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Review

VANADIUM ORGANOMETALLIC COMPOUNDS: ANALYSIS AND CLASSIFICATION OF CRYSTALLOGRAPHIC DATA

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CONTENTS

1. INTRODUCTION 43
2. VANADIUM ORGANOMETALLICS WITH UNIDENTATE CARBON LIGANDS 43
3. VANADIUM ORGANOMETALLICS WITH A MULTIDENTATE CARBON LIGAND 51
    A. Mononuclear Compounds With One Multidentate Carbon Ligand 51
    B. Mononuclear Compound With Two Multidentate Carbon Ligands 58
    C. Homo-Oligonuclear Compounds 67
    D. Hetero-Oligonuclear Compounds 74
4. CONCLUSIONS 77
5. REFERENCES 80

ABBREVIATIONS

As_2Ph_4	bis(diphenylarsine)
Cab	carborane, $Et_2C_2B_4H_4^{2-}$
CH_2O	oxymethylene
$CH_3C_3H_4$	3-methyl-allyl
C_3H_5	allyl
C_4H_3OCOO	furancarboxylate
C_5H_5BMe	1-methyl-boranobenzene
C_7H_7	cycloheptatrienyl
$C_{10}H_8$	fulvalene
CNC_6H_{11}	cyclohexylisocyanide
CN-t-Bu	tert-butyl-isocyanide
Cot	cyclooctatetraene

cp	cyclopentadienyl
cp*	pentamethylcyclopentadienyl
cp*Et	tetramethylethylcyclopentadienyl
cpMe	methylcyclopentadienyl
cpPr	iso-propylcyclopentadienyl
C_4Ph_4	tetraphenylcyclobutadiene
CSCBu	t-butylthioketene
$CSCR_2$	$R = CH(CH_2.C(CH_3)_3)_2$
def	diethylfumarate
dma	dimethylacetylenedicarboxylate
dpdae	1-diphenyl phosphino-2-diphenylarsinoethane
dppe	1,2-bis(diphenylphosphino)ethylene
Et	ethyl
L(ax)	axial ligand
L(eq)	equatorial ligand
m	monoclinic
ma	mesitylacetylide
Me	methyl
$Me_4H_2C_6$	1,2,4,5 -tetramethylbenzene
mes	mesityl
NPh	phenylimide
$N(PPh_3)_2$	bis(triphenylphosphine)iminium
$NSiMe_3$	trimethylsilylnitrene
$N_2(SiMe_3)_2$	(trimethylsilyl)isodiazene
$OCMe_2$	acetone
OC_2Ph_2	diphenylketene
or	orthorhombic
pdma	O-phenylenebis(dimethylarsine)
Ph	phenyl
ptd	4-phenyl-1,2,4-triazoline-3,5-dione
rb	rhombohedral
rh	rhombic
$SCPh_2$	thiobenzophenone
SPh	phenylsulphide
tcd	p-tolylcarbodiimide
tcdm	p-tolylcarbodiimide-N-methyl
TCNE	tetracyanoethylene
thf	tetrahydrofuran
tppb	1,1,4,4-tetraphenyl-1,4-diphosphabutane
tppe	bis(diphenylphosphinethane)phenyl-phosphine
tr	triclinic

1. INTRODUCTION

The rapid growth of transition metal organometallic chemistry since the 1950's has been remarkable. Many new classes of compounds have been prepared and numerous examples of new chemical reactions have been discovered. This has also led to the development of new methods in organic synthesis, and to a better understanding of catalytic processes. During the past few years there have been several developments in the theoretical aspects of structure and bonding which have promoted a better understanding of the nature of organometallic molecules.

The chemistry of the group VB organometallics has been an active field of study for some time, covering aspects of bonding and catalytic activity, and the number of determined crystal structures have increased rapidly. The available structural information for tantalum and niobium derivatives has already been presented (ref.1), and this review presents the structural data for vanadium organometallics. The material contained in this review has been obtained from published literature up to at least the end of 1984, or volume 101 of Chemical Abstracts. The activity and interest in the area is evident from the appearance of several new structures during the few months that this manuscript was in preparation, many of which have been included.

The aim of the review is to provide the first overall survey and classification of the structures for vanadium, and to compare and contrast the known structures of niobium and tantalum (ref.1a). A review of the coordination complexes of vanadium is concurrently in preparation, and is a sequel to the corresponding reviews of niobium and tantalum coordination complexes (ref.1b). In both the coordination and organometallic chemistries of these three elements the number of examples increases from tantalum to vanadium. The systems to be discussed here can be largely grouped into two classes, those containing only carbon σ-donor ligands, and those containing at least one aromatic multidentate ligand.

2. VANADIUM ORGANOMETALLICS WITH UNIDENTATE CARBON LIGANDS

The crystal and structural data for vanadium compounds in which the organic moiety is bonded by a unidentate carbon σ-donor atom are given in Table 1. The data has been arranged so that the structures are in increasing order of coordination number, increasing atomic number of the principal coordinating ligand, and increasing order of complexity of the coordination sphere.

The data in Table 1 show that the vanadium coordination number ranges from four to eight, and the nuclearity of the molecules includes mono- and binuclear, and larger clusters. The vanadium(IV) atom in $V(mes)_4$ (ref.2), as well as the vanadium(III) atom in $V(mes)_3(thf)$ (ref.3), has approximately tetrahedral coordination. The environment about the vanadium consists of four unidentate mesityl ligands with V–C bond distances ranging from 207.1(6) to 209.5(7)pm. The C–V–C angles vary from 96.41(28)° to 117.81(27)° which demonstrates the considerable deviation from an ideal tetrahedron. The distortion may be discussed in terms of a stretching along an "S" axis. It is noteworthy that the V–C bond distances for $V(mes)_3(thf)$ are larger, at 209.9(6) to 211.6(7)pm, indicating a tendency for elongation of the bond lengths with decreasing oxidation number of the central atom. These are the only two examples to date where the vanadium atom has a coordination number of four.

In all the other examples in Table 1 at least one of the ligands is carbonyl, CO. Vanadium hexacarbonyl has been extensively studied under a variety of conditions. The X-ray analysis of neutral paramagnetic $V(CO)_6$ shows tetragonal distortion about the metal atom, with V–C(ax) bond distances shorter than V–C(eq) values. This is believed to be due to both static and dynamic Jahn-Teller distortion (refs. 5&6). The gas phase electron diffraction value of 201.5(2)pm found in $V(CO)_6$ (ref.5) is somewhat higher than the mean, librationally corrected, distance of 200.8(3)pm found in the solid state (ref.6). However, the influence of bonding electrons on the apparent bond lengths obtained from these two different techniques is not the same, and this may account for the observed discrepancy.

X-ray analysis of pale yellow crystals of $[V(CO)_6].[N(PPh_3)_2]$ (ref.7) shows the geometry of the hexacarbonylvanadium anion to be that of an almost perfect octahedron, with six equivalent V–C bond lengths of 193.1(9)pm. The compound is isostructural with the corresponding niobium and tantalum derivatives (ref.17), the M–C bond distances increasing in the order: 193.1(9)pm (V) < 208.3(6)pm (Ta) < 208.9(5)pm (Nb). The C–O bond distances increase in the same order: 114.6(11)pm (VCO) < 114.9(8)pm (TaCO) < 116.0(7)pm (NbCO). This could indicate a maximization of $d\pi$–$p\pi$ back-bonding at niobium. However, it is also observed that both the P–N bond distances and the N–P–C angles in the cation also follow the same trend: 153.9(2)pm, 110.2(2)° (V complex) < 154.1(2)pm, 110.3(2)° (Ta complex) < 154.3(1)pm, 110.7(2)° (Nb complex). This is despite the fact that the cation and the anion are well separated from one another. These observations are of considerable interest and require further investigation if they are to be understood. Meanwhile, simplistic interpretations of bond lengths and angles from crystal structural data clearly need to be tempered with caution.

In another two examples, $[V(CO)_6]_2[V(CN\text{-}t\text{-}Bu)_6]$ (ref.8) and

$[V(CO)_6]_2[V(thf)_4]$ (ref.9) a distorted octahedral geometry is found about each vanadium atom because of interactions between the ions (Table 1). The molecular structure of $[V(CO)_6]_2[V(thf)_4]$ is shown in Figure 1. The vanadium(II) ion (V in the Figure), is coordinated by the oxygen atoms of the four thf ligands in a planar array, V–O(7) = 216.3(9)pm and V–O(8) = 217.7(10)pm. The axial positions of the distorted octahedron are occupied by oxygen atoms from the two $[V(CO)_6]^{-1}$ anions, V–O(5) = 207.9pm. The V(-1) (V2 in Figure) is coordinated by the carbons of the six CO ligands (V–C (mean) = 193.9(14,25)pm). The compound is the first known example with a linear M–C–O–M carbonyl bridge between two transition metal atoms. It is also unusual in that it serves to link an organometallic complex ion to a coordination complex ion. The coexistence of separate organometallic and coordination complex ions have been found in the chemistry of both niobium and tantalum (ref.1).

The crystal structure of $[V(CO)_4(\mu\text{-}PMe_2)]_2$ (ref.11) reveals that there are four crystallographically independent, structurally identical,

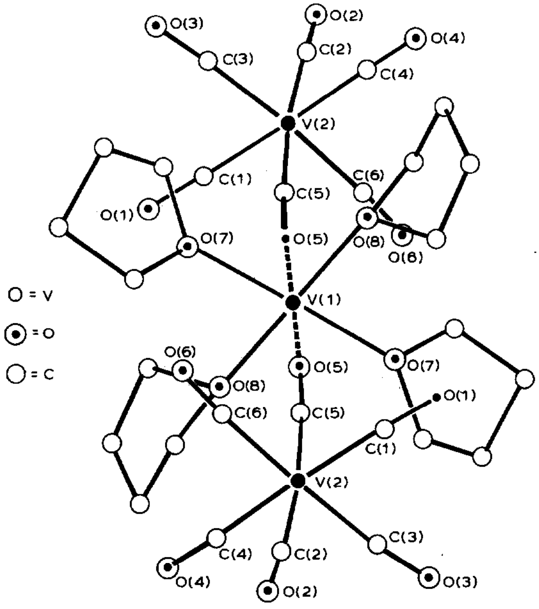

Figure 1. The molecular structure of $[V(CO)_6]_2[V(thf)_4]$
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centrosymmetric binuclear molecules. Two VC_4 moieties are double bridged by two P atoms of the PMe_2 ligands. The V-P-V angle (70.7° mean value) and P-V-P angle (109.2°) ensure that there is metal-metal bonding in the compound. The mean V-V distance of 273.3(1)pm clearly demonstrates this. In the four crystallographically independent binuclear molecules the V-V distance tends to increase as the V-P-V angle opens and the P-V-P angle simultaneously closes. For example, the V-V distance, V-P-V, and P-V-P angles are 272.6(1)pm, 70.5(1)° and 109.5(1)° respectively in one molecule, but in another are 274.1(1)pm, 71.1(1)°, and 109.0(1)° respectively (Table 1). The four independent molecules also show small differences in other bond lengths and angles. The coexistence of two or more species that differ only in degree of distortion within the same crystal is typical of the general class of distortion isomerisation (ref.18). Thus $[V(CO)_4.(\mu\text{-}PMe_4)]_2$ is a rather unique example of distortion isomerisation, and is the only example in the chemistry of vanadium, niobium, or tantalum organometallics where four such molecules coexist. The previous "record" for group VB was held by niobium, in $[(\eta\text{-}cp)C_5H_4NbH]_2$ (ref.19).

