solution was stirred under H_2 at 0 °C (1 h), then at 23 °C (1.5 h). While at the higher temprature the solution turned from a red to a stable green color, with accompanying evolution of N_2 (0.1195 mmol). Reaction of the product with HCl (1 mmol), −60 °C to 0 °C, gave H_2 (0.4312 mmol) as the only noncondensible gas. The ratio $\mathbf{5}:H_2 = 1:3.97$. The residue was analyzed (as detailed below) for hydrazine and ammonia. Found: NH_3, 0.006 mmol; N_2H_4, none detected (<0.001 mmol.).

Reactivity of 5 with I_2. In a glass reactor tube was made up a solution of **5** (49.18 mg, 0.0415 mmol) in THF (5 mL). Iodine (300 mg) was added to the solution from an evacuated side arm. N_2 gas evolved (0.044 mmol) was collected with the aid of a Töpler pump. Subsequently, 3 M aqueous HCl (5 mL) was added to the residue. This was analyzed for total N (Kjeldahl technique) with an appropriate blank made up of all the reagents employed. Found: 0.06 mg N (0.002 mmol). The ratio $\mathbf{5}:N_2 = 1:1.1$.

Reactivity of 5 with HCl and with Water. A deep red solution of **5** (96.45 mg, 0.0815 mmol) in diglyme (10 mL) was cooled to −196°C and HCl gas (~1 mmol) was added, in vacuo. The mixture was then warmed and stirred at −60 °C (30 min) and 0 °C (30 min). A deep purple solution was obtained. Noncondensible gases were measured with the aid of a Töpler pump. Collected: H_2 (0.1224 mmol) and N_2 (0.0841 mmol). The ratio $\mathbf{5}:H_2 = 1:1.50$ and $\mathbf{5}:N_2 = 1:1.03$.

In another experiment, a glass reactor tube equipped with an evacuable side arm was loaded with a mixture of **5** (42.41 mg, 0.0358 mmol) and **5** prepared from $^{15}N_2$ (14.82 mg, 0.0125 mmol). The crystals were dissolved in added THF to yield a deep red solution. Water (400 mg) was distilled onto the solution which was cooled to −196 °C. The mixture was warmed and stirred at 23 °C for 3 h. During this time, the solution turned from an initial purple to a light blue color, with the formation of a white precipitate. Collected noncondensible gases: H_2 (0.0372 mmol) and N_2 (0.0028 mmol). The ratio $\mathbf{5}:H_2 = 1:0.77$ and $\mathbf{5}:N_2 = 1:0.06$. The residue was then analyzed for hydrazine. From the side arm of the reaction tube, 10 mL of a scrupulously outgassed mixture of 0.015 M KIO_3 in 5 M H_2SO_4 was added. The dinitrogen formed (from N_2H_4 oxidation) was collected with the aid of a Töpler pump. Collected: dinitrogen (0.0057 mmol). The ratio $\mathbf{5}:N_2H_4 = 1:0.12$. Mass spectral analysis of this gas showed it to be a mixture of $^{14}N_2$ and $^{15}N_2$. Finally, Kjeldahl N analyses gave NH_3 (1.82 mg, 0.1037 mmol). The ratio $\mathbf{5}:NH_3 = 1:2.15$. (For the Kjeldahl analyses a blank titre, using THF, $KIO_3/H_2O/H_2SO_4$ solutions, was determined.) The Kjeldahl titration residue was then evaporated to near-dryness and heated with an excess of KOH to recover the NH_3, which was measured volumetrically (0.109 mmol). This NH_3 was heated in the presence of Pt black in a quartz tube at 500 °C. The dinitrogen formed was shown by mass spectral analysis to consist of a mixture of $^{14}N_2$, $^{14}N^{15}N$, and $^{15}N_2$.

