodium and degassed thoroughly prior to use. As soon as possible after preparation, the $V(CO)_6$ (and solvent, when used) was vacuum-distilled into a small ampoule prepared from a section of 9-mm Pyrex tubing, and the ampoule was sealed at the neck with a hot flame. Although the exact concentration of $V(CO)_6$ in the solution samples was not determined, based on other experiments[6] it was thought to be of the order of 1 mole %. The ampoule was then placed in an X-band TE012 rectangular cavity, quick-frozen by immersing the cavity in liquid nitrogen, and inserted into the liquid helium cryostat which is described elsewhere.[6] A Varian V-4502 esr spectrometer and 9-in. magnet equipped with Fieldial were employed in these experiments; 400-Hz modulation coils were attached to the outside of the cavity, and the entire assembly was immersed in liquid helium during the experiment. Temperatures down to 1.2°K were obtained by pumping on the liquid helium with a high-speed vacuum system.

Experimental Results

Reproducible esr spectra have been obtained at liquid helium temperatures for samples of pure $V(CO)_6$ and glasses of the carbonyl in *n*-pentane and benzene. Of particular interest here is the observation that some of the spectral line shapes depend in an unusual way on the intensity of microwave power incident on the cavity. For example, Figure 1 shows a series of esr spectra which were obtained from a sample of $V(CO)_6$ in *n*-pentane at various power levels. In spectrum a, the incident power level was -30 db ($\sim$0.5 mw) and the line has a peak-to-peak width of about 215 gauss. As the power level is increased, the line becomes considerably narrower and at -16 db is apparently narrowed to a width of about 100 gauss (b). However, when the power level is increased above -16 db (or when the field is swept at a slower rate at -16 db), the shape changes abruptly (see spectrum c). These changes were completely reversible. With the exception of the broad feature centered at about 3400 gauss, the spectrum at high power (c) is characteristic of a molecule possessing an axial spin Hamiltonian with $g_\perp > g_\parallel$.[7] The temperature of the sample in this experiment was estimated to be 1.3°K from liquid helium vapor-pressure data and did not vary noticeably with changes in power. A line shape similar to spectrum b is obtained from a sample of pure polycrystalline $V(CO)_6$ at the same temperature when the power level is such that no saturation occurs. In this case, the line width is 130 gauss.

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[1] G. Natta, R. Ercoli, F. Calderazzo, A. Alberola, P. Corradini, and G. Allegra, *Atti Accad. Nazl. Lincei, Rend., Classe Sci. Fis. Mat. Nat.*, 27, 107 (1959); see also R. Ercoli, F. Calderazzo, and A. Alberola, *J. Am. Chem. Soc.*, **82**, 2966 (1960), for a summary of this work.

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[4] H. Haas and R. K. Sheline, *J. Am. Chem. Soc.*, **88**, 3219 (1966).

[5] R. P. M. Werner and H. E. Podall, *Chem. Ind.* (London), 144 (1961).

[6] D. W. Pratt, Ph.D. Thesis, University of California, Berkeley, Calif., 1967, UCRL-17406.

[7] F. K. Kneubühl, *J. Chem. Phys.*, **33**, 1074 (1960). Our line shapes are very similar to those observed by Kneubühl, and we have followed his examples for the location of $g_\parallel$ and $g_\perp$.

The g values for $V(CO)_6$ obtained in these experiments are listed in Table I; these were determined by measuring the microwave frequency and comparing the field positions of the $V(CO)_6$ spectra with that of DPPH at this temperature.[6] The isotropic g value listed for the $V(CO)_6$–*n*-pentane sample at high power was calculated from the measured values of $g_\parallel$ and $g_\perp$, 1.981 and 2.103, respectively. It can be seen from Table I that there is excellent agreement between the g values for pure $V(CO)_6$ and for the $V(CO)_6$–*n*-pentane sample at medium and high power levels. This supports the assignment of the high-power spectrum described above and encourages a comparison of these results with semiempirical estimates.

Table I. $V(CO)_6$ (observed) g Values at 1.3° K

Sample	Isotropic g value	Power level, db
Pure $V(CO)_6$	2.063 ± 0.002[a]	−20
$V(CO)_6$–*n*-pentane	2.079 ± 0.002[a]	−30
$V(CO)_6$–*n*-pentane	2.061 ± 0.001[a]	−16
$V(CO)_6$–*n*-pentane	2.062 ± 0.001[b]	−6

[a] Center field determined by the point at which the signal crossed the base line. [b] Calculated from the values $g_\perp = 2.103$ and $g_\parallel = 1.981$.