In another four examples, $V(CO)_6AuPPh_3$ (ref.12), $[(Ph_3Sn)_2V(CO)_5]^-$ (ref.13), $HV(CO)_4(tpb)$ (ref.14), and $(\eta^2\text{-}COC_3Ph_3H_2)V(CO)_3(dpdae)$ (ref.15), the vanadium atom has a coordination number seven. For example, in the first case the vanadium atom is in a distorted capped octahedral geometry, with the three CO ligands in the capped face (V-C = 200.2(17)pm) and the remaining three forming the uncapped face (V-C = 193.2(33)pm). The gold atom occupies the unique capping position (V-Au = 269.0(3)pm). The V-C bond distances show that the capped position is more sterically crowded than the uncapped face, and generally follow the trends expected (refs. 20 & 21).

A distorted pentagonal bipyramidal geometry has been found for the seven coordinate vanadium atom in $HV(CO)_4(tpb)$ (ref.14).

Eight coordinate vanadium(0) has been found in the X-ray analysis of dark red $(Ph_3PAu)_3V(CO)_5$ crystals (ref.16). As can be seen in Figure 2, four metal atoms form a slightly distorted tetrahedral cluster with Au-V-Au angles of 62.03(2,1.50)°, Au-Au-V angles of 58.99(2,1.29)°, and Au-Au-Au angles of 60.00(1,1.70)°, essentially as expected. The mean V-C bond distance of 194.8(7)pm (Table 1) is in the range of 185.4-201.0pm found for other vanadium carbonyl complexes.

Examination of the data in Table 1 shows that the V-C(CO) bond distance is independent of the coordination polyhedra, and the mean value of 195.4(185.4-201.0)pm is smaller than that in the niobium and tantalum analogues (ref.1). The V-Au distance increases from 269.0(3) to 273.4(1)pm (mean value) on going from heterobinuclear to the tetranuclear metal

TABLE 1. STRUCTURAL DATA FOR VANADIUM ORGANOMETALLICS WITH UNIDENTATE CARBON LIGANDS

Compound	Crystal Class	Space Group	Z	Chromo- phore	a[pm] b[pm] c[pm]	α[°] β[°] γ[°]	V-L [pm]	C-V-C [°]	Ref.
$V^{IV}(mes)_4$	m	$P2_1/c$	4	VC_4	1217.7(3)		C^b207.9(16)	97.04(28,63)	2
					1919.8(3)	122.96(5)		116.27(28,1.82)	
					1551.3(3)				
$V^{III}(mes)_3(thf)$	m	$P2_1/c$	4	VC_3O	847.2(2)		C 210.9(7,17)	114.9(3,7.7)	3
					1427.3(4)	97.64(3)	O 206.9(4)	c	
					2238.5(6)				
$V(CO)_6$		$Pn2_1a$	4	VC_6	1197				4
		(Pnma)			1128				
					647				
$V(CO)_6{}^d$				VC_6			C 201.5(2)		5
$V(CO)_6$	or	Pnma	4	VC_6	1190.5(7)		C_{eq} 200.4(4,2)	89.9(2,1.2)	6
					1122.1(20)		C_{ax} 199.3(5,1)	179.5(1)^e	
					639.7(4)				
$[V(CO)_6][N(PPh_3)_2]$	rb	$R\bar{3}$	1	VC_6	976.1(6)	91.93(3)	C 193.1(9)(6x)	89.2;90.8(4)	7
$[V(CO)_6]_2[V^{II}(CN\text{-}t\text{-}Bu)_6]$		$P2_1/n$	2	VC_6	1074.1(1)		OC 189.2(19,30)	90.0(7,3.7)	8
					2312.2(5)	100.50(3)		176.0(7,1.2)	
					1214.2(5)				
				VC_6			-NC 210.2(14,22)	91.1(5,1.9)	

TABLE 1. continued 2

Compound	Crystal Class	Space Group	Z	Chromo-phore	a[pm] b[pm] c[pm]	α[°] β[°] γ[°]	V-L [pm]	C-V-C [°]	Ref.
$[V^{-I}(CO)_6]_2[V^{II}(thf)_4]$	tr	$P\bar{1}$	1	VC_6	946.7(2)	83.29(3)	OC 193.9(14,85)	90.6(7,6.8)	9
					1031.2(2)	109.56(3)		175.4(7)	
					1112.8(3)	117.26(2)			
				VO_6			O 214.0(9,61)	90.8(3,2.5)	
$V(CO)_3(NO)(PMe_3)_2$	m	$P2_1/n$	4	VC_3P_2N	960.6(8)		C 195.1(13,73)	91.9(5,3)	10
					1192.9(11)	95.48(6)	N 180.9(10)	176.0(5)	
					1377.5(11)		P 251.3(3,13)	f	
$[V(CO)_4(\mu\text{-}PMe_2)]_2{}^g$	tr	$P\bar{1}$	4	VC_4P_2	872.8(4)	94.89(2)	C 198(1,3)	88.9(3,12.1)	11
					1273.9(3)	91.96(2)	P 236.2(2,9)	167.0(3)	
					1228.3(3)	93.40(2)	V'272.6(1)	g	
				VC_4P_2			C 198(1,3)	89.7(3,12.8)	
							P 235.8(2,1)	168.9(3)	
							V'272.6(1)	g	
				VC_4P_2			C 197(1,3)	88.6(3,12.1)	
							P 235.8(2,1)	166.3(3)	
							V'273.7(1)	g	
				VC_4P_2			C 198(1,3)	89.0(3,12.3)	
							P 235.8(2,2)	166.7(3)	
							V'274.1(1)	g	

TABLE 1. continued 3

Compound	Crystal Class	Space Group	Z	Chromo-phore	a[pm] b[pm] c[pm]	α[°] β[°] γ[°]	V-L [pm]	C-V-C [°]	Ref.
$V(CO)_6AuPPh_3$	rb	$R\bar{3}$	2	VC_6Au	1108.8(10)	75.4(2)	C 193.2(33)	89.6(8,13.3)	12
							C 200.2(17)	168.5(12)	
							Au 269.0(3)	h	
$[(Ph_3Sn)_2V(CO)_5](Et_4N)$	m	$P2_1/n$	4	VC_5Sn_2	1042.8(2)	90.00	C 194(2,5)	105.8(8,13.7)	13
					2096.2(5)	95.67(1)	Sn 277.1(3,14)	i	
					2114.6(3)	90.00			
$HV^I(CO)_4(tppb)$	or	Pcab	8	VC_4P_2H	1463.3(30)	90	C 194.8(9,36)	91.3(4,5.3)	14
					1663.1(36)	90	H 155.2(93)	176.1(3)	
					2250.1(47)	90	P 246.5(2,12)	j	
$(\eta^2\text{-}COC_3Ph_3H_2)V(CO)_3\cdot$	m	$P2_1/c$	4	VC_4OPAs	965.1(7)		OC 190.5(16,16)	75.4(6,1.8)	15
$\cdot$(dpdae)					1708.7(12)	104.85(2)	(η)C 201.4(14)	104.6(7)	
					2658.5(18)		(η)O 224.3(11)	k	
							(As)P 254.2(3,17)		
$(Ph_3PAu)_3V^0(CO)_5$		$P\bar{1}$	2	VC_5Au_3	1284.0(6)	93.82(3)	C 194.8(7,54)	86.8(3,8.8)	16
					1908.8(6)	117.26(3)	Au 273.4(1,25)	167.3(3,2.0)	
					1238.0(4)	92.02(3)		ℓ	

TABLE 1 continued 4

a. Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in brackets is the e.s.d., and the second is the maximum deviation from the mean value.

b. The chemical identity of the coordinating atom or ligand.

c. The value of C-V-O = 103.6(3,12.8)°.

d. Electron-diffraction study.

e. The value of C_{ax}-V-C_{ax} angle.

f. The P-V-P = 96.9(1)°; P-V-C = 87.7(3,2.6) and 179.5(3)°; P-V-N = 89.6(3) and 173.1(3)°; C-V-N = 90.5(4,1.7)°.

g. There are four independent molecules. The values of P-V-C angles are: 74.7(2,2.1), 93.7(2,1.1) and 175.7(2,2.1°) (molecule 1); 74.0(2,4) 193.3(2,2) and 176.3(2,6)° (molecule 2); 75.1(2,8); 94.0(2,1.0) and 175.7(2,7)° (molecule 3); 74.9(2,1.3); 93.8(2,1.6) and 175.9(2,1.4)° (molecule 4). The values of V-P-V and P-V-P are: 70.5(1) and 109.5(1)°; 70.6(1) and 109.4(1)°; 70.9(1) and 109.1(1)°; 71.1(1) and 109.0(1)°, respectively.

h. The Au-V-C angles are 64.6(6) and 126.8(11)°;

i. Sn-V-C = 72.0(5,5.1); 81.4(6,5.3) 123.4(7,3.1)°; and Sn-V-Sn = 137.9(1)°.

j. The C-V-P angle = 90.4(3,5.4) and 172.8(3,2.6)°; C-V-H = 57.8(45), 87.3(54) and 92.9(54)°; H-V-P = 38.1(46)°; and P-V-P = 81.5(3)°.

k. OC-V-C(L) angle = 79.6(6,7) and 138.6(6)°; OC-V-O(L) = 99.0(5,9) and 170.2(5)°; (L)C-V-P(As) = 112.7(4,6)°; (L)O-V-P(As) = 88.4(3,8)°; and (L)C-V-O(L) = 32.0(5)°.

ℓ. The Au-V-Au angle = 62.03(2,1.5)°.

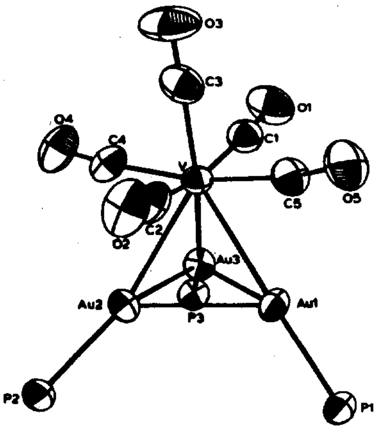

Figure 2. The structure of $(Ph_3PAu)_3V(CO)_5$, phenyls omitted Reproduced with permission from J. Am. Chem. Soc., (Ref.16)

cluster. Although rather long, the V-Au distances are shorter than the mean V-Sn distances (Table 1) which is probably a reflection of the van der Waal radii (217pm for Sn and 166pm for Au). In general, the V-L bond distance is expected to increase as the size of ligating atom increases.

