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The molecular structure of cyclopentadienyl vanadium tetracarbonyl determined by gas-phase electron diffraction

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Abstract

The molecular structure of cyclopentadienyl vanadium tetracarbonyl, $C_5H_5V(CO)_4$, has been determined by gas-phase electron diffraction at 95°C assuming local C_{4v} symmetry for the $V-(CO)_4$ moiety and C_{5v} symmetry for the C_5H_5-V group. The relative positions of these two groups could not be determined unequivocally. Models with an eclipsed (torsion angle, τ ($C-V-X-C$) = 0° where X is the centre of the cyclopentadienyl ring) or staggered configuration ($\tau = 9^\circ$) fit the experimental data equally as well as a model which allows for free rotation of the C_5H_5 ring with respect to the $V-(CO)_4$ group. The C–H bonds were allowed to bend out of the plane of the ring and $\angle V-C-O$ was allowed to be non-linear. For both the staggered and the eclipsed models $\angle X-C-H = 171(19)^\circ$ (C–H bent away from the metal) and $\angle V-C-O = 177(11)^\circ$ (C–O bent slightly towards the ring). The remaining parameter values are almost identical for both models and for the staggered model are: $r_g(V-C_{(ring)}) = 2.281(13)$ Å, $r_g(V-C_{(CO)}) = 1.963(7)$ Å, $r_g(C-C) = 1.405(6)$ Å, $r_g(C-O) = 1.135(4)$ Å, $\angle(OC-V-CO) = 75.4(2.0)^\circ$, $R = 11.4\%$.

Keywords: Vanadium; Carbonyl; Cyclopentadienyl; Electron diffraction

1. Introduction

Until recently there has been very little information in the literature on the structures adopted in the gas phase by mixed metal carbonyl–cyclopentadienyl derivatives. To date there are reports of only two such structures, $C_5H_5Co(CO)_2$ [1] and $C_5H_5Mn(CO)_3$ [2]. In contrast there has been interest in the solid state structures of such materials, primarily focused upon the nature of the bonding between the metal atom and the cyclopentadienyl ring [3,4]. Recently, attention has been directed towards organic derivatives of transition metal carbonyls because of their potential use as precursors in the deposition of thin metal films by MOCVD [5]. Very little is known of the mechanisms involved in the gas-phase thermal or photochemical decomposition of these compounds, but fundamental to these reactions is a knowledge of the molecular structures in the vapour phase. As part of our investigation into the gas-phase structures of first row transition metal carbonyl–cyclo-

pentadienyl complexes, a study of $C_5H_5V(CO)_4$ by gas-phase electron diffraction was undertaken.

2. Experimental

$C_5H_5V(CO)_4$ was obtained from Strem Chemicals Inc. and transferred under air and moisture free conditions to small glass ampoules having weakened ends which were inserted into the nozzle of the electron diffraction apparatus. Gas-phase electron diffraction data were recorded photographically using the Reading apparatus operating at 42.00 kV [6]. During the experiment the sample was held at a temperature of 95°C. Owing to the difficulty experienced in obtaining sufficient vapour in the chamber to produce measurable scattering, two runs were conducted at each camera length using a new sample ampoule for each run. In this way six plates were recorded at the shorter plate to nozzle distance (244.72, 244.80 mm) and six at the longer plate to nozzle distance (495.18, 495.22 mm). The electron wavelength (0.058575 Å) was calibrated against diffraction patterns of benzene [7]. The plates were traced on

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the microdensitometer of the Department of Chemistry at the University of Oslo (Joyce–Loebl) and all six plates from each camera distance were deemed suitable for use in the subsequent structural analysis. The data covering the regions $2.5 \leq s \leq 13.0 \text{ \AA}^{-1}$ and $6.0 \leq s \leq 24.5 \text{ \AA}^{-1}$ at intervals of $\Delta s = 0.25 \text{ \AA}^{-1}$ (where $s = 4\pi\lambda^{-1} \sin \theta$ and 2θ is the scattering angle) were processed as previously described [8] using scattering factors taken from Ref. [9].

