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# CRYSTAL AND MOLECULAR STRUCTURE AND PROPERTIES OF TETRAMESITYLVANADIUM

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## Summary

The crystal and molecular structure of tetramesitylvanadium has been determined by three-dimensional X-ray analysis. Its space group is $P2_1/c$ with the unit cell constants $a = 12.177$; $b = 19.158$; $c = 15.513$ Å; $\beta = 122.96°$. The experimental density of 1.15 g cm$^{-3}$ is in agreement with the calculated one with four molecules per unit cell. To determine the structure, Patterson and Fourier methods were used. The anisotropic least-squares refinement provided an $R$-factor of 0.061. The molecule has a distorted tetrahedral structure. The smallest C—V—C angle is 96.41°, the highest is 117.81°. The corresponding smallest and highest V—C distances are 2.071 and 2.095 Å, and the average value is 2.076 Å. The magnetic susceptibility in dependence upon temperature (95—285 K) and the spectral data were measured.

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## Introduction

Studies of the structures and resulting bonding parameters may provide useful hints for the behaviour of organometallic compounds of transition elements. In this respect little data on vanadium complexes is available. This holds especially true for compounds which have only σ-bound organyl ligands. Obviously, the structure of the V—C σ-bond in alkyl- or aryl-vanadium compounds has not been studied yet [1] although a number of stable vanadium(IV) complexes exist which have only σ-C-bound ligands [2—8]. A distorted tetrahedral structure resulted from ESR spectroscopic data for $V(CH_2Ph)_4$ [2] and for V(1-norb)$_4$ [6]. Via the synthesis of $LiV(C_9H_{11})_4$ [9] tetramesitylvanadium is obtained [10] which is especially suitable for studying its properties because of its stability. The results of an X-ray analysis of the structure, the spectral behaviour, and temperature-dependent magnetic measurements are reported in this paper.

