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Synthesis and molecular structure of the diamagnetic trigonal-bipyramidal cluster $(\pi\text{-MeC}_5\text{H}_4)_5\text{V}_5(\mu_3\text{-S})_6$

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Abstract

The reaction of $(\text{MeC}_5\text{H}_4)_2\text{V}$ with HSCMe_3 in boiling heptane leads together with the previously described tetranuclear cluster $\text{Cp}_4\text{V}_4(\mu_3\text{-S})_4$ (I) ($\text{Cp} = \eta\text{-CH}_3\text{C}_5\text{H}_4$) to the diamagnetic pentanuclear cluster $\text{Cp}_5\text{V}_5(\mu_3\text{-S})_6$ (II). The structure of II was confirmed by an X-ray study. The crystals of II are triclinic, *a* 9.9071(9), *b* 10.2952(9), *c* 16.9685(16) Å, α 94.062(7), β 90.399(7), γ 64.145(6)°, *V* 1553.0(4) Å^3, space group $P\bar{1}$. The metal framework of the cluster is in the form of a trigonal bipyramid with average $\text{V}_{\text{eq}}\text{–V}_{\text{ax}}$ and $\text{V}_{\text{eq}}\text{–V}_{\text{eq}}$ bond lengths of 3.062(2) and 3.206(2) Å, respectively. The μ_3-bridge sulphur atoms are situated over the faces of the bipyramid at average $\text{V}_{\text{eq}}\text{–S}$ and $\text{V}_{\text{ax}}\text{–S}$ bond lengths of 2.396(2) and 2.226(2) Å, respectively, forming also intramolecular S...S contacts of 2.8 Å.

Introduction

Recently the structures of the deltohedron clusters $(\text{C}_5\text{H}_5)_n\text{M}_n\text{O}_m$ (M = Cr, $n = m = 4$ [1]; M = V, $n = 5$, $m = 6$ [1]; M = Ti, $n = 6$, $m = 8$ [2]) were described, containing a μ_3-oxygen bridge over each triangular face. Our X-ray structure study of the μ_3-sulphide bridge analogue of the chromium-containing cluster $(\text{CH}_3\text{C}_5\text{H}_4)_4\text{Cr}_4\text{S}_4$ showed that this diamagnetic complex contains a regular metallatetrahedron with equal Cr–Cr bonds of 2.822 Å [3], whereas in the antiferromagnetic complex $(\text{C}_5\text{H}_5)_4\text{Cr}_4\text{O}_4$ the Cr–Cr bonds are respectively 2.706, 2.826 and 2.898 Å [1].

Comparison of the function of the bridge ligands in other deltohedron clusters is of great interest, in particular those containing a trigonal-bipyramidal V_5 frame-

Table 1

Atomic coordinates and anisotropic temperature factors for II

(Atomic coordinates multiplied by 10^4 (for V and S by 10^5). Anisotropic temperature factors are given in the form: $T = \exp - 1/4(B_{11}ah + B_{22} + bk + B_{33}cl + 2B_{12}abhk + 2B_{13}achl + 2B_{23}bckl)$