3. Structure refinements

Refinements were commenced on the structure of $C_5H_5V(CO)_4$ assuming local C_{4v} symmetry for the $V-(CO)_4$ moiety and C_{5v} symmetry for the C_5H_5-V group. The parameters chosen to define the structure of the molecule were: the distance of the vanadium atom above the centre of the Cp ring (X), the distance of the centre of the Cp ring (X) from the C atoms of the ring, the C–H, V–CO and C–O bond lengths, $\angle X-V-C$ (the angle formed between the carbonyl C atom, the V atom and the centre of the Cp ring), $\angle V-C-O$, $\angle X-C-H$ and τ , the $C_1-X-V-C_6$ torsion angle (for atom numbering see Fig. 1, n.b. H_n is bound to C_n). The torsion angle was defined as being equal to zero when the molecule was in the eclipsed position, i.e. when C_6O_6 lies over the carbon–hydrogen bond C_1H_1 of the Cp ring. Initial starting values for the parameters and for mean square vibrational amplitudes were obtained from a consideration of analogous gas-phase structures of vanadium carbonyl and cyclopentadienyl compounds.

Initial least squares refinements carried out on this model with the torsion angle τ fixed at 0.0° led to reasonable agreement between the theoretical intensity curves and the experimentally obtained one. Attempts to allow the torsion angle to vary failed to result in convergence in the least squares refinements. Therefore, refinements of a staggered model, that is with $\tau = 9^\circ$, were carried out. Values of the mean square vibrational

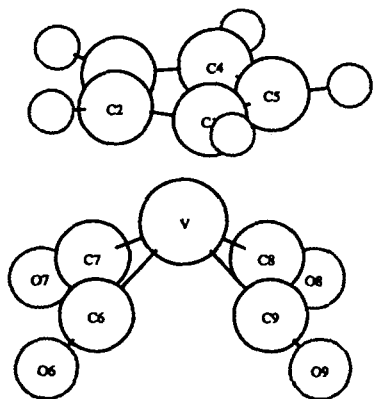


Fig. 1. Diagram of $C_5H_5V(CO)_4$ with atom numbering.

Table 1
Approximate valence force field for $C_5H_5V(CO)_4$

<i>Stretch</i> (mdyn \AA^{-1})			
V–C _(C=O)	1.9	C–O	15.0
V–C _(Cp)	1.5	C–C	6.5
		C–H	5.2
<i>Linear bend</i> (mdyn $\text{\AA} \text{ rad}^{-2}$)			
V–C–O	0.70		
<i>Bend</i> (mdyn $\text{\AA} \text{ rad}^{-2}$)			
C _(Cp) –C _(Cp) –H	0.55	C _(Cp) –C _(Cp) –C _(Cp)	1.20
C _(Cp) –V–C _(Cp)	0.55	C _(Cp) –V–C _(Cp)	0.25
C _(C=O) –V–C _(C=O)	0.65	C _(Cp) –V–C _(C=O)	0.20
<i>Out of plane bend</i> (mdyn $\text{\AA} \text{ rad}^{-2}$)			
C–C–C–H	0.25		
<i>Torsion</i> (mdyn $\text{\AA} \text{ rad}^{-2}$)			
C–C–C–C	0.24		

amplitudes and perpendicular amplitude corrections were then calculated [10] using an approximate force field close to the one given in Table 1. The values for the main stretching force constants were allowed to vary in the calculation until the average deviation between the experimental and calculated vibrational frequencies for the molecule were minimised. The new values for the vibrational amplitudes thus obtained were included in further least squares refinements for the molecule using fixed torsion angles of 0° and 9° . The values for selected vibrational amplitudes were allowed to refine as denoted in Table 2. Ultimately a final value of $R = 11.4\%$ was obtained for both models. The radial distribution curve for the staggered model is shown in Fig. 3 together with experimental and difference curves.