Reactivity of 4 (and 5) with Carbon Monoxide. An H-shaped apparatus, equipped with a filter disk in the horizontal arm, was loaded with N_2 complex **3** (800 mg) and THF (10 mL). The mixture was stirred giving a deep red solution of **4**. The solvent was then replaced with diglyme and after being stirred at room temperature the diglyme was removed in vacuo and THF once again added. Exposure of the resulting deep red (red-purple) solution to carbon monoxide (0.7 atm) gave an immediate, deep blue coloration. After being stirred (under CO) for ~2.5 h at 23 °C, the solution slowly turned to a deep green and carbon monoxide uptake ceased. The resulting solution was filtered, pumped to dryness, and extracted to exhaustion with octane. A dark, octane-insoluble material **6** was obtained. $^{15}N_2$- and ^{13}CO-labeled materials were also prepared. Infrared spectral data: $\nu(^{14}N{-}^{14}N) = 1502\ \mathrm{cm}^{-1}$, $\nu(^{15}N{-}^{15}N) = 1453\ \mathrm{cm}^{-1}$, $\nu(\mathrm{bridging})({>}^{12}C{-}O) = 1710\ \mathrm{cm}^{-1}$, $\nu(\mathrm{bridging})({>}^{13}C{-}O) = 1669\ \mathrm{cm}^{-1}$, and $\nu(\mathrm{terminal})(C{-}O) = 1875, 1965\ \mathrm{cm}^{-1}$. Atomic ratios from elemental analyses and the above spectral data suggest **6** to have the *approximate* composition $C_{20}H_{20}Ti_2N_2(CO)_2$. We were not able to prepare the compound in a crystalline form, which precluded any more definitive identification of its composition and structure.

Acknowledgment. We are grateful to Dr. J. N. Armor for many helpful discussions during the course of this work. Experimental assistance by Mr. J. Corsi in the preparation of the N_2 complexes is gratefully acknowledged. We thank Drs. I. L. Mador and L. R. Anderson for their encouragement and support, and Allied Corporation for permission to publish.

Registry No. 1, 61529-60-0; **5**, 79815-45-5.

Supplementary Material Available: A listing of structure factor amplitudes, general temperature factor expressions, intermolecular contacts to 3.75 Å, and a table of weighted least-squares planes and dihedral angles between planes (37 pages). Ordering information is given on any current masthead page.

Electron Paramagnetic Resonance Spectra and Molecular Structure of Vanadium Hexacarbonyl

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Abstract: Electron paramagnetic resonance spectra of vanadium hexacarbonyl have been measured in frozen cyclohexane (X- and Q-band frequencies) and in chromium hexacarbonyl (X band) hosts. The spectrum in cyclohexane is sensitive to alkene impurities. $V(CO)_6$ gives a nonaxial spectrum in both media. The EPR parameters in cyclohexane are $g_x = 2.066$, $g_y = 2.055$, and $g_z = 1.984$ and $A_x = 52.6$, $A_y = 49.1$, and $A_z = 15.7$ G. Measurements on ^{13}CO-enriched $V(CO)_6$ yield estimates for A_C. The highest symmetry distortion which is consistent with the g values, A values, and the Jahn–Teller modes is a D_{2h} angle bending distortion. Analysis of the hyperfine structure suggests considerable delocalization of spin density onto the ligands.

Vanadium hexacarbonyl is uniquely stable among binary paramagnetic metal carbonyls. Although much studied, the nature of the distortions from octahedral symmetry of this low-spin d^5 complex is far from understood. There are several lines of evidence which suggest a distortion. (i) The electron diffraction pattern of the vapor is consistent with an octahedral geometry with high amplitudes of vibration.[2] (ii) A recent single-crystal X-ray diffraction study[3] at 245 K indicates a marginally significant tetragonal distortion ($r_{V-C}(\mathrm{eq}) - r_{V-C}(\mathrm{ax}) = 0.012\ (3)$ Å). A vibrational analysis suggests that any dynamic distortions over

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[1] (a) University of Leicester. (b) University of Edinburgh. (c) University of Oxford. This work was initiated while R.N.P. was at the University of Edinburgh.