TABLE 1

FINAL POSITIONAL PARAMETERS WITH ESD IN PARENTHESES

| | $x$ | $y$ | $z$ | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| V | 0,1298(1) | 0,1464(1) | 0,2638(1) | 3,48(6) | 2,47(5) | 2,74(5) | −0,21(5) | 1,54(4) | −0,03(5) |
| C(1) | 0,2819(6) | 0,2129(3) | 0.3667(5) | 3,35(37) | 3,81(38) | 2,93(34) | −1,06(30) | 1,72(30) | −0,23(28) |
| C(2) | 0,3803(7) | 0,1848(4) | 0,4633(5) | 3,71(40) | 4,36(38) | 2,98(36) | −0,27(34) | 1,88(33) | 0,22(32) |
| C(3) | 0,3803(7) | 0,1081(4) | 0,4889(5) | 4,88(42) | 4,89(42) | 3,17(34) | −0,32(34) | 1,15(31) | 0,78(31) |
| C(4) | 0,4802(7) | 0,2256(4) | 0,5377(5) | 3,74(41) | 5,41(45) | 3,09(35) | −0.40(35) | 1,73(32) | −0,17(34) |
| C(5) | 0,4881(7) | 0,2966(4) | 0,5216(5) | 4,34(43) | 5,51(47) | 3,70(40) | −1,29(38) | 2,71(35) | −1,81(37) |
| C(6) | 0,6005(7) | 0,3393(4) | 0,6031(5) | 5,52(44) | 6,15(47) | 5,10(40) | −1,62(38) | 2,71(36) | −2,05(36) |
| C(7) | 0,3945(7) | 0,3236(3) | 0,4284(6) | 5,34(44) | 3,77(37) | 4.04(39) | −1,56(34) | 2,92(37) | −0,71(32) |
| C(8) | 0,2931(6) | 0,2846(4) | 0,3506(5) | 4,39(42) | 3,71(38) | 3,33(36) | −0,89(33) | 2,07(33) | −0,03(32) |
| C(9) | 0,2030(7) | 0,3222(3) | 0,2511(5) | 7,99(51) | 3,38(36) | 4,36(39) | −1,22(34) | 2,99(38) | 0,04(31) |
| C(10) | 0,0179(6) | 0,1051(3) | 0,3152(5) | 3,48(37) | 2,74(33) | 3,80(35) | −0,26(29) | 2,12(31) | −0,00(28) |
| C(11) | −0,0753(7) | 0,0537(3) | 0,2539(5) | 4,60(43) | 2,45(34) | 4,59(40) | 0,03(31) | 2,83(36) | 0,29(30) |
| C(12) | −0,0956(7) | 0,0274(3) | 0,1536(5) | 5,82(45) | 3,92(39) | 4,62(40) | −1,38(34) | 2,57(35) | −1,58(32) |
| C(13) | −0,1592(7) | 0,0255(3) | 0,2796(6) | 4,45(44) | 3,18(36) | 5,03(43) | −0,07(32) | 2,38(37) | 0,50(33) |
| C(14) | −0,1518(7) | 0,0457(4) | 0,3685(6) | 4,55(47) | 4,21(43) | 6,04(49) | 0,05(36) | 3,17(42) | 1,50(38) |
| C(15) | −0,2405(8) | 0,0149(4) | 0,3984(6) | 8,19(58) | 6,46(51) | 7,84(54) | −0,47(44) | 5,62(49) | 0,88(41) |
| C(16) | −0,0608(8) | 0,0959(4) | 0,4293(5) | 4,96(45) | 5,18(43) | 3,65(37) | 0,41(37) | 3,08(36) | 0,62(33) |
| C(17) | 0,0218(7) | 0,1262(3) | 0,4049(5) | 4,34(40) | 3,40(38) | 3,50(36) | 0,37(31) | 2,26(33) | 0,03(29) |
