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## STRUCTURE OF ORGANIC COMPOUNDS

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**Abstract**

New crystals of di- $\mu$ -methoxido-bis[(2-ethylhexanoato- $\kappa$ O)oxido(1,10-phenanthroline- $\kappa^2$ N,N')vanadium(IV)], C<sub>42</sub>H<sub>52</sub>N<sub>4</sub>O<sub>8</sub>V<sub>2</sub>, have been synthesized, characterized by elemental analysis, infrared spectroscopy, electron paramagnetic resonance and X-ray diffraction analysis. The compound crystallizes in monoclinic  $P2_1/c$  space group. The unit cell parameters are assessed to  $a = 13.0656(11)$ ,  $b = 9.1474(8)$ ,  $c = 17.0299(14)$  Å,  $\beta = 94.387(4)$ ,  $Z = 2$ ,  $R_{gt} = 0.0617$ ,  $wR(F^2) = 0.169$ ,  $T = 150(2)$  K. The dimeric oxidovanadium(IV) complex consists of two [V<sup>IV</sup>O(OCOC<sub>7</sub>H<sub>15</sub>)(phen)] units connected with two methanolate bridges. The vanadium atoms have a distorted octahedral environment with four oxygen and two nitrogen atoms. The V=O length is 1.601(3) Å; the V–O bond lengths in the symmetrical V<sub>2</sub>O<sub>2</sub> core are 1.973(2) and 2.007(3) Å. The bonds vanadium–carboxylate oxygen atom are V–O = 1.974 (3) Å. The bond distances V–N depend

on configuration toward oxido ligand. The preliminary experiments on a solvent-borne alkyd resin revealed promising catalytic activity in autoxidation process.

## INTRODUCTION

The vanadium(IV) complexes have been of great interest due to their biochemical significance [1] as pharmaceuticals with possible inhibition of several enzymes [2], antimicrobial activity [3], cytostatic activity [4] and treatment of diabetes [5–7]. Complexes containing oxidovanadium(IV) group are also studied for their catalytic activity in oxidation reactions of alkanes, alkenes, aromatic hydrocarbons and alcohols in presence of peroxides [8,9]. They have been used as soluble Ziegler-Natta catalysts for polymerization and co-polymerization of  $\alpha$ -olefins [10–12]. The coordination chemistry of vanadium(IV) mostly represents an octahedral or square-pyramidal coordination of monomeric structures, whereas dinuclear or polynuclear complexes of oxidovanadium(IV) with distorted octahedral geometry are much less common [13]. As an example of dinuclear coordination compounds could be taken  $\mu$ -oxo bridged vanadium(IV) compounds bearing 1,10-phenanthroline ligand and  $\mu$ -arsenate [14,15] or  $\mu$ -selenite bridges [16].

Alkyd resins, as saturated polyesters modified with unsaturated fatty acids, are spontaneously auto-oxidatively crosslinked polymers. However, the autoxidation process is very slow without addition of driers [17]. It is well known, that transition metal complexes are widely used for their ability to undergo redox changes necessary for acceleration of film-forming process of alkyd resins [18, 19]. Acknowledged studies report toxic and genotoxic properties of cobalt(II) compounds [20,21], whereby the most widely used drier is cobalt(II) 2-ethylhexanoate. In recent studies, the oxidovanadium(IV) complexes [22,23] along with complexes containing manganese [24] and iron [25] have been found to be powerful alkyd driers and could serve as a possible replacement for cobalt(II) compounds.

In this work, a new binuclear oxidovanadium(IV) complex containing methanolate bridges was synthesized and its catalytic activity in autoxidation process was

studied. Structure of the title compound was determined by single-crystal X-ray diffraction analysis.

