

THE CRYSTAL AND MOLECULAR STRUCTURE OF π -CYCLOPENTADIENYLVANADIUM TETRACARBONYL

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INTRODUCTION

Most of the known stable simple π -cyclopentadienyl metal carbonyls have been studied by X-ray diffraction¹⁻⁶. However, many of these structures have been reported without detailed information³⁻⁶ and only one vanadium complex has been studied⁵. A detailed 3-dimensional X-ray examination of $(\pi\text{-C}_5\text{H}_5)\text{V}(\text{CO})_4$ is now reported.

PROCEDURE

A set of 350 visually estimated intensities was obtained from crystals of $(\pi\text{-C}_5\text{H}_5)\text{V}(\text{CO})_4$, sealed into capillary tubes to minimise decomposition (Cu K α radiation, equi-inclination Weissenberg photographs). The structure was determined by standard Patterson, Fourier and isotropic least-squares refinement techniques.

RESULTS

Unit cell and space group

Crystals of $(\pi\text{-C}_5\text{H}_5)\text{V}(\text{CO})_4$ are orthorhombic; $a = 7.485 \pm 0.005 \text{ \AA}$, $b = 12.25 \pm 0.01 \text{ \AA}$; $c = 10.43 \pm 0.01 \text{ \AA}$; $U = 956.6 \text{ \AA}^3$. $M = 228$, $D_m = 1.56 \text{ g}\cdot\text{cm}^{-3}$ (float-

TABLE I

FINAL ATOMIC PARAMETERS AND STANDARD DEVIATIONS

Atom	X	Y	Z	$10^2\sigma(X)$	$10^2\sigma(Y)$	$10^2\sigma(Z)$	$10^2 U$	$10^2\sigma(U)$
V	0.5889	0.2500	0.4825	0.071	0	0.034	1.538	0.154
O ₁	0.5921	0.4028	0.2500	0.272	0.150	0.158	7.109	0.528
O ₂	0.2784	0.4054	0.5381	0.237	0.132	0.134	5.099	0.478
C ₁	0.5946	0.3459	0.3415	0.386	0.175	0.175	4.015	0.555
C ₂	0.3922	0.3505	0.5120	0.352	0.164	0.177	3.729	0.530
C ₃	0.6720	0.2500	0.6934	0.851	0	0.470	0.882	1.219
C ₄	0.7445	0.3508	0.6365	0.626	0.307	0.334	1.099	0.867
C ₅	0.8678	0.3112	0.5390	0.614	0.361	0.348	2.087	1.103
C ₆	0.8925	0.2500	0.5069	0.733	0	0.360	0.430	0.890
C ₇	0.8143	0.3457	0.5814	0.775	0.434	0.536	3.069	1.186
C ₈	0.7055	0.2965	0.6696	0.635	0.342	0.293	1.178	0.930

Temperature factors are in Å^2 units.

tion, aqueous KI), $D_c = 1.58 \text{ g}\cdot\text{cm}^{-3}$ for 4 molecules per unit cell. Linear absorption coefficient for Cu $K\alpha$ radiation, $\mu = 90.9 \text{ cm}^{-1}$. The observed systematic absences $0kl$ for $k+l$ odd and $hk0$ for h odd, are consistent with space groups $Pnma$ and $Pn2_1a$.

Determination of the structure

The vanadium atom (found from Patterson projections) is in a special position on a mirror plane in the centrosymmetric space group $Pnma$. This requires the molecule to have mirror symmetry. Fourier syntheses revealed the carbonyl group positions but showed a toroid of electron density for the cyclopentadienyl ring. Suitable positions for the ring atoms were calculated, on the assumption of a regular pentagon of side 1.425 \AA , as found for related structures^{1,2,5}. Various possible arrangements of either a single ring, or a number of staggered rings which preserved mirror symmetry were tested. The best agreement with the observed structure factors

TABLE 2
INTERATOMIC DISTANCES AND BOND ANGLES
"Ring" is taken as the centroid of the 5 atoms.