| C(18) | 0,1137(7) | 0,1818(4) | 0,4785(5) | 5,57(43) | 5,47(40) | 3,32(34) | −0,09(35) | 2,72(33) | −0,60(32) |
| C(19) | 0,2419(6) | 0,0761(3) | 0,2423(5) | 3,38(38) | 3,38(50) | 2,98(33) | 0,83(31) | 1,45(30) | 0,06(30) |
| C(20) | 0,2973(7) | 0,1022(4) | 0,1887(5) | 3,49(41) | 5,57(45) | 3,39(37) | −0,12(36) | 1,75(32) | −0,26(34) |
| C(21) | 0,2869(7) | 0,1782(4) | 0,1590(5) | 4,33(43) | 6,77(47) | 4,31(39) | −0,36(36) | 2,77(35) | 1,23(35) |
| C(22) | 0,3626(7) | 0,0571(5) | 0,1597(6) | 3,80(44) | 7,92(57) | 5,26(45) | −0,39(42) | 3,22(37) | −0,84(42) |
| C(23) | 0,3768(8) | −0,0125(5) | 0,1847(7) | 4,10(48) | 7,64(63) | 5,35(49) | 0,58(45) | 2,16(38) | −2,20(47) |
| C(24) | 0,4439(8) | −0,0604(5) | 0,1495(7) | 8,25(62) | 9,02(61) | 10,30(63) | 0,56(49) | 5,83(54) | −3,78(51) |
| C(25) | 0,3297(8) | −0,0373(4) | 0,2404(6) | 4,20(47) | 4,27(42) | 5,23(46) | 0,94(35) | 1,56(38) | −1,35(35) |
| C(26) | 0,2609(7) | 0,0049(4) | 0.2090(5) | 3.70(41— | 4,08(42) | 3,70(27) | 0.44(34) | 1.41(32) | 0,19(32) |
| C(27) | 0,2165(8) | −0,0304(3) | 0,3222(6) | 7,58(53) | 2,69(35) | 6,44(46) | 0,75(35) | 3,42(43) | 0,28(34) |
| C(28) | −0,0246(6) | 0,1893(3) | 0,1294(5) | 3,39(36) | 2,91(34) | 2.74(34) | −0,69(29) | 1,34(29) | −0,39(27) |
| C(29) | −0,0723(6) | 0,1601(3) | 0,0266(5) | 3,14(38) | 3,55(38) | 3,80(37) | −0,45(29) | 1,92(32) | 0,01(30) |
| C(30) | −0,0160(7) | 0,1118(4) | −0,0042(5) | 5,20(43) | 6,10(44) | 3,76(35) | −0,18(35) | 2,33(33) | −1,19(32) |
| C(31) | −1,1817(7) | 0,2026(4) | −0,0551(5) | 4,15(44) | 5,61(45) | 2,63(35) | −0,61(37) | 1,60(34) | 0,28(34) |
| C(32) | −0,2479(7) | 0,2552(4) | −0,0423(6) | 4,25(44) | 4,81(44) | 4,03(42) | −0,39(36) | 1,89(36) | 1,47(37) |
| C(33) | −0,3682(7) | 0,2889(4) | −0,1320(5) | 6,19(50) | 7,74(53) | 4,09(40) | 1,48(43) | 1,62(38) | 1,35(38) |
| C(34) | −0,2031(7) | 0,2748(3) | 0,0582(6) | 4,09(42) | 3,57(37) | 4,73(41) | 0,41(32) | 2,28(38) | 0,52(34) |
| C(35) | −0,0940(7) | 0,2436(3) | 0,1426(5) | 3,69(39) | 2,98(36) | 3,58(47) | −0,16(31) | 1,72(33) | 0,00(30) |
| C(36) | −0,0586(7) | 0,2677(4) | 0,2475(5) | 6,11(45) | 3,55(37) | 4,41(38) | 1,42(33) | 2,64(35) | 0,26(31) |