Discussion

Formally, the electronic structure of the zerovalent vanadium in $V(CO)_6$ is (Ar)$3d^5$, and crystal-field theory predicts a $^2T_{2g}$ ground state for the low-spin configuration in a field of octahedral symmetry. According to the theorem of Jahn and Teller, an octahedral complex in a $^2T_{2g}$ electronic state is unstable with respect to distortion. Group theoretical considerations show that either a trigonal distortion (D_{3d}) or a tetragonal distortion (D_{4h}) will remove the orbital degeneracy of the $^2T_{2g}$ state and satisfy the Jahn–Teller theorem. With a trigonal distortion, crystal-field calculations for the g values show[6] that $g_\parallel$, $g_\perp$, and the isotropic g value must be less than the free-electron value of 2.0023. This is clearly not characteristic of $V(CO)_6$. If, however, a tetragonal distortion with a decreased crystal field along the tetragonal axis is assumed, then the observed order of $g_\parallel$, $g_\perp$, and the free-electron value results. Of course, not all this distortion must be due to the Jahn–Teller theorem, for it is difficult to quantify, but such a distortion is consistent with this theorem.

If one then assumes that the molecule undergoes a small tetragonal distortion (yielding a $^2B_{2g}$ ground state), application of perturbation theory in the usual way[8] gives the following predicted g values for the elongated octahedron, correct to first order.

$$g_\parallel = g_e - 8(|\xi|/\Delta_1) \qquad (1)$$

$$g_\perp = g_e + 2(|\xi|/\Delta_2) \qquad (2)$$

In these expressions, g_e is the free-electron g value, ξ is the one-electron spin–orbit parameter, and Δ_1 and Δ_2 are crystal-field splittings defined by $\Delta_1 = E(b_{1g}) - E(b_{2g})$ and $\Delta_2 = E(b_{2g}) - E(e_g)$. Taking $\xi \leqslant 95$ cm^{-1}[9] and the observed values of $g_\parallel$ and $g_\perp$ for the $V(CO)_6$–*n*-pentane sample, one obtains from (1) and (2) the estimates $\Delta_1 \leqslant 36{,}200$ cm^{-1} and $\Delta_2 \leqslant 1880$ cm^{-1}. The value of Δ_1 found in this way is in good agreement with the values of $10Dq$ ($\sim\Delta_1$) observed for other low-spin, strong-field complexes such as $Cr(CO)_6$, for which $10Dq = 34{,}150$ cm^{-1}.[10] Further, although the optical spectrum of $V(CO)_6$ has not been assigned, this result is consistent with existing ultraviolet data.[4]

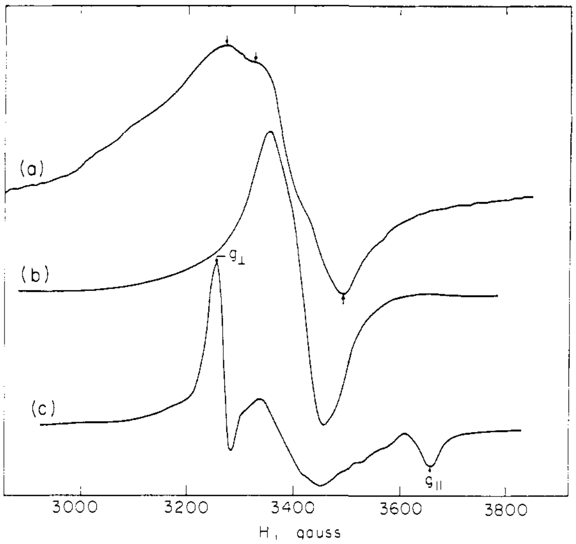

Figure 1. Esr spectra of $V(CO)_6$ in *n*-pentane at 1.3°K: (a) −30 db, (b) −16 db, (c) −6 db.

Although the value of Δ_2 is less amenable to direct comparison with other results, some qualitative remarks can be made. First, the parameter Δ_2 is considerably larger than the splitting on the t_{2g} manifold by a spin–orbit interaction acting alone, which produces a separation of about $3\xi/2$.[6,11] It is therefore necessary to postulate the existence of other mechanisms which might contribute to the distortion. One possibility[12] is that a change in the π character of the metal–carbon bonds from that normally present in the mononuclear carbonyls occurs in $V(CO)_6$. For example, in $Cr(CO)_6$ the metal atom has the configuration $(t_{2g})^6$ and the π bonding which is thought to exist between the t_{2g} orbitals and the antibonding π orbitals of the ligands would strengthen all M–C bonds equally. Thus the octahedral symmetry resulting from the d^2sp^3 hybridization of the σ orbitals is preserved. In $V(CO)_6$ the $^2B_{2g}$ ground state has only one electron in the b_{2g} orbital. This orbital corresponds to the d_{xy} orbital for octahedral symmetry. In this case there would be less "back-donation" to the ligands in the x,y plane. This is equivalent to a stronger crystal field in the x,y plane, for it would result in less charge compensation in this plane in agreement with the crystal-field calculation. At the same time the CO bonds in the x,y plane would be strengthened because of the decreased "back-dona-

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(8) See, for example, A. Carrington and A. D. McLachlan, "Introduction to Magnetic Resonance," Harper and Row, Publishers, New York, N. Y., 1967, Chapter 10. For a tetragonally distorted low-spin $3d^5$, see J. J. Fortman and R. G. Hayes, *J. Chem. Phys.*, 43, 15 (1965).

(9) T. M. Dunn, *Trans. Faraday Soc.*, 57, 1441 (1961).

