Accepted Manuscript

Synthesis, characterization and magnetic properties of a dinuclear oxidovanadium(IV) complex: magneto-structural DFT studies on the effects of out-ofplane -OCH₃ angle

Nader Noshiranzadeh, Marzieh Emami, Rahman Bikas, Joaquin Sanchiz, Marta Otręba, Pavlo Aleshkevych, Tadeusz Lis

PII:	S0277-5387(16)30607-6
DOI:	http://dx.doi.org/10.1016/j.poly.2016.11.026
Reference:	POLY 12334
To appear in:	Polyhedron
Received Date:	27 August 2016
Revised Date:	14 November 2016
Accepted Date:	15 November 2016



Please cite this article as: N. Noshiranzadeh, M. Emami, R. Bikas, J. Sanchiz, M. Otręba, P. Aleshkevych, T. Lis, Synthesis, characterization and magnetic properties of a dinuclear oxidovanadium(IV) complex: magneto-structural DFT studies on the effects of out-of-plane -OCH₃ angle, *Polyhedron* (2016), doi: http://dx.doi.org/10.1016/j.poly. 2016.11.026

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Synthesis, characterization and magnetic properties of a dinuclear oxidovanadium(IV) complex: magneto-structural DFT studies on the effects of out-of-plane -OCH₃ angle

Nader Noshiranzadeh,^a Marzieh Emami,^a Rahman Bikas,^{a,*} Joaquin Sanchiz,^{b,*} Marta Otręba,^c Pavlo Aleshkevych,^d and Tadeusz Lis^c

^a Department of Chemistry, Faculty of Sciences, University of Zanjan 45371-38791, Zanjan, Iran.

^b Department of Chemistry, Faculty of Science, University of La Laguna, Tenerife 38206, Spain
 ^c Faculty of Chemistry, University of Wroclaw, Joliot-Curie 14, 50-383 Wroclaw, Poland
 ^d Institute of Physics, Polish Academy of Sciences (PAN), Al. Lotnikow 32/46, PL-02-668
 Warsaw, Poland

Abstract

A new dinuclear oxidovanadium(IV) complex with a symmetric heptadentate N_4O_3 -donor ligand, $[V_2O_2L(\mu-OCH_3)]$ CH₃OH (1), was synthesized and characterized by elemental analysis, spectroscopic methods (FT-IR, UV-Vis and EPR) and single crystal X-ray analysis, where H₃L is the Schiff base ligand obtained by the condensation of triethylenetetramine and 5-bromosalicylaldehyde. Single crystal X-ray analysis indicated that the vanadium(IV) ions have distorted octahedral geometry and are connected together by phenoxy and methoxy bridging groups. The EPR and magnetic susceptibility measurements show weak V^{...}V antiferromagnetic interactions. The analysis of the magnetic susceptibility data with the Bleaney-Bowers equation

^{*} Corresponding author. Tel.: +98 243 3052583; Fax: +98 243 2283203. *E-mail addresses:* <u>bikas_r@yahoo.com</u> (R. Bikas), <u>jasnchiz@ull.es</u> (J. Sanchiz)

gave a value for the magnetic coupling constant of $J = -1.60 \text{ cm}^{-1}$ ($H = -JS_1S_2$). A Broken-Symmetry DFT study also agreed with an intramolecular character of the magnetic coupling giving a comparable value for J and showed an important dependence of the magnetic interaction with the out-of-plane shift of the methyl group of the methoxy bridging group.

Keywords: Dinuclear oxidovanadium(IV), Magnetic studies, X-ray structure, DFT calculation, Magneto-structural studies

Introduction

The coordination chemistry of vanadium has received increasing interest in the past years due to its biological activities and catalytic applications [1]. Although vanadium plays a limited role in human biology, it is a bio-essential element found in remarkably high concentration in certain mushrooms, polychaete worms and marine environments [2]. Vanadium plays a significant role in the reduction of N₂ to NH₃ (in nitrogenases) [3], it is seen in vanadate-dependent haloperoxidases [4], and its complexes show insulin-mimetic behaviour [5]. The most commonly coordination compounds of vanadium(IV) exist as oxidovanadium derivatives, VO²⁺, which binds four other ligands strongly and one weakly (the one *trans* to the oxidovanadium centre) [6]. Vanadium(IV) complexes with d¹ electronic configuration (S =1/2) are interesting candidates to be studied by EPR [7] that can be easily correlated to other magnetic and structural studies. Having only a single unpaired electron vanadium(IV) and copper(II) complexes resemble to each other from the magnetic and electronic point of view[8] and the magnetic properties of their complexes are described comparatively. However, it should be noted that there are some important differences between them since in the octahedral and square-pyramidal geometry the

orbital bearing the unpaired electron in the oxovanadium(IV) case is of the d_{xy} type whereas in the case of copper(II) it is of the d_{x-y}^{2-2} type [9].

