

Synthesis and Catalytic Activity of Alkoxyoxovanadium(IV) Diketonates, Crystal and Molecular Structure of Bis-[Methoxyoxovanadium(IV) Acetylacetonate]

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Methoxyoxovanadium(IV) acetylacetonate crystallizes in the monoclinic system, space group $P2_1/n$, with $a = 10.50(1)$, $b = 11.10(1)$, $c = 7.67(1)$ Å, and $\beta = 107.63(3)^\circ$. The complex consists of dimeric $[VO(OCH_3)acac]_2$ units with molecular and crystallographic C_i symmetry, in which the vanadium atoms are in the tetragonal pyramidal coordination geometry. The $V=O$ length is $1.587(3)$ Å and all other $V-O$ lengths are in the range $1.953(3)$ – $1.968(3)$ Å. The $V \cdots V$ separation (3.104 Å) compares well with metal–metal separations in binuclear complexes of atoms of comparable dimensions.

The synthesis and the catalytic activity in ethylene–propylene co-polymerization of three other diketonates are reported.

Introduction

The coordination chemistry of vanadium mainly concerns the oxygenated species VO(IV) and VO(V). A powerful stimulation to research in this field is the possible use of such compounds as soluble Ziegler–Natta catalysts, particularly in the synthesis of ethylene–propylene elastomers [1–3].

Oxovanadium compounds, simultaneously bearing chelating ligands and alkoxy groups, have been prepared in which the metal atom is in the higher oxidation state (V). For instance, alkoxyoxovanadium(V) complexes are known in which the chelating ligands are β -diketonates [4], 8-quinolinol derivatives [5], salicylamidoxime [6], tri- and tetra-dentate Schiff bases [7]. The ways to synthesise these compounds are:

a) the reaction of $VO(OR_3)$ ($R = \text{alkyl group}$) with a tri- or tetradentate divalent ligand in a 1:1 molar ratio [7];

b) the reaction with an excess alcohol of the corresponding hydroxyoxovanadium(V) chelate [4–6].

At the present time no alkoxyoxovanadium(IV) chelate is known to us. This paper relates the synthesis of some alkoxyoxovanadium(IV) β -diketonates, their characterization, and their use as catalysts in ethylene–propylene co-polymerization to yield saturated elastomers. The X-ray structure of methoxyoxovanadium(IV) acetylacetonate is also reported.

Experimental

Materials and Equipment

All the syntheses were carried out in nitrogen atmosphere. All chemicals, except the Schiff bases, are commercially available and were used without previous purification. Oxovanadium(IV) dichloride was used in the form of a 50% water solution purchased from Carlo Erba. The Schiff bases were prepared by reacting salicylaldehyde with the suitable amine in methanol medium.

Infrared data were recorded on a Perkin Elmer 580B spectrophotometer. Magnetic moments were measured by the Gouy method using a Brucker-Sartorius instrument.

Ethylene–propylene co-polymerization tests were performed in a 1.5 l glass reactor equipped with 2 gas inlet tubes and a mechanical stirrer, kept at a constant temperature of 20°C by a refrigerating bath.

General method of Preparation of the Alkoxyoxovanadium(IV) Diketonates

To a solution of the β -diketone (4 mmol) and LiOH (8 mmol) in 40 ml of the appropriate alcohol,

VOCl_2 (4 mmol) diluted in 10 ml of the same alcohol was added. The mixture was stirred at boiling temperature for 2 hrs and then cooled at room temperature. The alkoxyoxovanadium(IV) β -diketonates separated from the reaction mixture either during the heating or on standing overnight. In the case of methoxyoxovanadium(IV) acetylacetonate, $\text{VO}(\text{OCH}_3)\text{acac}$, slow cooling allowed to obtain blue crystals suitable for X-ray work. Possible variations of the above procedure are as follows:

a) the alkaline hydroxide may be replaced by an organic base (e.g. triethylamine and pyridine gave good results)

b) the heating is not essential to perform the reaction: in fact, $\text{VO}(\text{OCH}_3)\text{acac}$ was obtained after 24 hrs stirring of the reaction mixture at room temperature.