(10) H. B. Gray and N. A. Beach, *J. Am. Chem. Soc.*, 85, 2922 (1963).

(11) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, Chapter 6.

(12) This explanation is a logical extension of the description of the bonding in metal carbonyls as found in L. E. Orgel, "An Introduction to Transition-Metal Chemistry," Methuen & Co., Ltd., London, 1960, Chapter 9.

tion" to the antibonding CO orbitals. Haas and Sheline[4] have observed, in the gas-phase infrared spectrum, a broadening in the CO stretching region which could be ascribed to such an effect on the CO bonds. This explanation of our results, though probably oversimplified, supports the concept of "back-donation" in metal carbonyls. In our experiments, the existence of intermolecular effects cannot, of course, be entirely ruled out and further experiments to test these ideas are in progress.

No resolvable hyperfine structure was observed in any of the spectra recorded in these experiments. Since the nuclear spin of ^{51}V is $^{7}/_{2}$, an upper limit for the isotropic coupling constant would be about one-seventh of the line width, or 30 gauss or less for the widest lines observed. This is considerably smaller than normally observed for paramagnetic vanadium compounds and suggests the presence of an exchange interaction in our samples. Further evidence for exchange is provided by a closer inspection of the line shapes.[6] The existence of such an interaction in the *n*-pentane glass samples could be the result of precipitation of V(CO)$_6$ which may occur during the freezing process; however, experiments with benzene as a solvent also yielded no hyperfine structure. The benzene spectra were asymmetric even at low power levels; the *g* values measured from the benzene spectrum ($g_{\|} = 2.023$ and $g_{\perp} = 2.126$) do not agree with those calculated on the basis of either tetragonal or trigonal models. It is possible that this is due to the formation of an associated V(CO)$_6$–benzene species.

The presence of rather strong exchange forces can, in some cases, produce unusual variations in esr line shapes when the spectrum is power saturated. For example, Goldsborough, *et al.*,[13] have observed that in pure crystalline free-radical systems such as DPPH, a pronounced narrowing of the resonance line occurs when it is power saturated. In such systems, spin-lattice relaxation occurs *via* an exchange reservoir and the narrowing occurs when the exchange "temperature" exceeds the lattice temperature. It is possible that such a mechanism accounts for some, if not all, of the observed variations in the shape of the V(CO)$_6$ spectra.

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Nuclear Resonance Studies of Vanadium(III) Complexes. III.[1] Synthesis, Stereochemistry, and Electron Delocalization Properties of Tris(salicylaldehydes) and Tris(salicylaldimines)

F. Röhrscheid, R. E. Ernst,[2] and R. H. Holm[3]

Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin. Received August 14, 1967

Abstract: The first synthesis of a series of tris(salicylaldehydo)- (**1**) and tris(salicylaldimino)vanadium(III) complexes (**2**) is reported. The complexes prepared are V(X-sal)$_3$ (**1**) (X = 3-, 5-Me) and V(X-R-sal)$_3$ (**2**) (R = Me, X = H; R = *n*-Pr, X = H, 3-, 4-, 5-Me). These complexes exhibit large isotropic proton contact shifts which unequivocally demonstrate the *trans* stereochemistry for all. No amount of *cis* isomer was detected in any case. A necessarily qualitative analysis of the contact shifts has led to the conclusion that they are effected principally by delocalization of parallel spin from the metal to the lowest unoccupied π-molecular orbital of the ligands. The mechanisms of spin delocation in V(III) and Ni(II) salicylaldimine complexes are compared.

Previous work in this series[1,4] together with the results of Eaton[5] has demonstrated that the line widths of most signals in the proton magnetic resonance spectra of pseudo-octahedral vanadium(III) complexes containing conjugated ligand systems are sufficiently narrow that useful information concerning stereochemistry and unpaired electron delocalization can be obtained. Tris-β-diketone[4,5] and -β-ketoamine[1] V(III) complexes exhibit extremely large chemical shifts which at room temperature occur in the range *ca.* +150 to −60 ppm relative to tetramethylsilane. The overwhelming contribution to these shifts is the isotropic electron–nuclear contact interaction, which is highly sensitive to the fine details of molecular structure.[6] This situation has facilitated the unambiguous identification of the geometrical isomers (*cis*, *trans*) of the tris-chelate V(III) complexes in solution.[1,4]

In order to further our investigation of the stereochemistry of tris-chelate complexes, we have prepared a

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(2) National Institutes of Health Predoctoral Fellow.

(3) Alfred P. Sloan Foundation Fellow; Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Mass. 02139.

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(5) D. R. Eaton, *J. Am. Chem. Soc.*, **87**, 3097 (1965).

(6) For examples, *cf.* (a) R. H. Holm, A. Chakravorty, and G. O. Dudek, *ibid.*, **86**, 397 (1964); (b) A. Chakravorty and R. H. Holm, *ibid.*, **86**, 3999 (1964); (c) R. E. Ernst, M. J. O'Connor, and R. H. Holm, *ibid.*, **89**, 6104 (1967).