3. VANADIUM ORGANOMETALLICS WITH MULTIDENTATE CARBON LIGANDS

A. Mononuclear Compounds with One Multidentate Carbon Ligand

Crystal and structural data for mononuclear vanadium organometallics with one multidentate carbon ligand are gathered in Table 2. There are three examples where η^3-allyl (or its methyl derivative) are coordinated to a vanadium(0) central atom. In all three examples, $(\eta^3\text{-}C_3H_5)V(CO)_4.PPh_3$ (ref.22), $(\eta^3\text{-}C_3H_5)V(CO)_3(dppe)$ (ref.23), and $(\eta^3\text{-}CH_3C_3H_4)V(CO)_3(pdma)$ (ref.24), the arrangement of the allyl group with respect to the vanadium atom is asymmetric (Figure 3). In general the V-C(central) distance is shorter than the V-C(terminal) distance.

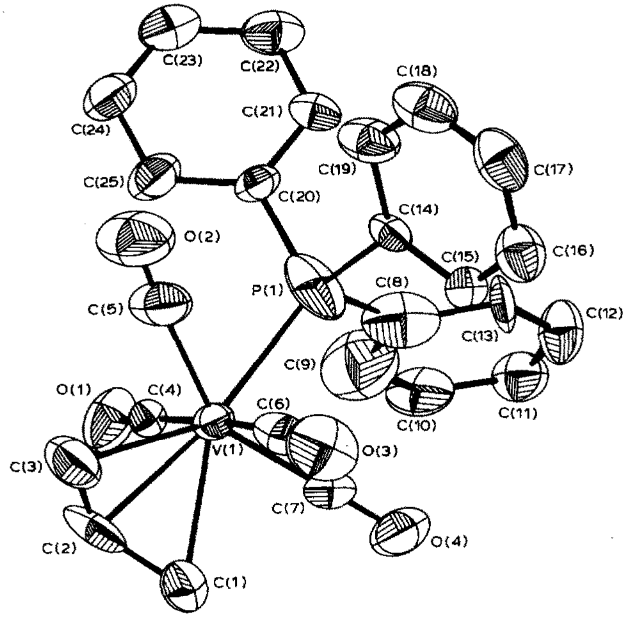

Figure 3. The crystal structure of $(\eta^3\text{-}C_3H_5)V(CO)_4PPh_3$
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There is also a difference between the allyl complex and its methyl derivative. While the mean V-C(terminal) and V-C(central) distances in $(\eta^3\text{-}C_3H_5)V(CO)_4PPh_3$ (ref.22), and $(\eta^3\text{-}C_3H_5)V(CO)_3(dppe)$ (ref.23), are 235.3 and 223.2pm respectively, in $(\eta\text{-}CH_3C_3H_4)V(CO)_3(pdma)$ (ref.24) they are 242.8 and 222.6pm respectively. The mean V-C (CO) distance of 194.7pm (Table 2) is in the range found for other vanadium carbonyl complexes (Table 1). The mean V-P bond distance of 248.0pm is about 2.9pm shorter than that of V-As (250.9pm) and corresponds to the difference in van der Waal radii, 180pm (P) and 185pm (As).

In $(\eta^3\text{-}C_3H_5)V(CO)_4PPh_3$ and $(\eta^3\text{-}CH_3C_3H_4)V(CO)_3(pdma)$ two crystallographically independent molecules are present differing only by degree of distortion, representing two more examples of distortion isomerisation (ref.18).

In general, the cyclopentadienyl radical is one of the most widely found π-electron donor, and vanadium organometallic chemistry is no exception. The crystal structure of (η^5-cp)V(CO)$_3$As$_2$Ph$_4$ (ref.26) is shown in Figure 4 as a representative example of the monocyclopentadienyl compounds from Table 2. The vanadium atom is centered between two planes defined by the cyclopentadienyl ring and by the three CO ligands and the arsenic of the As$_2$Ph$_4$ ligand. The mean V-C (cp) bond distance of 225.9(9)pm is one of the shortest found in the monocyclopentadienyl organometallics.

X-ray analysis of [(Me$_4$H$_2$C$_6$)V(CO)$_4$][V(CO)$_6$] (ref.31) shows that the complex cation and the [V(CO)$_6$]$^-$ anion exist as discrete units in the crystal. The hexacarbonylvanadate anion is elongated along a trigonal axis with a molecular symmetry of D_{3d}. The mean V-C bond distance of 193 pm is comparable to that found in other carbonyl compounds (Table 1). The tetracarbonyl cation, which has C_{4v}, symmetry has C-V-C angles in the range 72.9-76.3°, with V-C (CO) distances in the range 192-196(2) pm, and V-C (C$_6$H$_2$Me$_4$) mean value of 233(2) pm. While the values of V-C (CO)

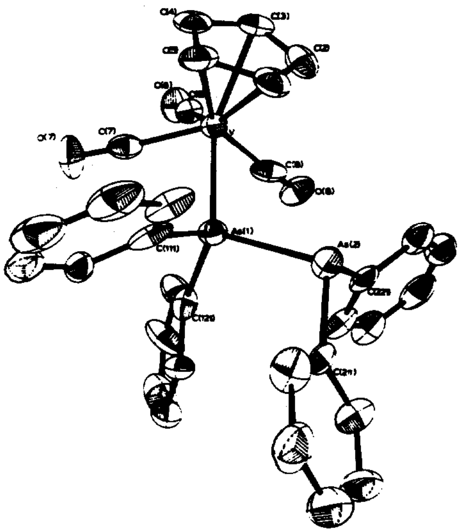

Figure 4. The crystal structure of (η^5-cp)V(CO)$_3$As$_2$Ph$_4$
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distances are in the range of and comparable to the other vanadium carbonyls, the V–C ($C_6H_2Me_4$) bond distance is about 5 pm longer than the mean V–C (cp) bond distance but equal to the mean V–C (C_3H_5) distance (Table 2). Further examples would be necessary to present these observations as a generalisation.

The crystal structure of the brown compound $(\eta^5\text{-cp*})V(\eta^2\text{-PhN-C(S)-cp*})_2$ is shown in Figure 5. Only one cp* ring is η^5 bonded to the vanadium atom (V–cp*(centroid) = 198.3(7)pm), and two thioamido ligands are chelated through the sulphur (V–S = 244.9(3) and 245.8(4)pm) and the nitrogen atoms (V–N = 215.0(4) and 215.4(4)pm). The coordination polyhedron has been described as a severely distorted trigonal bipyramid, with the sulphur atom at the apices (ref.32).

Inspection of the data in Table 2 shows that the mean V–C bond distance increases in the order: 192.5pm (CO) < 227.8 pm (cp) < 233.1 pm (η^3-C_3H_5) < 233.5 pm ($C_6H_2Me_4$). The reasons include both steric and electronic factors. In general, the mean V–L bond distance increases with increasing

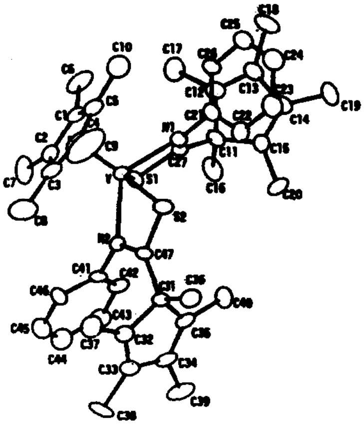

Figure 5. The crystal structure of $(\eta^5\text{-cp*})V(\eta^2\text{-PhN-C(S)-cp*})_2$
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TABLE 2. STRUCTURAL DATA FOR VANADIUM ORGANOMETALLICS WITH ONE MULTIDENTATE CARBON LIGAND[a]

Compound	Crystal Class	Space Group	Z	Chromo- phore	a[pm] b[pm] c[pm]	α[°] β[°] γ[°]	M–L [pm]	OC-M-CO cis trans [°]	Ref.
$(\eta^3\text{-}C_3H_5)V^0(CO)_4PPh_3$[c]	m	$P2_1/c$	8	$(\eta^3\text{-}C_3)VC_4P$	862.7(1)		OC[b]195.3(6,37)	90.4(2,12.4)	22
					1629.4(3)	90.09(2)	P 248.6(2)		
					3245.1(31)		(η^3)C 230.7(6,84)		
				$(\eta^3\text{-}C_3)VC_4P$			OC 196.0(6,32)	90.2(3,13.4)	
							P 248.5(2)		
							(η^3)C 231.3(7,68)		
$(\eta^3\text{-}C_3H_5)V^0(CO)_3(dppe)$	or	Pbcn	8	$(\eta^3\text{-}C_3)VC_3P_2$	1580.5(2)		OC 194.1(6,11)	90.3(2,8.3)	23
					1711.2(2)		P 247.4(2,13)	179.0(2)	
					2051.4(2)		(η^3)C 230.6(6,78)	d	
$(\eta^3\text{-}CH_3C_3H_4)V^0(CO)_3\cdot$	rh	$Pbc2_1$	8	$(\eta^3\text{-}C_3)VC_3As_2$	988.1(8)		OC 193.6(26,71)	90.2(13,6.0)	24
·(pdma)[c]					1892.3(15)		As 250.5(3,19)	172.3(11)	
					2151.5(16)		(η^3)C 234.8(28,136)	e	
				$(\eta^3\text{-}C_3)VC_3As_2$			OC 194.4(21,25)	88.6(12,4.4)	
							As 251.2(4,2)	173.6(10)	
							(η^3)C 237.4(28,135)	f	
$(\eta^5\text{-}cp)V(CO)_4$	or	Pnma	4	$cpVC_4$	748.5(5)		OC 191(3,3)	76.2(1.3;9)	25
		$(Pn2_1a)$			1225(1)		(cp)C g		
					1043(1)				

TABLE 2. continued 2

Compound	Crystal Class	Space Group	Z	Chromo-phore	a[pm] b[pm] c[pm]	α[°] β[°] γ[°]	M-L [pm]	OC-M-CO cis trans [°]	Ref.
$(\eta^5\text{-cp})V(CO)_3As_2Ph_4$		$P2_1/c$	4	$cpVC_3As$	1347.8		OC 190.4(7,41)	74.9(3,7)	26
					1020.0	82.3	As 253.6(1)	h	
					2085.2		(cp)C 225.9(9,29)		
$(\eta^5\text{-cp})V^I(CO)(tppe)$		$P2_1/c$	8	$cpVP_3C$	1807.1		OC 187.8(11)	i	27
					1088.7	94.3	P 239.1(4,88)		
					3461.6		(cp)C 232.2(12,26)		
$cis\text{-}(\eta^5\text{-cp})V^I(CO)_2\cdot$	m	$P2_1/c$	4	$cpVC_2P_2$	1228.6(6)		OC 189.0(5,1)	74.6(4)	28
$\cdot(tppb)$					846.0(4)	103.94(3)	P 244.2(2,17)	j	
					2771.1(9)		(cp)C 226.7(5,44)		
$(\eta^5\text{-cp})VC\ell_2(PMe_3)_2$		$P2_1/a$	4	$cpVC\ell_2P_2$	1232.6(4)		$C\ell$ 240.3(1,2)	k	29
					1014.8(3)	94.15(2)	P 250.8(1,2)		
					1305.6(4)		(cp)C 230.5(3,27)		
$(C_5H_5BMe)V(CO)_4$	or	Pbca	8	C_5BVC_4	1397.0(2)		OC 192.9(6,5)	75.7(3,8)	30
					1276.0(1)		B 249.6(8)		
					1294.5(2)		C 230.4(7,43)		