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
V(1)	26378(12)	43102(12)	66537(6)	1.93(5)	2.11(5)	1.16(4)	−1.12(4)	−0.07(4)	0.29(3)
V(2)	34388(13)	23875(12)	81547(7)	1.82(5)	1.87(5)	1.54(4)	−0.74(4)	−0.29(4)	0.43(4)
V(3)	234(12)	45435(12)	78289(6)	1.57(4)	2.08(5)	1.21(4)	−0.87(4)	−0.05(3)	0.12(3)
V(4)	17600(13)	18067(12)	67425(7)	2.17(5)	2.04(5)	1.60(5)	−1.16(4)	0.07(4)	−0.06(4)
V(5)	23388(13)	56623(12)	83463(6)	2.13(5)	2.07(5)	1.36(4)	−1.17(4)	−0.25(4)	0.20(4)
S(1)	3747(19)	40614(18)	64290(9)	1.96(7)	2.33(7)	1.19(6)	−1.03(6)	−0.20(5)	0.15(5)
S(2)	6941(19)	63538(18)	73795(10)	2.09(7)	1.87(6)	1.52(7)	−0.82(6)	−0.24(5)	0.35(5)
S(3)	43599(19)	39972(18)	76930(10)	1.77(7)	2.45(7)	1.66(7)	−1.13(6)	−0.19(5)	0.29(5)
S(4)	40317(19)	17511(18)	67663(10)	1.74(7)	2.12(7)	1.86(7)	−0.81(6)	0.21(5)	0.02(5)
S(5)	12228(20)	20039(18)	80296(10)	2.25(7)	2.13(7)	1.66(7)	−1.14(6)	0.05(6)	0.29(5)
S(6)	15384(19)	42816(18)	89671(9)	2.02(7)	2.29(7)	1.13(6)	−1.08(6)	−0.12(5)	0.24(5)
C(11)	4609(8)	4047(8)	5806(4)	3.5(4)	3.7(4)	1.3(3)	−2.2(3)	0.5(2)	0.5(2)
C(12)	3526(8)	3757(8)	5353(4)	3.3(4)	4.1(4)	1.1(3)	−2.2(3)	0.2(2)	0.6(2)
C(13)	2116(9)	5071(9)	5379(4)	3.8(4)	4.9(4)	1.4(3)	−2.3(3)	−0.3(3)	1.8(3)
C(14)	2329(9)	6180(9)	5857(4)	4.3(4)	4.0(4)	2.1(3)	−2.3(3)	0.3(3)	1.4(3)
C(15)	3869(9)	5539(8)	6126(4)	4.2(4)	3.8(4)	1.8(3)	−2.5(3)	0.5(3)	0.7(3)
C(16)	6213(8)	3028(9)	5873(5)	2.1(3)	5.1(5)	3.0(4)	−1.2(3)	0.4(3)	0.6(3)

C(21)	5930(8)	808(8)	8350(5)	1.9(3)	3.0(3)	3.6(4)	−0.4(3)	−1.1(3)	1.6(3)
C(22)	5448(9)	1818(9)	9017(5)	3.5(4)	3.4(4)	3.7(4)	−0.5(3)	−2.3(3)	1.6(3)
C(23)	4279(9)	1627(9)	9410(5)	3.4(4)	4.5(4)	2.4(4)	0.0(3)	−1.5(3)	1.9(3)
C(24)	4037(9)	509(8)	8980(5)	3.6(4)	3.3(4)	3.4(4)	−0.6(3)	−1.1(3)	2.4(3)
C(25)	5048(8)	15(8)	8323(5)	2.2(3)	2.4(3)	3.6(4)	−0.3(3)	−0.9(3)	1.4(3)
C(26)	7235(9)	550(10)	7798(6)	2.1(4)	5.6(5)	6.0(5)	−1.2(4)	0.0(4)	2.1(4)
C(31)	−2445(8)	6029(8)	7536(4)	1.4(3)	4.0(4)	2.3(3)	−0.8(3)	−0.1(2)	0.3(3)
C(32)	−2295(8)	4591(9)	7625(5)	1.8(3)	4.5(4)	3.3(4)	−1.8(3)	0.4(3)	−0.4(3)
C(33)	−1918(8)	4272(9)	8416(5)	2.1(3)	4.5(4)	2.9(4)	−1.6(3)	0.9(3)	0.2(3)
C(34)	−1834(7)	5477(8)	8820(4)	1.5(3)	3.8(4)	2.4(3)	−0.8(3)	0.5(2)	0.0(3)
C(35)	−2151(8)	6572(8)	8276(4)	1.5(3)	3.6(4)	2.1(3)	−0.7(3)	0.3(2)	−0.2(3)
C(36)	−2953(9)	6864(10)	6805(5)	3.0(4)	5.3(5)	2.2(3)	−0.2(3)	−0.9(3)	1.1(3)
C(41)	1745(9)	696(8)	5498(4)	4.0(4)	2.9(3)	2.1(3)	−2.0(3)	0.0(3)	−0.7(3)
C(42)	318(9)	1110(9)	5878(5)	3.4(4)	4.2(4)	4.9(5)	−2.4(4)	0.0(3)	−2.1(4)
C(43)	572(12)	330(11)	6562(5)	8.4(7)	6.3(6)	4.0(5)	−6.2(5)	2.2(4)	−2.1(4)
C(44)	2122(12)	−545(9)	6609(5)	9.3(7)	3.1(4)	3.1(4)	−3.7(4)	−0.8(4)	0.0(3)
C(45)	2864(9)	−340(8)	5954(5)	4.0(4)	2.7(3)	3.6(4)	−1.1(3)	−0.6(3)	−0.9(3)
C(46)	2005(13)	1191(11)	4710(5)	10.3(8)	6.5(6)	2.1(4)	−5.8(6)	−0.3(4)	0.4(4)
C(51)	1393(9)	7563(8)	9324(4)	3.5(4)	2.9(3)	2.5(3)	−1.8(3)	0.1(3)	−0.6(3)
C(52)	2775(9)	6467(8)	9581(4)	4.4(4)	3.6(4)	1.9(3)	−2.5(3)	−0.5(3)	−0.3(3)
C(53)	3962(9)	6326(9)	9060(5)	3.8(4)	4.0(4)	3.4(4)	−2.4(3)	−0.7(3)	−0.5(3)
C(54)	3330(10)	7311(9)	8474(5)	5.0(5)	3.9(4)	3.1(4)	−3.3(4)	0.0(3)	−0.2(3)
C(55)	1751(10)	8094(8)	8647(5)	5.2(5)	2.8(3)	2.4(3)	−2.2(3)	−0.5(3)	0.1(3)
C(56)	−109(10)	8126(10)	9730(5)	4.2(5)	5.3(5)	3.9(4)	−2.3(4)	1.7(4)	−1.6(4)