Magneto-structural studies on phenoxy- and alkoxy-bridged multinuclear transition metal complexes show important correlations between the magnetic coupling constant (*J*) and some geometrical parameters such as M–O bond distances, M–O–M bridging angle (θ), O–M–O angle (β), M[…]M distances and out-of-plane displacement of the O–C group [10] Although this latter parameter has usually being disregarded in the interpretation of the magnetic properties of coordination compounds, recent studies showed that it plays a significant role in determining the sign and magnitude of the exchange coupling. In this sense, theoretical methods based on density functional theory (DFT) have been established as valuable tools in developing magneto-structural correlations, in the accurate calculation of the values of the magnetic coupling constants and in modelling the magnetic properties of transition metal complexes, as well as to gain insight into the magnetic coupling mechanism [11].

From both the experimental and theoretical points of view dinuclear copper(II) and vanadium(IV) complexes make relatively simple magnetic models for magneto-structural studies [12]. However, although magnetic properties of dinuclear copper(II) complexes have been theoretically and experimentally extensively studied [13], this is not the case of vanadium(IV) complexes. This is particularly due to the limited number of available dinuclear vanadium(IV) complexes and to the general interest to the spectroscopic and catalytic properties of such compounds in oxidation reactions [14]. Thus, magneto-structural relationships have not yet been well established for vanadium(IV) complexes. In addition, due to the presence of the V=O bond and several possible configuration related to this group, vanadium(IV) complexes have higher structural diversity in comparison with copper(II) complexes.

The reaction of triethylenetetramine and o-hydroxybenzaldehydes with 1 : 3 molar ratios (Scheme 1) forms a class of multidentate N- and O-donor ligands that almost behave as compartmental donor when they bind to metals ions [15]. This kind of ligands usually acts as trinegative hepta-dentate N₄O₃ donor ligand to form dinuclear complexes [16]. Accordingly, they are suitable target ligands to form dinuclear vanadium complexes and stabilize it in IV oxidation state.

In the present paper we report synthesis, characterization, crystal structure and magnetic properties of a new dinuclear oxidovanadium(IV) complex. The aim of this work is to study the magnetic exchange interactions in a dinuclear oxidovanadium(IV) complex by focusing on the out-of-plane influences of $O-CH_3$ group. The magnetic exchange interaction has been studied by DFT calculations in order to have some evidences about the effects of this structural parameter in the magnetic interactions of vanadium(IV) complexes.

Scheme 1.

2. Experimental

2.1. Materials and instruments

Oxidovanadium(IV) bis(acetylacetonate), VO(acac)₂, 5-bromo-2-hydroxybenzaldehyde, triethylenetetramine and the other chemical materials were purchased from Merck and used as received. Solvents of the highest grade commercially available (Merck) were used without further purification. ¹H and ¹³C NMR spectra of ligand in CDCl₃ solution were measured on a Bruker 250 and 62.9 MHz spectrometer, respectively, and chemical shifts are indicated in ppm relative to tetramethylsilane (TMS). IR spectra were recorded as KBr disks with a Bruker FT–IR spectrophotometer. UV–Vis spectra of solutions were recorded on a thermo spectronic, Helios

Alpha spectrophotometer. The atomic absorption analysis was carried out using Varian Spectra AA-220 equipment.