A further refinement was also attempted which allowed for free rotation of the Cp ring with respect to the $V(CO)_4$ fragment. Owing to the numbers of different interactions generated in such a model, free rotation is best described by defining only three different positions for the carbonyl groups representing conformers having torsion angles of 1.5° , 4.5° and 7.5° each with equal occupancy of $\alpha = 0.333$. Refinements for this model gave a slightly poorer fit to the observed data ($R = 11.9\%$) than did those from models with a fixed torsion angle; however, the difference is very small, as would be expected in a molecule having a 20-fold barrier to rotation.

Initial values of $\angle X-C-H$ in the range $170-190^\circ$ were tested, where a value smaller than 180° for the angle indicates the hydrogen atoms are displaced away from the vanadium atom. The V–C–O angle refined to values very close to 180° , but for both the staggered and eclipsed models a value slightly less than 180° (C–O bent towards the ring) was the final result. None of the values for $\angle V-C-O$ or $\angle X-C-H$ are significantly

Table 2
Internuclear distances, angles and mean square vibrational amplitudes for the final refinements of $C_5H_5V(CO)_4$ staggered model^b

	r_g, \angle	l_{calc}	l_{ref}
Independent parameters			
$r(V-C_{(C=O)})$	1.963(7)	0.060	
$r(C-O)$	1.135(4)	0.039	
$r_{\alpha}(V-X^\circ)$	1.942(17)		
$r(C-C)$	1.405(6)	0.050	
$r(C-H)$	[1.123]	0.077	
$\angle(V-C-O)$	177(11)		
$\angle(X-V-C_{(C=O)})$	120.1(2.2)		
$\angle(H-C-X)$	171(19)		
Dependent parameters			
$r(V...O_6)$	3.091(10)	0.062	
$r(C_6...C_7)$	2.405(54)	0.133	
$r(O_6...O_7)$	3.825(94)	0.224	
$r(C_6...O_7)$	3.236(42)	0.163	0.192(88)
$r(C_6...O_8)$	4.425(61)	0.144	0.177(84)
$\angle(C_6-V-C_7)$	75.4(2.0)		
$r(V-C_1)$	2.282(13)	0.059	0.107(8)
$r(V...H_1)$	3.117(202)	0.132	
$r(C_1...C_3)$	2.270(10)	0.054	
$r(C_1...H_2)$	2.243(20)	0.097	
$r(C_1...H_3)$	3.336(35)	0.112	
R^d	11.4		

The number in parentheses are the estimated standard deviations $\times 2$.

^a Distances and vibrational amplitudes (l_{ref} and l_{calc}) in angstroms, angles in degrees. Values in square brackets were kept constant in the final refinement. ^b $\tau = 9^\circ$ (torsion angle, $C_1-X-V-C_6$). ^c X is the geometrical centre of the Cp ring. ^d R is weighted agreement factor (%) for curves from both distances combined.

different from linear, but refinements started with these angles larger than 180° always converged back to the reported values. The average experimental and final theoretical intensity curves for the staggered model are shown in Fig. 2 and the radial distribution curves calculated from them for this model are shown in Fig. 3. The curves for the eclipsed model are almost identical to those shown. The correlation matrix for the parameters of the staggered model is shown in Table 3.

Table 3
Correlation matrix ($\times 100$) for parameters of $C_5H_5V(CO)_4$ ^a

1	$r(X-C_1)$	100										
2	$r(X-V)$	-70	100									
3	$\angle(X-V-C_6)$	-3	25	100								
4	$r(V-C_6)$	-33	41	6	100							
5	$r(C-O)$	-6	-1	6	-10	100						
6	$\angle(X-C-H)$	16	-4	29	-37	-6	100					
7	$\angle(V-C-O)$	-8	24	76	10	6	15	100				
8	$l(V...C_1)$	18	-11	43	-31	18	22	32	100			
9	$l(C_6...O_7)$	-8	30	52	2	13	77	25	26	100		
10	$l(C_6...O_8)$	8	-9	-10	-9	-1	7	-18	-3	4	100	
11	σ_{LS}^b	-0.9	-0.5	-19.2	-10.2	17.3	27.5	-9.2	22.9	27.3	1.8	

^a Distances and amplitudes are in angstroms, angles in degrees. ^b Standard deviations taken from final least squares refinement with $\tau = 9^\circ$.