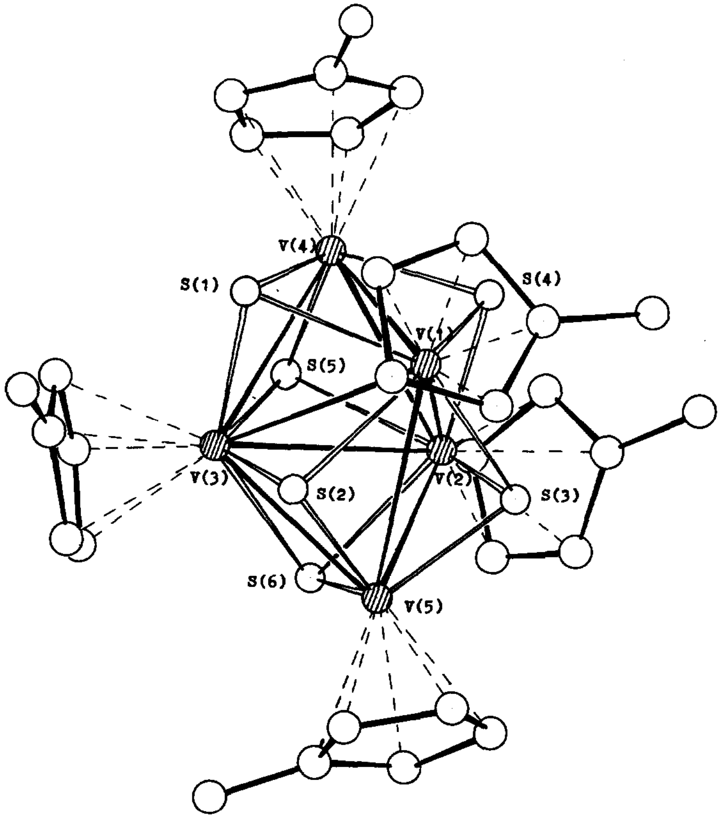

Fig. 1. The molecular structure of $(\pi\text{-MeC}_5\text{H}_4)_5\text{V}_5(\mu_3\text{-S})_6$.

work. Therefore we carried out an X-ray study of the cluster $(\text{CH}_3\text{C}_5\text{H}_4)_5\text{V}_5\text{S}_6$ (II), briefly mentioned in ref. 4, which was recently obtained by Rauchfuss and coworkers, independently of us, via the reaction of $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{V}_2\text{S}_4$ with PBu_3 and separated from the tetrahedron $(\text{CH}_3\text{C}_5\text{H}_4)_4\text{V}_4\text{S}_4$ (I) by sublimation in vacuum [4].

