Crystal and Molecular Structure of Vanadium Hexacarbonyl

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Abstract

$V(CO)_6$ is orthorhombic with $a = 11.905$ (7), $b = 11.221$ (20), $c = 6.397$ (4) Å at 244.7 ± 1.5 K, space group *Pnma*, $Z = 4$. The structure was refined to $R = 0.0329$ for 990 unique reflexions. Mean V—C and C—O distances are 2.001 (2) and 1.128 (2) Å respectively before librational correction and 2.008 and 1.139 Å after. The molecular structure is very close to regular octahedral although there is a marginally significant tetragonal distortion with uncorrected bond lengths: V—C (axial) 1.993 (2), (equatorial) 2.005 (2), C—O (axial) 1.136 (3), (equatorial) 1.123 (2) Å. This represents a lower limit on a possible static Jahn–Teller distortion since a dynamic distortion is also possible; however, a vibrational analysis shows that dynamic effects, if present, are also small.

Introduction

EPR investigation of vanadium hexacarbonyl (Rubinson, 1976) showed that it is a paramagnetic low-spin d^5 molecule, with an axial Jahn–Teller distortion in a frozen cyclohexane glass. The MCD spectra (Barton, Grinter & Thomson, 1978) also indicate a Jahn–Teller distortion. However, the vapour-phase electron diffraction data (Schmidling, 1975) were interpreted in terms of a regular octahedral structure and a dynamic Jahn–Teller effect. We undertook a single-crystal X-ray structure determination to establish the nature of any distortion and also to throw some light on the absorption band arising at 1500 mm^{-1} in the solid phase (Rubinson, 1976). Comparison with the structure of $[V(CO)_6]^-$ provides a rare opportunity to study the effect of a change in oxidation state on the V—C lengths without a change in geometry or coordinating ligands. Previous X-ray investigation of $V(CO)_6$ has been limited to powder work (Ercoli, Calderazzo & Alberola, 1960) which suggested that the structure was approximately isostructural with $Cr(CO)_6$ and $Mo(CO)_6$. Because the crystals sublime and decompose at room temperature, we collected X-ray data at low temperature.

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Experimental

Satisfactory crystals were grown by sublimation *in vacuo* at −15°C. They were transferred to 0.5 mm Lindemann-glass capillaries and fixed in place with Apiezon L grease, the transfer being performed in an argon-filled dry-bag because the compound is sensitive to oxygen. The capillaries were flame-sealed and the seals covered with wax.

Intensities were measured with a Stoe STADI-2 two-circle diffractometer and graphite-monochromated Mo $K\alpha$ radiation. The temperature was maintained at 244.7 ± 1.5 K (Bellard & Sheldrick, 1978). The a and c cell dimensions were determined by least squares from the ω medians of the zero-layer reflexions, whilst b was determined from diffractometer μ angle measurements. 4564 reflexions (layers $h0$–$17l$) were measured for a crystal $0.46 \times 0.46 \times 0.5$ mm, and corrected for Lp and absorption. Equivalent reflexions were averaged to give 990 unique reflexions with $F > 4\sigma(F)$ based on counting statistics.

Crystal data

$V(CO)_6$, orthorhombic, *Pnma*, $a = 11.905$ (7), $b = 11.221$ (20), $c = 6.397$ (4) Å at 244.7 K, $U = 854.6$ Å^3, $Z = 4$, $M_r = 219.005$, $D_x = 1.70$ Mg m^{-3}, μ(Mo $K\alpha$) = 1.078 mm^{-1}.

Structure solution and refinement

From the systematic absences ($0kl$ with $k + l$ odd, $hk0$ with h odd), the space group is *Pnma* or *Pn2₁a*. The former was chosen by analogy with chromium hexacarbonyl, and confirmed by successful refinement. The V atom was located in a special position on the mirror plane by inspection of the Patterson function, and the C and O atoms found from difference syntheses. The structure was refined by full-matrix least-squares calculations, complex neutral-atom scattering-factors being taken from *International Tables for X-ray Crystallography* (1974). Interlayer scale factors were fixed at the values obtained from a refinement in which all atoms were isotropic. Although this introduces some uncertainty into the U_{22} values we consider it to be justified in this example by the high molecular

symmetry. Because of the difficulties in handling the crystals we did not succeed in obtaining a crystal mounted about another axis. In the final anisotropic refinement the weighting scheme $w = [\sigma^2(F) + 0.0001F^2]^{-1}$ gave a flat analysis of variance in terms of $\sin \theta$ and F_o. Refinement converged to $R' = \sum w^{1/2}\Delta/\sum w^{1/2}|F_o| = 0.0341$ and $R = 0.0329$. Final positional and thermal parameters are presented in Tables 1 and 2, bond lengths and angles in Table 3 and Fig. 1.*