2.2. Synthesis of 2-(5-Bromo-2-hydroxyphenyl)-1,3-bis(2-(5-bromo-2hydroxybenzylideneamino)ethyl)imidazolidine (H₃L)

A methanol solution (10 mL) of triethylenetetramine (0.45 mL, 3 mmol) was added to a methanolic solution of 5-bromosalicylaldehyde (1.81 g, 9 mmol). The solution was refluxed for 2 h at the 70 °C. The obtained yellow solid was separated, filtered off and washed with cold methanol and finally recrystallized from ethanol. Yield 78% (1.81g). M.p. 155-157 °C. Anal. Calc. for $C_{27}H_{27}Br_3N_4O_3$ (MW = 695.24): C, 46.64; H, 3.91; N, 8.06 %. Found: C, 46.68; H, 3.94; N, 7.99%. FT-IR (KBr, cm⁻¹): 3424 (w, br), 2956 (w), 2923 (m), 2839 (m), 1635 (s), 1613 (m), 1576 (w), 1477 (vs), 1439 (w), 1395 (w), 1367 (m), 1355 (m), 1377 (w), 1282 (s), 1261 (s), 1238 (w), 1197 (m), 1167 (m), 1085 (w), 1074 (w), 1040 (w), 1008 (w), 937 (w), 918 (m), 880 (m), 821 (s), 783 (m), 686 (m), 627 (s), 626 (w), 544 (w), 454 (w). ¹H NMR (250 MHz, CDCl₃, 25 °C, TMS): δ 13.80 (s, 2H, external phenolic OH); 13.14 (s, 1H, central phenolic OH); 8.26 (s, 2H, CH=N); 7.85-6.42 (m, 9H, arom); 3.89 (s, 1H, CH); 3.77-3.40 (m, 6H, 3CH₂), 3.05-2.27 (m, 6H, 3CH₂) ppm. ¹³C NMR (62.90 MHz, CDCl₃): δ = 165.07, 164.94, 160.12, 157.26,135.35, 134.96, 133.52, 133.23, 133.08, 122.92, 120.01, 119.00, 118.67, 109.99, 88,79, 58.17, 57.43, 55.23, 53.31, 52.60, 50.99 ppm. UV-Vis (in CH₃OH, c = 2.5×10^{-5} M, λ_{max} [nm] with ϵ [M⁻¹ cm⁻¹ ¹]): 221 (54000), 325 (6640), 424 nm (2400).

2.3. Synthesis of the complex $[V_2(O)_2(L)(\mu - OCH_3)]$ ·CH₃OH (1)

The ligand H_3L (0.695 g, 1 mmol) and VO(acac)₂ (0.530 g, 2 mmol) were placed in the main arm of branched tube. Methanol was carefully added to fill the arms the tube was sealed and the

reagents containing arm immersed in an oil bath at 60 °C while the other arm was kept at ambient temperature. After 2 days, black crystals were appeared in the cooler arm, which were separated and washed by methanol, Yield 79%. Anal. Calc. for $C_{29}H_{31}Br_3N_4O_7V_2$ (MW) = 889.19): C, 39.17; H, 3.51; N, 6.30; V, 11.46. Found: C, 39.25; H, 3.57; N, 6.22; V, 11.53%. FT-IR (KBr, cm⁻¹): 3450 (w, br), 2924 (w), 2912 (w), 1633 (vs), 1589 (m), 1564 (w), 1523 (m), 1479 (s), 1458 (s), 1396 (w), 1383 (s), 1367 (w), 1339 (w), 1313 (s), 1293 (s), 1241 (w), 1195 (w), 1172 (m), 1133 (w), 1095 (w), 1067 (w), 1042 (m), 1026 (w), 972 (s), 947 (vs), 939 (vs), 879 (w), 822 (m), 803 (m), 686 (m), 649 (m), 636 (m), 570 (m), 555 (m), 532 (m), 501 (w), 461 (w), 428 (w). UV-Vis (in CH₃OH, c = 2.5×10^{-5} M, λ_{max} [nm] with ϵ [M⁻¹ cm⁻¹]): 233 (59200), 390 nm NAT (8800).

2.4. X-ray crystallography

A summary of the crystal data and refinement details for complex 1 are given in Table 1. Only special features of the analyses are mentioned here. Single crystal data collection for 1 was performed on Xcalibur diffractometer with CCD Ruby detector, equipped with an Oxford Cryosystems open-flow nitrogen cryostat, using ω scan and a graphite-monochromated Mo K α $(\lambda = 0.71073 \text{ Å})$ radiation at 90 K. The structure was solved by direct methods with SHELXS-97 [17], and refined with full-matrix least-squares techniques on F^2 with SHELXL-97 [18]. The C-bonded hydrogen atoms were calculated included in idealized geometry riding on their parent atoms. The O-bonded hydrogen atom was located from the difference map. The molecular structure plot was prepared using Diamond [19].

Table 1.

2.5. EPR and magnetic studies

The EPR measurements were carried out using a Bruker EMX spectrometer working at fixed frequency 9.25 GHz (X-band) with Oxford Instruments helium-flow cryostat operating in the temperature range from 3.8 to 300 K. A 100 kHz magnetic field modulation and phase sensitive detection were used to record the derivative of the absorbed microwave power. The samples were maintained to a rotatable sample holder to record angular variation of the EPR spectra.