## EXPERIMENTAL

**Synthesis.** The binuclear oxidovanadium(IV) complex was prepared under nitrogen atmosphere, 2-ethylhexanoic acid (1.9 mL, 12.0 mmol) and 1,10-phenanthroline (0.356 g, 2.0 mmol) was added to mixture of oxidovanadium(IV) sulfate (0.5 g, 2.0 mmol) in methanol (5 mL). The reaction mixture was stirred and a green powder precipitated immediately. Then sodium methanolate was added to neutralize the excess of 2-ethylhexanoic acid, meanwhile red-brownish powder precipitated. All product was filtered off and washed with diethyl ether (3 x 10mL). The resulting product was vacuum dried to give orange-red powder (0.256 g, yield 31 %). The single crystal was obtained by slow diffusion of hexane into saturated solution of title complex in dichloromethane. Complex  $[\text{VO}(\text{OCH}_3)(\text{C}_8\text{H}_{15}\text{O}_2)(\text{C}_{12}\text{H}_8\text{N}_2)]_2$  characterization data: Anal. Calcd. for  $(\text{C}_{42}\text{H}_{48}\text{N}_4\text{O}_8\text{V}_2)$ : C, 60.13%; H, 5.77%; N, 6.68%. Found: C, 60.01%; H, 5.85%; N, 6.70%.

**X-ray diffraction analysis.** Crystallographic data for  $[\{\text{V}^{\text{IV}}\text{O}(\text{OCH}_3)(\text{OCOC}_7\text{H}_{15})(\text{phen})\}_2]$ , were collected on Nonius KappaCCD diffractometer equipped with Bruker APEX-II CCD detector by monochromatized  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at a temperature of 150(2) K. The structure was solved by direct methods (SHELXT2014/4) [26] and refined by full matrix least squares based on  $F^2$  (SHELXL2018/8) [27]. The absorption corrections were carried on using multi-scan method. The hydrogen atoms were found on difference Fourier map and were recalculated into idealized positions. All hydrogen atoms were refined as fixed (riding model) with assigned temperature factors  $H_{\text{iso}}(H) = 1.2 U_{\text{eq}}(\text{pivot atom})$  or  $1.5 U_{\text{eq}}$  for methyl moiety. Crystal data, data collection and structure refinement details are summarized in Table 1-4.

**Infrared spectroscopy.** The infrared spectra were measured on a FTIR spectrometer Nicolet iS50 using ATR technique (built-in all-reflective diamond

crystal) in the range of 4000–500  $\text{cm}^{-1}$  with resolution of 0.5  $\text{cm}^{-1}$  (16 scans) under standard laboratory conditions ( $T = 23\text{ }^{\circ}\text{C}$ , rel. humidity = 50%). FT-IR spectrum (ATR-C): 3054vw, 2956vw, 2926vw, 2870vw, 2858vw, 2813vw, 1623m, 1604w, 1578m, 1517w, 1494vw, 1454w, 1425s, 1378vw, 1365w, 1348w, 1309w, 1289w, 1246vw, 1226vw, 1210vw, 1140vw, 1105w, 1062m, 988vw, 963s, 951vs, 903vw, 868vw, 845s, 807vw, 775vw, 760vw, 726vs, 670w, 643m, 589w, 551vs, 544vs, 507w, 487w, 471m, 438m, 426m.

**Electron paramagnetic resonance.** The spectra were measured on Miniscope MS 300 spectrometer (World Precision Instruments, Sarasota, FL, USA) in microwave X-band ( $\sim 9.5\text{ GHz}$ ). The apparatus was gauged on DPPH value ( $g_{\text{iso}} = 2.0036 \pm 2$ ). Solution spectrum was measured in dimethylsulfoxide in glass capillary (ID = 0.5 mm) at room temperature (293 K).