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* A list of structure factors and a table of non-bonded distances have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33966 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
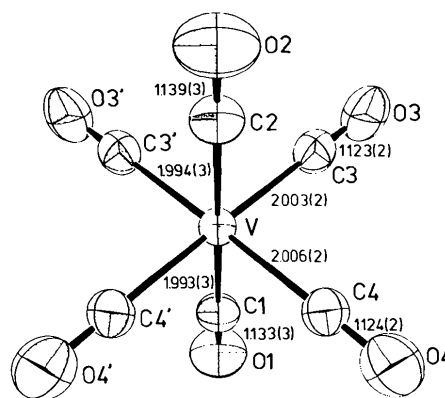

Fig. 1. ORTEP plot of the $V(CO)_6$ molecule, with 50% probability thermal ellipsoids, atom labelling, and unique bond lengths (in Å).

Table 1. Atom coordinates ($\times 10^4$)

	x	y	z
V	1277 (1)	2500	622 (1)
C(1)	2204 (2)	2500	3216 (4)
C(2)	361 (2)	2500	−1989 (4)
C(3)	268 (2)	1252 (2)	1843 (3)
C(4)	2269 (2)	1236 (2)	−606 (3)
O(1)	2734 (2)	2500	4685 (3)
O(2)	−160 (2)	2500	−3482 (3)
O(3)	−305 (1)	557 (2)	2519 (3)
O(4)	2815 (1)	517 (2)	−1287 (3)

Table 2. Anisotropic temperature factors ($\text{Å}^2 \times 10^3$)

The temperature factor exponent takes the form:
$$-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^*b^*).$$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
V	30 (1)	29 (1)	31 (1)	0	0 (1)	0
C(1)	41 (1)	50 (1)	40 (1)	0	−2 (1)	0
C(2)	44 (1)	46 (1)	40 (1)	0	−5 (1)	0
C(3)	42 (1)	42 (1)	47 (1)	−2 (1)	1 (1)	−2 (1)
C(4)	43 (1)	41 (1)	48 (1)	−6 (1)	1 (1)	0 (1)
O(1)	67 (1)	102 (2)	49 (1)	0	−20 (1)	0
O(2)	72 (1)	90 (2)	51 (1)	0	−21 (1)	0
O(3)	67 (1)	60 (1)	79 (1)	11 (1)	13 (1)	−23 (1)
O(4)	64 (1)	63 (1)	88 (1)	−25 (1)	5 (1)	18 (1)

Table 3. Bond lengths (Å) and angles (°)

C(1)–V	1.993 (5)	O(1)–C(1)	1.133 (4)
C(2)–V	1.994 (5)	O(2)–C(2)	1.139 (4)
C(3)–V	2.003 (4)	O(3)–C(3)	1.123 (3)
C(4)–V	2.006 (4)	O(4)–C(4)	1.124 (3)
C(3)–V–C(1)	90.4 (2)	C(2)–V–C(1)	179.5 (1)
C(4)–V–C(1)	90.0 (2)	O(1)–C(1)–V	179.7 (1)
C(4)–V–C(2)	89.7 (2)	O(2)–C(2)–V	179.9 (1)
C(2)–V–C(3)	89.9 (2)	O(3)–C(3)–V	179.4 (2)
C(4)–V–C(3)	90.7 (2)	O(4)–C(4)–V	179.1 (2)
C(3')–V–C(3)	88.7 (2)		
C(4')–V–C(4)	90.0 (2)		

