



## New sulfate-bridged dinuclear oxidovanadium complexes

Evgenia S. Bazhina<sup>a,\*</sup>, Marina E. Nikiforova<sup>a</sup>, Grigory G. Aleksandrov<sup>a</sup>, Nikolay N. Efimov<sup>a</sup>, Helena A. Ugolkova<sup>a</sup>, Oleg M. Nikitin<sup>b</sup>, Tatiana V. Magdesieva<sup>b</sup>, Artem S. Bogomyakov<sup>c</sup>, Vadim V. Minin<sup>a</sup>, Aleksei A. Sidorov<sup>a</sup>, Vladimir M. Novotortsev<sup>a</sup>, Igor L. Eremanko<sup>a</sup>

<sup>a</sup>N.S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Leninsky Prosp. 31, 119991 Moscow, Russian Federation

<sup>b</sup>M.V. Lomonosov Moscow State University, Department of Chemistry, Leninskie Gory 1/3, 119991 Moscow, Russian Federation

<sup>c</sup>International Tomography Center, Siberian Branch of the Russian Academy of Sciences, Institutskaya Str. 3a, 630090 Novosibirsk, Russian Federation

### ARTICLE INFO

#### Article history:

Received 22 February 2012

Received in revised form 11 May 2012

Accepted 1 June 2012

Available online 9 June 2012

#### Keywords:

Oxidovanadium(IV)

Chelate complexes

4,4'-Di-*tert*-butyl-2,2'-bipyridine

X-ray diffraction

ESR spectroscopy

Cyclic voltammetry

### ABSTRACT

The reaction of oxidovanadium sulfate  $\text{VO}\text{SO}_4 \cdot 3\text{H}_2\text{O}$  with 4,4'-di-*tert*-butyl-2,2'-bipyridine (dtb-bpy) in methanol was found to give the complex  $(\text{VO})_2(\mu_2\text{-SO}_4)_2(\text{dtb-bpy})_2(\text{CH}_3\text{OH})_2 \cdot 4\text{CH}_3\text{OH}$  (**1**). Single crystal X-ray diffraction reveals that molecule **1** is a centrosymmetric dimer consisting of two  $\{\text{VO}(\mu_2\text{-SO}_4)(\text{dtb-bpy})(\text{CH}_3\text{OH})\}$  moieties linked by two bridging sulfate anions. Each vanadium atom is in a distorted octahedral environment formed by two nitrogen and four oxygen atoms. The further reaction of an ethanolic solution of compound **1** with sodium pivalate in  $\text{CH}_3\text{CN}$  produces the new dinuclear complex  $[(\text{VO})_2(\mu_2\text{-O})_2(\mu_2\text{-SO}_4)(\text{dtb-bpy})_2] \cdot 2\text{CH}_3\text{CN}$  (**2**), which does not include pivalate ligands, but contains one bridging sulfate anion and two bridging oxygen atoms. The X-ray study, cyclic voltammetry and magnetic measurements were performed allowing to conclude that both vanadium centers in **2** are in +5 oxidation state. According to ESR studies the dinuclear complex **1** undergoes dissociation upon dissolution in ethanol yielding mononuclear species  $\text{VO}(\mu_2\text{-SO}_4)(\text{dtb-bpy})(\text{CH}_3\text{OH})$ , while solution of **1** in dichloromethane contains "dimers" exhibiting spin–spin exchange interactions between two paramagnetic monomeric fragments.

© 2012 Elsevier B.V. All rights reserved.

## 1. Introduction

The design and synthesis of hybrid materials based on inorganic transition metal salts and organic ligands are of great interest due to unusual structural features of these materials and their possible use as catalysts, bioactive agents, and model systems in magnetochemistry and material science [1–3]. Many molecular polyvanadates and vanadium complexes with organic ligands have been reported [4–8]. In contrast, the dinuclear oxidovanadium complexes containing 2,2'-bipyridine ligands and bridging inorganic acid anions remain much less investigated [9–14]. To date, only a few structurally characterized vanadium compounds containing sulfate bridges have been reported. For example, coordination polymers  $[\text{V}_2\text{O}_2(\text{OH})_2(\text{SO}_4)_2(2,2'\text{-bpy})_2]_n$  [15] and  $[\text{VO}(\text{SO}_4)(2,2'\text{-bpy})_n]$  [16] are known. Unfortunately, low solubility of these complexes in organic solvents substantially limits the field of their research and application. In the present study we used 4,4'-di-*tert*-butyl-2,2'-bipyridine, because this ligand substantially increases the solubility of complexes in organic solvents. This allows one to isolate the newly formed compounds as crystals suitable for