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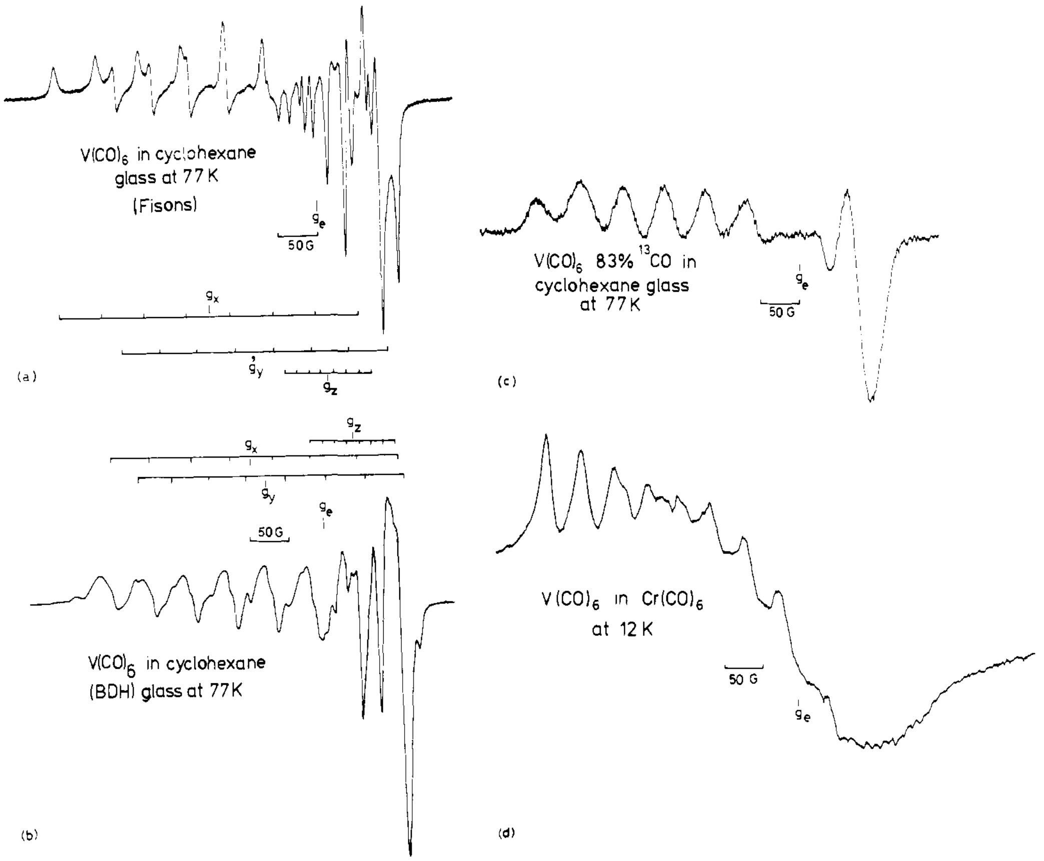

Figure 1. X-band (9.235-GHz) EPR spectra of $V(CO)_6$: (a) in cyclohexane (Fisons) at 77 K (The host is probably contaminated by cyclohexene); (b) in cyclohexane (BDH) at 77 K; (c) in cyclohexane (Fisons at 77 K; $V(CO)_6$ 83% enriched with ^{13}CO); (d) in $Cr(CO)_6$ at 14 K.

and above this static effect are also small. (iii) The CO stretching band in the IR spectrum in solution,[4] vapor,[5] and matrices[4,6,7] is far broader than that of $Cr(CO)_6$. (iv) The analysis of the magnetic circular dichroism of $V(CO)_6$ suggests that a distortion splits the t_{2g} orbitals by about 1350 cm^{-1}.[8] (v) The EPR spectra show clear evidence that $g_{\parallel} = g_{\perp}$.[9,10] The distortions probably arise from the Jahn–Teller instability of the T_{2g} octahedral term; they are thought to be dynamic in the vapor but static in solids at low temperature. The EPR spectrum gives evidence of the geometric nature of the distortion, yet even this is ambiguous.[10] In this paper we report the results of EPR experiments which we started in the hope of detecting ^{13}C superhyperfine structure in the spectrum of ^{13}C-enriched $V(CO)_6$. Our experiments provide evidence that $V(CO)_6$ has a different geometry and electron distribution from that deduced from earlier measurements. While these experiments were in progress, we heard of complementary single-crystal measurements on $Cr(CO)_6$ doped with $V(CO)_6$ which are consistent with our own results.[11]

Experimental Section

$V(CO)_6$ was prepared by oxidation of $Na(diglyme)_2V(CO)_6$ (Strem) with 100% H_3PO_4 at room temperature.[12] The $V(CO)_6$ was pumped into a U-trap cooled to −78 °C containing P_2O_5, from which it was sublimed into epr tubes. All manipulation of $V(CO)_6$ was carried out on a vacuum line. Cyclohexane (Fisons spectrograde, BDH Aristar or BDH spectroscopic grade) was dried with Na or CaH_2, thoroughly degassed, and distilled into the EPR tubes.