## Experimental

The organometallic compound under investigation crystallizes in the shape of distorted rhombohedra from concentrated benzene solution. Cu-$K_\alpha$ radiation with ($\lambda$ = 1.5418 Å) and a crystal of the size 0.18 × 0.18 × 0.20 mm were used.

Crystal data: V(mesityl)$_4$; mol. wt. 527.69, monoclinic, space group $P2_1/c$, $a$ = 12.177(3), $b$ = 19.198(3), $c$ = 15.513(3) Å, $\beta$ = 122.96(5)°, $V$ = 3042.0 Å$^3$, $\mu$ = 30.3 cm$^{-1}$. The experimental density which was determined by flotation is $d_m$ = 1.15 g cm$^{-3}$ and is in agreement with the calculated one, $d_c$ = 1.15 g cm$^{-3}$,

TABLE 2

FINAL POSITIONAL HYDROGEN ATOMS

| | $x$ | $y$ | $z$ | $B$ |
|---|---|---|---|---|
| H(1) | 0.427 | 0.102 | 0.565 | 4.8 |
| H(2) | 0.429 | 0.082 | 0.462 | 4.8 |
| H(3) | 0.293 | 0.089 | 0.450 | 4.8 |
| H(4) | 0.551 | 0.204 | 0.608 | 4.8 |
| H(5) | 0.667 | 0.310 | 0.667 | 4.8 |
| H(6) | 0.564 | 0.379 | 0.621 | 4.8 |
| H(7) | 0.646 | 0.361 | 0.571 | 4.8 |
| H(8) | 0.401 | 0.376 | 0.414 | 4.8 |
| H(9) | 0.136 | 0.289 | 0.198 | 4.8 |
| H(10) | 0.254 | 0.341 | 0.226 | 4.8 |
| H(11) | 0.158 | 0.359 | 0.263 | 4.8 |
| H(12) | −0.147 | −0.017 | 0.117 | 4.8 |
| H(13) | −0.004 | 0.022 | 0.167 | 4.8 |
| H(14) | −0.135 | 0.067 | 0.102 | 4.8 |
| H(15) | −0.229 | −0.012 | 0.232 | 4.8 |
| H(16) | −0.221 | 0.030 | 0.466 | 4.8 |
| H(17) | −0.243 | −0.036 | 0.388 | 4.8 |
| H(18) | −0.335 | 0.032 | 0.340 | 4.8 |
| H(19) | −0.057 | 0.112 | 0.496 | 4.8 |
| H(20) | 0.121 | 0.219 | 0.437 | 4.8 |
| H(21) | 0.201 | 0.162 | 0.522 | 4.8 |
| H(22) | 0.076 | 0.198 | 0.518 | 4.8 |
| H(23) | 0.201 | 0.197 | 0.152 | 4.8 |
| H(24) | 0.362 | 0.204 | 0.219 | 4.8 |
| H(25) | 0.276 | 0.185 | 0.096 | 4.8 |
| H(26) | 0.400 | 0.078 | 0.117 | 4.8 |
| H(27) | 0.384 | −0.094 | 0.093 | 4.8 |
| H(28) | 0.517 | −0.089 | 0.206 | 4.8 |
| H(29) | 0.489 | −0.033 | 0.119 | 4.8 |
| H(30) | 0.345 | −0.089 | 0.264 | 4.8 |
| H(31) | 0.169 | −0.074 | 0.293 | 4.8 |
| H(32) | 0.296 | −0.042 | 0.401 | 4.8 |
| H(33) | 0.155 | −0.001 | 0.335 | 4.8 |
| H(34) | −0.035 | 0.065 | 0.013 | 4.8 |
| H(35) | 0.084 | 0.114 | 0.033 | 4.8 |
| H(36) | −0.052 | 0.111 | −0.081 | 4.8 |
| H(37) | −0.214 | 0.185 | −0.130 | 4.8 |
| H(38) | −0.429 | 0.250 | −0.178 | 4.8 |
| H(39) | −0.409 | 0.322 | −0.107 | 4.8 |
| H(40) | −0.340 | 0.313 | −0.177 | 4.8 |
| H(41) | −0.251 | 0.315 | 0.071 | 4.8 |
| H(42) | 0.039 | 0.252 | 0.300 | 4.8 |
| H(43) | −0.067 | 0.320 | 0.248 | 4.8 |
| H(44) | −0.112 | 0.241 | 0.269 | 4.8 |

$Z = 4$. The measurements were carried out with a four-circle Syntex P2 diffractometer equipped with a scintillation counter and a graphite monochromator. The parameters of the unit cell were refinement by means of the least-squares method. The intensities of 3063 reflections were measured with the help of the $\theta$—$2\theta$ scan method. 2354 reflections with $F > 3.92\ \sigma(F)$ were used for further calculations. Corrections for Lorentz and polarisation effects were carried out, but not for the absorption.

The coordinates of the vanadium atom were derived from the three-dimensional Patterson function. The coordinations of all carbon atoms were calculated by two successive three-dimensional Fourier syntheses. The full-matrix least-squares refinement excluded the hydrogen atoms, but the assigned individual anisotropic thermal parameters of all the other atoms provides a conventional $R_c$ of 0.96 and a weighted $R_w$ of 0.092.

Positions (atomic coordinates) of most hydrogen atoms were found in two successive difference Fourier syntheses and positions of other hydrogen atoms were introduced by the geometrical methods, using the HPOSN programme.

Final refinement by the full-matrix method of least squares with all hydrogen atoms and isotropic temperature factors (4.8) allowed for enabled us to determine the final values of conventional $R_c$ and weighted $R_w$ to be 0.061 and 0.060, respectively. The parameters obtained from the final refinement are presented in Tables 1 and 2 together with their standard estimated deviations. All calculations were performed with the Syntex XTL Structure Determination System.

The magnetic susceptibilities were measured by means of the Gouy method in the temperature range 80—300 K. The electron spectra of chloroform solutions were taken with the help of a Unicam SP 700 and a Cary 14 spectrophotometer.