studies by different physical methods and extend the scope of application of these compounds as separate materials and as the starting compounds for the synthesis of polynuclear complexes.

In the present study, we report the synthesis and structures of oxidovanadium complexes and the results of their investigation by X-ray new dinuclear diffraction, ESR spectroscopy and cyclic voltammetry.

## 2. Experimental

### 2.1. Synthesis

New complexes were synthesized in air with the use of  $\text{CH}_3\text{OH}$ ,  $\text{C}_2\text{H}_5\text{OH}$ ,  $\text{CH}_3\text{CN}$ , hexane,  $\text{VO}\text{SO}_4 \cdot 3\text{H}_2\text{O}$  (99%), sodium trimethylacetate (NaPiv), and 4,4'-di-*tert*-butyl-2,2'-bipyridine (dtb-bpy, 98%). NaPiv was prepared by the neutralization of NaOH (99%) with HPiv (99%), and the final product was washed with hexane.

#### 2.1.1. $[(\text{VO})_2(\mu_2\text{-SO}_4)_2(\text{dtb-bpy})_2(\text{CH}_3\text{OH})_2] \cdot 4\text{CH}_3\text{OH}$ (**1**)

4,4'-Di-*tert*-butyl-2,2'-bipyridine (0.247 g, 0.92 mmol) was added to a solution of  $\text{VO}\text{SO}_4 \cdot 3\text{H}_2\text{O}$  (0.2 g, 0.92 mmol) in  $\text{CH}_3\text{OH}$  (30 ml). The reaction mixture was stirred for 20 min, after which the solution was kept at room temperature. Green crystals suitable for X-ray diffraction were obtained by slow evaporation for a few

\* Corresponding author.

E-mail addresses: [evgenia-vo@mail.ru](mailto:evgenia-vo@mail.ru) (E.S. Bazhina), [tvm@org.chem.msu.ru](mailto:tvm@org.chem.msu.ru) (T.V. Magdesieva).

days. Crystals of **1** were separated from the mother liquor by decantation, washed with CH<sub>3</sub>OH, and dried in air up to constant weight. The yield of complex **1** was 0.317 g (74.3% based on the starting amount of vanadium). Elemental analysis: *Anal. Calc.* for V<sub>2</sub>C<sub>38</sub>H<sub>56</sub>N<sub>4</sub>O<sub>12</sub>S<sub>2</sub>: C, 49.24; H, 6.09; N, 6.04; S, 6.92. For **1**, Found: C, 48.94; H, 5.88; N, 6.05; S, 6.77% (All calculations were made without four solvate methanol molecules). IR (KBr, cm<sup>-1</sup>): 3600–3250 br.s, 3228.68 s, 3074.32 s, 2962.36 s, 2909.1 s, 2873.07 s, 1618.23 s, 1548.93 s, 1485.86 s, 1466.54 s, 1413.89 s, 1367.02 s, 1306.89 w, 1246.98 s, 1229.72 s, 1204.59 s, 1116.02 s, 1054.79 s, 1033.23 s, 981.74 s, 899.87 s, 881.08 m, 850.32 s, 742.51 w, 721.56 m, 676.23 m, 607.58 s, 589.53 s, 555.13 m, 486.42 w, 430.94 w, 411.94 w.