Table I summarizes the elemental analysis and infrared spectroscopy data of the prepared complexes.

Methoxyoxovanadium(IV) 2,2,6,6-tetramethylheptanedionate, $\text{VO}(\text{OCH}_3)\text{tmh}$, was prepared also using a different method. Oxovanadium(IV) bis(2,2,6,6-tetramethylheptandionate) (1 mmol), triethylamine (2 mmol) and VOCl_2 (1 mmol) were dissolved, in the above order, in 25 ml methanol.

The reaction mixture was boiled for 2 hrs. After cooling a blue powder was collected by filtration and dried under reduced pressure. *Anal.* Found: C, 50.88; H, 7.69. Calcd. for $\text{C}_{12}\text{H}_{22}\text{O}_4\text{V}$: C, 51.24; H, 7.83%. The IR spectrum was the same as the compound obtained by the general procedure.

Some reactions were performed according to the general procedure by using 8-quinolinol and three Schiff bases as ligands. A very poor yield of $\text{VO}(\text{OCH}_3)\text{L}$ was obtained with 8-quinolinol, while the Schiff bases gave complexes having the structure VOL_2 , as shown by elemental analysis data (see Table II) and infrared spectroscopy.

Ethylene-Propylene Co-polymerization Tests

In each test the reactor was filled with 0.6 l of dry n-heptane. Ethylene and propylene were bubbled

into the solvent at rates of 1 and 2 l/min respectively. An air-free solution containing ethylene and propylene in a molar ratio 1:10 was obtained after 1 hr. Diethylaluminium chloride (3×10^{-3} mol/l), n-butyl perchlorocrotonate (6×10^{-4} mol/l) and the tested vanadium compound (6×10^{-5} mol/l) were then added. Immediately after the last addition an exothermic reaction started. The feeding of the monomers was continued for 60 min. After this time no more heat was evolved by the reacting system.

The addition of 0.5 l acetone to the (clear) solution caused the precipitation of the ethylene-propylene co-polymer, which was separated by filtration, dried at 100–110 °C and weighed. The catalytic activities were then calculated as (grams of copolymer produced)/(grams of vanadium introduced). Table III shows the results obtained by testing some alkoxyoxovanadium(IV) β -diketonates. The data relating vanadium tris-acetylacetonate and vanadium oxytrichloride (which are presently used in industrial processes for the production of ethylene-propylene elastomers [8]) are also reported for comparison. The same Table shows the values for the propylene content [9], intrinsic viscosity $[\eta]$ and the product of the reactivity ratios [10].

X-Ray Diffraction Data

Well-formed crystals of methoxyoxovanadium(IV) acetylacetonate were obtained from methanol solution. The crystallographic data are given in Table IV. The cell dimensions were obtained from a least squares analysis of the setting angles of 25 reflections which had been centered on a Philips PW 1100 diffractometer with Mo-K α radiation. Intensity data were collected by the ϑ -2 ϑ scan out to 2 ϑ (Mo) of 50° with a scan rate of 2° in 2 ϑ min⁻¹. The intensities were corrected for Lorentz and polarization factors, but not for absorption. Only the 'observed' reflections were used in subsequent calculations. Two standard reflections, measured at intervals of 100, were constant within counting statistics. The structure is governed by the heavy atom and was solved by standard methods.

TABLE I. Elemental Analysis and Infrared Data of Alkoxyoxovanadium(IV) Diketonates.

Compound	Elemental analysis						$\nu_{\text{V=O}}$ (cm^{-1})
	C %		H %		V %		
	Calc.	Found	Calc.	Found	Calc.	Found	
$\text{VO}(\text{OCH}_3)\text{acac}$	36.55	36.75	5.08	5.27	25.89	26.03	990
$\text{VO}(\text{OC}_2\text{H}_5)\text{acac}$	39.81	39.18	5.69	5.67	24.17	24.10	995
$\text{VO}(\text{OCH}_3)\text{tmh}^{\text{a}}$	51.24	51.00	7.83	7.69	18.15	17.95	995
$\text{VO}(\text{OCH}_3)\text{ach}^{\text{a}}$	45.57	45.16	5.91	5.97	21.52	21.33	990
$\text{VO}(\text{OCH}_3)\text{tta}^{\text{a}}$	33.85	33.00	2.19	2.42	15.99	16.21	925

^aHtmh = 2,2,6,6-tetramethylheptandione, Hach = 2-acetylcyclohexanone, Htta = 2-thenoyltrifluoroacetone.