Results and discussion

Cluster II results together with the previously described tetrahedron $(\text{CH}_3\text{C}_5\text{H}_4)_4\text{V}_4\text{S}_4$ (I) [5] on heating bis(methylcyclopentadienyl)vanadium with t-butylmercaptane in boiling heptane (the products were separated chromatographically on Al_2O_3; yields: 13.5 and 60%, respectively):

$$(\text{CH}_3\text{C}_5\text{H}_4)_2\text{V} + \text{Me}_3\text{CSH} \xrightarrow[\text{heptane}]{100\,^\circ\text{C}} \underset{\text{(I)}}{(\text{CH}_3\text{C}_5\text{H}_4)_4\text{V}_4\text{S}_4} + \underset{\text{(II)}}{(\text{CH}_3\text{C}_5\text{H}_4)_5\text{V}_5\text{S}_6}$$

The mass spectrum of II shows a molecular ion peak P^+ (m/e 842) and also peaks of the products of successive cleavage of $\text{CH}_3\text{C}_5\text{H}_4$ ligands up to $\text{V}_5\text{S}_6{}^+$ (m/e 763, 684, 605, 526 and 447, respectively). The X-ray study of cluster II was carried out for objective determination of its structure (see Fig. 1 and Tables 1–3).

Table 2

Bond lengths *d* (Å) for II

Bond	*d*	Bond	*d*
V(1)–V(2)	3.217(2)	V(3)–S(2)	2.405(2)
V(1)–V(3)	3.194(2)	V(3)–S(5)	2.403(2)
V(1)–V(4)	3.071(2)	V(3)–S(6)	2.395(2)
V(1)–V(5)	3.059(2)	V(3)–C(31)	2.323(8)
V(1)–S(1)	2.390(2)	V(3)–C(32)	2.300(9)
V(1)–S(2)	2.405(2)	V(3)–C(33)	2.304(9)
V(1)–S(3)	2.384(2)	V(3)–C(34)	2.326(8)
V(1)–S(4)	2.404(2)	V(3)–C(35)	2.335(8)
V(1)–C(11)	2.341(8)	V(4)–S(1)	2.223(2)
V(1)–C(12)	2.319(7)	V(4)–S(4)	2.226(2)
V(1)–C(13)	2.331(7)	V(4)–S(5)	2.226(2)
V(1)–C(14)	2.340(8)	V(4)–C(41)	2.333(7)
V(1)–C(15)	2.327(9)	V(4)–C(42)	2.330(9)
V(2)–V(3)	3.206(2)	V(4)–C(43)	2.30(1)
V(2)–V(4)	3.078(2)	V(4)–C(44)	2.282(9)
V(2)–V(5)	3.050(2)	V(4)–C(45)	2.316(8)
V(2)–S(3)	2.389(2)	V(5)–S(2)	2.229(2)
V(2)–S(4)	2.406(2)	V(5)–S(3)	2.224(2)
V(2)–S(5)	2.400(2)	V(5)–S(6)	2.228(2)
V(2)–S(6)	2.388(2)	V(5)–C(51)	2.329(7)
V(2)–C(21)	2.326(8)	V(5)–C(52)	2.305(8)
V(2)–C(22)	2.347(8)	V(5)–C(53)	2.309(9)
V(2)–C(23)	2.342(8)	V(5)–C(54)	2.300(9)
V(2)–C(24)	2.329(8)	V(5)–C(55)	2.327(8)
V(2)–C(25)	2.299(8)	S(1)–S(2)	2.894(2)
V(3)–V(4)	3.062(2)	S(3)–S(4)	2.839(2)
V(3)–V(5)	3.081(2)	S(5)–S(6)	2.869(2)
V(3)–S(1)	2.388(2)		

Cluster II crystallizes as violet needles in the triclinic space group $P\bar{1}$, *a* 9.9071(9), *b* 10.2952(9), *c* 16.9685(16) Å, α 94.062(7), β 90.399(7), γ 64.145(6)°, *V* 1553.0(4) Å^3, $Z = 2$.