TABLE 2. continued 3

Compound	Crystal Class	Space Group	Z	Chromophore	a[pm] b[pm] c[pm]	α[°] β[°] γ[°]	M-L [pm]	OC-M-CO cis trans [°]	Ref.
$[(Me_4H_2C_6)V(CO)_4]^+$.	m	$P2_1/a$	4	C_6VC_4	1813.5(5)		OC 194(2,2)	74.9(8,2.0)	31
$.[V(CO)_6]^-$					1274.6(4)	93.03(2)	C 233(2,1)		
					1002.5(4)				
				VC_6			OC 193(2,5)	90.0(10,3.4)	
								178.9(11,4)	
$(\eta^5$-cp*)V(η^2-PhN-	or	Pbca	8	$cpVN_2S_2$	2997.1(7)	90	N 215.2(4,2)	ℓ	32
-C(S)-cp*$)_2$					1429.2(4)	90	S 245.4(4,5)		
					1869.8(5)	90	(cp)C not given		
$(\eta$-$C_7H_7)V(CO)_3$	or	$P2_12_12_1$	4	C_7VC_3	1347(7)				33
					1130(6)				
					652(3)				

a. Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in brackets is the e.s.d., and the second is the maximum deviation from the mean value.
b. The chemical identity of the coordinating atom or ligand. c. There are two crystallographically independent molecules. d. The value of P-V-P = 76.98(5)°; P-V-C(CO) = 88.7(2,11.5) and 152.0(2)°. e. The value of As-V-As = 78.7(1)°; As-V-C(CO) = 86.4(8,3.9) and 159.8(11)°.
f. The value of As-V-As = 78.6(1)°; As-V-C(CO) = 87.1(8,7.1) and 159.4(10)°. g. The V-cp(centroid) = 193.0(7)pm; the (OC)C-V-cp(centroid = 118.7(8,1.1)°. h. The value of As-V-C(CO) = 79.2(2,2.4)°. i. The value of P-V-P = 76.5(1,2)°; P-V-C(CO) = 77.2(3,8)°. j. The value of P-V-C(CO) = 81.2(2,5)°. k. The value of Cℓ-V-Cℓ = 126.1(0)°; Cℓ-V-P = 79.5(0.8); P-V-P = 132.6(0)°; Cℓ-V-cp (centroid) = 117.0(0,1.0)°; P-V-cp (centroid) = 113.7(0,1)°. ℓ. The V-cp(centroid) = 198.3(7)pm; the N-V-cp (centroid) = 119.5(3,2)°; S-V-cp (centroid) = 116.5(2,1)°; N-V-N = 120.9(2)°; N-V-S = 66.0(1,2) and 88.1(1,1.3)°; S-V-S = 126.8(1)°.

van der Waal radius of the ligating atom, as noted above. For example, the V-L distance (van der Waal radius) increases in the order: 240.3 pm (Cℓ, 175 pm) < 246.0 pm (P, 180 pm) < 251.4 pm (As, 185 pm).

The mean M-L bond distances increase from V to Ta to Nb. For example the mean M-cp distances are: 227.8 pm (Vcp) < 242.1 pm (Tacp) < 242.5 pm < (Nbcp). The mean M-Cℓ bond distances are 240.3 pm (V-Cℓ) < 244.4 pm (Ta-Cℓ) < 248.1 (Nb-Cℓ), the values taken from Table 2 and reference 1.

B. Mononuclear Compounds with Two Multidentate Carbon Ligands

Crystal and structural data for mononuclear vanadium organometallics with two multidentate carbon ligands are listed in Table 3. Almost half of the known structures for organovanadium compounds belongs to this group. Vanadocene has been studied by gas phase electron diffraction and by X-ray methods. The electron diffraction value of 228.0 pm found for the V-C bonds in $(\eta^5\text{-cp})_2V$ (ref.35) is slightly higher than the mean value of 224 pm found in the solid state (refs.36,37), probably due to minor differences in the bonding. The crystal structure has been determined twice, in 1979 (ref.36) and in 1981 (ref.37). Although the latter work does not mention the former, the crystal and structural data (Table 3) are in close agreement except for the unit cell parameters, a and c. The molecule has C_i symmetry with vanadium at the centre of inversion, with the planar cyclopentadienyl rings staggered.

The red compound decamethylvanadocene (ref. 38) has two crystallographically independent molecules in the asymmetric unit (Table 2). One of the two molecules has Cmm symmetry, with eclipsed cyclopentadienyl rings, while the other molecule is statistically disordered.

Vanadocene and its derivatives are highly reactive towards unsaturated molecules in particular, and are able to bind various types of ligand. From a structural point of view, vanadocene with additional ligands, listed in Table 3, can be divided into two groups. In compounds of the general formula $(\eta^5\text{-cp})_2VL$, the extra ligand L is unidentate, such as: CO, CN, or $OCMe_3$ (ref.38); Cℓ (ref.41); $NSiMe_3$ (ref.43); $NN(SiMe_3)_2$ (ref.44); NPh (ref.45); and $C{\equiv}CC_6H_2Me_3$ (ma) (ref.47). The crystal structure of $[(\eta^5\text{-cp})_2V(OCMe_2)]^+$ is shown in Figure 6 as a representative example. It can be seen (Table 3) that as the V-cp (centroid) distance increases the cp(centroid)-V-cp(centroid) angle closes. For example, the corresponding angle and distances in the CO derivative (ref.38) are 153.6(4) and 192.8 pm, compared to 130.9(8) and 205.4 pm in the NSiMe derivative (ref.43).

The second group has the general formula $(\eta^5\text{-cp})_2VL_2$, where both L can be unidentate, or L_2 can be a bidentate ligand. Examples of the former include two identical L such as CO (ref.48), Cℓ (ref.50), SPh (ref.52), or

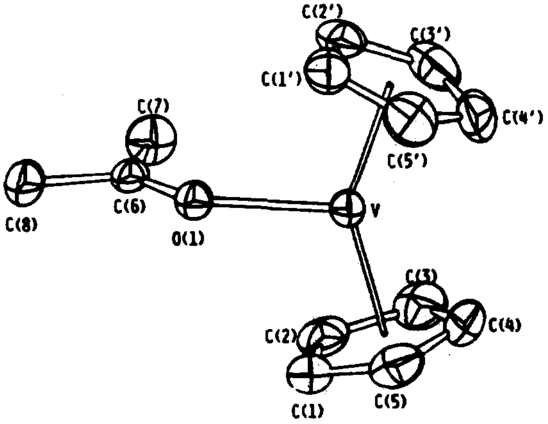

Figure 6. The crystal structure of $[(\eta^5\text{-cp})_2V(OCMe_2)]^+$
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two different L (eg. refs.38,49 and 50). The bidentate L_2 examples are much more common and include systems with identical bonding atoms such as two C atoms (ref.53), two S atoms (ref.51), or more commonly two different atoms such as C and N (ref.54), C and O (refs.42 and 55), C and S (refs. 32, 56-59). The crystal structure of $(\eta^5\text{-cp})_2V(\eta^4\text{-CSCBu})$ is shown in Figure 7, where it can be seen that the two cyclopentadienyl rings incline to form a cavity in the equatorial plane for the thioketene ligand.

Inspection of the data in Table 3 shows that the additional ligand causes the cp(centroid)-V-cp(centroid) angle to decrease from its 180° value in vanadocene. When there is only one unidentate ligand present the value of this angle ranges from 153.6° to 130.9°. A smaller range is found for the cases where two unidentate ligands are present, 142.1° to 133.4°, and also for the cases where one bidentate is present, 143.1° to 133.4°. The mean values of the angle are 144.0° in the first case, 136.1° in the second, and 137.7° in the third case. In addition, in all cases the angle decreases with increasing V-cp(centroid) distance in all of these "clino"-sandwich compounds.

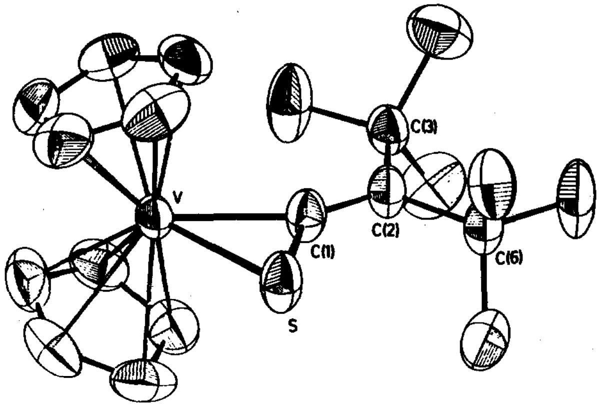

Figure 7. The crystal structure of $(\eta^5\text{-cp})_2V(\eta^2\text{-CSCBu})$
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Comparison of the V–C (cp) distances for the mono- and bis-cyclopentadienyl compounds reveals that the mean value is similar for both (227.8 pm and 227.9 pm respectively). By contrast, in the niobium and tantalum analogues (ref.1) the mean M–C (cp) distance is noticeably shorter in the bis-cyclopentadienyl derivatives than in the mono-cyclopentadienyls. The difference between the two mean values increases from -0.1 pm for vanadium to 2.2 pm for niobium, to 3.7 pm for tantalum. A similar trend is seen for the M–C (CO) bond distances for the carbonyl derivatives of the mono- and bis-cyclopentadienyls: -3 pm (vanadium), 3 pm (niobium), and 7 pm (tantalum). While it is tempting to attribute this to the relative covalent radii of the metal atoms, the effect is certainly not linear, and suggests that other effects are operative.

There is a tendency for the V–cp (centroid) distance to increase with increasing oxidation number of the vanadium atom: 190.0–194.8 pm (mean 192.2 pm) for V(II), 193.0–197.3 pm (mean 195.0 pm) for V(III), and 196.6–205.4 pm (mean 200.6 pm) for V(IV).