TABLE II. Elemental Analysis Data of the Products of the Reaction among VOCl_2 , LiOH and HL (where HL = 8-quinolinol, Schiff base) in Methanol.

Ligand (HL)	Found (%)			Theoretical for VOL_2			Theoretical for $\text{VO}(\text{OCH}_3)\text{L}$		
	C	H	N	C	H	N	C	H	N
8-quinolinol	50.02	4.04	5.88	60.85	3.38	7.89	49.59	3.72	5.79
2-[N-(4'-tolyl)iminomethyl]-phenol	68.03	5.32	5.46	68.99	5.78	4.93	58.44	4.87	4.55
2-[N-(4'-chlorophenyl)iminomethyl]phenol	54.84	3.42	9.62	56.82	3.28	10.20	49.56	3.54	8.26
2-[N-(4'-nitrophenyl)iminomethyl]phenol	59.12	3.28	4.99	59.09	3.41	5.30	51.14	3.65	4.26

TABLE III. Ethylene-propylene Copolymerization Tests.

Compound	Catalytic activity	Propylene content ^a	$[\eta]^b$	$[r_1 \times r_2]^c$
$\text{VO}(\text{OCH}_3)\text{acac}$	12,200	45	2.47	0.57
$\text{VO}(\text{OC}_2\text{H}_5)\text{acac}$	19,900	48	2.53	0.57
$\text{VO}(\text{OCH}_3)\text{tmh}$	19,300	49	2.46	0.49
$\text{VO}(\text{OCH}_3)\text{ach}$	14,300	42	2.56	0.67
$\text{VO}(\text{OCH}_3)\text{tta}$	14,900	42	2.68	0.71
$\text{V}(\text{acac})_3$	20,800	51	2.30	0.48
VOCl_3	24,400	50	2.41	0.46

^aDetermined by IR spectroscopy (% by weight). ^bMeasured in decaline at 135 °C. ^cDetermined by IR spectroscopy.

TABLE IV. Crystal Data for Methoxyoxovanadium(IV) Acetylacetonate.

$\text{C}_{12}\text{H}_{40}\text{O}_8\text{V}_2$	FW 414
Crystal description	Blue-green prisms
Systematic absences	$h0l, h + 1 \text{ odd}; 0k0, k = \text{odd}$
Crystal system and space group	Monoclinic, $P2_1/n$
General positions	$\pm(x, y, z; 1/2 - x, 1/2 + y, 1/2 - z)$
Cell constants	$a = 10.50(1), b = 11.10(1), c = 7.67(1) \text{ \AA}, \beta = 107.63(3)^\circ; V = 852 \text{ \AA}^3$ Calcd. 3.22 g cm^{-3} for $Z = 4$
Density $\mu(\text{Mo-K}\alpha)$	23.9 cm^{-1}
Crystal dimensions	$0.10 \times 0.15 \times 0.12 \text{ mm}$
Data collection	4-circle Philips PW 1100 diffractometer (Mo-K α)
Number of observations	1576 (1210 with I greater than $2\sigma(I)$)

Isotropic refinement of the coordinates of all non-hydrogen atoms resulted in an R factor of 10.1%. Further refinement with the introduction of the anisotropic temperature factors gave an R factor of 4.9%. At this point an electron difference synthesis was calculated, from which the appropriate positions of the hydrogen atoms were determined. Two more

cycles with a fixed isotropic temperature factor B of 8.0 \AA^2 for the hydrogen atoms reduced the conventional R factor to the final value of 4.0%, when the shift/error values in the last cycle were less than 0.3 for the non-hydrogen atoms and less than 1.0 for the hydrogen atoms.