The framework of the molecule is an unsymmetrical trigonal bipyramide from the V atoms, compressed along the axis, passing through the V_{ax} atoms and the centre of the $(V_{eq})_3$ triangle. The V_{ax}–V_{eq} bond lengths of 3.050–3.081(2) Å are close to the sum of the covalent radii (3.0 Å), whereas the V_{eq}–V_{eq} bonds are noticeably lengthened to 3.194–3.217(2) Å. Analogous non-equivalence is observed for the values of the V–S bond lengths of 2.223–2.229(2) Å for V_{ax}–S and 2.384–2.406(2) Å for V_{eq}–S. This may be a consequence of intramolecular bonding of the sulphur atoms, situated over the faces of the $V_{ax}(V_{eq})_2$ triangles, while short S...S contacts of sulphur atoms are observed, both connected with one V_{ax} apex (3.15 Å) and with different V_{ax} apexes (2.85 Å). The geometry of cluster II agrees principally with that recently found for the dication $[(CH_3C_5H_4)_5V_5S_6]^{2+}(TCNQ^-)_2$ (III) [4], in which the V_{eq}–V_{eq} bonds are only slightly lengthened (3.21–3.25 Å) and the V_{eq}–V_{ax} bonds are shortened (2.97–3.01 Å). In addition, the S...S contacts between the S atoms bridged for equatorial V–V bonds are also shortened (to 2.77 Å). At the same time, the lengths of the V–S bonds remain practically unchanged (V_{ax}–S of 2.22 Å, V_{eq}–S