Magnetic susceptibility measurements on polycrystalline samples were carried out by means of a Quantum Design SQUID MPMS XL magnetometer. The *dc* measurements were performed in the temperature range 2.0-300 K at applied magnetic fields of 5T. Diamagnetic corrections of the constituent atoms were estimated from Pascal's constants and experimental susceptibilities were also corrected for the temperature-independent paramagnetism and the magnetization of the sample holder.

2.6. Theoretical calculations

Spin-unrestricted DFT calculations were performed at the B3LYP level by means of the *Gaussian09* code with a triple- ξ all-electron Gaussian basis set for all the elements and with the *tight* convergence criteria, SCF = tight [20]. The general zero-field Heisenberg-Dirac-Van Vleck Hamiltonian for a dinuclear system can be written as $H = -J_{12}(S_1S_2)$, where 1 and 2 refer to the VO²⁺ centres and J_{12} corresponds to the magnetic coupling constants between those two VO²⁺ centres. Most oxidovanadium(IV) (d¹ electronic configuration) complexes follow a spin-only behaviour with magnetic moments consistent with one unpaired electron and their magnetic coupling constant can be calculated from the difference in energy between the high spin (HS, *S* = 1) and the low spin (LS, *S* = 0) states. The energy of the LS state can be obtained directly from the energy of the broken-symmetry (BS) solution, E_{BS} when using DFT-based wave functions.

Thus, single-point calculations were performed for the triplet S = 1 (HS = ++), with mean $S^2 \approx 2.0$ and the BS singlet state S = 0 (LS = +-) with mean $S^2 \approx 1.0$. The value of the magnetic coupling constant can now be obtained from the difference $E_{HS}-E_{BS}=-J_{12}$ [21]. The chk files generated by the calculation can be used for the figures of the HOMO orbitals and the spin density plots showed. The calculations have been performed for the atomic positions taken directly from the crystal structure without minimization. The study of the dependence of the magnetic coupling constant with the out-of-plane shift of the methyl group was done in the same condition, except by the replacement of Br atoms by H atoms in order to save calculation time.

3. Results and Discussions

3.1. Synthesis and Characterization

The reaction of triethylenetetramine with 5-bromosalicylaldehyde with 1 : 3 molar ratios in methanol gave the desired symmetric heptadentate Schiff base ligand, H₃L (Scheme 1), as confirmed by elemental analysis and spectroscopic data. In ¹H NMR spectrum of H₃L the presence of two broad singlet signals at δ 13.50 and 10.50 ppm were assigned to the phenolic O-H groups, which were consistent with the observation of a rapid loss of this signal when D₂O was added to the solution. The singlet peak at δ 8.64 ppm is assigned to the hydrogen atom of azomethine (-CH=N-) group [22], and confirms that the Schiff base ligand is formed. There is a singlet peak at δ 4.42 ppm in the ¹H NMR spectrum of H₃L which is due to the formation of five membered aliphatic ring and confirms that the third mol of 5-bromosalicylaldehyde has reacted with two central NH groups of triethylenetetramine. The NH peak was not detected in the ¹H NMR spectrum of the ligand which is another evidence for involving the central NH groups in condensation reaction with aldehyde. Four aliphatic peaks and thirteen aromatic peaks were

observed in the ¹³C NMR spectrum of ligand which is another evidence for existence of H_3L in the proposed structure shown in Scheme 1. The FT-IR spectrum of the H_3L shows no evidence of the N-H stretching vibrations (in which usually observes around 3150 cm⁻¹) [23] indicating that all NH groups have reacted with 5-bromosalicylaldehyde. The absorption band at 1635 cm⁻¹ in the FT-IR spectrum of H_3L , can be assigned to the imine C=N stretching frequency [24].

Complex $[V_2(O)_2(L)(\mu$ -OCH₃)]⁻CH₃OH (1) was synthesized by the reaction of H₃L and VO(acac)₂ with molar ratios 1 : 2 in methanol. Slow change in the color of reaction mixture from green-yellow to dark violet was the first evidence for the complexation of ligand to the vanadium ion and formation of a new complex. Comparison the IR spectrum of the complex 1 with the IR spectrum of the free ligand shows considerable differences between them, but also express some evidences for the coordination of Schiff base ligand to the vanadium ion. The infrared spectrum of 1 displays a band at 1631 cm⁻¹ which can be assigned to the C=N stretching frequency of the coordinated Schiff base ligand [23,24] and is red shifted with respect to the free ligand. Furthermore, in the IR spectra of 1 one strong band at 972 cm⁻¹ is observed, which is assigned to the V=O and V–N vibrations, respectively. These three bands are observed as new peaks for the complex and not exist in the spectrum of the free ligand. Very broad band around 3450 cm⁻¹ expresses the presence of –OH group and uncoordinated methanol molecule involved in hydrogen bonding [26].