$Cr(CO)_6$ was doped with $V(CO)_6$ by condensing $V(CO)_6$ into a tube containing excess $Cr(CO)_6$. The two materials were sublimed together to yield a homogeneous salmon-colored crystalline solid which was air-stable! The vanadium-doped $Cr(CO)_6$ showed shoulders in its optical absorption spectrum at 77 K at 465 and 540 nm which are absent from vapor,[5] solution,[10] or matrices[8,9] containing $V(CO)_6$.

$[V(CO)_6]^-$ was enriched with ^{13}CO by photolyzing degassed THF solutions (0.002 M) of $Na(diglyme)_2V(CO)_6$ in the presence of ^{13}CO (Prochem 97%) at −22 °C. In a typical run a 13-cm^3 solution in a 75-cm^3 Pyrex tube with 250 torr of ^{13}CO was photolyzed with a Philips HPK 125W mercury arc for 5 h. The THF was pumped off at −22 °C and 100% H_3PO_4 added under a nitrogen atmosphere. The oxidation to $V(CO)_6$ was carried out as above. Analysis of IR spectra of solutions of $V(CO)_6$ and of matrix-isolated samples showed stoichiometric exchange with ^{13}CO. The photochemical reaction proved very sensitive to traces of oxygen which caused decomposition.

The X-band EPR spectra were measured on a Varian E line spectrometer calibrated with DPPH. The Q-band spectra were measured on the Leicester instrument which has been described elsewhere.[13]

Results

$V(CO)_6$ in Cyclohexane. Although the early EPR spectra of $V(CO)_6$ showed no hyperfine splitting, Rubinson's use of frozen cyclohexane solutions[9,10] led to the detection of an axial spectrum with hyperfine coupling to ^{51}V ($I = {}^7/_2$, 99.8% abundant). No isotropic spectra were obtained because the signal disappeared above 130 K. When we attempted to repeat Rubinson's work, we obtained a much sharper and more complex spectrum than his, which could no longer be interpreted in terms of axial symmetry. The resolution could be improved slightly by cooling from 88 K (as used by Rubinson) to 77 K (Figure 1a), but cooling to 15 K resulted in no further change. At 77 K the full width at half-maximum (fwhm) of the lowest field line was 10 G compared with Rubinson's 27 G. Only when we used deliberately more

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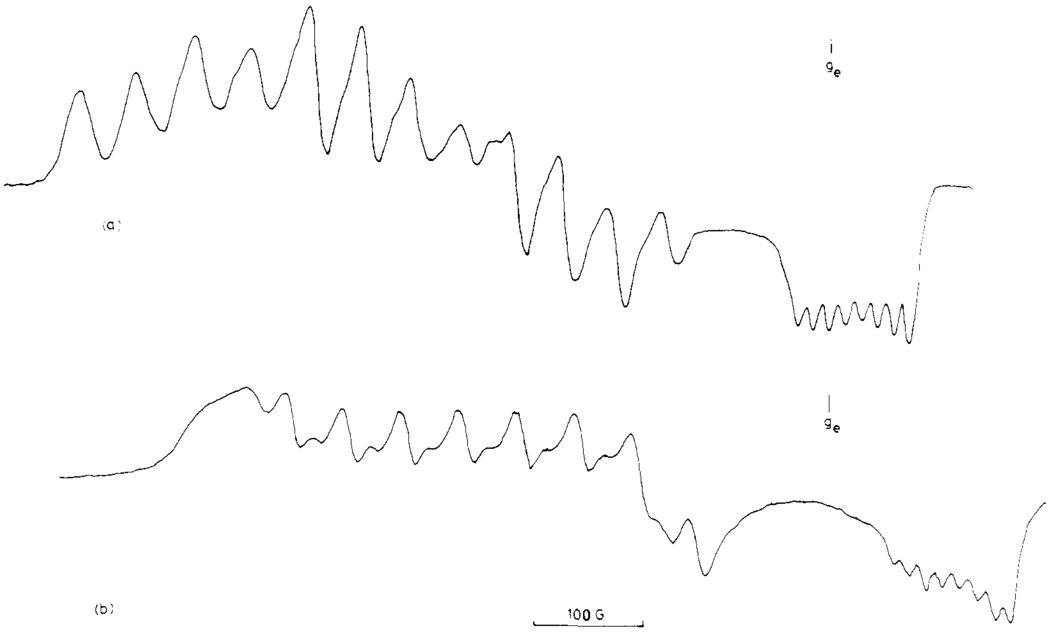

Figure 2. Q-band (33.3-GHz) epr spectra of $V(CO)_6$ at 120 K: (a) in cyclohexane (Fisons); (b) in cyclohexane (BDH).