Bond	Length (Å)	Angle	Size (°)	Angle	Size (°)
V-C ₁	1.88 ± 0.03	C ₁ -V-C ₂	75.3 ± 1.2	C ₄ -C ₃ -C ₄	114 ± 5
V-C ₂	1.94 ± 0.03	C ₁ -V-C ₁	77.1 ± 1.3	C ₃ -C ₄ -C ₅	104 ± 4
V-Ring	1.93 ± 0.007	C ₁ -V-Ring	119.8 ± 0.8	C ₄ -C ₅ -C ₅	109 ± 4
C ₁ -O ₁	1.18 ± 0.03	C ₂ -V-Ring	117.7 ± 0.8		
C ₂ -O ₂	1.12 ± 0.03			C ₇ -C ₆ -C ₇	101 ± 5
		O ₁ -C ₁ -V	176.7 ± 2.5	C ₆ -C ₇ -C ₈	103 ± 5
C ₃ -C ₄	1.48 ^a	O ₂ -C ₂ -V	174.7 ± 2.3	C ₇ -C ₈ -C ₈	116 ± 5
C ₄ -C ₅	1.46 ^a				
C ₅ -C ₅	1.50 ^a	O ₁ -V-Ring	121.0 ± 0.4	C ₁ -V-C ₅	88.6 ± 1.5
		O ₂ -V-Ring	116.5 ± 0.4	C ₂ -V-C ₄	86.2 ± 1.4
C ₆ -C ₇	1.52 ^a			C ₁ -V-C ₇	90.9 ± 1.7
C ₇ -C ₈	1.37 ^a			C ₂ -V-C ₈	108.7 ± 1.5
C ₈ -C ₈	1.14 ^a				

^a These values and their e.s.d.'s are unreliable.

(F_0) was found for two such rings, each with an atom on the mirror plane. A weighting scheme

$$1/W = 1 + (F_0 - p_2)^2 / p_1^2 \quad \text{with } p_1 = p_2 = 27.4$$

was chosen. With F_0 re-scaled in relation to the final calculated values, the R value was 11.6%.

Ring arrangements based on the space group $Pn2_1a$ were also investigated. These attempted refinements gave some negative temperature factors for the ring and chemically unreasonable bond lengths and angles for the $V(\text{CO})_4$ group. Moreover, as this group retained approximate mirror symmetry it could not be refined satisfactorily in the noncentrosymmetric space group^{9,10}. The electron density maps were very similar to those obtained for space group $Pnma$. The structure is therefore described in terms of this space group.

TABLE 3

OBSERVED AND CALCULATED STRUCTURE FACTORS

l	F_0	F_c	l	F_0	F_c	l	F_0	F_c	l	F_0	F_c
$k=0, h=0$			$k=0, h=5$			$k=1, h=4$			$k=2, h=3$		
			1	23	-39	2	35	-41	2	33	33
2	114	115	3	31	-32	3	8	6	3	19	-16
4	119	119	4	22	-18	4	35	-34	4	23	16
6	70	67	5	27	-23	7	13	10	5	14	11
8	37	35	6	26	-24	8	19	-16	6	29	26
			7	27	-25	9	13	18	8	34	33
									10	18	20
$k=0, h=1$			$k=1, h=0$			$k=1, h=5$			$k=2, h=4$		
2	13	6	3	52	49	2	22	27	0	39	51
3	38	40	5	17	-12	6	29	24	1	11	13
4	43	-42	9	28	-25	7	27	-17	2	49	55
5	60	64				8	38	33	3	17	16
6	41	-37	$k=1, h=1$						4	40	36
7	44	43	1	61	-60	$k=2, h=0$			6	30	27
8	32	-29	2	32	-35	2	87	-90	7	32	32
9	15	12	3	29	30	4	44	-42	9	13	18
10	22	-22	4	20	-21	6	76	-69	$k=2, h=5$		
11	12	11	5	22	-20	8	22	-20	1	39	43
12	10	-13	6	24	-21	10	22	-17	3	39	42
$k=0, h=2$			7	23	-21	$k=2, h=1$			5	30	23
2	19	-14	8	32	-29	1	55	-63	7	14	19
3	29	-26	10	20	-20	2	26	-24	$k=3, h=0$		
4	36	37	11	8	-7	3	35	-34	1	48	-48
5	67	-66	12	14	-15	4	12	8	3	92	91
6	8	8	$k=1, h=2$			5	43	-45	5	31	36
7	37	-32	1	50	-60	7	35	-30	7	50	46
8	24	22	2	43	34	8	12	7	9	25	31
9	48	-46	3	31	-26	9	18	-13	11	25	30
11	17	-20	4	24	-23	10	18	15	$k=3, h=1$		
$k=0, h=3$			5	15	-13	$k=2, h=2$			1	80	100
1	19	-24	6	29	-30	0	23	-24	2	8	9
2	43	-43	7	27	-24	1	8	-6	3	74	66
4	15	15	8	20	-16	2	55	-56	4	36	38
5	29	-25	9	19	-17	3	49	42	5	44	51
7	13	-12	$k=1, h=3$			4	38	-33	6	31	32
8	34	-31	1	62	-73	5	25	25	7	21	16
10	17	-18	3	64	-61	6	21	-16	8	27	28
$k=0, h=4$			4	23	16	7	36	31	10	28	28
2	25	-25	5	47	-45	8	13	-13	12	13	20
3	20	19	7	27	-24	9	31	29			
4	55	-52				11	19	23			
6	29	-24									
7	29	-21									
8	19	-20									
9	19	-22									