**Film drying time measurements.** The catalytic effect of  $[\{\text{V}^{\text{IV}}\text{O}(\text{OCH}_3)(\text{OCOC}_7\text{H}_{15})(\text{phen})\}_2]$  during autoxidation process were studied on solvent-borne alkyd resin modified by soybean oil. Alkyd resins CHS-ALKYD S 471 X 60 (oil length = 47%, AV = 6 mg KOH/g) was supplied from Spolchemie. The drying performance has been determined by Beck Koller method on a BYK Drying Time Recorder according to ASTM D5895 [28] and under standard laboratory conditions ( $T = 23\text{ }^{\circ}\text{C}$ , rel. humidity = 50%). Films on glass test strips ( $305 \times 25 \times 2\text{ mm}$ ) were placed into holders of the device. The instrument is a straight-line recorder equipped with hemispherical-ended needle ( $D = 1\text{ mm}$ ) placed to beginning of wet film clamped in horizontal direction with 5 g weight. The straight-line groove resulting during 24 h is usually used for determination of set-to-touch time ( $\tau_1$ ), tack-free time ( $\tau_2$ ), dry-hard time ( $\tau_3$ ) and dry-through time ( $\tau_4$ ).

## RESULTS AND DISCUSSION

The quest for non-toxic driers ensuring the acceleration of drying of alkyd resins led us to synthesize a new oxidovanadium(IV) compound with a structure providing sufficient stability during autoxidation process. The title compound was

synthesized *in situ* by a direct reaction of oxidovanadium(IV) sulfate with monodentate (2-ethylhexanoic acid) and bidentate (1,10-phenanthroline) ligands. Reaction proceeds in methanolic solution and then the excess of 2-ethylhexanoic acid was neutralized by sodium methanolate. Composition and purity of the title compound were checked by elemental analysis, infrared and EPR spectroscopy. The crystal structure was determined by X-ray diffraction analysis of the single crystal prepared from saturated solution in dichloromethane by slow diffusion of hexane.

The unit cell of the title compound consists of  $[\{V^{IV}O(\mu-OCH_3)(OCOC_7H_{15})(phen)\}_2]$  molecules and crystallizes in the monoclinic space group  $P2_1/c$ . The oxidovanadium(IV) complex has the rigorous overall  $C_i$  symmetry with two  $[V^{IV}O(OCOC_7H_{15})(phen)]$  units connected by  $\mu$ -methoxido groups ensuring approximately planar  $V_2O_2$  core (see Fig.1). The bond angles  $V1-O2-V1a$   $[103.49(11)^\circ]$ ,  $O2-V1-O2a$   $[76.51(11)^\circ]$  and the  $V\cdots V$  separation  $[3.1254(8) \text{ \AA}]$  near the values previously reported for oxido-bridged dimers  $[(V^{IV}O(\mu-OC_2H_5)\{OV^{VO}(OC_2H_5)_2\}(phen))_2]$  [29] and  $[(V^{IV}O(\mu-O)\{OC_6H_3(OCH_3-2)(CHO-4)\}(phen))_2]$  [30]. The oxidovanadium groups ( $V=O$ ) are in the *anti*-configuration. Coordination sphere of vanadium atoms forms a distorted octahedron with  $N_2O_4$  ensemble. It is occupied by three different types of oxygen atoms; terminal oxido group  $[V1-O1 = 1.601(3) \text{ \AA}]$ , bridging methoxido groups  $[V1-O2 = 1.973(2) \text{ \AA}, V1-O2a = 2.007(3) \text{ \AA}]$  and  $\kappa^1$ -bonded carboxylato group  $[V1-O3 = 1.974(3) \text{ \AA}]$ . The observed  $V-O$  bond lengths for terminal ligands well correlate with data previously reported for oxidovanadium(IV) complexes [31]. The 1,10-phenanthroline ligand is  $\kappa^2$ -bonded to the vanadium atom through nitrogen donor atoms. The  $V-N$  bond distances differ considerably due to different configuration with respect to oxidovanadium(IV) group. The nitrogen atom in *cis*-position gives the value  $[V-N1 = 2.154(3) \text{ \AA}]$  that fits to common  $V-N$  distances in vanadium complexes bearing the phenanthroline ligand [30,32]. The  $V-N2$  bond

length was found to be considerably longer [2.333(3) Å] due to the *trans*-effect of the oxido group.