The electronic spectrum of H₃L in methanol displays bands at 217 and 325 nm. Based on their extinction coefficients they are assigned to intraligand $\pi \to \pi^*$ (217 nm) and $n \to \pi^*$ (325 nm) transitions. Shifts of the bands in complex **1** relative to H₃L bands, indicate the coordination of the ligand to the vanadium ion. For complex the higher energy band at ~370 nm with high

extinction coefficient value is due to the ligand to metal charge transfer (LMCT) transition. The other higher energy intense transitions in the range 222 nm and 320 nm are due to the intraligand transitions [27].

3.2. Description of structure

Single crystals of 1 suitable for X-ray structure determination were obtained by thermal gradient method in methanol. The molecular structure of 1 is shown in Fig. 1a and selected bond distances and angles are summarized in Table 2. Single crystal X-ray analysis indicates that 1 is a neutral dinuclear complex of vanadium(IV) and a methanol molecule is located as solvent molecule. The molecular structure features a $O=V-(\mu-OCH_3)-V=O$ couple trapped by chelate $(L)^{3-}$, which the oxygen atom of central phenolate arm of Schiff base ligand acts as bridging group between two vanadium ions. Therefore, two vanadium atoms are doubly bridged by one phenolate oxygen atom (O2C) and an oxygen atom (O1M) provided by methanolate bridging group. The Schiff base ligand acts as a heptadentate trianionic compartmental donor, with two tridentate N₂O cavities and a central bridging phenolate group. Both vanadium centers are sixcoordinated with VN₂O₄ coordination environment and the coordination geometry around them can be described as distorted octahedral (Fig. 1b). It may be assumed that the amine and azomethine nitrogen atoms and the phenolate oxygen of Schiff base ligand together with oxygen atom of bridged methoxy group form the equatorial plane. Then, the oxygen atom of oxido group occupies one axial position and the oxygen atom of phenolate bridging group is located on the remaining axial position. The metal centers are displaced by 0.283 Å (V1) and 0.284 Å (V2) from the mean plane defined by the equatorial donor atoms towards the V=O moiety. In both centers, the vanadium to oxygen bond lengths follow the order V=O_{\text{oxido}} < V-O_{\text{phenolate}} < V-O_{methoxy} < V–O_{bridged phenolate}. The V–O_(bridged phenolate) bonds are longer than all other bonds, which

can be attributed to the *trans* influence of the oxido group [6,25]. The V–N(azomethine) bond lengths (V1–N1A = 2.073(3) Å and V2–N1B = 2.056(2) Å) are significantly shorter than the V– N(amine) bond lengths (V1–N2A = 2.215(3) and V2–N2B = 2.222(3) Å) which can be attributed to the differences in the hybridization of coordinated N atoms and also weaker *trans* influence of methoxy group in comparison with phenolate moiety.

The V1^{···}V2 separations through V₂O₂ cyclic unit is 3.203(1) Å and the bridging angle at the phenoxy oxygen atom, V1–O2C–V2 = 95.67(8)°, is smaller than that at the methoxy oxygen atom, V1–O1M–V2 = 108.49(9)°. The dihedral angle between the V1,O1M,O2C and V2,O1M,O2C planes is 18.38(1)°. The whole molecule has a nearly *Cs* symmetry with the mirror plane perpendicular to the vanadium-oxygen V₂O₂ metallacycle. The bridging methoxy and 5-bromophenoxy groups together with C7C atom lie approximately on this mirror plane (maximum deviation from the mean calculated plane is 0.051 Å). The crystal package of complex 1 is stabilized by several C–H^{···}O, C–H^{···}Br, C–Br^{···}O and C–H^{···} π interactions (Table 3). The methanol molecule of solvation is connected to dinuclear unit by O–H^{···}O hydrogen bonding interaction.

Fig. 1.

Table 2.

Table 3.