Molecular symmetry: constrained refinements

The molecule contains a crystallographic mirror plane which passes through the V atom and two of the carbonyl groups: the structure is isostructural with that of $Cr(CO)_6$ (Rees & Mitschler, 1976) although all the cell dimensions are larger because of the longer V—C bonds and the higher temperature at which the structure was determined. The C—V—C and V—C—O angles are all close to the ideal values of 90 and 180° respectively, the most significantly different being C(3')–V–C(3) [88.7 (2)°]. Crystal packing effects are thus small but possibly detectable, since this is also the smallest C—Cr—C angle found in both the X-ray and neutron refinements for $Cr(CO)_6$. The bond lengths in Table 3 provide evidence of a small tetragonal distortion: the pair of *trans* carbonyls which lie in the mirror plane have shorter V—C and longer C—O distances than the remaining carbonyls [a smaller and less regular effect is seen in $Cr(CO)_6$, although the Cr—C and C—O distances are correlated in the same way: this correlation presumably arises because the C atoms have the largest positional uncertainties]. Refinement with the bond lengths constrained so as to represent a tetragonal distortion from octahedral symmetry increased the generalized index R_g by only 0.0001, and gave V—C (axial) 1.993 (2), (equatorial) 2.005 (2), C—O (axial) 1.136 (3), (equatorial) 1.123 (2) Å. There is no evidence to favour a symmetry lower than tetragonal. On the other hand, octahedral constraints increased R_g by 0.0006 and gave V—C 2.0005 (13), C—O 1.1277 (17) Å; thus an almost significant tetragonal distortion is indicated. This would be consistent with the axial Jahn–Teller distortion found by EPR (Rubinson, 1976) and as such would be the first determination of a structural distortion that uniquely can cause a spectroscopic energy splitting. However, X-ray diffraction can only put a lower limit on the distortion because there may be (partial)
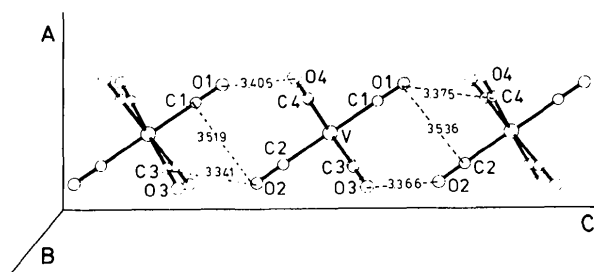
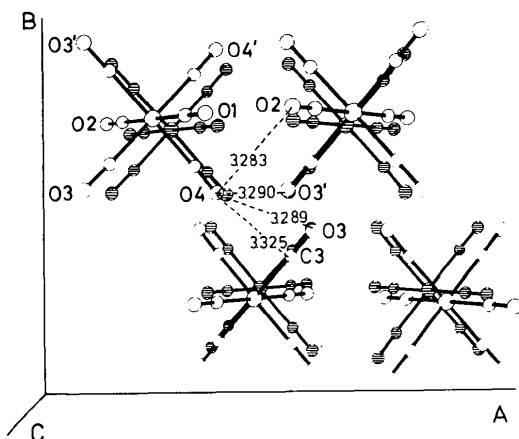Fig. 2. Packing diagram for $V(CO)_6$ showing some non-bonded distances (in Å).

Fig. 3. Alternative view of $V(CO)_6$ packing, with further non-bonded distances (in Å).

dynamic averaging between the various possible orientations of the unique axis.

More puzzling is the optical absorption of crystalline $V(CO)_6$ and the deep bluish-black colour of the crystals. Before determining the structure we had suspected some association of the paramagnetic molecules in the solid, but the packing and intermolecular distances (Figs. 2 and 3) provide no evidence to support this idea. Theoretical calculations (Bullett & Woolley, 1978) based on possible chain interactions along c (Fig. 2) also cannot account for the absorption. A possible explanation would be interactions with an impurity trapped in the lattice. In view of this one should be cautious about the significance of the tetragonal distortion, since a small percentage of an impurity containing a V=O bond would effectively move some C atoms towards the V atom but leave the O atom positions unchanged: the V$\cdots$O intramolecular distances are in fact remarkably constant (3·129 and 3·128 Å for the tetragonally constrained refinement).

Molecular vibrations and librational corrections

The vibrational motion of the V atom is effectively isotropic. By assuming that the V atom tensor results only from translational motion of the whole molecule, we calculate the mean amplitudes parallel and perpendicular to the V—C—O directions for C as 0·093 (11) and 0·126 (12) Å respectively and for O as 0·075 (8) and 0·241 (6) Å (the uncertainties are estimated from the spread of values). If we then assume a riding model, we obtain librational corrections (for all V—C bonds) of about +0·008 Å and (for all C—O bonds) +0·011 Å. The mean librationally corrected distances are then V—C 2·008 (3) and C—O 1·139 (3) Å; the gas-phase electron-diffraction values are 2·015 (2) and 1·138 (2) Å. (The influence of bonding electrons on the apparent bond lengths obtained from X-ray and electron diffraction is slightly different.)