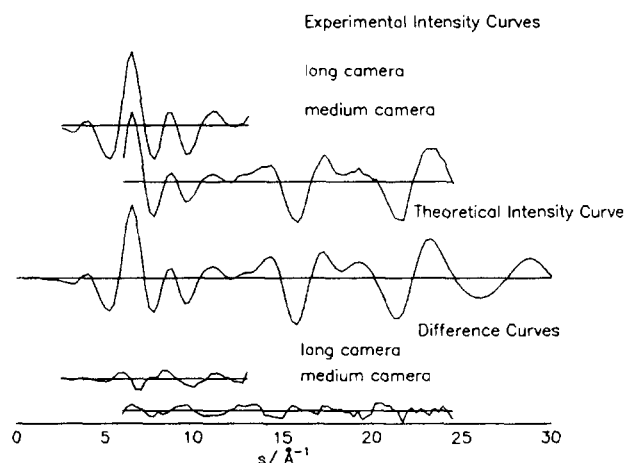


Fig. 2. Intensity curves $sI_m(s)$ for $C_5H_5V(CO)_4$. The experimental curves are averages of all plates for the two camera distances. The theoretical curve was calculated using the parameter values of the staggered model given in Table 2.

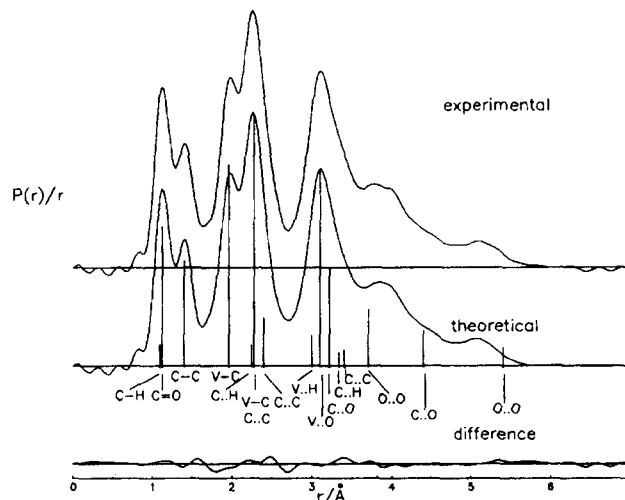


Fig. 3. Radial distribution curves for $C_5H_5V(CO)_4$. The experimental curve was calculated from the average of the intensity curves after multiplication by $(Z_V Z_C / f_V f_C) \exp(-0.0025s^2)$ and using theoretical data for the region $0 \leq s \leq 2.25 \text{ \AA}^{-1}$. The contributions from the most important distances are indicated on the radial distribution curves and the heights of the bars are proportional to the weights of the distances.

4. Discussion

The results from the structural study on $C_5H_5V(CO)_4$ in the vapour phase demonstrate that the molecule has the expected mixed sandwich arrangement of ligands above and below the central vanadium atom. However, it was very difficult to determine, from the available data, the exact relative positions of the Cp group and the $V-(CO)_4$ group. A model having the C–H bonds of the Cp group and the C–O bonds of the $V-(CO)_4$ groups in a staggered arrangement showed equally good fit to the data as did an eclipsed arrangement or one possessing free rotation of the Cp group. This suggests, as expected, that there is a very low barrier to internal rotation of the Cp group. Additionally, data could only be collected to a maximum value of $s = 24.50 \text{ \AA}^{-1}$ because of the very weak scattering observed beyond this limit. The same problem was encountered in the gas-phase determination of the structure of $(C_5H_5)_2V$ where data could not be obtained beyond $s = 20 \text{ \AA}^{-1}$ [11]. In the study of $C_5H_5Mn(CO)_3$ [2] a similar situation was found where it was not possible to state whether the ligands assume a staggered arrangement with respect to each other or whether free rotation takes place. In $C_5H_5V(CO)_4$ there is a difference in torsion angle of only 18° between one eclipsed conformation and another. Accordingly there will be little difference in expected scattering across the central vanadium atom due to the main interactions for either an eclipsed or a staggered model; thus, with the available data it is difficult to select the best fit.