TABLE 3. STRUCTURAL DATA FOR MONONUCLEAR VANADIUM COMPOUNDS WITH TWO MULTIDENTATE CARBON LIGANDS[a]

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] β[°] γ[°]	M-L [pm]	M-cp [pm] centroid cp-M-cp centroid[°]	L-M-L L-M-cp centroid [°]	Ref.
$(\eta^5\text{-cp})V(CO)_2(\eta^4\text{-}C_4Ph_4)$	rh	$P2_12_12_1$	4	2093(3)		OC[b] 195(3)(2x)		89(3)	34
				1239(2)		(η^4)C 226(3)(4x)		105	
				1005(2)		(η^5)C 224(3)(5x)			
$(\eta^5\text{-cp})_2V^{II}$ c						C 228.0(5)			35
$(\eta^5\text{-cp})_2V^{II}$		$P2_1/n$	2	589.0(1)		(cp)C 224.5(6,11)	192.0		36
				802.2(3)	91.16(3)		180		
				927.0(4)					
$(\eta^5\text{-cp})_2V^{II}$	m	$P2_1/n$	2	926.9(3)		(cp)C 226.0(10,30)	192		37
				802.0(3)	91.21(3)				
				589.2(2)					
$(\eta^5\text{-cp*})_2V^{II}$ d	or	Cmcm	8	1504.9(6)		(cp*)C 225(3,3)	190(3)		38
				866.0(4)	90		177(2)		
				2966.3(10)		(cp*)C 229(7,20)	191(5,4)		
$(\eta^5\text{-cp})V^{II}(\eta^7\text{-}C_7H_7)$	or	Pnma	4	1105.8(14)		(η^5)C 223	190		39
				1084.5(10)		(η^7)C 225			
				792.9(7)					
$(\eta^8\text{-Cot})V^{IV}(\eta^5\text{-Cab})$		$Pna2_1$	4	1426.4(5)		(η^8)C 228.2(8,83)			40
				1259.5(4)		(η^5)C not given			
				844.9(2)					

TABLE 3. Continued 2

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] β[°] γ[°]	M-L [pm]	M-cp [pm] centroid cp-M-cp centroid[°]	L-M-L L-M-cp centroid [°]	Ref.
$(\eta^5\text{-cp*})_2V^{II}(CO)$	m	$P2_1n$	4	1569.9(7)		OC 187.9(8)	192.8(0,5)		38
				1335.3(6)	99.26(5)	(η^5)C 226.1(9,37)	153.6(4)	103.2(4,3)	
				945.2(5)					
$(\eta^5\text{-cp*})_2V^{III}(CN)$	m	$P2_1n/$	4	1589.5(4)		NC 208.8(7)	197.0(7,7)		38
				1344.1(3)	97.92(2)	(cp*)C 229.8(7,25)	151.5(3)	104.2(3,8)	
				920.9(2)					
$(\eta^5\text{-cp})_2V^{III}C\ell$	or	Ama2	4	913.4(8)		Cℓ 239.0(4)	194.5(7,1)		41
				1352.2(10)		(cp)C 227.8(10,18)	139.5(3)		
				748.4(6)					
$(\eta^5\text{-cp})_2V^{III}(OCMe_2)$.	or	Pnam	4	2401.4(3)	90	O 208.1(4)	193.4(6)		42
$.(BPh_4)$				928.0(1)	90	(cp)C 226.5(6,14)	144.4(3)	107.7(1)	
				1369.2(2)	90				
$(\eta^5\text{-cp})_2V^{IV}NSiMe_3{}^e$		Pnma	4	1652(3)		N 166.5	205.4		43
				1012(1)		(cp)C 236.4(0,75)	130.9(8)		
				814.5(9)					
$(\eta^5\text{-cp})_2VN_2(SiMe_3)_2$		Fdd2	8	1692(1)		N 166.6(6)	not given		44
				2140(1)		(cp)C not given			
				1105.3(7)					

TABLE 3. Continued 3

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] β[°] γ[°]	M-L [pm]	M-cp [pm] centroid cp-M-cp centroid[°]	L-M-L L-M-cp centroid [°]	Ref.
$(\eta^5\text{-cp*})_2V^{IV}NPh$	m	$P2_1/c$	4	1395.1(5)		N 173.0(5)	205.3(8,5)		45
				1219.9(4)	103.92(4)	(cp*)C not given	138.4(3)		
				1384.5(5)					
$(\eta^5\text{-cp*Et})_2V^{III}(ma)$	m	$P2_1/c$	4	1142.9(10)		(ma)C 203.2(13)	197.3(0,3)		46
				1595.8(11)	102.21(9)	(cp)C 231(1,3)	149.7(1)	105.1(4,3)	47
				1585.4(12)					
$[(\eta^5\text{-cp})_2V(CO)_2]\cdot$	or	$Pna2_1$	4	2053.2(2)		OC 197(3,2)	192(2,3)		48
$\cdot(BPh_4)$				1008.4(1)		(cp)C 227(2,7)	134(1,4)	105(1,2)	
				1391.4(1)					
$(\eta^5\text{-cp})_2V^{III}(CN)(CNC_6H_{11})$	m	$P2_1/c$	4	1034.2(5)		NC 207(2)	199.5(2)		38
				1314.6(7)	92.60(6)	C 200(2)	142.1(7)	104.2(7,8)	
				1895.6(10)		(cp*)C 232(2,7)			
$(\eta^5\text{-cp})V^{IV}Br(TCNE)$	or	Pccn	8	2109(4)		Br 259(1)			49
				1108(2)		C not given			
				1279(2)		(cp)C not given			
$(\eta^5\text{-cpMe})_2V^{IV}C\ell_2$	m	C2/c	4	1361.4(2)		Cℓ 239.8(2)(2x)	199.1	87.06(9)	50
				672.0(1)	105.99(1)	(cp)C 237.2(6,44)	133.4	106.7(0,8)	
				1376.3(2)					

TABLE 3. Continued 4

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] β[°] γ[°]	M–L [pm]	M–cp [pm] centroid cp–M–cp centroid[°]	L–M–L L–M–cp centroid [°]	Ref.
$(\eta^5\text{-cp*})_2V(S_2)$	or	Fdd2	8	1766.4(9)		S 241.5(4)	202(2)	49.7(1)	51
				2619.9(14)		(cp*)C not given	141.7(4)	107.3(3,1.5)	
				866.4(3)					
$(\eta^5\text{-cp})_2V^{IV}(SPh)_2$	m	C2/c	8	3145.4(5)		S 245.9(3,11)	196.8	94.1(1)	52
				783.5(1)	104.35(1)	(cp)C 231(0,4)	135	105.3(0,2.9)	
				1554.5(2)					
$(\eta^5\text{-cp})_2V^{II}(\eta^2\text{-def})$	m	$P2_1/c$	4	787.1(1)		(η^2)C 220.0(12,14)	195.5(12,4)	39.0(3)	53
				1860.4(3)	121.32(2)	(cp)C 229.0(11,32)	135.9(5)	110.7(4,9)	
				1371.2(3)					
$(\eta^5\text{-cp})_2V^{II}(\eta^2\text{-dma})$	m	C2/c	8	2508.9(2)		(η^2)C 209.1(3,7)	196.0(5,1)	35.8(1)	53
				794.8(1)	112.14(1)	(cp)C 228.1(5,24)	138.4(2)	109.8(2,1.2)	
				1597.9(2)					
$(\eta^5\text{-cp})_2V(tcd)^d$	or	$Pna2_1$	8	1444.6(3)		C 199(3)	195(2,1)	42.0(12)	54
				1418.6(2)		N 212(3)	140.0(7)	108.3(8,3.1)	
				2090.3(4)		(cp)C 230(2,6)			
						C 200(2)	195(2,0)	40.1(6)	
						N 209(2)	140.0(10)	108.8(8,2.1)	
						(cp)C 229(3,12)			

TABLE 3. Continued 5

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] β[°] γ[°]	M-L [pm]	M-cp [pm] centroid cp-M-cp centroid [°]	L-M-L L-M-cp centroid [°]	Ref.
$[(\eta^5\text{-cp})_2V(\text{tcdm})]I_3$	m	$P2_1/c$	4	1426.0(6)		C 203(2)	194(4,1)	36.0(6)	54
				1917.6(5)	106.92(5)	N 204(1)	138.9(18)	109.5(13,1.4)	
				1062.8(4)		(cp)C 225(3,2)			
$(\eta^5\text{-cp})_2V^{II}(\eta^2\text{-}CH_2O)$	m	$C2/c$	8	1363.4(3)		C 209.2(8)	195.4(9,11)		55
				681.2(1)	103.24(2)	O 195.5(5)			
				2052.8(4)		(cp)C not given			
$(\eta^5\text{-cp})_2V(\eta^2\text{-}OC_2Ph_2)$	or	$P2_12_12_1$	4	1851.0(2)	90	C 201.3(6)	194.3(7,3)	37.3(2)	42
				971.2(1)	90	O 202.0(4)	139.4(3)	109.1(3,9)	
				1002.1(1)	90	(cp)C 226.6(7,22)			
$(\eta^5\text{-cp})_2V(\eta^2\text{-}CSCR_2)$	m	$P2_1/m$	2	847.8(2)		C 214.8(5)		44.3(1)	56
				1207.4(2)	99.91(2)	S 238.3(3)	133.5(4)		
				914.2(2)		(cp)C 229.9(4)			
$(\eta^5\text{-cp})_2V(\eta^2\text{-}CSCBu)$	rh	Pnma	4	1344.3(3)		C 217.2(5)		44.5(1)	56
				1258.3(4)		S 236.6(2)	132.5(4)		
				1107.1(2)		(cp)C 229.9(4)			
$(\eta^5\text{-cp})_2V^{IV}(\eta^2\text{-}SCPh_2)$	m	$P2_1/n$	4	1028.0(1)		C 230.6(4)	197.1(4,1)	44.2(1)	57
				1124.9(1)	99.27(1)	S 237.4(2)	133.9(2)	111.2(1,2.8)	
				1588.9(2)		(cp)C not given			

TABLE 3. Continued 6

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] β[°] γ[°]	M-L [pm]	M-cp [pm] centroid cp-M-cp centroid [°]	L-M-L L-M-cp centroid [°]	Ref.
$(\eta^5\text{-cp*})_2V^{IV}(\eta^2\text{-SCNPh})$	m	$P2_1/n$	4	987.6(3)	90	C 204.2(7)	200.7(7,8)	44.7(2)	32
				1465.0(5)	94.40(3)	S 244.4(2)	143.1(3)	106.9(3,2.8)	
				1678.4(6)	90	(cp*)C not given			
$(\eta^5\text{-cp})_2V^{IV}(\eta^2\text{-S}_5).0.5H_2O$	or	$P2_12_12$	4	1349.1(1)		S 246.4(2)	196.6(0,7)	89.3(1)	58
				1274.8(1)		S 245.0(2)	134.1	106.0(0,4.0)	
				771.5(1)		(cp)C 229.9(0,22)			
$(\eta^5\text{-cp})_2V^{II}(\eta^2\text{-CS}_2)^d$	m	$P2_1/c$	8	1180.3(2)		C 207.5(4)	194.8(5,1)	42.5(1)	59
				1231.0(2)	90.07(3)	S 243.2(2)	138.8(3)	109.0(2,1.6)	
				1446.3(3)		(cp)C 227.4(5,26)			
						C 209.0(5)	194.2(6,4)	42.2(1)	
						S 244.4(2)	138.1(3)	109.4(2,1.6)	
						(cp)C 226.5(5,22)			
$[(\eta^5\text{-cp})_2V^{III}(\eta^2\text{-SCSMe})].$	m	$P2_1/n$	4	937.7(2)		C 208(1)	193(2,1)	41.0(4)	59
$.(I_3)$				2660.1(3)	108.95(2)	S 245.2(4)	137.9(7)	109.5(6,1.1)	
				757.9(1)		(cp)C 227(2,2)			

a. Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in brackets is the e.s.d., and the second is the maximum deviation from the mean value. b. The chemical identity of the coordinating atom or ligand. c. By gas phase electron diffraction. d. There are two independent molecules. e. At 253 K.