A three-dimensional difference synthesis showed no significant anomaly at this stage. The atomic form factors for vanadium were from Cromer and Waber [11], for oxygen and carbon from Cromer and Mann [12], and for hydrogen from International Tables for X-ray Crystallography [13]. The effects of the anomalous dispersion of vanadium were included in the calculations of Fc; the values of f' and f'' were taken from Cromer and Libermann [14]. All calculations were performed using the X-ray '72 programs system. Fractional atomic coordinates and thermal parameters are given in Table V. Bond and contact distances are given in Table VI. Bond angles are reported in Table VII. The equations of selected molecular planes are reported in Table VIII.

Results and Discussion

The reaction in alcoholic medium of a β -diketone, a base and oxovanadium(IV) dichloride in 1:2:1 molar ratios leads to the formation of alkoxyoxovanadium(IV) β -diketonates. This is a surprising result considering that oxovanadium(IV) bis- β -diketonates are formed in the reaction of the same species in molar ratios of 2:2:1 (or 1:1:1, thus leaving one half of the VOCl_2 unreacted). Therefore the stoichiometry by which the reagents are mixed is able to drive the reaction either toward one product or the other.

On the other hand an oxovanadium(IV) bis- β -diketonate may be transformed to the corresponding alkoxydiketonate in the presence of two moles of a base and one mol of VOCl_2 . However, the unreacted bis- β -diketonate is recovered when it is refluxed in alcoholic solution in the presence of the base, but without adding VOCl_2 .

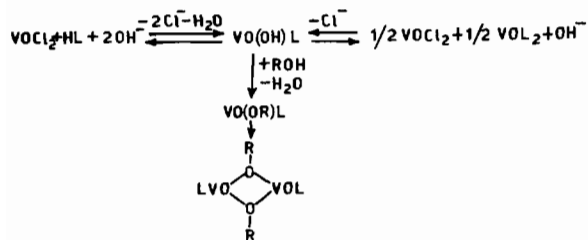
TABLE V. Atomic Parameters ($\times 10^4$).

Atom	x	y	z
V	4383(1)	3985(1)	3612(1)
O(1)	4003(3)	2809(3)	4522(4)
O(2)	2858(3)	4408(3)	1487(4)
O(3)	5278(3)	3409(2)	1868(4)
O(4)	6092(3)	4601(2)	5167(4)
C(1)	6326(7)	381(6)	3555(9)
C(2)	7664(5)	771(4)	4771(6)
C(3)	8593(5)	1300(4)	4077(6)
C(4)	4842(5)	3303(4)	123(6)
C(5)	5756(6)	2719(6)	-755(8)
C(6)	2623(6)	5930(6)	4494(8)
H(11)	6228(62)	-347(54)	3673(91)
H(12)	5701(66)	729(57)	3598(96)
H(13)	6499(60)	252(52)	2396(87)
H(31)	8296(58)	1374(50)	2876(84)
H(51)	5521(59)	2788(53)	8085(86)
H(52)	6584(59)	2927(54)	-261(89)
H(53)	5892(63)	2003(52)	-395(90)
H(61)	1948(59)	5331(51)	3733(84)
H(62)	2481(60)	6380(55)	3549(87)
H(63)	2533(56)	6107(52)	5668(88)

TABLE V (continued). Thermal Parameters ($\times 10^3$). The temperature factor is in the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^{*}b^{*} + 2U_{13}hla^{*}c^{*} + 2U_{23}k lb^{*}c^{*})]$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
V	60	38	39	0	17	-5
O(1)	83	47	54	-7	25	4
O(2)	66	60	48	12	13	-7
O(3)	68	50	42	8	21	-4
O(4)	58	45	47	5	16	-12
C(1)	75	78	65	-10	9	1
C(2)	67	42	45	5	9	0
C(3)	70	54	39	8	18	2
C(4)	65	38	42	-8	23	-2
C(5)	83	78	48	8	30	-3
C(6)	64	68	62	12	17	-10