Table I. Experimental EPR Parameters of $V(CO)_6$

host	temp, K	g_x	g_y	g_z	A_x, G	A_y, G	A_z, G
cyclohexane (Fisons)[a]	77	2.093 (3)	2.055 (3)	1.995 (6)	55.0 (5)	48.8 (5)	15.8 (3)
cyclohexane (BDH)[a]	77	2.066 (3)	2.055 (3)	1.984 (6)	52.6 (5)	49.1 (5)	15.7 (3)
methylcyclohexane	77	2.066[b]		2.00 (1)	53.5[b]		c
$Cr(CO)_6$	14	2.125 (3)	2.074 (6)	1.96 (1)	44 (1)	50 (2)	20 (4)

[a] Fisons cyclohexane contaminated by cyclohexene. [b] g_x and g_y not resolved. [c] A_z not resolved.

concentrated solutions could we reproduce Rubinson's spectra. Like Rubinson we observed that the yellow frozen solutions turned blue on warming, the color being similar to that of solid $V(CO)_6$. On melting a yellow solution was restored. More dilute solutions showed the same EPR spectrum as in Figure 1a, but the blue color was no longer observed on warming.[14] We conclude that the blue color is due to aggregation and that Rubinson used too high a concentration to obtain an optimal spectrum. However, further investigation showed complications in our own spectra when the Fisons cyclohexane was replaced by BDH cyclohexane. The spectrum obtained with BDH cyclohexane (Figure 1b) is not so sharp as that of Figure 1a, but it still differs substantially from Rubinson's. However adding a small proportion of cyclohexene restores the spectral type of Figure 1a. Conversely, adding cyclohexene has no effect on samples made with Fisons cyclohexane. Thus the spectrum of Figure 1a is complicated by cyclohexene or similar contamination of the solvent, which interacts sufficiently to alter the position and structure of the spectral bands.

The X-band spectra in Figure 1a,b suggest a nonaxial distortion of $V(CO)_6$, but the high field region does not lend itself to simple interpretation. However, at Q-band frequencies and 120 K the spectrum is simplified considerably (Figure 2), so that g_z and A_z may be unambiguously measured and transferred to the X-band spectra for comparison (Figure 1). The g and A values (Table I) show three striking differences from Rubinson's: (i) g_x, g_y, and g_z are all unequal, (ii) A_x and A_y are unequal, (iii) A_z is about 16 G compared with Rubinson's estimate of 5 G.[10] These parameters establish a nonaxial distortion for $V(CO)_6$ in solid cyclohexane, both in the presence and in the absence of cyclohexene.

The EPR spectrum in frozen cyclohexane of $V(CO)_6$ enriched to 13% with ^{13}CO was indistinguishable from that of unenriched material. However, the spectrum of much more heavily enriched material (83% ^{13}CO) was considerably broadened in all three components (Figure 1c). For instance the lowest field line increased in width (fwhm) from 10 to 30 G. No superhyperfine structure was detected, but this broadening is consistent with coupling of four ^{13}C nuclei of ca. 12 G and much weaker coupling ($\sim$4 G) to the remaining two. However under these circumstances a slight increase in width from 10 to 13 G is predicted with 13% ^{13}CO. The relatively high value of A_C suggests direct coupling to ^{13}C rather than spin polarization.

$V(CO)_6$ in Chromium Hexacarbonyl. The results described for cyclohexane hosts indicate a nonaxial distortion of $V(CO)_6$. In order to establish whether the distortion was unique to this medium, we measured the EPR spectrum at 14 K of polycrystalline $Cr(CO)_6$ which had been doped with $V(CO)_6$ (Figure 1d). The spectrum was extremely temperature sensitive, disappearing altogether at 40 K. Although the spectrum is not as well resolved as in cyclohexane, it is clearly nonaxial. The hyperfine coupling is similar to that in cyclohexane, but g_x and g_y are appreciably larger (Table I). This higher orbital contribution probably reduces the relaxation time so that lower temperatures are needed to observe the spectrum. Although the site symmetry of $Cr(CO)_6$ is very low (space group P_{nma}, site symmetry C_s),[15] the combination of these results with those for cyclohexane hosts provides strong evidence that the nonaxial distortion of $V(CO)_6$ is not imposed by the host.