3.3. EPR studies

EPR spectroscopy is a convenient and effective way to probe the electronic structure of paramagnetic molecules. The examples of resonance spectra obtained for the powdered complex 1 are shown in Fig. 2. The spectrum consists of one intense resonance line located around 338.5 mT ($g \approx 1.985$). In order to better expose the weak temperature changes, the intensity of the showed spectrum was multiplied by temperature. As it is seen on Fig. 2, the intensity of the

resonance line increases upon heating. The inset to Fig. 2 shows enlarged region of the spectrum, where a small resonance absorption clearly visible at around 150 mT. As it was shown above in the structural analysis, the vanadium core adopts six coordinate distorted octahedral geometry with the closest apical oxygen atom is 1.61 Å away from metal ion and much greater distances from the metal ion (1.94 - 2.21 Å) for equatorial ligands. Therefore, it is expected to observe at least the axial EPR spectrum. The lack of hyperfine structure typical for a mononuclear oxidovanadium(IV) compounds (⁵¹V, I = 7/2) indicates on the magnetic interactions [28]. Apparently, the thermally activated absorption at 338.5 mT points on antiferromagnetic character of weak magnetic interactions however it is remains inconclusive whether this interactions are attributed to exchange intramolecular coupling or/and dipolar couplings to other paramagnetic centers. The small half-field absorption located at 150 mT might belong to the "forbidden" $\Delta M =$ 2 resonance transition within the spin triplet separated from the singlet state. However this separation, proportional to the isotopic exchange interaction constant J, is so small that temperatures well below 4K are required in EPR studies to ambiguously determine what is the ground state: singlet for antiferromagnetically coupled oxidovanadium pair (AFM) or triplet for ferromagnetically coupled pair (FM). The best can be say from experimental observation is that the AFM coupling is unusually weak.

Fig. 2.

3.4. Magnetic properties

The temperature-dependence of the molar magnetic susceptibility, χ , for complex 1 was measured on a powdered sample at B = 5 T in the temperature range of 2 K to 300 K. Results are depicted in a graph χT versus temperature in Fig. 3. At 300 K, the value for χT is 0.738

 $(\text{cm}^3 \cdot \text{K} \cdot \text{mol}^{-1})$, which is in good agreement with the expected contribution of two vanadium(IV) ions per formula unit, giving effective magnetic moment $\mu_{eff} = \sqrt{8\chi T/2} \approx 1.72 \ \mu_{\text{B}}$ per metal ion, as expected for spin-only value for an S = 1/2 system. The value of χT depends steady of temperature upon cooling down to ~ 70 K, then with further cooling χT decreases. The decrease indicates the presence of antiferromagnetic interactions between two oxidovanadium (IV) ions.

Fig. 3.

To account for the observed temperature dependence of χT , the intra-molecular exchange interaction only has been considered while inter-molecular exchange was neglected. Assuming an isotropic model, the expression based on the spin Hamiltonian ($H = -JS_1S_2$) is given by Bleaney-Bowers equation:

$$\chi T = (2N_A \beta^2 g^2) / k[3 + \exp(-J/kT)] \qquad ($$

where N_A is the Avogadro's number, g the Landé factor, k the Boltzmann constant and J the exchange coupling constant. The solid line in Fig. 3 shows the least-squares fit of the experimental data $\chi T(T)$ with adjustable parameter J = -1.60(5) cm⁻¹ and fixed value of g = 1.985, taken from EPR spectrum. The good concordance between the experimental and theoretical plot indicates the good correlation between the data and the model.

The electronic configuration of a oxidovanadium(IV) ion is d¹ having only one unpaired electron *per* metal centre. In square-pyramidal or octahedral geometry this electron is placed in a t_{2g} orbital with d_{xy} symmetry if the oxygen atom of the oxidovanadium group is considered to be in the *z* axis and the donor atoms of the ligands in the *x* and *y* axis. However, the variable configuration of the oxidovanadium oxygen and the bridging groups can lead to different geometries of the $[VO(\mu-OR)_2VO]^{2+}$ cores that display different mechanism for the transmission of the magnetic coupling which may result in very different intensities of the magnetic coupling.

In this sense, the classification given by W. Plass becomes critical for the comparison and the description of the magnetic properties of oxidovanadium(IV) compounds [29].

Scheme 2.