l	F_0	F_c
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 $k=3, h=2$

0	41	44
1	18	-16
2	84	93
4	37	28
5	20	-16
6	50	46
7	12	10
8	9	7
10	20	16

 $k=3, h=3$

1	42	45
3	55	52
4	25	-22
5	33	36
6	11	-10
7	33	32
8	10	-9
9	26	26

 $k=3, h=4$

1	17	18
2	41	45
4	21	18
6	27	22
7	13	-10
8	16	18

 $k=3, h=5$

1	18	18
3	26	20
6	23	-18

 $k=4, h=0$

0	54	-43
2	54	52
4	31	31
6	39	40
8	7	10
10	27	26
12	18	5

l	F_0	F_c
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 $k=4, h=1$

1	25	25
3	39	37
4	13	-10
5	25	21
7	8	9
9	20	12
10	12	-12

 $k=4, h=2$

0	43	42
1	44	43
2	63	61
3	26	-23
4	21	17
5	15	-11
6	8	12
7	20	-18
8	9	11
9	21	-18
11	17	-23

 $k=4, h=3$

3	12	13
4	30	-32
6	37	-36
8	23	-19
10	20	-19

 $k=4, h=4$

0	26	-26
2	39	-42
3	25	-26
4	19	-16
5	19	-20
6	22	-17
7	27	-25

 $k=4, h=5$

1	23	-24
3	36	-38
5	23	-17
8	19	-7

l	F_0	F_c
-----	-------	-------

 $k=5, h=0$

3	41	-35
5	50	-42
7	20	-16
9	29	-31

 $k=5, h=1$

1	22	-21
2	8	9
3	46	-52
4	30	-30
5	44	-42
6	31	-26
7	15	-15
8	20	-21
9	24	-17
10	28	-28