$V(CO)_6$ in Other Hosts. The EPR spectrum of $V(CO)_6$ was also measured in methylcyclohexane: the bands were considerably broader than those in cyclohexane so g_x and g_y remained unresolved (Table I). Attempts to measure the spectrum in tetramethylsilane and cyclohexene were frustrated by aggregation of the $V(CO)_6$ to give a blue solid on freezing.

Analysis and Discussion

The spectra of vanadium hexacarbonyl in cyclohexane are sufficiently sharp to merit detailed analysis. Since the g values

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(14) The concentrations ranged from about 10^{-2} M (dilute) to 10^{-1} M. More accurate values are difficult to obtain because of the problems in handling $V(CO)_6$. The dilute solutions were very pale yellow (cf. Rubinson's "bright yellow").

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Table II. Derived EPR Parameters of $V(CO)_6$

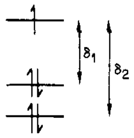
					pop,[a] %	
host	A_z, G	"$A_\perp$", G	A_{iso}, G	$2B$, G	V-(4s)	V-(3d)
cyclohexane (Fisons)	+15.8	+51.9	38.1	23.0	9.7	31.1
	−15.8	+51.9	26.1	42.1	8.5	56.9
cyclohexane (BDH)	+15.7	+50.9	37.6	23.1	9.7	31.2
	−15.7	+50.9	25.8	42.5	8.5	57.4
$Cr(CO)_6$	+20	+47	35.9	18.1	9.5	24
	−20	+47	19.9	41.9	7.9	57

[a] Populations derived by assuming that A_{iso} could range from -60 (0%) to 950 G (100% 4s) and that $2B$ could range from 0 to 74.0 G (100% 3d) (Symons, M. C. R. "Chemical and Biochemical Aspects of Electron Spin Resonance Spectroscopy"; Van Nostrand: New York, 1978).

Table III. d Orbital Splitting Parameters (cm^{-1}) Derived from Calculations of g Values[a]

host	δ_1	δ_2
cyclohexane (Fisons)	980	1200
cyclohexane (BDH)	680	1200
$Cr(CO)_6$	500	850

[a] δ_1 and δ_2 are defined as follows:



are not far removed from 2, we may use first-order perturbation methods to analyze the experimental results. At this stage we note that a trigonal compression of the molecule would result in a $d^4_{xy,x^2-y^2}d^1_{z^2}$ configuration and $g_\parallel = 2$ and $g_\perp < 2$, whereas D_{4h} or D_{2h} distortions which place the unpaired electron in a $d_{x^2-y^2}$ or d_{xy} orbital should give the observed $g_\parallel \lesssim 2$ and $g_\perp > 2$. Accordingly we use the equations appropriate to these electron configurations to correct the hyperfine coupling for orbital contributions and to calculate A_{iso} and $2B$, the isotropic and anisotropic contributions to the hyperfine coupling (Table II).[16]

$$A_\parallel = A_{iso} - 2B[1 + \tfrac{7}{4}(g_\parallel - g_e)]$$

$$A_\perp = A_{iso} + B[1 + \tfrac{7}{2}(g_\perp - g_e)]$$

In making these corrections we have taken the average of A_x and A_y and g_x and g_y and have assumed that A_x and A_y have the same sign. However, there are two choices for the relative signs of $A_\perp$ and $A_\parallel$. With both positive, $2B$ drops to 23 G and the 3d population is only 31%. We reject this possibility as implausible in comparison with that with $A_\perp$ positive and $A_\parallel$ negative which yields $2B$ of 42 G and a 3d population of 57%. The corresponding value of A_{iso} is +26 G, giving a 4s population of 8.5% if we assume a contribution of −60 G by spin polarization. The population analysis is similar for cyclohexane (Fisons and BDH) and $Cr(CO)_6$ hosts (Table II). In summary, this analysis shows the electron to have the following distribution: $3d_{xy}$ or $3d_{x^2-y^2}$, 57%; 4s, 8.5%; leaving 34% ligand character.