If we assume that the C—O bond is much stiffer than the V—C bond, i.e. that the carbonyl moves as a unit, we can estimate the r.m.s. vibrational amplitude $u(V—C) = u(V\cdots O) = 0·084$ Å, in good agreement with the electron diffraction values $[u(V—C) 0·079 (2), u(V\cdots O) 0·074 (3)$ Å]. The amplitudes calculated for $Cr(CO)_6$ from spectroscopic data (Jones, McDowell & Goldblatt, 1969) were $u(Cr—C) 0·058$ and $u(Cr\cdots O) 0·057$ Å. The apparently large amplitudes for $V(CO)_6$ were quoted by Schmidling (1975) as evidence for a dynamic Jahn–Teller distortion. An analogous analysis applied to the X-ray/neutron thermal parameters for $Cr(CO)_6$ (Rees & Mitschler, 1976) produces the even more anomalous value of $u(Cr—C) = (Cr\cdots O) = 0·090$ Å, despite the fact that $Cr(CO)_6$ does not have a degenerate electron state and so cannot exhibit a dynamic Jahn–Teller effect. Another explanation for the large amplitudes could be a dynamic trigonal distortion, which, in an extreme case, would affect only the perpendicular amplitudes. However, the perpendicular amplitudes would then be much more sensitive to temperature and to interactions with other molecules. Therefore, no definite conclusions can be drawn except that any effect, if present, must be small.

Effect of oxidation state on bond lengths

Swanson, Hamburg & Ryan (1974) observed that the Fe—C distance in $[Fe(CN)_6]^{4-}$ is 0·026 (8) Å shorter than in $[Fe(CN)_6]^{3-}$, although the ionic radius of Fe^{2+} is about 0·06 Å larger than that of Fe^{3+}. Exactly the same effect arises in the isoelectronic $[V(CO)_6]^-$ and $V(CO)_6$. The V—C distance of 1·931 (9) Å observed by Wilson & Bau (1974) in $[(Ph_3P)_2N]^+$ $[V(CO)_6]^-$ is 0·070 Å shorter than the librationally uncorrected value reported here for $V(CO)_6$ even though the ionic radius of V^- is expected to be larger than that of V^0. It is difficult to reconcile these results quantitatively with valence-bond analyses, such as that for the closely related $Cr(CO)_6$ by Pauling (1968), since corrections for the differing double-bond character to the V—C bonds in the vanadium carbonyls are small relative to

the radius change. The molecular orbital model, on the other hand, correctly predicts the sense of the bond length changes. This is ascribed to changes in π back-donation from the loss of the sixth d electron upon oxidation.

Mean librationally corrected bond lengths for $Cr(CO)_6$ [Cr—C 1·920 (2), C—O 1·140 (1) Å] can be obtained in the same way as for $V(CO)_6$. The reduction in M—C distance going from $V(CO)_6$ to $Cr(CO)_6$ can again be attributed in part to π back-bonding by the extra d electron. Although the corrected C—O distances in the neutral V and Cr carbonyls agree to within 0·001 Å, the uncorrected value in $[V(CO)_6]^-$ of 1·146 (11) Å indicates that the corrected† value would be longer, consistent with the idea that the negative charge increases the population of the CO π^* orbitals (Paetzold & Abd-el-Mottaleb, 1975).

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† Corrected values should be compared since the three determinations were at different temperatures and the C—O librational correction is relatively large and temperature sensitive; however the thermal parameters are not available for $[V(CO_6)]^-$

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Kristallstruktur von Zirkoniumtetrajodid ZrI4: Ein neuer AB_4-Strukturtyp

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Abstract

The crystal structure of ZrI_4 was determined from X-ray diffractometer data and was refined by full-matrix least-squares methods to an R index of 0·045 for 1985 observed reflexions. The crystals are monoclinic, space group $P2/c$ with $a = 8.356$ (2), $b = 8.326$ (2), $c = 17.926$ (4) Å, $\beta = 103.21$ (3)°, $V = 1214.1$ Å^3, $D_x = 4.914$ Mg m^{-3}, $Z = 6$ ZrI_4. The structure consists of infinite chains of ZrI_6 octahedra sharing non-opposite edges in such a way that a helical arrangement with an identity period of six octahedra along the chain results. It appears to be the first AB_4 structure of its type, different from the α-NbI_4, $ZrCl_4$, and β-$ReCl_4$ chain structures. Zr—I distances range from 2·692 (1) to 3·030 (1) Å, Zr—Zr separations along the chains are

uniform [4·394 (1) and 4·416 (1) Å]; I—I distances within the c.c.p. anion arrangement are 3·899–4·199 (1) Å within the chains and 4·103–4·413 (1) Å between the chains.

Einleitung

Die Tetrahalogenide der Übergangsmetalle zeigen eine Vielfalt des strukturellen Aufbaus, die durch Unterschiede der Elektronenkonfiguration und der Möglichkeiten von Metall—Metall-Bindungen sowie durch unterschiedliche Polarisations- und Radienverhältnisse verursacht ist. Eine Systematik ist jedoch bisher nicht sichtbar. So bilden z.B. $NbCl_4$ (Taylor, Calabrese & Larsen, 1977; Schäfer & von Schnering, 1964), α-NbI_4