 $k=5, h=2$

0	56	-65
1	6	9
2	63	-68
4	63	-59
5	27	-22
6	26	-22
7	18	-16
8	25	-18
10	17	-18

 $k=5, h=3$

1	70	-72
3	72	-69
5	47	-39
7	32	-32
9	30	-27

 $k=5, h=4$

0	24	-23
2	39	-40
4	43	-38
5	36	30
6	23	-20
7	19	15
8	19	-21

l	F_0	F_c
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 $k=5, h=5$

3	15	-18
4	29	24
6	27	25

 $k=6, h=0$

0	67	-61
2	44	-41
4	73	-82
6	11	-14

 $k=6, h=1$

1	35	-37
2	23	23
3	38	-44
4	41	38
5	24	-21
6	24	20
8	22	17
9	16	-10
10	16	16

 $k=6, h=2$

0	13	-15
5	36	34
8	16	-16
9	26	24

 $k=6, h=3$

1	19	16
2	17	-16
3	12	8
6	24	18

 $k=6, h=4$

0	11	14
5	23	21
8	13	17

 $k=6, h=5$

3	21	23
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 $k=7, h=0$

1	20	19
5	33	29

l	F_0	F_c	l	F_0	F_c	l	F_0	F_c
$k=7, h=1$			$k=8, h=2$			$k=10, h=1$		
3	22	18	0	18	21	1	30	-38
4	22	15	2	17	18	3	24	-25
5	24	20	5	11	-13	5	25	-28
6	20	15	6	9	14	7	16	-20
7	18	13	$k=8, h=3$			$k=10, h=2$		
8	18	16	8	14	-21	0	19	-21
9	12	18	$k=8, h=4$			2	20	-25
10	18	19	0	20	-24	3	21	18
$k=7, h=2$			2	18	-19	$k=10, h=4$		
0	47	57	4	19	-21	0	30	28
2	30	30	$k=9, h=0$			$k=11, h=0$		
4	43	47	3	26	-24	1	7	4
5	25	26	$k=9, h=1$			$k=11, h=1$		
6	16	12	1	31	-32	1	20	22
8	22	16	2	12	-12	$k=11, h=2$		
$k=7, h=3$			3	20	-16	0	13	23
1	51	58	5	18	-11	$k=11, h=4$		
3	50	51	7	11	-10	0	16	23
5	34	35	$k=9, h=2$			$k=12, h=0$		
7	28	25	0	29	-29	0	40	46
$k=7, h=4$			2	28	-32	2	27	34
0	29	38	$k=9, h=3$			4	21	30
2	29	28	5	17	-26	6	13	20
4	29	33	7	13	-18	$k=12, h=1$		
5	30	-29	$k=9, h=4$			1	22	25
8	17	15	2	13	-18	$k=10, h=0$		
$k=8, h=0$			$k=9, h=3$			$k=10, h=0$		
0	53	55	5	17	-26	0	41	-42
2	45	43	7	13	-18	2	41	-41
4	40	42	$k=9, h=4$			4	19	-17
6	28	30	2	13	-18	6	35	-35
8	20	26	$k=10, h=0$			$k=10, h=0$		
$k=8, h=1$			0	41	-42	$k=10, h=0$		
1	39	44	2	41	-41	$k=10, h=0$		
3	33	36	4	19	-17	$k=10, h=0$		
4	17	-12	6	35	-35	$k=10, h=0$		
5	26	29	$k=10, h=0$			$k=10, h=0$		
7	20	17	$k=10, h=0$			$k=10, h=0$		
8	19	-18	$k=10, h=0$			$k=10, h=0$		

DISCUSSION

Determination of this crystal structure was rendered difficult for two reasons. Decomposition of the crystals under X-rays resulted in lower quality data than desired for a very accurate structure determination. The space group was not uniquely determined from the systematic absences and could not be selected by consideration of a known molecular symmetry. Moreover, intensity statistics⁷ cannot be used for each of the reasons given by Sim⁸.

The structure is shown in Fig. 1. It consists of discrete molecules with all

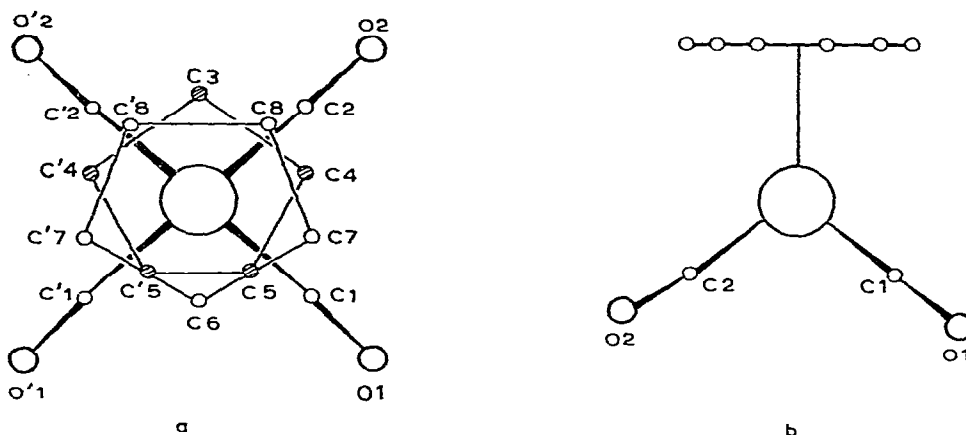


Fig. 1. Two projections of $(\pi\text{-C}_5\text{H}_5)\text{V}(\text{CO})_4$ with respect to the plane of the cyclopentadienyl ring.