These results allow a more detailed analysis of the g values and the energy levels of vanadium hexacarbonyl. The energy levels may be derived from the equations of first-order perturbation theory,[16]

$$g_i = g_e \pm n_i \lambda k^2/\delta_i$$

where k is the orbital reduction factor, λ is the spin–orbit coupling constant, the values of n_i are given by the magic pentagon, and the positive sign is appropriate to occupied orbitals, and the negative sign is appropriate to unoccupied orbitals; δ_i is the energy separation between the half-filled orbital and the orbital to which it couples. Both for the configuration $d^2_{xz}d^2_{yz}d^1_{xy}$ and for $d^2_{xz}d^2_{yz}d^1_{x^2-y^2}$ (see discussion of geometry below), the value of n_i appropriate to coupling of the occupied levels is 2. Using this equation and $\lambda = 95$ cm^{-1} [17] and $k = 0.57$ (deduced from the population analysis above), we obtain the d orbital splitting parameters shown in Table III. We do not consider the values of g_z accurate enough to calculate useful values of the energy separation between the half-occupied and the unoccupied levels. The values of δ_i shown in Table III indicate that $\lambda/\delta_i >> 1$ in accord with the use of first-order perturbation theory.

Chart I

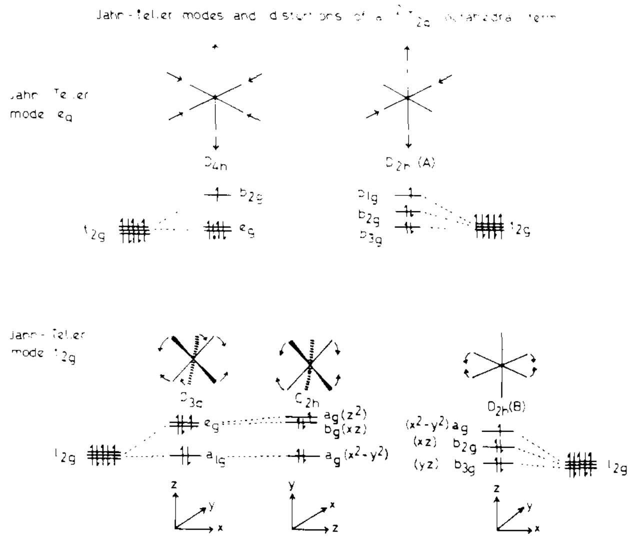
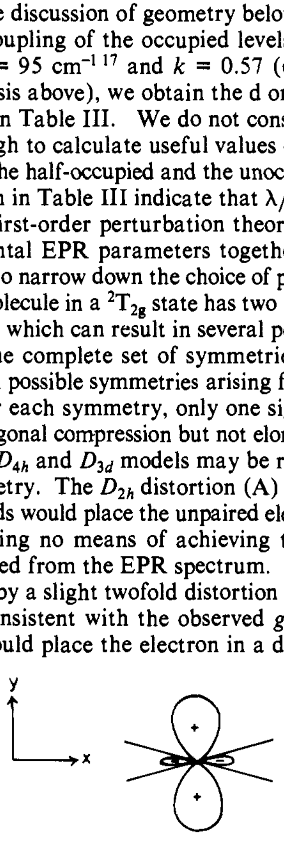


Table IV. EPR Parameters of Cyanide Ions Isoelectronic with $V(CO)_6$ (from ref 20)

ion	host	g_x	g_y	g_z	A_x, G	A_y, G	A_z, G
$Fe(CN)_6^{3-}$	$K_3Co(CN)_6$	2.35	2.10	0.915			
$Mn(CN)_6^{4-}$	$K_4Fe(CN)_6$	2.624	2.182	0.63	69.0	45.6	354

The experimental EPR parameters together with the above analysis allow us to narrow down the choice of possible distortions. An octahedral molecule in a $^2T_{2g}$ state has two Jahn–Teller active modes, t_{2g} and e_g, which can result in several possible distortions. Chart I shows the complete set of symmetries arising from e_g distortions and all possible symmetries arising from t_{2g} distortions except C_i.[18] For each symmetry, only one sign of distortion is shown (e.g., tetragonal compression but not elongation). Of these possibilities, the D_{4h} and D_{3d} models may be rejected since they have axial symmetry. The D_{2h} distortion (A) with twofold axes through the ligands would place the unpaired electron in a $b_{1g}(d_{xy})$ orbital so providing no means of achieving the substantial 4s population deduced from the EPR spectrum. The C_{2h} geometry which may arise by a slight twofold distortion of a D_{3d} geometry (Chart I) is inconsistent with the observed g values. The D_{2h} distortion (B) would place the electron in a $d_{x^2-y^2}$ orbital (**1**) of a_g symmetry which could mix directly with 4s. The anisotropy



1 D_{2h} (B)

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of g_x and g_y arises from the unequal coupling of the electron to the b_{2g} (yz) and b_{3g} (xz) orbitals. The anisotropy of A_x and A_y must then arise from spin polarization. Thus there are strong grounds for preferring the D_{2h} (B) distortion as the highest symmetry distortion compatible with the experimental evidence.