Such behaviour may be rationalized on the basis of the following reaction scheme:



This scheme indicates that an intermediate VO(OH)L (never isolated) is in equilibrium with VOCl_2 , VOL_2 and the free ligand in alkaline alcoholic medium, and

TABLE VI. Bond and Contact Distances (Å).

a) Bond distances			
V-O(1)	1.587(3)	O(2)-C(2)	1.286(6)
V-O(2)	1.965(3)	O(3)-C(4)	1.282(5)
V-O(3)	1.961(4)	C(1)-C(2)	1.50(1)
V-O(4)	1.953(3)	C(2)-C(3)	1.38(1)
V-O(4 ⁱ)	1.968(3)	C(3)-C(4)	1.38(1)
O(4)-C(6)	1.422(7)	C(4)-C(5)	1.48(1)
C(1)-H(11)	0.82(6)	C(5)-H(52)	0.87(6)
C(1)-H(12)	0.77(7)	C(5)-H(53)	0.84(6)
C(1)-H(13)	0.97(7)	C(6)-H(61)	1.02(5)
C(3)-H(31)	0.88(6)	C(6)-H(62)	0.86(6)
C(5)-H(51)	0.85(6)	C(6)-H(63)	0.95(7)
b) Contact distances			
V...V ⁱ	3.102(1)		
O(4)...O(4 ⁱ)	2.399(4)	O(1)...O(4 ⁱ)	2.890(4)
O(1)...O(2)	2.885(4)	O(2)...O(3)	2.706(5)
O(1)...O(3)	2.834(5)	O(2)...O(4 ⁱ)	2.704(4)
O(1)...O(4)	2.890(4)	O(3)...O(4)	2.753(4)
Symmetry code			
none	x, y, z		
i	1 - x, 1 - y, 1 - z		

TABLE VII. Bond Angles ($^\circ$).^a

O(1)-V-O(2)	108	V-O(2)-C(2)	130
O(1)-V-O(3)	106	V-O(3)-C(4)	130
O(1)-V-O(4)	109	V-O(4)-C(6)	128
O(1)-V-O(4 ⁱ)	108	V ⁱ -O(4)-C(6)	127
O(2)-V-O(3)	87	O(2)-C(2)-C(1)	115
O(2)-V-O(4 ⁱ)	87	O(2)-C(2)-C(3)	123
O(3)-V-O(4)	89	O(3)-C(4)-C(5)	116
O(4)-V-O(4 ⁱ)	75	O(3)-C(4)-C(3)	123
V-O(4)-V ⁱ	105	C(2)-C(3)-C(4)	125

For symmetry code see Table IV. ^aStandard deviations are all less than 1° .

that it is irreversibly transformed to the corresponding VO(OR)L . The formation of the latter is only allowed when the stoichiometry favours a high concentration of VO(OH)L , *i.e.* in the systems $\text{VOCl}_2/\text{HL}/\text{Base}$ (1:1:2) and $\text{VOL}_2/\text{VOCl}_2/\text{Base}$ (1:1:2). When VOCl_2 and HL are reacted in the presence of an amount of base just enough to neutralize the ligand (or when the ligand anion L^- removed from OH^- cannot find another oxovanadium group (from VOCl_2) to coordinate), no VO(OH)L is formed and no VO(OR)L may be produced.

The reaction of VO(OH)L with alcohol to give VO(OR)L is similar to the one suggested by Blair [5] as the way by which VO(OH)Q_2 is transformed to VO(OR)Q_2 ($\text{HQ} = 8\text{-quinolinol}$). The overall reaction is fast enough. In fact, $\text{VO(OCH}_3\text{)tmh}$ starts to precipitate from the reaction mixture a few minutes after mixing.

As regards the magnetic behaviour in the binuclear complexes the similar geometry of the metal ions and

TABLE VIII. Equations of Least-Squares Planes Referred to Monoclinic Axes with Distances (Å) of Relevant Atoms from the Planes.