Infrared spectroscopy has confirmed the presence of 1,10-phenanthroline and 2-ethylhexanoate ligands. The phenanthroline gives characteristic band of C–H stretching at 3054 cm<sup>-1</sup>. Alkyl chain of 2-ethylhexanoate gives four bands of characteristic vibrations modes assigned to C–H stretching of methyl ( $\nu_a = 2956$  cm<sup>-1</sup>,  $\nu_s = 2870$  cm<sup>-1</sup>) methylene groups ( $\nu_a = 2926$  cm<sup>-1</sup>,  $\nu_s = 2858$  cm<sup>-1</sup>). The C=O stretching band ( $\nu = 1623$  cm<sup>-1</sup>) appears in the range typical for monodentate carboxylate ligand. The methanolate bridges provide antisymmetric C–H stretching vibration mode at 2926 cm<sup>-1</sup> that overlaps with  $\nu_a(\text{CH}_2)$  of the 2-ethylhexanoate. Symmetric C–H stretching appears at 2813 cm<sup>-1</sup>. The infrared spectrum also shows two strong V=O stretching bands at 964 and 951 cm<sup>-1</sup>.

The EPR measurements reveal that the title compound is EPR inactive in solution due to communication of vanadium(IV) atoms in the V<sub>2</sub>O<sub>2</sub> core. It well correlates with the X-ray structure and proves the absence of EPR active contaminants (e.g. starting oxovanadium(IV) sulfate and monomeric oxovanadium(IV) compounds).

The drying activity of [ $\{\text{V}^{\text{IV}}\text{O}(\mu\text{-OCH}_3)(\text{OCOC}_7\text{H}_{15})(\text{phen})\}_2$ ] on air-drying process was followed in solvent-borne alkyd resin modified with soybean oil. This semi-drying solvent-borne alkyd resin is commonly used in the preliminary examination of drying activity of the potential alkyd driers. Without additives, the alkyd is not spontaneously tack-free dried ( $\tau_2$ ) within 24 h.

Our experiments on the title compound revealed considerable improvement of the drying performance at the metal concentrations 0.06 and 0.03 wt.%. In case of 0.06 wt.%, the cured film achieves tack-free time ( $\tau_2$ ) in 1.2 h and total drying time ( $\tau_3 = \tau_4$ ) was determined to 7.2 h. For comparison, the formulation cured by commercial drier (cobalt(II) 2-ethylhexanoate) at the same metal concentration reached tack-free time ( $\tau_2$ ) in 0.5 h, dry-hard time ( $\tau_3$ ) in 9.4 h and dry-through time ( $\tau_4$ ) in 20.4 h. In contrary to cobalt compound, the oxidovanadium(IV) complex exhibits a

good drying activity even at lower concentration. At 0.03 wt.%, cured film achieves tack-free time in 1.7 h ( $\tau_2$ ) and total drying time ( $\tau_3$ ) in 9.3 h.



Table 1 Crystallographic parameters and the X-ray-data-collection and structure-refinement statistics for [ $\{V^{IV}O(\mu-OCH_3)(OCOC_7H_{15})(phen)\}_2$ ]

Crystal data	
Empirical formula	$C_{42}H_{52}N_4O_8V_2$
Formula weight	842.75
Crystal form	orange bar
Size (mm)	$0.30 \times 0.10 \times 0.09$
Crystal system, sp. gr., Z	Monoclinic, $P2_1/c$ , 2
$a, b, c$ (Å)	13.0656 (11), 9.1474 (8), 17.0299 (14)
$\beta$ (°)	94.387 (4)
$V$ (Å <sup>3</sup> )	2029.4 (3)
Radiation type	Mo $K\alpha$
$\mu$ (mm <sup>-1</sup> )	0.52
Data collection	
Diffractometer	Nonius Kappa+Bruker APEX-II CCD
Absorption correction	Multi-scan <i>SADABS</i> V2014/5 (Bruker AXS Inc.)
$T_{\min}, T_{\max}$	0.84, 0.95
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	26193, 3997, 3043
$R_{\text{int}}$	0.053
$(\sin \theta/\lambda)_{\text{max}}$ (Å <sup>-1</sup> )	0.617
Refinement	