## Discussion

Fig. 1 shows the structure which results from the X-ray investigations. The atom distances and the valence angles are summarized in Tables 3 and 4. C—H distances vary from 0.92 and 1.09 Å and the angles correspond to the values predicted by the bond geometry. The central atom has approximately a tetrahedral coordination, which was already suggested from different data [2,6] and the electron spectrum [10]; The vanadium—carbon bond distances vary only slightly from 2.071(6) to 2.095(7) Å, and the average value is 2.076 Å whereas the C—V—C valence angles considerably deviate from the ideal tetrahedral angle. The distortion may be explained as due to stretching of the molecule along an "$S_4$"-axis. The two angles which are decreased by this stretching are 97.67 and 96.41°, whereas the others are in the range from 114.45—117.81°. This phenomenon which may be due to various reasons is frequently observed in similar organometallic compounds of transition elements with the coordination number four.

In the case of the tetrabenzyls of titanium [11] and zirconium [12] this deformation is related to the interaction of the $C_\beta$-atoms with the central atoms. The compounds $Cr(CH_2CPhMe_2)_4$ [13] and $LiLu(2,6\text{-}Me_2C_6H_3)_4$ [14] are well comparable to tetramesitylvanadium and the Jahn—Teller effect is to be excluded from the first two compounds. The analogous deviation of the valence angles

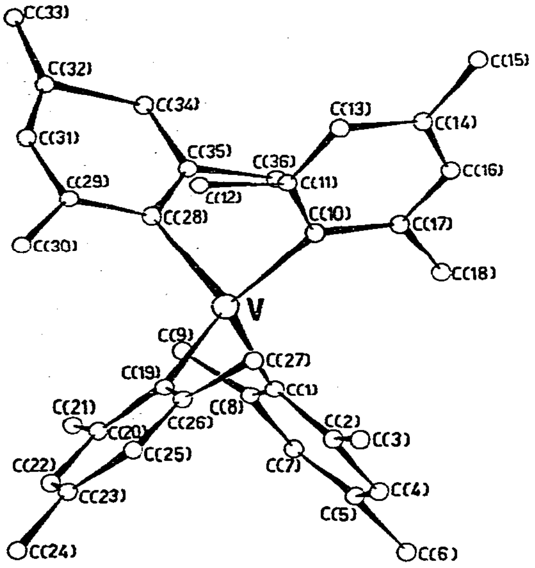

*Fig. 1. Structure of V(mesityl)$_4$.*

is found in both the former compounds regardless of the different sizes of the central atoms. However, the deviation in the chromium(IV) complex is not so eivdent as in the lutetium complex [4]. Thus, is the first place, steric hindrance of the ligands and packing effects must be responsible for the disturbed symmetry. In addition studies on a model show that steric hindrance of the $CH_3$ groups excludes ideal tetrahedral symmetry. The distances between the metal and carbon atoms in δ-organometallic compounds of transition elements are

TABLE 3

INTERATOMIC DISTANCES (Å)

| | | | |
|---|---|---|---|
| V—C(1) | 2.095(7) | V—C(19) | 2.071(8) |
| V—C(10) | 2.075(8) | V—C(28) | 2.073(6) |
| C(1)—C(2) | 1.420(9) | C(19)—C(20) | 1.416(12) |
| C(2)—C(3) | 1.524(10) | C(20)—C(21) | 1.515(11) |
| C(2)—C(4) | 1.378(10) | C(20)—C(22) | 1.393(13) |
| C(4)—C(5) | 1.398(11) | C(22)—C(23) | 1.395(14) |
| C(5)—C(6) | 1.504(11) | C(23)—C(24) | 1.514(15) |
| C(5)—C(7) | 1.365(11) | C(23)—C(25) | 1.358(14) |
| C(7)—C(8) | 1.387(10) | C(25)—C(26) | 1.400(13) |
| C(8)—C(9) | 1.504(9) | C(26)—C(27) | 1.513(12) |
| C(8)—C(1) | 1.419(9) | C(26)—C(19) | 1.410(10) |
| C(10)—C(11) | 1.410(10) | C(28)—C(29) | 1.423(9) |
| C(11)—C(12) | 1.521(10) | C(29)—C(30) | 1.505(11) |
| C(11)—C(13) | 1.394(13) | C(29)—C(31) | 1.400(10) |
| C(13)—C(14) | 1.387(12) | C(31)—C(32) | 1.372(12) |
| C(14)—C(15) | 1.508(14) | C(32)—C(33) | 1.511(11) |
| C(14)—C(16) | 1.383(11) | C(32)—C(34) | 1.394(11) |
| C(16)—C(17) | 1.380(13) | C(34)—C(35) | 1.394(10) |
| C(17)—C(18) | 1.519(10) | C(35)—C(36) | 1.511(9) |
| C(17)—C(10) | 1.425(10) | C(35)—C(28) | 1.425(11) |