intermolecular distances greater than 3.3 \AA . The cyclopentadienyl ring is disordered, having two possible orientations with respect to the carbonyl groups, as shown in Fig. 1(a). In Fig. 1(b) some of the atoms overlap. Unless there is some form of free rotation of part of the molecule, the carbonyl groups cannot have an environment in which they interact equally with each of the ring atoms. This might lead to distortion of the ring from its normal symmetry or of the carbonyl groups from four-fold symmetry. If this occurs, the deviations would be in opposite directions for the two ring orientations. Hence in the structure as determined, the carbonyl groups would also be disordered or ill-defined. However, these atoms could be located reliably, and if this type of distortion occurs it is very small.

Bond angles found are similar to those reported for the isomorphous complex $(\pi\text{-C}_5\text{H}_5)\text{Nb}(\text{CO})_4$ by Doedens and Dahl⁶, who mention it in view of a relationship to the geometry of another molecule. It was not disordered but no other details were given and no further comparisons can be made. In the vanadium complex, the two ring positions are equally occupied; a similar disorder was reported¹¹ for $(\pi\text{-C}_5\text{H}_5)\text{-Cr}(\text{NO})_2\text{Cl}$.

Disordering of cyclopentadienyl rings in crystal structures is common¹⁴. Even for ordered structures there is considerable libration of the ring in its plane^{1,2}, as found for ferrocene². Molecular orbital theory suggests a low energy barrier to rotation of the rings¹². This has recently been estimated¹³ to be 1.1 kcal per mole.

The molecular structure found is closely related⁵ to that of $(\pi\text{-C}_5\text{H}_5)\text{V}(\pi\text{-C}_7\text{H}_7)$. The space group was chosen as $Pnma$ and the vanadium atoms were located

on mirror planes. Disorder of the rings was not investigated but the high R value (18.6% on 969 reflections) suggests that either disorder or considerable libration occurs.

As a result of the disorder in the present compound, it was not possible to obtain accurate bond lengths between ring atoms (Table 2). However, the carbon atoms deviate by less than 0.05 Å from their least-squares best plane, which is well defined. The distance from the ring centroid to the vanadium atom (1.930 ± 0.007 Å) agrees with that reported⁵ for $(\pi\text{-C}_5\text{H}_5)\text{V}(\pi\text{-C}_7\text{H}_7)$. It is longer than found for other π -cyclopentadienyl complexes of the first row transition metals¹⁴, probably because the applicable covalent radius of the vanadium atom is greater than that of its neighbours in the row.

Two crystallographically independent carbonyl groups are present in the molecule. The mean metal carbonyl bond length (1.90 ± 0.03 Å) is slightly longer than found for $(\pi\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$ (1.80 ± 0.01 Å)¹ or $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ (1.75 Å)⁴. The mean carbonyl bond length (1.15 ± 0.03 Å) agrees well with other reported values^{1,3,4,15}. The carbonyl groups deviate from linearity by approximately 5°, as found for other carbonyls¹⁵. This is an expected result of the two non-equivalent π^* anti-bonding orbitals of terminal carbonyl groups, as discussed by Kettle¹⁶. The carbonyl groups are bent in opposite ways with respect to the ring, probably as a result of intermolecular packing considerations. The angles that the M–C(O) axes make with each other (76°) are comparable with the smallest angle that they make with a V–C (ring) atom (86°), suggesting that these are determined largely by steric factors¹⁵.

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SUMMARY

The crystal structure of $(\pi\text{-C}_5\text{H}_5)\text{V}(\text{CO})_4$ has been found from a 3-dimensional X-ray analysis. The orange crystals are orthorhombic, space group $Pnma$, with the vanadium atom occupying a special position on a mirror plane. The cyclopentadienyl ring was disordered over two equally preferred orientations. The vanadium atom and carbonyl groups are ordered. Bond lengths are compared with related structures.

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