Plane I

V, O(4), O(4¹).

$$3.314x + 6.473y - 6.207z = 1.790 \text{ \AA}$$

Plane II

O(2), O(3), O(4), O(4¹).

$$4.152x + 8.970y - 4.112z = 4.505 \text{ \AA}$$

[O(2), 0.02; O(3), -0.02; O(4), 0.03; O(4¹), -0.03]

Plane III

O(2), O(3), C(2), C(3), C(4).

$$4.446x + 10.010y - 1.621z = 5.448 \text{ \AA}$$

[O(2), -0.01; O(3), 0.01; C(2), 0.01; C(3), 0.00; C(4), -0.01]

Angles (°) between the planes

Planes	Angle
I-II	22.6
I-III	43.6
II-III	20.9

bridging oxygens implies that differences in the strengths of exchange are caused by differences in the symmetry of the exchanging electrons [23]. Since the unpaired (d_{xy}) electron in copper(II) is directed to the ketonic oxygen and is able to participate directly in bonding it is logical that d^9-d^9 exchange is the strongest so far observed in the first-row transition metal ions. The μ_{eff} for the (acac)VO(OCH₃) is 1.80 B.M.; for the other binuclear vanadyl(IV) complexes the $\mu_{\text{eff}} = 1.80-1.90$ B.M.. Regardless of the details of the exchange mechanisms, the strength of the exchange is much higher in the copper complexes than in the vanadyl(IV) analogues. In the vanadyl complexes the exchange pathway is obviously different. As regards the use of the alkoxyoxovanadium(IV) β -diketonates as Ziegler-Natta catalysts, Table III gives a clear picture. A random copolymer having about 45% propylene content is obtained with these compounds. Compositions, homogeneity and molecular weights are almost the same as those which may be obtained by using commercial catalysts V(acac)₃ and VOCl₃. However the latter ones show somewhat higher activities.

Description of the Structure

The complex consists of dimeric VO(OCH₃)acac₂ units. The structure of the dimer is shown in Figs. 1-3. The dimeric molecule adopts a chair-like arrangement. The geometry around the vanadium atom is best described as tetragonal bipyramidal with O(2), O(3), O(4) and O(4¹) forming the base and O(1) occupying the apical position. The basal atoms are almost coplanar, with O(2) and O(4) lying only 0.02 and 0.03 Å, respectively, below the best least-squares plane through the four atoms and O(3) and O(4¹)

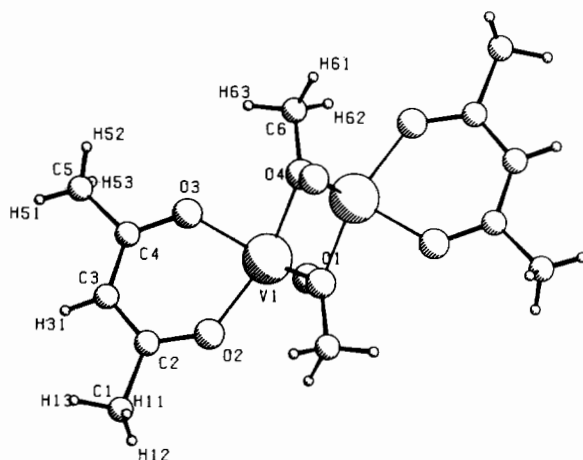


Fig. 1. Numbering scheme in [VO(OCH₃)acac]₂.

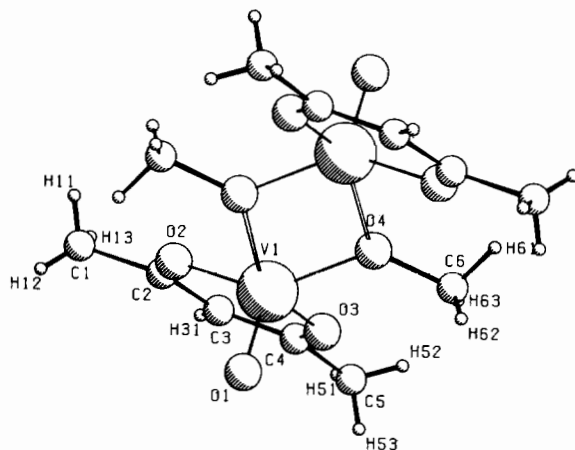


Fig. 2. Projection of the molecule along the *c* axis.