According to that classification, compound **1** is of the *syn*-coplanar type, and for such complexes the magnetic coupling is expected to be moderate antiferromagnetic [29,30] however, compound **1** exhibits a rather weak antiferromagnetic coupling, somewhat lower than that expected. Concerning the magnetic coupling mechanism, some authors point to a through-the-space mechanism, but others say the superexchange mechanism to predominante [30a]. Thus, with the aim of giving a good comparison of the magnetic coupling and a good description of the magnetic coupling mechanism we have performed a theoretical study based on a DFT calculation.

3.5. DFT calculations

Although there are many experimental and some theoretical studies concerning the orthogonal and the *anti*-coplanar cores [29,30] there are just a few experimental studies concerning the magnetostructural correlations in *syn*-coplanar oxidovanadium(IV) compounds [31,32]. Compared to them, the magnetic coupling constant obtained for **1** is somewhat smaller, however this comparison is not good since the only found two compounds have important differences respect to **1**.

 $NH_4[V_2O_2(OH)(C_4O_4)_2(H_2O)_3] \cdot H_2O$ (with J = -153 cm⁻¹) [31] has three bridges in the adequate configuration to mediate magnetic coupling between the two oxidovanadium(IV) centres, so it hardly compares to 1 with one single active bridge and $[{VO(L)}_2{VO(acac)}_2(\mu_2 - \mu_2 - \mu_2)]$

 $OMe)_2$]·MeOH (with $J = -167 \text{ cm}^{-1}$) [32] is a tetranuclear complex with butterfly core-structure and only one magnetic coupling constant (of the three existing magnetic exchange-pathways) was determined which can be contaminated by the rest of the magnetic exchange path-ways. [H₂L=N,N-bis(2-hydroxyethyl)-N'-(2-pyrrolylmethyli-dene)ethylenediamine]. In any case, we investigate herein the low value found for **1**.

The Broken Symmetry DFT calculation afforded a LS ground state, but very close in energy to the HS state, resulting in a very weak antiferromagnetic coupling with J = -5.5 cm⁻¹ very close to the value obtained from magnetic susceptibility data, J = -1.60 cm⁻¹ (Table S1).

Fig. 4.

The spin density iso-surface plot of the HS state shown in Fig. 4 (a) (iso-val density 0.004), displays positive spin density in both d_{xy} oxidovanadium orbitals and in the bridging methoxy-oxygen. This clearly suggests a participation of the methoxy group in the transmission of the magnetic coupling and therefore supports the superexchange mechanism in detriment of the through-the-space mechanism in this compound. On the other hand, the spin density of the LS broken symmetry state shows opposite spin density in both d_{xy} oxidovanadium and oxo orbitals and little spin density in the bridging methoxy-oxygen, suggesting, in this case, a little participation of the bridging group in the antiferromagnetic coupling. These plots of the spin density are indicators of the good quality of the calculation results since they show non-zero spin in the $[VO(\mu-OR)_2VO]^{2+}$ core in the HS and in the LS states.

Fig. 5 shows the two alpha SOMO orbitals (the HOMO and HOMO-1) of the S = 1 state. The d_{xy} orbitals point to the diagonals of the equatorial planes of the oxidovanadium(IV) ions and they are delocalized into the Schiff-base ligand through the phenolate oxygen. Also some electronic density is shared with a p orbital of the bridging methoxy-oxygen (p_y).

Fig. 5.

This (O=V)-O(methoxy)-(V=O) is clearly the operative magnetic exchange pathway and as above mentioned, supports the super-exchange mechanism [30a]. The symmetry of the magnetic orbitals are of type π which usually show weaker overlaps than those of the σ type [33]. So, here we have one of the reasons for the weak coupling observed in 1. In this sense, it is essential the relative orientation of the methoxy-oxygen p_y orbital and the d_{xy} oxidovanadium orbitals. In this π type interactions, the out-of-plane shift of the methyl group from the O=V-O(methoxy) plane is of strong influence (Fig. 5) [30a]. The magnetic coupling is related to the overlap between the orbital bearing the unpaired electrons of the paramagnetic centers with those of the bridge, in such a way that the larger the overlap the larger the magnetic coupling [33]. The maximum overlaps takes place when there is a perfect alignment of the py orbital of the methoxy-oxygen with the d_{xy} of the oxidovanadium(IV) ions and this occurs when the methyl group lies in the same plane of the oxidovanadium oxo groups (the XZ plane) Fig. 6. Compound 1 shows a deviation from that plane of 56.3° which seriously displaces the p_y orbital from the ideal situation (Fig. 5) and clearly reduces the overlap and therefore the intensity of the antiferromagnetic coupling.