### 2.1.2. [(VO)<sub>2</sub>(μ<sub>2</sub>-O)<sub>2</sub>(μ<sub>2</sub>-SO<sub>4</sub>)(dtb-bpy)<sub>2</sub>]-2CH<sub>3</sub>CN (**2**)

Complex **1** (0.15 g, 0.16 mmol) was dissolved in C<sub>2</sub>H<sub>5</sub>OH (15 ml) and then NaPiv (0.02 g, 0.32 mmol) was added. The reaction mixture was stirred until it turned brown. Ethanol was distilled off under reduced pressure. The residue was dissolved in CH<sub>3</sub>CN (15 ml) at room temperature. The black-blue solution was kept at room temperature for 7 days. Yellow rectangular crystals suitable for X-ray diffraction were separated from the mother liquor by decantation, washed with cold CH<sub>3</sub>CN, and dried in air up to constant weight. The yield of compound **2** was 0.0548 g (42.4% based on the starting amount of vanadium). Elemental analysis: *Anal. Calc.* for V<sub>2</sub>C<sub>40</sub>H<sub>54</sub>N<sub>6</sub>O<sub>8</sub>S: C, 54.13; H, 6.06; N, 7.01; S, 4.01. For **2**, Found: C, 53.83; H, 5.83; N, 6.91; S, 3.87% (All calculations were made without two solvate acetonitrile molecules). IR (KBr, cm<sup>-1</sup>): 3688.5–3163.8 br.w, 3116.6 v.w, 3075.99 v.w, 3059.54 v.w, 2964.51 s, 2907.59 m, 2871.97 w, 1617.90 s, 1548.98 m, 1481.10 m, 1465.5 w, 1411.73 s, 1367.09 w, 1281.21 s, 1253.38 m, 1201.96 w, 1150.62 v.s, 1082.55 v.w, 1034.02 w, 1021.14 w, 936.77 s, 850.29 s, 898.92 s, 748.13 v.w, 740.71 v.w, 719.24 v.w, 666.82 v.w, 637.36 v.w, 605.98 m, 555.47 v.w, 530.22 v.w, 513.05 v.w, 485.00 v.w, 411.96 v.w.

## 2.2. Methods

The IR spectra of compounds **1** and **2** were measured on a Perkin Elmer Spectrum 65 FT-IR spectrometer in the range of 400–4000 cm<sup>-1</sup> in KBr pellets. The elemental analysis was carried out on an EA1108 CHNS automatic analyzer (Carlo Erba Instruments). The static magnetic susceptibility was measured on a Quantum Design MPMSXL SQUID magnetometer in the temperature range of 5–300 K at an external magnetic field strength of up to 5 kOe. The molar magnetic susceptibility ( $\chi$ ) was calculated taking into account the diamagnetism according to Pascal's additivity rules. In the paramagnetic region, the effective magnetic moment was calculated by the equation  $\mu_{\text{eff}} = [(3k/N_A\beta^2)T]^{1/2} \approx (8T)^{1/2}$ , where  $k$  is the Boltzmann constant,  $N_A$  is Avogadro's number, and  $\beta$  is the Bohr magneton [17]. The X-band ESR spectra were recorded on a Bruker Elexsys E680-X spectrometer at  $T = 293$  and 100 K.

### 2.3. X-ray diffraction studies

The X-ray diffraction data sets for complexes **1** and **2** were collected on a Bruker APEX II diffractometer equipped with a CCD detector and a graphite-monochromated Mo K $\alpha$  radiation source ( $\lambda = 0.71073$  Å) [18]. For both compounds, semiempirical absorption corrections were applied [19]. The structures were solved by direct methods and using Fourier techniques and were refined by the full-matrix least squares against  $F^2$  with anisotropic displacement parameters for all non-hydrogen atoms. The hydrogen atoms of the carbon-containing ligands were positioned geometrically and refined using the riding model. All calculations were carried out with the use of the SHELXL97 program package [20]. The

**Table 1**

Crystallographic parameters and structure refinement statistics for dinuclear oxovanadium complexes.