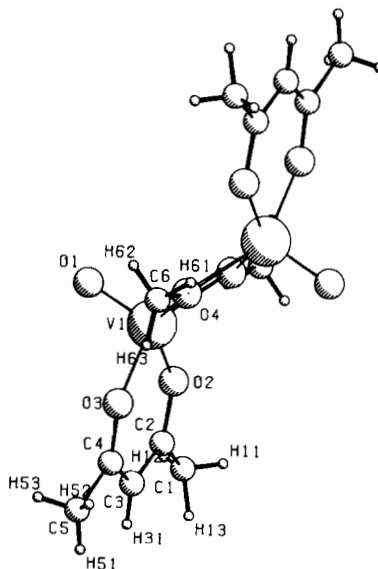


Fig. 3. Representation of the [VO(OCH₃)acac]₂ molecule, showing the chair-like configuration.

lying only 0.02 and 0.03 Å above it. The vanadium atom lies 0.60 Å above the plane, *i.e.*, toward the apical O(1) atom; this is normal for tetragonal pyramidal complexes. The distance of 1.587(3) Å is typical of V=O lengths found in similar structures, and its shortness is evidence of multiple bonding. The bridging V–O(4)–V¹–O(4¹) unit is strictly planar as the dimer has symmetry C_i, there being a crystallographic inversion center in the middle. The plane of the bridging unit is inclined by 22.6° with respect to the base plane. Chelation gives rise to a quasi-planar six-membered ring which is inclined 20.9 degrees with respect to the base plane.

The equatorial V–O distances to the terminal oxygens (1.961(4) and 1.965(3) Å) are not significantly different from the V–O distances to the bridging oxygens (1.953(3) and 1.968(3) Å) and compare well with the average of 1.969(4) Å found in VO(acac)₂ [15] and with 1.950(6) Å in VOacacen [16]. Both V–O–C angles are 130°. This value is almost identical to those found in VOacacen and in VOH₂(BAA)₂en.(CH₃)₂CO [17] where the vanadium atom is in the same square pyramidal coordination geometry, and also in the α and β forms of V(acac)₃ [18] where it is six-coordinated in a distorted octahedral geometry: an indication that these angles are largely determined by the ligand geometry, irrespective of the coordination around the vanadium atom. The same can be said about the (ligand) O–V–O angle (87°). It must be noted that this angle remains practically unchanged if one or both oxygen atoms of the six-membered ring are substituted by nitrogen atoms, as in the β-ketimine complex VOacacen [16] or in the porphyrin complex CO(OEP) [19] (OEP = 2,3,7,8,12,13,17,18-octaethylporphinato). Bond distances and angles within the diketone do not differ from the normal values. The average C–O and C–C (ring) bond distances of 1.284(6) and 1.38(1) Å, respectively, indicate the presence of a diffuse delocalization of the π electrons which probably extends to the metal atom to form a pseudo-aromatic system. The high symmetry of the bridge (due to the good accordance of the V–O (bridge) bond lengths) is an indication that the bridging interaction is strong. The separation of the oxygen atoms involved, O(4) and O(4¹) (2.40 Å) is less (by about 0.3 Å) than those involving oxygen atoms bonded to the same vanadium atom. The vanadium atom's separation (3.102 Å) is comparable to that (3.09 Å) in the symmetric di-μ-fluoro bridge system in vanadium trifluoride [20], and to that (3.175 Å) in (bipy)VO₂F [21]. It must be noted, however, that similar values were found also in mixed binuclear complexes as in NiVO-

(BAA)₂en [22], (O···O = 2.36 Å, Ni···V = 2.991(2) Å), and in NiZn(py)(BAA)₂en [22] (O···O = 2.37 Å, Ni···Zn = 3.120(2) Å), indicating that the values are comparable for atoms of comparable dimensions.

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