The mean V-L (unidentate) distance increases with the van der Waal radius of the coordinated atom (ref.60) as might be expected. Thus V-L = 168.8 pm (L = N, r(ion) = 155 pm), 211.7 pm (C, 170 pm), 239.4 pm (Cℓ, 175 pm), 245.9 pm (S, 180 pm), and 259 pm (Br, 185 pm).

Two independent molecules differing only by degree of distortion are present in $(\eta^5\text{-cp*})_2V$ (ref.38), $(\eta^5\text{-cp})_2V(tcd)$ (ref.54) and $(\eta^5\text{-cp})_2V(\eta^2\text{-}CS_2)$ (ref.59). These are typical examples of distortion isomerism (ref.18).

C. Homo-oligonuclear Compounds

Crystal and structural data for homo-bi-, tetra- and pentanuclear vanadium organometallics are listed in Table 4. The data are tabulated by increasing nuclearity and by increasing V-V bond distances. The brown, binuclear compound $(C_6H_6)_2V_2(CO)_4$ (ref.61) is extremely air sensitive, and the preliminary structural data indicate two $(C_6H_6)_2V$ moieties are linked by four bridging CO ligands. The V-V distance, at 225 pm, is the shortest found in the organometallic derivatives of vanadium. It also ensures that the shortest metal-metal bond distance for group VB belongs to vanadium.

In another two binuclear derivatives, $(\eta^5\text{-cp})_2V_2(CO)_5$ and $(\eta^5\text{-cp})_2V_2(CO)_4PPh_3$ (refs.62-64), two nonequivalent moieties, $(cp)V(CO)_2$ and (cp)V(CO) in the former and $(cp)V(CO)_2$ and $(cp)V(PPh_3)$ in the latter, are linked by two CO ligands in what is described as "semibridges" through the C atoms. The mean V-C (CO) distances are very asymmetric in both cases. The distances in the former are 193.6 and 242.1 pm at 295K, and 194.0 and 241.7 pm at 123K. In the latter the distances are 192.5 and 240.0 pm at 143K, the only temperature studied in this case (Table 4). All the distances are longer than the corresponding V-C (CO) terminal distances of 193.3, 193.8, and 192.2 pm respectively. The V-V distances of 246.2 and 245.9(2) pm in the former, and 246.6(2) pm in the latter, indicate multiple bonding. The mean V-C (cp) distances of 223.9(11,20) pm (at 295K) and 226.2(5,34) pm (at 123K) in the former, as well as 227.2(6,25) pm in the latter, are in the range found for monocyclopentadienyl vanadium organometallic derivatives (Table 2).

A decrease in bond length on cooling has been noted for the V-V bond distance in $(\eta^5\text{-cp})_2V_2(CO)_5$, and also for the longer V-C (CO) bridge distances. At the same time, the shorter V-C (CO) bridge, V-C (CO) terminal and V-C (cp) distances all increase when the temperature drops from 295K to 123K.

The crystal structure of $(\eta^5\text{-cp})_2V_2S_2[S_2C_2(CF_3)_2]$ and $(\eta^5\text{-cpPr})_2V_2S_4$ are shown in Figure 8. The V-V bond distances of 257.4(3)pm in the former and 261.0pm in the latter indicate a direct bond between the central atoms. In

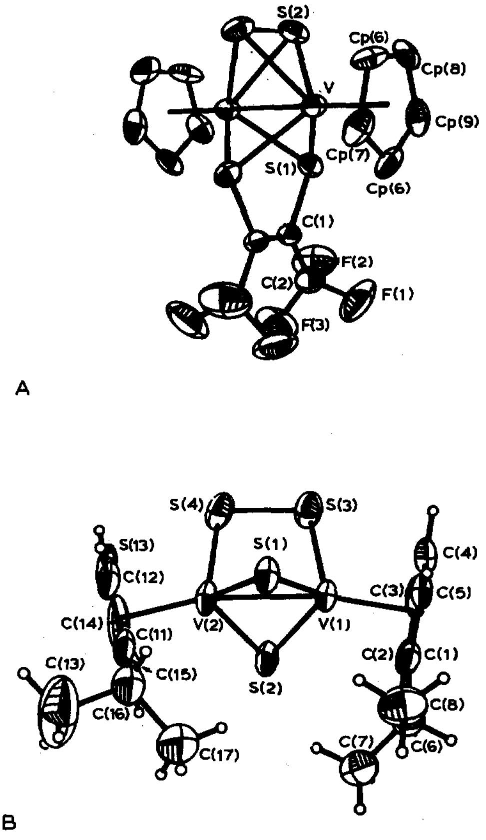

Figure 8. The crystal structures of $(\eta^5\text{-cp})_2V_2S_2\{S_2C_2(CF_3)_2\}$ (top) and $(\eta^5\text{-cpPr})_2V_2S_4$ (bottom)
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the black crystals of $(\eta^5\text{-cpMe})_2V_2S_5$ (ref.66) the two $(\eta^5\text{-cpMe})V$ moieties are symmetrically bridged by three different types of sulphur ligands with V-V bond distances of 265.8(1) pm. The V-S bridge distances decrease in the order 237 pm $(\mu\text{-}\eta^2\text{-}S_2)$ > 232 pm $(\mu\text{-}\eta^1\text{-}S_2)$ > 227 pm $(\mu\text{-}S)$.

By contrast, the distance between the vanadium atoms in $[(cp)V(RCOO)_2]$, 362.5 pm for R = C_6H_4O (ref.68), and 370.4 pm for R = F_3C (ref.69) indicates no direct bonding interaction. The compounds are both binuclear with a structure similar to that of copper(II) acetate monohydrate (ref.75), having two vanadium atoms bridged by four carboxylate groups. Each vanadium atom has square pyramidal coordination with the π-cyclopentadienyl ligand in the axial position. The absence of a metal-metal bond in a dimer of this type is rare, however, in this case there is probably considerable steric hindrance between the bulky cyclopentadienyl ligands in the axial positions and the carboxylate ligands (refs. 68 and 69).

The deep maroon compound $[(\eta^5\text{-cp})_2V]_2(COS_2)$ (ref.70), has two $(\eta^5\text{-cp})_2V$ moieties held together by a COS_2 ligand, bonded through S to one of the V atoms and by C to the other (Table 4). The V-cp (centroid) distances are in the range from 193.0 to 195.0 pm (mean value 194.0 pm) and indicate that the central atoms are probably in an oxidation state of +3.

There are two tetranuclear examples (Table 4). The structures of $[(\eta^5\text{-cpVI})_2\{(\eta^5\text{-cp})V(NO)\}_2(\mu\text{-}O)_4]$ (ref.71) and $[(\eta^5\text{-cpMe})VS]_4$ (ref.72) are shown in Figure 9.

Hexakis(μ_3-oxo)pentabis(η^5-cyclopentadienylvanadium) (ref.74) is a trigonal bipyramid of vanadium atoms with an oxygen atom over each triangular face. The cyclopentadienyl rings that cap each vanadium atom have perpendicular distances from the axial vanadium atoms of 199.7 pm, and from the equatorial vanadium atoms of 197.3 pm. The V(ax)-O distance of 186.1(6,15) pm is shorter than the V(eq)-O distance of 199.2(6,11) pm. The differing equatorial and axial V-cp and V-O distances are due to the different oxidation states of the vanadium atoms, V(ax) being +4, and V(eq) being +3. The V(ax)-V(eq) average distance of 275.2(2) pm is about 1.2 pm larger than the V(eq)-V(eq) distance of 274.0(2) pm. This compound appears to be the only pentanuclear vanadium organometallic, and also the highest cluster determined to date. The data in Table 4 shows the expected shorter V-C (CO) bond lengths for unidentate compared to the semibridge situations, 192.9 pm versus 217.5 pm. The mean values of V-S (S) distances increase in the order 223.5 pm (unidentate) < 229.2 pm (tridentate). The mean V-C (cp) distance of 226.9 pm is shorter than the values for mono- and biscyclo-pentadienyl mononuclear compounds (227.8 and 227.9 pm respectively) shown in Tables 2 and 3.

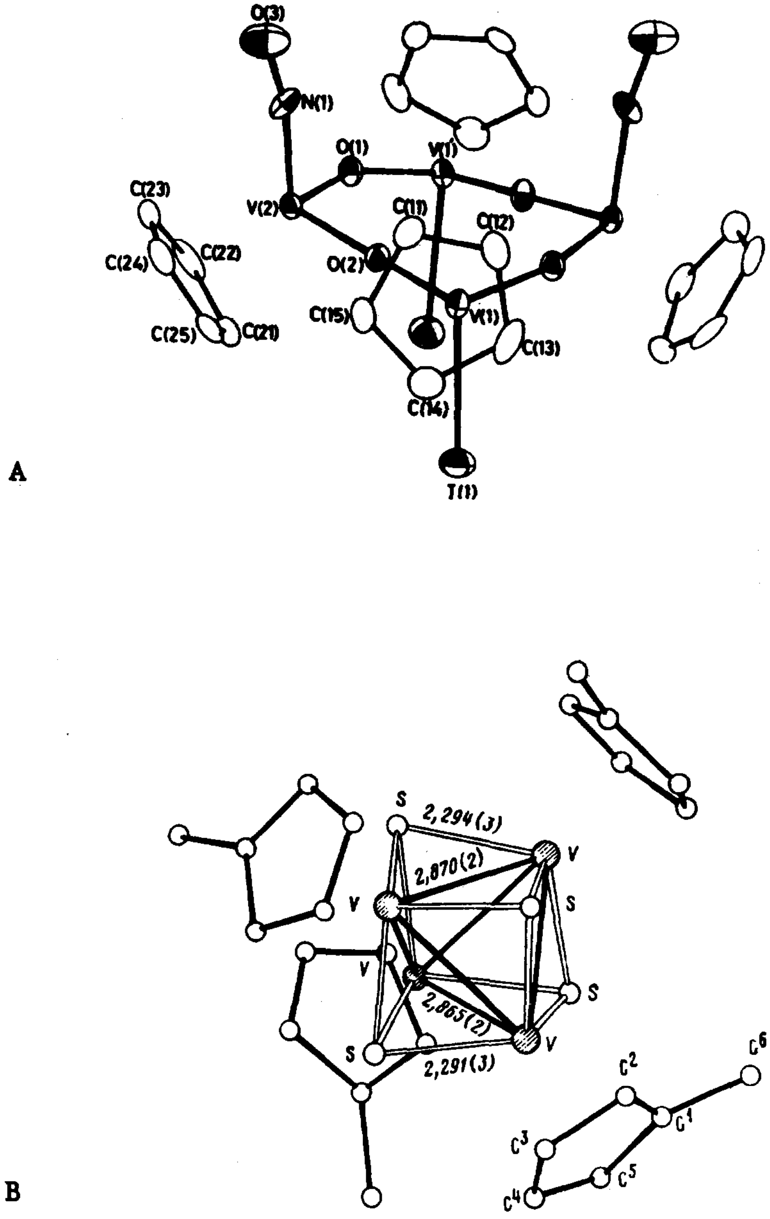

Figure 9. The structure of $[(\eta^5\text{-cpVI})_2\{(\eta^5\text{-cp})V(NO)\}_2(\mu\text{-}O)_4]$ (top) Reproduced with permission from J. Chem. Soc., Chem. Commun. (Ref.71) and $[(\eta^5\text{-cpMe})VS]_4$ (bottom) Reproduced with permission from Izv. Akad. Nauk SSSR (Ref.72)