TABLE 4

BOND ANGLES (°)

| | | | |
|---|---|---|---|
| C(1)—V—C(10) | 115.66(28) | C(10)—V—C(19) | 116.16(28) |
| C(1)—V—C(19) | 97.67(28) | C(10)—V—C(28) | 96.41(28) |
| C(1)—V—C(28) | 117.81(27) | C(19)—V—C(28) | 114.45(28) |
| V—C(1)—C(2) | 117.44(30) | V—C(19)—C(20) | 115.46(30) |
| C(1)—C(2)—C(3) | 121.4(7) | C(19)—C(20)—C(21) | 122.1(7) |
| C(1)—C(2)—C(4) | 121.4(7) | C(19)—C(20)—C(22) | 120.9(7) |
| C(3)—C(2)—C(4) | 117.1(7) | C(21)—C(20)—C(22) | 117.0(7) |
| C(2)—C(4)—C(5) | 121.3(7) | C(20)—C(22)—C(23) | 120.5(8) |
| C(4)—C(5)—C(6) | 120.0(7) | C(22)—C(23)—C(24) | 120.0(9) |
| C(4)—C(5)—C(7) | 117.4(7) | C(22)—C(23)—C(25) | 119.0(9) |
| C(6)—C(5)—C(7) | 122.5(7) | C(24)—C(23)—C(25) | 121.0(9) |
| C(5)—C(7)—C(8) | 123.5(8) | C(23)—C(25)—C(26) | 122.2(8) |
| C(7)—C(8)—C(9) | 124.1(7) | C(25)—C(26)—C(27) | 124.4(7) |
| C(7)—C(8)—C(9) | 119.7(7) | C(25)—C(26)—C(19) | 119.9(7) |
| C(9)—C(80—C(1) | 116.2(7) | C(27)—C(26)—C(19) | 115.6(7) |
| C(8)—C(1)—C(2) | 116.6(6) | C(26)—C(19)—C(20) | 117.4(7) |
| C(8)—C(1)—V | 125.93(30) | C(26)—C(19)—V | 126.96(30) |
| V—C(10)—C(11) | 117.63(30) | V—C(28)—C(29) | 127.32(30) |
| C(10)—C(11)—C(12) | 123.1(7) | C(28)—C(29)—C(30) | 125.3(7) |
| C(10)—C(11)—C(13) | 121.6(7) | C(28)—C(29)—C(31) | 119.8(7) |
| C(12)—C(11)—C(13) | 115.3(7) | C(30)—C(29)—C(31) | 115.0(7) |
| C(11)—C(13)—C(14) | 121.0(7) | C(29)—C(31)—C(32) | 123.5(7) |
| C(13)—C(14)—C(15) | 121.7(8) | C(31)—C(32)—C(33) | 122.2(7) |
| C(13)—C(14)—C(16) | 117.9(8) | C(31)—C(32)—C(34) | 117.2(8) |
| C(15)—C(14)—C(16) | 120.4(8) | C(33)—C(32)—C(34) | 120.6(7) |
| C(14)—C(16)—C(17) | 122.7(8) | C(32)—C(33)—C(35) | 121.8(7) |
| C(16)—C(17)—C(18) | 123.6(7) | C(34)—C(35)—C(36) | 122.2(6) |
| C(16)—C(17)—C(10) | 120.4(7) | C(34)—C(35)—C(28) | 121.1(7) |
| C(18)—C(17)—C(10) | 116.0(7) | C(36)—C(35)—C(28) | 116.6(7) |
| C(17)—C(10)—C(11) | 116.4(7) | C(35)—C(28)—C(29) | 116.6(6) |
| C(17)—C(10)—V | 125.93(30) | C(35)—C(28)—V | 115.55(30) |