Table 3

Bond angles ω (°) for II

Angle	ω	Angle	ω
V(2)V(1)V(3)	60.00(4)	S(2)V(1)S(4)	137.98(8)
V(2)V(1)V(4)	58.56(4)	S(3)V(1)S(4)	72.72(7)
V(2)V(1)V(5)	58.09(4)	V(1)V(2)V(3)	59.64(4)
V(2)V(1)S(1)	92.70(6)	V(1)V(2)V(4)	58.35(4)
V(2)V(1)S(2)	92.55(6)	V(1)V(2)V(5)	58.36(4)
V(2)V(1)S(3)	47.67(5)	V(1)V(2)S(3)	47.55(5)
V(2)V(1)S(4)	48.05(5)	V(1)V(2)S(4)	47.99(5)
V(3)V(1)V(4)	58.47(4)	V(1)V(2)S(5)	92.52(6)
V(3)V(1)V(5)	58.98(4)	V(1)V(2)S(6)	92.42(6)
V(3)V(1)S(1)	48.02(5)	V(3)V(2)V(4)	58.28(4)
V(3)V(1)S(2)	48.39(5)	V(3)V(2)V(5)	58.94(4)
V(3)V(1)S(3)	93.11(6)	V(3)V(2)S(3)	92.73(6)
V(3)V(1)S(4)	92.65(6)	V(3)V(2)S(4)	92.32(6)
V(4)V(1)V(5)	105.84(5)	V(3)V(2)S(5)	48.17(5)
V(4)V(1)S(1)	45.96(5)	V(3)V(2)S(6)	48.00(5)
V(4)V(1)S(2)	105.58(6)	V(4)V(2)V(5)	105.90(5)
V(4)V(1)S(3)	104.62(6)	V(4)V(2)S(3)	104.31(6)
V(4)V(1)S(4)	46.01(5)	V(4)V(2)S(4)	45.90(5)
V(5)V(1)S(1)	105.72(6)	V(4)V(2)S(5)	45.91(5)
V(5)V(1)S(2)	46.26(5)	V(4)V(2)S(6)	104.88(6)
V(5)V(1)S(3)	46.19(3)	V(5)V(2)S(3)	46.31(5)
V(5)V(1)S(4)	104.64(6)	V(5)V(2)S(4)	104.85(6)
S(1)V(1)S(2)	74.25(7)	V(5)V(2)S(5)	105.73(6)
S(1)V(1)S(3)	138.00(8)	V(5)V(2)S(6)	46.43(5)
S(1)V(1)S(4)	91.33(7)	S(3)V(2)S(4)	72.61(7)
S(2)V(1)S(3)	91.81(7)	S(3)V(2)S(5)	137.75(8)
S(3)V(2)S(6)	92.25(7)	S(1)V(3)S(2)	74.28(7)
S(4)V(2)S(5)	91.15(7)	S(1)V(3)S(5)	91.61(7)
S(4)V(2)S(6)	137.58(8)	S(1)V(3)S(6)	138.06(8)
S(5)V(2)S(6)	73.64(7)	S(2)V(3)S(5)	138.31(8)
V(1)V(3)V(2)	60.35(4)	S(2)V(3)S(6)	91.06(7)
V(1)V(3)V(4)	58.76(4)	S(5)V(3)S(6)	73.44(7)
V(1)V(3)V(5)	58.32(4)	V(1)V(4)V(2)	63.09(4)
V(1)V(3)S(1)	48.07(5)	V(1)V(4)V(3)	62.77(4)
V(1)V(3)S(2)	48.38(5)	V(1)V(4)S(1)	50.63(6)
V(1)V(3)S(5)	93.02(6)	V(1)V(4)S(4)	50.98(6)
V(1)V(3)S(6)	92.85(6)	V(1)V(4)S(5)	100.11(7)
V(2)V(3)V(4)	58.77(4)	V(2)V(4)V(3)	62.95(4)
V(2)V(3)V(5)	58.01(4)	V(2)V(4)S(1)	99.98(7)
V(2)V(3)S(1)	93.02(6)	V(2)V(4)S(4)	50.91(6)
V(2)V(3)S(2)	92.83(6)	V(2)V(4)S(5)	50.75(6)
V(2)V(3)S(5)	48.08(5)	V(3)V(4)S(1)	50.74(6)
V(2)V(3)S(6)	47.81(5)	V(3)V(4)S(4)	99.96(7)
V(4)V(3)V(5)	105.54(5)	V(3)V(4)S(5)	51.12(6)
V(4)V(3)S(1)	46.11(5)	S(1)V(4)S(4)	100.84(8)
V(4)V(3)S(2)	105.85(6)	S(1)V(4)S(5)	101.10(8)
V(4)V(3)S(5)	46.14(5)	S(4)V(4)S(5)	100.87(8)
V(4)V(3)S(6)	105.16(6)	V(1)V(5)V(2)	63.55(4)
V(5)V(3)S(1)	105.13(6)	V(1)V(5)V(3)	62.69(4)
V(5)V(3)S(2)	45.93(5)	V(1)V(5)S(2)	51.21(6)
V(5)V(3)S(5)	104.74(6)	V(1)V(5)S(3)	50.68(6)
V(5)V(3)S(6)	45.94(5)	V(1)V(5)S(6)	100.03(7)
V(2)V(5)V(3)	63.05(4)	V(1)S(2)V(5)	82.54(7)
V(2)V(5)S(2)	100.81(7)	V(3)S(2)V(5)	83.24(7)

Table 3 (continued)