Complex	<b>1</b>	<b>2</b>
Empirical formula	V <sub>2</sub> C <sub>42</sub> H <sub>72</sub> N <sub>4</sub> O <sub>16</sub> S <sub>2</sub>	V <sub>2</sub> C <sub>40</sub> H <sub>54</sub> N <sub>6</sub> O <sub>8</sub> S
Formula weight (g mol <sup>-1</sup> )	1055.04	880.83
$T$ (K)	120(2)	173(2)
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
$a$ (Å)	10.9943(7)	11.514(1)
$b$ (Å)	11.2068(7)	14.516(1)
$c$ (Å)	11.9861(8)	15.242(2)
$\alpha$ (°)	93.563(1)	115.275(1)
$\beta$ (°)	103.708(1)	91.836(2)
$\gamma$ (°)	116.386(1)	92.638(1)
$V$ (Å <sup>3</sup> )	1261.3(1)	2297.3(4)
$Z$	1	2
$D_{\text{calc}}$ (g cm <sup>-3</sup> )	1.389	1.273
$\theta_{\text{min}}-\theta_{\text{max}}$ (°)	2.07–28.70	1.48–25.68
$\mu$ (mm <sup>-1</sup> )	0.523	0.505
Reflections number	12684	13932
Reflections with $ I  > 2\sigma(I)$	5259	5228
$R_{\text{int}}$	0.023	0.0523
$R_1, wR_2$ [ $ I  > 2\sigma(I)$ ]	0.0380, 0.1177	0.0486, 0.1238
$R_1, wR_2$ (all data)	0.0482, 0.1254	0.0885, 0.1740

crystallographic parameters and the refinement statistics are given in Table 1.

## 2.4. Electrochemistry

For electrochemical studies, CH<sub>3</sub>CN (high-purity grade) was stirred for 12 h over calcium hydride, distilled, refluxed over P<sub>2</sub>O<sub>5</sub> for 2 h, and again distilled, the fraction with b.p. = 81–82 °C being collected at atmospheric pressure. The electrochemical redox potentials were measured with the use of an IPC-Win digital potentiostat/galvanostat connected to a PC. Cyclic voltammograms were obtained by cyclic voltammetry (CV) with stationary platinum ( $d = 3.1$  mm) and glassy-carbon ( $d = 3.3$  mm) electrodes at different potential scan rates using 0.05 M *n*-Bu<sub>4</sub>NBF<sub>4</sub> as the supporting electrolyte at 20 °C in a 10 ml electrochemical cell. Oxygen was removed from the cell by purging with dry argon. A platinum wire served as the auxiliary electrode. A saturated silver chloride electrode was used as the reference electrode (the potential with respect to Fc/Fc<sup>+</sup> was 0.46 V in CH<sub>3</sub>CN). The measured potentials were corrected for Ohmic losses.

## 3. Results and discussion

### 3.1. Synthesis and IR spectra

The reaction of vanadyl sulfate with 4,4'-di-*tert*-butyl-2,2'-bipyridine easily proceeds in methanol at room temperature to form the dinuclear complex [(VO)<sub>2</sub>(μ<sub>2</sub>-SO<sub>4</sub>)(dtb-bpy)<sub>2</sub>(CH<sub>3</sub>OH)<sub>2</sub>] (**1**) isolated as a solvate with four methanol molecules (**1**·4CH<sub>3</sub>OH). An attempt to replace sulfate groups by pivalate anions in the reaction of NaPiv with an ethanolic solution of complex **1** in air followed by recrystallization of a glassy substance from CH<sub>3</sub>CN led to the formation of yellow crystals of the dinuclear complex **2**, which does not include pivalate ligands (Scheme 1).

The infrared spectra of **1** and **2** exhibit, besides bipyridine bands (1618–1367 cm<sup>-1</sup>) and bands of C–H vibrations in *tert*-butyl groups (2964–2860 cm<sup>-1</sup>), very strong bands at 982 and 937 cm<sup>-1</sup>, respectively attributed to the  $\nu(\text{V}=\text{O})$ . The multiple strong bands in 1247–1033 cm<sup>-1</sup> region in spectrum of **1** are attributable to the  $\mu_2\text{-SO}_4^{2-}$  groups connecting two vanadium(IV) centers [15].

Download English Version:

<https://daneshyari.com/en/article/1305997>

Download Persian Version:

<https://daneshyari.com/article/1305997>

[Daneshyari.com](https://daneshyari.com)