TABLE 4. STRUCTURAL DATA FOR HOMO-OLIGONUCLEAR VANADIUM ORGANOMETALLICS[a]

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] β[°] γ[°]	M–L [pm]	M–M [pm] M–L–M[°] L^c–M–L^c[°]	L–M–L L^c–M–L L^c(L)–M–Cp [°]	Ref.
$(\eta^6\text{-}C_6H_6)_2V^I_2(CO)_4$	m	$P2_1/c$	4	1499.4(12)		$OC^{b,c}$ d	225	d	61
				660.5(7)	108.46(8)	CO^c d			
				1525.3(14)		$(\eta^6)C$ d			
$(\eta^5\text{-cp})_2V^I_2(CO)_5$[e]		$P2_1/n$	4	837.6(8)	90	OC 193.8(4,36)	245.9(3)	81.9(2)	62
				1554.7(18)	91.78(9)	OC^c194.0(5,1)	–	76.8(2,5.7);126.8(2,4.3)	
				1118.3(11)	90	OC^c241.7(5,31)	84.0(2),113.0(2)	117.0(0,8.6)	
						(cp)C 226.2(5,34)			
$(\eta^5\text{-cp})_2V^I_2(CO)_5$[f]		$P2_1/n$	4	824.6(2)		OC 193.3(11,34)	246.2(2)	81.4(4)	63,64
				1576.9(5)	91.66(2)	OC^c193.6(11,11)	67.7(3,3)	76.8(4,4.9),126.9(4,3.3)	
				1172.9(2)		OC^c242.1(10,19)	84.1(4),113.7(4)		
						(cp)C 223.9(11,20)			
$(\eta^5\text{-cp})_2V^I_2(CO)_4PPh_3$[g]		$P\bar{1}$	2	822.5(2)	102.13(2)	OC 192.2(6,10)	246.6(2)	82.8(2)	62
				1680.6(4)	101.91(2)	P 247.2(2)		77.6(2,6.3);127.9(2,2.3)	
				1019.3(3)	83.84(1)	OC^c192.5(5,0)	84.0(2);113.1(2)	117.6(0,6.1)	
						OC^c240.0(5,0)			
						(cp)C 227.2(6,25)			

TABLE 4. Continued 2

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] β[°] γ[°]	M-L [pm]	M-M[pm] M-L-M[°] L^c-M-L^c[°]	L-M-L L^c-M-L L^c(L)-M-Cp [°]	Ref.
$(\eta^5\text{-cp})_2V_2S_2\{S_2C_2(CF_3)_2\}$	m	C2/c	4	1320.6(3)		$(S_2)S^c$ 238.0(2,0)	257.4(3)	d	65
				1529.4(4)	114.40(1)	$(L)S^c$ 242.9(2,1)			
				1008.6(1)		(cp)C d			
$(\eta^5\text{-cpPr})_2V_2S_4$	m	$P2_1/c$	4	1039.0(3)		S^c 223.5(2,45)	261.0(1)	d	65
				1010.3(2)	102.08(2)	(cp)C d			
				1848.5(5)					
$(\eta^5\text{-cpMe})_2V_2S_5$	m	C2/c	8	1270.3(5)		S^c 235.1(1,89)	265.8(1)	d	66
				791.7(2)	102.22(4)	(cp)C d	68.6(1,3.3)		
				3130(1)			d		
$[(\eta^5{:}\eta^5\text{-}C_{10}H_8)_2V^{III}{}_2\cdot$	or	$Cmc2_1$	4	777.1(1)		N 209(1,2)	332.9(4)	d	67
$\cdot(CH_3CN)_2]\cdot$				2055.6(3)		C 228(1,10)			
$\cdot(PF_6)_2\cdot CH_3CN$				1832.4(3)					
$[(\eta^5\text{-cp})V^{III}(C_4H_3OOOO)_2]_2$	m	B2/b	4	1880(2)		O^c 204(1,1)	362.5		68
				1874(2)		(cp)C 234(2,5)	-		
				822(2)	106.2(5)		83.0(5,2.4)		

TABLE 4. Continued 3

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] β[°] γ[°]	M-L [pm]	M-M[pm] M-L-M[°] L^c-M-L^c[°]	L-M-L L^c-M-L L^c(L)-M-Cp [°]	Ref.
$[(\eta^5\text{-cp})V^{III}(F_3CCOO)_2]_2$	tr	$P\bar{1}$	1	900(1)	65.9(3)	O^c 205	370.4		69
				875(1)	105.5(3)	(cp)C 228	–		
				888(1)	102.8(3)		82.0		
$[\{(\eta^5\text{-cp})_2V\}_2(COS_2)]$.		$P2_1/c$	4	1631.7(5)	90.0	O 200.6(6)		69.5(1)	70
$.C_6H_6$				1056.6(2)	114.72(4)	S 247.5(4,9)			
				1541.6(5)	90.0	(cp)C 226.2(10,82)		107.9(4,8)	
$[(\eta^5\text{-cpVI})_2\{(\eta^5\text{-cp})$.	m	C2/c	4	1835.8(3)		I d	d	d	71
$.V(NO)\}_2(\mu\text{-}O)_4]$				815.2(1)	91.27(2)	O^c d	148.1;179.3(3)		
				1759.0(2)		(cp)C d			
$(\eta^5\text{-cpMe})_4V^{III}{}_4S_4$	c	$P\bar{4}3n$	6	1634.8(6)		S^c 229.2(3,2)	286.7(2,3)		72
						(cp)C d			
$(\eta^5\text{-cp})_5V_5O_6$	m	$P2_1/c$	4	982.5(4)		O^c 194.8(6,95)	274.8(2,15)	h	73,
				1558.4(9)	125.83(3)	(cp)C d	89.69(26,3.01)		74
				1959.2(8)			84.6(2,9.2);132.4(2,6)		

a. Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in brackets is the e.s.d., and the second is the maximum deviation from the mean value. b. The chemical identity of the coordinating atom or ligand. c. The bridge atom (ligand). d. not given. e. at 123 K. f. At 295 K. g. At 143 K. h. The values of cp(centroid)-V-cp(centroid) angles are: 89.9(0,2.5) and 120.0(0,3.5)°; the V-cp(centroid) bond distance is 197.8(0,16)Å.

The V-V distances can be separated into four types in the binuclear derivatives. A triple bond with a V-V distance of 225 pm (ref.61), where the vanadium atoms are bridged by four CO ligands. A double bond with the V-V distance in the range 245.9-246.6 pm (refs.62-64), where there are two CO ligands as semi-bridges between the metal atoms. A single bond with a V-V distance in the range 257.4-261.0 pm (ref.65) as shown in Figure 8. Finally, two examples with V-V distances of 362.5 and 370.4 pm (refs. 68 and 69), indicating an absence of metal bonding, with the two vanadium atoms bridged by four carboxylate groups.

The mean values of the V-V distances in tetranuclear and pentanuclear clusters, 286.7 pm (ref.72) and 274.8 pm (ref.74) respectively, indicate single bond character in these cases.

D. Hetero-oligonuclear Compounds

Crystal and structural data for hetero-oligonuclear compounds are given in Table 5. The data are tabulated in order of increasing V-V distance. The crystal structure of the red $(\eta^5\text{-cpMe})_2V_2S_3Fe(CO)_3$ (ref.76) is shown in Figure 10. The three metal atoms are arrayed in the approximate form of an

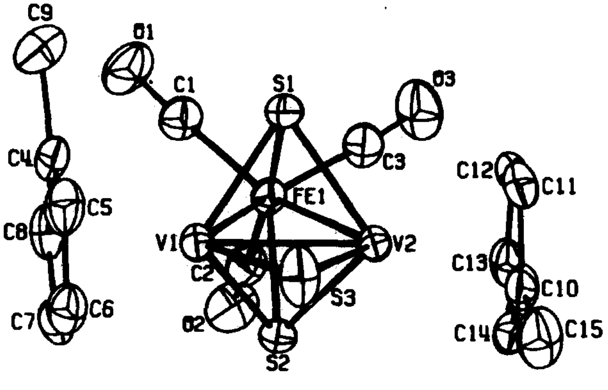

Figure 10. The crystal structure of $(\eta^5\text{-cpMe})_2V_2S_3Fe(CO)_3$ Reproduced with permission from J. Am. Chem. Soc., (Ref.76)

isosceles triangle, with a V-V distance of 251 pm and two V-Fe distances of 282(1) pm. The V-S(3) distance of 223(1) pm is the only one mentioned in the report, but clearly indicates some multiple bond character. In another isosceles triangle of metal atoms (ref.77), with two vanadium atoms and one iron, the triangle is capped by two μ_3-S ligands and the V-V edge is spanned by a μ-S and a μ-η^1-ptd ligand (Table 5).

X-ray analysis of the black crystals of $(\eta^5\text{-cpMe})_2V_2S_4Fe_2(NO)_2$ (ref.78) shows a distorted cubane core of $V_2Fe_2S_4$ (Figure 11) with a Fe-Fe distance of 275 pm and V-V distance of 295 pm, which is indicative of a weak but significant interaction.

In hetero-binuclear $[(\eta^5\text{-cp})_2Nb(CO)](\mu\text{-H})[(\eta^5\text{-cp})V(CO)_3]$, the Nb and V containing moieties are bridged by a hydrogen atom (ref.79). There are two independent molecules in the structure with respective Nb...V distances of 370.1(3) and 372.5(4) pm, indicative of an absence of metal bonding. The V-L distances are shorter than those of Nb-L (Table 5) as expected. The two independent molecules differing by degree of distortion is another example of distortion isomerism.