The $V-C_{(\text{ring})}$ distance, $r_a = 2.277(13) \text{ \AA}$, is almost identical to that found in vanadocene, $V(C_5H_5)_2$ [11] $r_a = 2.280(5) \text{ \AA}$. When the analogous $Mn-C_{(\text{ring})}$ bond lengths in $C_5H_5Mn(CO)_3$ [2] ($r_a(Mn-C) = 2.147(3) \text{ \AA}$) and $(C_5H_5)_2Mn$ ($r_a(Mn-C) = 2.380(6) \text{ \AA}$) [12] were compared, a difference of 0.233 \AA was observed. Yet in the analogous cobalt compounds the M–C distance in $Co(C_5H_5)_2$ ($2.119(3) \text{ \AA}$) [13] is slightly shorter than that in $C_5H_5Co(CO)_2$ ($2.129(6) \text{ \AA}$) [1]. However, this can perhaps be explained by looking at the electronic structures of such cyclopentadienyl compounds. In Ref. [11] the lengths and strengths of the M–C bonds in $(C_5H_5)_2M$ ($M = V, Cr, Mn, Fe, Co, Ni$) are explained in terms of the electron imbalance due to the number of

holes in the a_{1g} and e_{2g} bonding orbitals and the number of electrons in the e_{1g} antibonding orbitals. The metal to ring strength was found to decrease as a result of this imbalance for the series $M(C_5H_5)_2$ such that the longest M–C bond, $2.383(3) \text{ \AA}$, was found in the 17 electron $Mn(C_5H_5)_2$. In the mixed Cp–transition metal carbonyl compounds whose gas-phase structures are known so far, namely $C_5H_5V(CO)_4$, $C_5H_5Mn(CO)_3$ and $C_5H_5Co(CO)_2$, the total number of outer electrons is 18 in each case. Thus the electronic structures would be expected to be comparable. Along the series the M–C distance decreases with decreasing size of the metal atom ($V-C = 2.277(13) \text{ \AA}$, $Mn-C = 2.147(3) \text{ \AA}$ [2], $Co-C = 2.129(6) \text{ \AA}$ [1]) as might be expected. Thus it is not meaningful to compare the M–C distance in the mixed sandwich compounds with those in the metal-locenes without taking the differences in electronic structures into account.

The distance of the vanadium atom above the centre of the Cp ring (X) in $C_5H_5V(CO)_4$ ($1.942(17) \text{ \AA}$) compares well with that found in the X-ray diffraction study of the crystalline material (1.93 \AA) [14], being slightly longer in the vapour phase as might be expected.

The V–C distance found in the $V-CO_4$ group ($r_a = 1.961(7) \text{ \AA}$) is also longer than the two V–C distances found in crystalline $C_5H_5V(CO)_4$ ($1.88, 1.94 \text{ \AA}$) [14]. The only other vanadium carbonyl compound for which the vapour phase structure has been determined is the 17 electron species $V(CO)_6$ [15] in which the value of $r_g(V-C)$ was found to be $2.015(2) \text{ \AA}$. The values of the M–CO distances in the series of compounds $C_5H_5-V-(CO)_4$ ($r_a(V-C) = 1.961(7) \text{ \AA}$), $C_5H_5Mn(CO)_3$ ($r_a(Mn-C) = 1.806(3) \text{ \AA}$) [2] and $C_5H_5Co(CO)_2$ ($r_a(Co-C) = 1.674(4) \text{ \AA}$) [1] decrease with increasing atomic number Z of the transition metal; this leads to a decrease of atomic radius and an increase in the back donation from the metal to the carbonyl groups as the number of d electrons rises. A similar decrease in M–CO distances is observed within the series of first row transition metal carbonyls, $r_a(V-C) = 2.015(2) \text{ \AA}$ in $V(CO)_6$ [15], $r_a(Cr-C) = 1.92(4) \text{ \AA}$ in $Cr(CO)_6$ [16], $r_a(Mn-C_{ax}) = 1.803(16) \text{ \AA}$ and $r_a(Mn-C_{eq}) = 1.873(5) \text{ \AA}$ in $Mn_2(CO)_{10}$ [17], $r_a(Fe-C) = 1.8205(10) \text{ \AA}$ in $Fe(CO)_5$ [18]. Associated with this decrease in $r_a(M-C)$