$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.062, 0.169, 1.05
No. of reflections	3997
No. of parameters	256
No. of restraints	12
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\max}, \Delta\rho_{\min}$ ( $e \text{ \AA}^{-3}$ )	0.93, -0.44

Computer programs: Bruker Instrument Service v2014.11.0.1, *SAINTE* V8.34A (Bruker AXS Inc., 2013), *SHELXT* 2014/4 (Sheldrick, 2014), *SHELXL2018/1* (Sheldrick, 2018).

Table 2 Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ ) for  $[\{\text{V}^{\text{IV}}\text{O}(\mu\text{-OCH}_3)(\text{OCOC}_7\text{H}_{15})(\text{phen})\}_2]$

Atom	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
V1	0.38938 (4)	0.54341 (6)	0.52026 (4)	0.0204 (2)
C1	0.5659 (3)	0.6324 (4)	0.6288 (2)	0.0275 (8)
C2	0.1777 (3)	0.6100 (5)	0.4357 (3)	0.0392 (11)
C3	0.0778 (3)	0.5884 (6)	0.4048 (3)	0.0459 (12)
C4	0.0376 (3)	0.4510 (6)	0.4074 (3)	0.0450 (12)
C5	0.0948 (3)	0.3354 (6)	0.4387 (3)	0.0414 (11)
C6	0.0602 (4)	0.1902 (6)	0.4418 (3)	0.0502 (13)
C7	0.1208 (4)	0.0808 (5)	0.4733 (3)	0.0431 (12)
C8	0.2231 (4)	0.1113 (5)	0.5080 (3)	0.0394 (10)
C9	0.2890 (4)	0.0095 (5)	0.5443 (3)	0.0441 (12)
C10	0.3845 (4)	0.0454 (5)	0.5753 (3)	0.0474 (12)
C11	0.4162 (4)	0.1948 (5)	0.5701 (3)	0.0406 (11)
C12	0.2604 (3)	0.2553 (5)	0.5051 (2)	0.0342 (9)
C13	0.1970 (3)	0.3677 (5)	0.4699 (2)	0.0341 (9)
C14	0.2626 (3)	0.5979 (4)	0.6575 (2)	0.0273 (8)
C15	0.2576 (3)	0.5646 (5)	0.7454 (2)	0.0384 (10)
C16	0.2543 (4)	0.4041 (5)	0.7609 (3)	0.0451 (12)
C17	0.1696 (3)	0.3172 (5)	0.7192 (3)	0.0414 (11)
C18	0.1762 (4)	0.1536 (5)	0.7313 (3)	0.0430 (11)
C19	0.0875 (4)	0.0680 (6)	0.6950 (3)	0.0575 (15)

C20	0.3409 (5)	0.6435 (6)	0.7939 (3)	0.0575 (14)
C21	0.3507 (5)	0.8024 (6)	0.7775 (3)	0.0615 (16)
N1	0.2371 (2)	0.5015 (4)	0.46750 (19)	0.0304 (8)
N2	0.3567 (3)	0.2948 (4)	0.5362 (2)	0.0311 (8)
O1	0.3768 (2)	0.7109 (3)	0.49400 (16)	0.0316 (6)
O2	0.53197 (18)	0.5345 (3)	0.56740 (14)	0.0214 (5)
O3	0.34301 (19)	0.5441 (3)	0.62789 (15)	0.0269 (6)
O4	0.1962 (2)	0.6722 (3)	0.62208 (17)	0.0357 (7)

Table 3 Selected bond lengths  $d$  for [ $\{V^{IV}O(\mu-OCH_3)(OCOC_7H_{15})(phen)\}_2$ ]