The striking effect of alkene impurity on the EPR spectrum of $V(CO)_6$ indicates that the exact g and A values are very sensitive to small pertubations. Unfortunately it is not possible to define the nature of the interaction from these results. However, we would be reluctant to postulate a 19-electron species, $V(CO)_6$-(alkene).

It is useful to compare the results on $V(CO)_6$ with those obtained earlier[19,20] on the isoelectronic ions $Mn(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$ (Table IV). These ions show much larger deviations of their g values from the free-spin value. This can be understood as a consequence of spin-orbit coupling energies which exceed the distortion energies. (For $Fe(CN)_6^{3-}$ $\lambda = 280$, $\delta_1 = 120$, and $\delta_2 = 160$ cm^{-1}.) Although the distortions are far smaller than for $V(CO)_6$, they are also nonaxial and may have the same symmetry.

Finally we may ask why $V(CO)_6$ is so much more stable than other paramagnetic binary metal carbonyls. This stability cannot be attributed solely to coordinative saturation of vanadium since the existence of seven-coordinate compounds $RV(CO)_6$ with very bulky R groups is well documented[21,22] (R = $AuPPh_3$, $SnPh_3$, SiH_3, etc.). A seven-coordinate binary cyanide ion, $V(CN)_7^{4-}$, has also been characterized.[23] Our results show that $V(CO)_6$ is a delocalized π radical with a distortion from octahedral symmetry which does not provide a directional orbital suitable for attack by σ radicals. We conclude that the reorganization energy necessary to generate an appropriate σ radical is prohibitive for most R groups including $V(CO)_6$ itself.[24] Only with certain large and polarizable R groups can seven-coordination be achieved. The stability of $V(CO)_6$ (**2**) may be contrasted with the reactivity of doublet σ^* radicals such as $Co(CO)_4$ (**3**) and $Mn(CO)_5$ (**4**) which require only very minor reorganization in order to react.[25-27]


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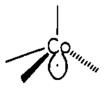
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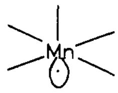
4

Conclusions

We have observed hyperfine structure in the EPR spectra of $V(CO)_6$ in frozen cyclohexane and in $Cr(CO)_6$ hosts. The spectra in cyclohexane are perturbed by small proportions of alkene impurity and are at their sharpest in the presence of such impurity. Unlike spectra reported previously,[10] our spectra are best interpreted in terms of a nonaxial distortion to D_{2h} symmetry in which two cis pairs of ligands are pinched together in a plane. This model represents the highest symmetry which is consistent with all our EPR data and the Jahn-Teller modes of the molecule. Analysis of the g values shows that the distortion energy greatly exceeds the spin-orbit coupling energy and that the t_{2g} orbitals are split into three levels with separations of 500-1000 cm^{-1}. Two lines of evidence, the value of A_C estimated from spectra of ^{13}C-enriched samples, and the analysis of A_V both point to considerable delocalization of spin density onto the ligands. The analysis of A_V gives 57% $d_{x^2-y^2}$, 8.5% 4s, and 34% ligand character. The stability of $V(CO)_6$ is attributed not only to steric constraints but also to the nature of the distortion from octahedral symmetry and to the delocalization of spin density.

Registry No. $V(CO)_6$, 14024-00-1.

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(28) **Note Added in Proof**: Since submitting this paper, a very brief account of the EPR spectra of $V(CO)_6$ in powders and single crystals of $M(CO)_6$ (M = Cr, Mo, W) has appeared (Ammeter, J. H.; Zoller, L.; Bachmann, J.; Baltzer, P.; Gamp, E.; Bucher, R.; Deiss, E. *Helv. Chim. Acta* **1981**, *64*, 1063). We are also grateful to Dr. J. R. Morton for communicating further details of his work on single crystals of $Cr(CO)_6$ doped with $V(CO)_6$ (Boyer, M. P.; Le Page, Y.; Morton J. R.; Preston K. F.; Vuolle, M. J. *Can. J. Spectrosc.*, in press). These single-crystal measurements are in reasonable agreement with our own more approximate powder results for the same host. While Ammeter et al. agree with us in suggesting a low-symmetry distortion, Boyer et al. assume an essentially tetragonal distortion modified slightly by low site symmetry.