Table 4

Electron diffraction bond lengths r_a for M–C and C–O in some gaseous transition metal carbonyls and Cp-substituted metal carbonyls

Metal carbonyl	$r(M-C)$	$r(C-O)$	Ref.	Cp metal carbonyl	$r(M-C)$	$r(C-O)$	Ref.
$V(CO)_6$	2.015(2)	1.138(2)	[15]	$CpV(CO)_4$	1.961(7)	1.134(4)	– ^a
$Cr(CO)_6$	1.92(4)	1.16(5)	[16] ^b	$CpMn(CO)_3$	1.806(3)	1.147(2)	[2]
$Mn_2(CO)_{10}$	1.803(16)	1.147(2)	[17]	$CpCo(CO)_2$	1.679(4)	1.191(4)	[1]
	1.873(5)						
$Fe(CO)_5$	1.8205(10)	1.1531(11)	[18]				

^a This work. ^b Visual method.

in the above metal carbonyls there is an increase in the C–O bond length of the carbonyl group. The value of $r_a(\text{C–O})$ increases from 1.138(2) Å in $(\text{V}(\text{CO})_6)$ [15], to 1.147(2) Å in $\text{Mn}_2(\text{CO})_{10}$ [17] to 1.1531(11) Å in $\text{Fe}(\text{CO})_5$ [18]. The quoted value of $r(\text{C–O}) = 1.16(5)$ Å for $\text{Cr}(\text{CO})_6$ is somewhat high for this series, but the uncertainty associated with this figure is rather large as the structure was determined by the visual method. In the same way the value of $r_a(\text{C–O})$ in the mixed sandwich complexes $(\text{C}_5\text{H}_5)\text{M}(\text{CO})_n$, ($\text{M} = \text{V}$, $n = 4$; $\text{M} = \text{Mn}$, $n = 3$; $\text{M} = \text{Co}$, $n = 2$) increases from a minimum value of 1.134(4) Å in $\text{C}_5\text{H}_5\text{V}(\text{CO})_4$ to the relatively long value of 1.191(4) Å in $\text{C}_5\text{H}_5\text{Co}(\text{CO})_2$ [1]. A comparison of these bond lengths is given in Table 4.

The exact positions of the hydrogen atoms in Cp- and C_4H_4 -substituted metal carbonyls is a question of current interest. As discussed previously [2], there is to date no precedent for the direction of inclination of the hydrogen atoms. In $\text{C}_5\text{H}_5\text{Co}(\text{CO})_2$ the C–H atoms were reported as being bent away from the cobalt atom by $16(4)^\circ$ [1], whereas in $\text{C}_4\text{H}_4\text{Fe}(\text{CO})_3$ the H atoms were found to be bent towards the metal atom by an angle of $8.6(6.3)^\circ$ [19]. In $\text{C}_5\text{H}_5\text{Mn}(\text{CO})_3$ the H atoms were found to be inclined towards the metal atom by a very small angle, $1.7(3.4)^\circ$, but the uncertainty associated with this angle was so high that the exact positions could not be unequivocally stated [2]. In this investigation the MnCO groups were assumed to be linear and this could also have an effect on the results for the position of the hydrogen atoms. In $\text{C}_5\text{H}_5\text{V}(\text{CO})_4$ we found that the H atoms are bent away from the vanadium atom by an angle of $9(19)^\circ$ (where the quoted uncertainties are equal to 2σ). Here no assumption about the linearity of the VCO groups has been made. The large uncertainty in the value of the H–C–X angle is, however, again too large for us to make any definitive statements about the positions of the hydrogen atoms relative to the ring. More information is needed before any final conclusions about the hydrogen positions in molecules like these can be made.

Acknowledgements

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