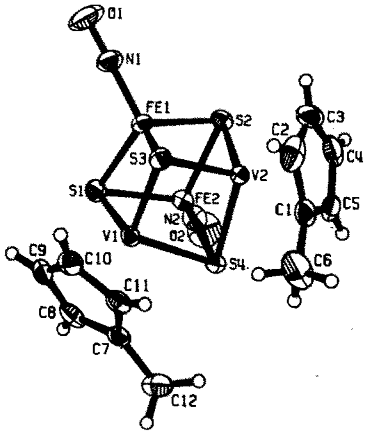

Figure 11. The crystal structure of $(\eta^5\text{-cpMe})_2V_2(NO)_2S_4Fe_2$
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TABLE 5 STRUCTURAL DATA FOR HETERO-OLIGONUCLEAR VANADIUM ORGANOMETALLICS[a]

Compound	Crystal Class	Space Group	Z	a[pm] b[pm] c[pm]	α[°] β[°] γ[°]	V-L [pm]	V-V [pm]	Ref.
$(\eta^5\text{-cpMe})_2V_2S_3Fe(CO)_3$[d]	m	$P2_1/c$	8	1039.7(2)		$S^{b,c}$ 223(1)	251	76
				2550.4(7)	102.63(2)	Fe^c 282(1)		
				1413.5(4)		(cp)C e		
$(\eta^5\text{-cpMe})_2V_2{}^{IV}S_3(ptd)$.		$P2_1/c$	4	2218.1(7)		N 199.0(9)	255.6(2)	77
$.Pt(PPh_3)_2$				1317.6(4)	111.10(2)	S^c 237.5(3,112)	f	
				1930.3(5)		(cp)C e		
$(\eta^5\text{-cpMe})_2V_2S_4Fe_2(NO)_2$	m	$P2_1/n$	4	961.6(2)		S^c e	295	78
				2021.9(5)	99.16(2)	Fe^c 275		
				974.6(2)		(cp)C e		
$[(\eta^5\text{-cp})V(CO_3)](\mu\text{-H})$.		$P\bar{1}$	4	1103.3(4)	68.90(3)	OC 193.5(19,28)	g	79
$.[(\eta^5\text{-cp})_2Nb(CO)]$[d]				1320.6(5)	71.17(3)	H^c 163(20)		
				1476.3(5)	68.91(3)	(cp)C 227.5(20,29)		
						OC 191.5(20,25)		
						H^c 169(16)		
						(cp)C 227.2(17,39)		

a. Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in brackets is the e.s.d., and the second is the maximum deviation from the mean value.

b. The chemical identity of the coordinating atom or ligand. c. The bridge atom. d. There are two crystallographically independent molecules.

e. Not given. f. The values of V-S-V angles, 65.2(1,3.1)°; the V-cp (centroid) distances, 1.98(1) and 1.97(1). g. There is V ... Nb distance, 372.5(4) and 370.1(3)pm; the bond distances around Nb(1) and Nb(2) are Nb-H = 206(18) and 187(15)pm; Nb-C(CO) = 202.4(15) and 203.8(22)pm; Nb-C(cp) = 238.7(17,91) and 238.5(21,70)pm, respectively.

4. CONCLUSION

From 1963, when the first organovanadium structure was characterized by X-ray analysis, to the end of 1984 almost eighty crystal structures have been determined. The majority of these can be seen to be mono- and binuclear, with only four tetranuclear and one each of tri- and pentanuclear examples.

The oxidation numbers of the vanadium ranges from +4 to -1, with a few examples of mixed valency compounds (section 3C). There are three examples (refs. 8, 9, and 31) with the vanadium hexacarbonyl anion and a vanadium containing cation in which a different oxidation number is observed for the vanadium atoms.

Two crystallographically independent molecules, differing by degree of distortion, are present in seven examples (refs.22,24,38,54,59,76, and 78). There is even an example, $[V(CO)_4(\mu\text{-}(PMe_2))]_2$ (ref.11), in which four such molecules are present. Such types of distortion have also been found for niobium and tantalum organometallics (ref.1). The coexistence of two or more species with the same coordination number of the central atom, but different degrees of distortion within the same crystal, is typical of the general class of distortion isomerism (ref.18).

The temperature dependence of V-L bond distances has been noted in one compound (refs. 62-64) which has been examined at different temperatures.

Vanadium organometallic compounds with a unidentate carbon ligand show a coordination number from four to eight. For the carbonyl compounds, the V-C (CO) distance is independent of the coordination polyhedron. In a series of compounds with one multidentate ligand, the mean V-C bond distance increases in the order: 192.5 pm (CO) < 227.8 pm (cp) < 233.1 pm $(\eta^3\text{-}C_3H_5)$ < 233.5 pm $(C_6H_2Me_4)$.

There is a relationship between the cp(centroid)-V-cp(centroid) angle and the V-C (cp) distance, such that the angle closes as the distance increases. The mean value of this angle decreases in the order: 144.0° $[(cp)_2VL$, L = unidentate] < 137.7° $[(cp)_2VL$, L = bidentate] < 136.1° $[(cp)_2VL_2$, L = unidentate]. The mean value of the V-cp(centroid) distance increases with the oxidation number of the vanadium atom: 190- 194.8 pm (192.2 pm mean) for V(+2) < 193-197.3 pm (195.0 pm mean) for V(+3) < 196.6-205.4 pm(200.6 pm mean) for V(+4).

An overall summary of the structural data for the organometallic compounds of vanadium, niobium and tantalum is given in Table 6. Some points of interest arising from the data are listed below.

(a) In general, V-L bond distances are found to be shorter than corresponding Nb-L and Ta-L distances.

(b) Mean M-L bond distances in mononuclear compounds of Nb and Ta with one

TABLE 6 SUMMARY OF THE VANADIUM-ATOM (LIGAND), NIOBIUM-ATOM (LIGAND) AND TANTALUM-ATOM (LIGAND) BOND DISTANCES (pm)^{a}

Coord. Atom (Ligand)		Mononuclear		Homobinuclear
		Mono-cp	Bis-cp	
C(cp)	V	222.3-234.7(227.8)	217.0-243.9(227.9)	218.0-238.0(226.9)
	Nb	236.4-248.0(242.5)	234.0-246.0(240.3)	232.0-248.8(242.2)
	Ta	224.0-262.0(242.1)	230.0-245.7(238.4)	
C(cp*)	V		213.0-239.0(227.5)	
	Ta	237.1-251.8(243.0)		240.0-263.3(247.0)
C(cp*Et)	V		228-234(231)	
	Ta			230.0-253.2(243.3)
C(CO)	V	186.3-196.0(192.0)	187.9-199.0(195.0)	189.0-197.2(192.9)
	Nb	200.0-211.5(206.0)	202.0-204.0(203.0)	196.0-211.5(206.5)
	Ta	201.0		194.0
C^{b}	V		203.2-221.3(211.7)	
	Nb	210.0-251.0(231.0)	227.7-234.6(230.6)	209.0-235.0(222.0)
	Ta	185.0-242.0(220.0)	207.0-233.0(220.2)	219.5-235.4(229.7)
Cℓ	V	240.1-240.5(240.3)	239.0-239.8(239.4)	
	Nb	246.3-250.5(248.1)	246.4-248.3(247.4)	232.0-237.0(234.5) (255.7-257.0(256.5))^{c}
	Ta	236.2-259.6(244.4)	243.9-247.9(245.4)	231.9-247.2(237.6) (246.1-269.0(257.3))^{c}
S	V		241.5-247.0(244.4)	221.0-228.0(223.5) (238.0-243.0(241.3))^{c} (229.1-229.4(229.3))^{d}
	Nb		243.2-260.2(251.2)	(242.8-264.8(253.7))^{c}
P	V	230.3-251.0(243.9)		
	Ta	250.7-265.0(259.4)	253.4-253.6(253.5)	

a. The mean value is in parenthesis. The values for Nb and Ta compounds (ref.1). b. Excluding all ligands listed above. c. The values of a bridge atom (ligand).d. The values of a triple bridge atom (ligand).

cyclopentadienyl ligand are shorter than those with two such ligands. For vanadium this is not the case. The mean extent of the decrease of M-C (cp) is 3.7 pm for Ta, 2.2 pm for Nb, and -0.1 pm for V. The mean extent of the decrease for M-C (CO) is 7 pm for Ta, 3 pm for Nb, and -3pm for V. Presumably both steric and electronic effects play a role in these variations.

(c) In the mononuclear biscyclopentadienyl compounds with S_2 or CS_2 bonded via two atoms, the M-L distances correspond to the van der Waal radii. For example: L = CS_2; V-C = 208.2 pm, V-S = 243.8 pm, Nb-C = 222.4 pm; Nb-S = 250.9 pm: L = S_2; V-S = 241.5 pm, NbS = 252.2 pm. All are mean values.

(d) The M-L bridge distances tend to be somewhat longer than the M-L terminal distances, and the M-L distances in homo-oligonuclear derivatives are somewhat longer than those of heteronuclear compounds.

(e) In heterobinuclear derivatives the M-M' distance increases with increasing M-L-M' angle, and at the same time the M-L bridge distance also increases. The shortest V-V distance of 225 pm is found for the homobinuclear compounds, and increases in the order: 251 pm for heteronuclear < 273.7 pm for pentanuclear < 286.5 pm for tetranuclear. The shortest distances for niobium and tantalum are larger by 48.2 pm and 42.7 pm respectively.

(f) From environments containing zero, one, two, three or four bridging atoms, the most favourable for M-M bonding is that in which there are two bridging atoms.

(g) As the M-L-M angle opens the M-M distance increases, as expected. Increased steric hindrance of the coordinated ligands also serves to increase the M-M distance.

The factors governing the choice of geometry in these complexes include electronic configuration of the central atom, crystal packing forces, and the nature of the ligands. For example, chelating ligands are often found to play a substantial role in the nature of the overall structure, stereochemistry, and fluxional behaviour of the organometallic derivatives of the Group Vb metals. This review, together with those for niobium and tantalum (ref.1), represents an overview of the almost two hundred structures which have been determined for this group of transition metals. To our knowledge, it is the first such survey of an entire subgroup, and illustrates the rich chemistry of this group and the many systematic trends which have been observed. A related series for the coordination complexes of these metals has also been undertaken (ref.80).

Although applications of organometallic compounds in biological and medical research are widespread (ref.81), there have been relatively few studies with the vanadium subgroup. However, antineoplastic properties have been reported for $cp_2MC\ell_2$ compounds, where M is a d^0, d^1 or d^2 metal ion. Thus both $cp_2VC\ell_2$ (ref.82) and $cp_2NbC\ell_2$ (ref.83) have been shown to be very effective against Ehrlich ascites tumor in mice, but also very toxic (LD_{50} = 30mg/kg). It has been suggested (ref.83) that the biological properties are related to the $C\ell$-M-$C\ell$ bite, which is almost the same for $cp_2NbC\ell_2$ and the well known anti-tumor dichloroplatinum complexes at 335 pm. An estimate for the vanadium derivative, based on the methyl-cyclopentadienyl analogue (ref.50) suggests a $C\ell$–M–$C\ell$ bite of about 320 pm, slightly less than another actively antineoplastic compound $cp_2MoC\ell_2$ (ref.83). In this respect, a possible candidate to test the bite hypothesis might be the d^2 system $(\eta^5\text{-cp})VC\ell_2(PMe_3)_2$ with a bite of approximately 415 pm, and probably therefore inactive.

It is hoped that this series of structural reviews will serve to stimulate further investigations in these interesting and useful areas of chemistry.

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