Angle	ω	Angle	ω
V(2)V(5)S(3)	50.96(6)	V(1)S(3)V(2)	84.77(7)
V(2)V(5)S(6)	50.92(6)	V(1)S(3)V(5)	83.13(7)
V(3)V(5)S(2)	50.83(6)	V(2)S(3)V(5)	82.72(7)
V(3)V(5)S(3)	99.57(7)	V(1)S(4)V(2)	83.96(7)
V(3)V(5)S(6)	50.56(6)	V(1)S(4)V(4)	83.01(7)
S(2)V(5)S(3)	101.14(8)	V(2)S(4)V(4)	83.19(7)
S(2)V(5)S(6)	100.43(8)	V(2)S(5)V(3)	83.75(7)
S(3)V(5)S(6)	101.31(8)	V(2)S(5)V(4)	83.35(7)
V(1)S(1)V(3)	83.91(7)	V(3)S(5)V(4)	82.74(7)
V(1)S(1)V(4)	83.41(7)	V(2)S(6)V(3)	84.19(7)
V(3)S(1)V(4)	83.15(7)	V(2)S(6)V(5)	82.65(7)
V(1)S(2)V(3)	83.23(7)	V(3)S(6)V(5)	83.49(7)

of 2.38 Å). The same relatively weak influence of the removal of two electrons on the framework geometry was observed earlier for the series of clusters (i-$PrC_5H_4)_4Mo_4S_4{}^{n+}$ ($n = 0, 1, 2$) [6].

On the other hand, the metalla framework of the known oxygen-bridge cyclopentadienyl analogue $Cp_5V_5O_6$ seems to be much more compressed (V_{ax}–V_{eq} of 2.752(2) Å, V_{eq}–V_{eq} of 2.740(2) Å, V_{ax}–O of 1.861(5) Å, V_{eq}–O of 1.992(6) Å, O...O 2.444(8) Å) [1]. It is worth noting that this oxygen-containing cluster has antiferromagnetic properties while cluster II is diamagnetic, in contrast to the data [4] on its weak paramagnetism ($\mu_{\text{effective}}$ was equal to 0.98 μ_B). The same influence of the nature of the bridge ligands on the magnetic properties of clusters was observed in the tetrahedral chromium clusters $Cp_4Cr_4X_4$, which are diamagnetic when X = S [7] and antiferromagnetic when X = O [1]. Apparently, the electronic structure of $Cp_5V_5X_6{}^n$ clusters has the same pecularities as those in the case of the tetrahedral clusters $Cp_4M_4X_4{}^n$ [8], where the extended Hückel method calculation has shown the slightly antibonding character of the HOMO and also the approach of the HOMO and LUMO upon going from X = S to X = O.

Experimental

All operations were carried out in a pure argon atmosphere. Heptane was purified by distillation over dispersed Na in a pure argon stream. IR spectra were measured with a Specord IR-75 instrument. Mass spectra were recorded on an automatic DS-50 system. X-Ray data were obtained with an automatic four-circle Hilger & Watts diffractometer (λMo-K_α, $\theta/2\theta$ scan, $2 \leqslant \theta \leqslant 60°$). The structure was solved by direct methods and refined using block-diagonal approximation for all non-hydrogen atoms to $R = 0.048$ ($R_w = 0.061$) for 5420 reflections. All calculations were performed on an Eclypse S/200 computer using INEXTL programs [9].

$(MeC_5H_4)_5V_5(\mu_3\text{-}S)_6$

3.5 cm^3 of $HSCMe_3$ (33.3 m*M*) was added to a violet solution of 3.45 g (16.5 m*M*) of $(MeC_5H_4)_2V$ in 60 ml of heptane and the reaction mixture obtained was refluxed for 3 h. The brown solution obtained was concentrated to 10 ml at 50 °C/10 Torr and was chromatographed on a 15 × 3 cm Al_2O_3 column; brown (A) and then violet (B) zones were eluted with heptane. 1.6 g (2.46 m*M*) of $(MeC_5H_4)_4V_4S_4$ [5] was isolated from the brown eluant (A). The violet eluant (B) was concentrated to 10 ml and cooled to $-5°$C. The precipitated violet needles were separated from the solution, washed with cool pentane and dried in vacuo. Yield: 0.36 g (0.43 mM, 13.5%). IR spectrum (ν, cm^{-1}): 435w, 595w, 795w, 805w, 1020m, 1355m, 1435m, 1485w, 1505w, 2840m, 2905m, 2940m, 3080w.

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