dependent on various factors. Organotitanium complexes have a vast range of Ti—C distances [1], whereas for example $CrR_2(dipy)_2^+$ cations have the same distances for the Cr—C(alkyl) and Cr—C(aryl) bonds [15]. In addition a decrease of the average M—C distances can be expected in the series of 3*d*-elements from titanium towards nickel [1]. The average V—C distance in tetramesitylvanadium of 2.08 Å fits well into the range (av. Cr—C: 2.05 Å [13]; Ti—C 2.156 Å [1]). The C—C distances in the aryl rings of the investigated compound average 1.397 Å (1.358—1.425). The bond lengths between the C atoms of the methyl substituents and the corresponding ring atoms are characteristic of single bonds (average values 1.512 Å). The bond angles, too, do not differ considerably from each other within the rings. This also holds true for the ring valence angle at the metal-binding C atom which differs considerably from the other ones (112.1°) in the case of the complex $Co(C_9H_{11})_2 \cdot (PEt_2Ph)_2$ [16]. However, it is evident that the angles between the V—C—C atoms differ to a greater extent. Thus the line from C (found with vanadium) to C(*para*) does not cross through the V-atom.

The methyl groups are closely packed. Therefore they essentially contribute to the screening of the central atom. In this way the relative chemical inertness of tetramesitylvanadium can be explained.

The magnetic behaviour was studied in the range 90—285 K. It had already

TABLE 5

MAGNETIC PROPERTIES OF V(mesityl)$_4$ ($\theta$ = +5°K)

| Temp. (K) | $\chi_{mol}$ corr. | $\mu_{eff.}$ (BM) |
|---|---|---|
| 77 | 4673.44 | 1.65 |
| 98 | 3961.16 | 1.72 |
| 111 | 3343.50 | 1.69 |
| 124 | 3090.37 | 1.72 |
| 138 | 2662.94 | 1.69 |
| 151 | 2567.95 | 1.74 |
| 164 | 2378.00 | 1.75 |
| 177 | 2161.63 | 1.73 |
| 190 | 1913.67 | 1.69 |
| 203 | 1887.23 | 1.74 |
| 229 | 1707.82 | 1.76 |
| 245 | 1581.70 | 1.75 |
| 260 | 1517.88 | 1.77 |
| 272 | 1474.32 | 1.78 |
| 285 | 1422.87 | 1.79 |
| 297 | 1343.72 | 1.78 |

been investigated at room temperature and clearly shown vanadium(IV) [10]. The susceptibilities and the effective moments are summarized in Table 5. The deviation of the moments from the spin value (1.75 BM) is essentially due to crystal effects. The susceptibilities are in accordance with the Curie—Weiss law; for $\theta$ = 5 K the magnetic moment of 1.76 BM results.

The electron spectrum ($CHCl_3$ solution) indicates four transitions at: 23870 cm$^{-1}$ (I; $\epsilon_{mol}$ = 8440); 21480 cm$^{-1}$ (II; 5660); 18350 cm$^{-1}$ (III; 6650); 13370 cm$^{-1}$ (IV; 254). The values of the extinction coefficients make it evident that I, II, and III are assigned to CT-transitions. IV should represent a *d-d* band according to $^2E \rightarrow {}^2T_2$. The ratio of the $\Delta(V^{IV})$ value (13370 cm$^{-1}$) to the value of $\Delta(V^{III})$ (9400 cm$^{-1}$) [9] estimated for the anion $V(C_9H_{11})_4^-$ is 1.42. This ratio is not only to be expected from the different oxidation states but corresponds also with the ratio of the corresponding chloro derivatives $VCl_4$ ($\Delta(V^{IV})$ = 7900 cm$^{-1}$) [18] and $VCl_4^-$ ($\Delta(V^{III})$ = 5520 cm$^{-1}$) [17] which is 1.43.

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