Bond	$d$
V1—O1	1.601 (3)
V1—O2	1.973 (2)
V1—O3	1.974 (3)
V1—O2a	2.007 (3)
V1—N1	2.154 (3)
V1—N2	2.333 (3)
C1—O2	1.422 (4)
C2—N1	1.348 (5)
C2—C3	1.384 (6)
C3—C4	1.364 (7)
C4—C5	1.378 (7)
C5—C6	1.406 (7)
C5—C13	1.430 (6)
C6—C7	1.361 (7)
C7—C8	1.447 (6)
C8—C9	1.381 (7)
C8—C12	1.407 (6)
C9—C10	1.358 (7)
C10—C11	1.433 (7)
C11—N2	1.306 (6)

C12—N2	1.377 (5)
C12—C13	1.423 (6)
C13—N1	1.333 (6)
C14—O4	1.225 (5)
C14—O3	1.297 (5)
C14—C15	1.533 (6)
C15—C16	1.493 (6)
C15—C20	1.500 (6)
C16—C17	1.498 (6)
C17—C18	1.512 (6)
C18—C19	1.493 (6)
C20—C21	1.487 (7)

Table 4 Selected bond angles  $\omega$  for  $[\{V^{IV}O(\mu-OCH_3)(OCOC_7H_{15})(phen)\}_2]$

Atoms	$\omega$
O1—V1—O2	103.11 (13)
O1—V1—O3	102.93 (13)
O2—V1—O3	88.27 (10)
O1—V1—O2a	100.35 (13)
O2—V1—O2a	76.51 (11)
O3—V1—O2a	154.55 (11)
O1—V1—N1	88.95 (14)
O2—V1—N1	167.34 (12)
O3—V1—N1	92.78 (12)
O2a—V1—N1	97.80 (11)
O1—V1—N2	161.69 (14)
O2—V1—N2	95.03 (11)
O3—V1—N2	79.82 (12)
O2a—V1—N2	81.32 (11)
N1—V1—N2	72.78 (13)
N1—C2—C3	123.0 (5)
C4—C3—C2	118.2 (5)
C3—C4—C5	121.4 (4)

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C4—C5—C6	125.0 (4)
C4—C5—C13	116.6 (4)
C6—C5—C13	118.4 (5)
C7—C6—C5	122.1 (4)
C6—C7—C8	120.7 (4)
C9—C8—C12	116.2 (4)
C9—C8—C7	125.2 (4)
C12—C8—C7	118.5 (4)
C10—C9—C8	122.2 (4)
C9—C10—C11	117.9 (5)
N2—C11—C10	122.0 (4)
N2—C12—C8	122.7 (4)
N2—C12—C13	117.2 (4)
C8—C12—C13	120.0 (4)
N1—C13—C12	117.4 (4)
N1—C13—C5	122.4 (4)
C12—C13—C5	120.2 (4)
O4—C14—O3	125.7 (4)
O4—C14—C15	120.7 (4)
O3—C14—C15	113.6 (3)
C16—C15—C20	113.9 (4)
C16—C15—C14	111.9 (4)
C15—C16—C17	117.9 (4)
C16—C17—C18	115.4 (4)
C19—C18—C17	115.3 (4)
C21—C20—C15	115.9 (5)
C13—N1—C2	118.3 (4)
C13—N1—V1	120.2 (3)
C2—N1—V1	121.4 (3)
C11—N2—C12	118.8 (4)
C11—N2—V1	128.8 (3)
C12—N2—V1	112.4 (3)
C1—O2—V1	120.3 (2)
C1—O2—V1a	128.5 (2)

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V1—O2—V1a	103.49 (11)
C14—O3—V1	132.7 (2)
C16—C17—C18	115.4 (4)

Figure 1 Structure of [ $\{V^{IV}O(\mu-OCH_3)(OCOC_7H_{15})(phen)\}_2$ ]

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