3.6. Influence of the out-of-plane shift of the methyl group in the intensity of the magnetic coupling. The DFT study has shown the relative orientation of the p_y orbital of the methoxy-oxygen to play an important role in the mediation of the magnetic interaction, also the value found for the magnetic coupling in 1 seems to be rather small compared with other *syn*-coplanar oxidovanadium(IV) dinuclear complexes. In order to give an explanation and to further investigate these facts we have extended the calculation to the effect of the out-of-plane shift of the methyl group, τ . For this calculations we have replaced the bromine atoms by hydrogens in

the Schiff-base and we have rotated the methyl group to have angles of 0°, 30°, 60° and 90° respect to the O=V1–O1M plane keeping the rest of the molecule unchanged. The values obtained for the magnetic coupling constant, J, are shown in Fig. 7 as a function of τ .

Fig. 6.

Fig. 7.

It can be observed that there is an important influence of the τ parameter in the value of the magnetic coupling constant. It clearly shows that the maximum of antiferromagnetic coupling is found for the minimum deviation from the O=V–O plane. In this situation the p_y orbital of the methoxy-oxygen is in the best alignment with the vanadium d_{xy} orbitals Fig. 8 (a). As soon as the methyl group deviates from the O=V–O1M plane, the p_y orbital decreases its overlap with the d_{xy} orbitals of the oxidovanadium(IV) ions leading to a lower antiferromagnetic coupling. The *J* parameter decreases continuously reaching a minimum value around 60°. Below this value, the antiferromagnetic coupling remains almost constant which may indicate the predominance of the through-the-space mechanism below a certain out-of-plane shift. This study gives also a good concordance of the value of *J* with other *syn*-coplanar complexes that have little deviation of the bridging group [31,32].

Fig 8.

4. Conclusion

In summary, a new dinuclear oxidovanadium(IV) complex has been synthesized and characterized by spectroscopic methods and X-ray analysis. The EPR spectrum of complex allowed to identification of vanadium(IV) ions. The vanadium(IV) atoms in the dinuclear complex are coupled antiferromagnetically. Magnetic measurements of complex **1** confirmed the existence of a weak antiferromagnetic exchange coupling between the vanadium(IV) ions (J = -

1.60(5) cm⁻¹ and g = 1.98(5)), also observed by means of the EPR technique. A Broken-Symmetry DFT study has validated the intramolecular character of the magnetic coupling and has showed an important dependence of the magnetic interaction with the out-of-plane shift of the methyl group of the methoxy bridging group, giving the explanation for the very weak antiferromagnetic coupling found in compound **1**.

Acknowledgments

The authors are grateful to the University of Zanjan and Institute of Physics, Polish Academy of Sciences for financial support of this study.

Appendix

CCDC 1479603 contains the supplementary crystallographic data for complex **1**, which can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html. Electronic Supplementary Information (ESI) of this article can be found online at <u>DOI</u>:

References

c) T. Uek, Vanadium in the Environment and Its Bioremediation, Springer (2015) 13-26.

^[1] a) M. Sutradhar, L.M.D.R.S. Martins, M.F.C. Guedes da Silva, A.J.L. Pombeiro, Coord. Chem. Rev., 301–302 (2015) 200-239;

b) Hélène Pellissier, Coord. Chem. Rev., 284 (2015) 93-110;

c) M.A. Fik, A. Gorczyński, M. Kubicki, Z. Hnatejko, A. Wadas, P.J. Kulesza, A. Lewińska, M. Giel-Pietraszuk, E. Wyszko, V. Patroniak, Polyhedron 97 (2015) 83–93;

d) I.N. Booysen, T. Hlela, M.P. Akerman, B. Xulu, Polyhedron 85 (2015) 144–150;

e) P. Paciorek, J. Szklarzewicz, A. Jasińska, B. Trzewik, W. Nitek, M. Hodorowicz, Polyhedron 87 (2015) 226–232;

⁽f) J.C. Pessoa, S. Etcheverry, D. Gambino, Coord. Chem. Rev., 301–302, 15 (2015) 24-48.

^[2] a) L.J. Carpenter, S.D. Archer, R. Beale, Chem. Soc. Rev. 41 (2012) 6473-6506;

b) D. Rehder, *Bioinorganic Vanadium Chemistry*; John Wiley & Sons, (2008) Chichester, UK;

[3] G. Stacey, R.H. Burris, H.J. Evans, *Biological Nitrogen Fixation*, Springer-Verlag, (1992) New York.

[4] a) C. Leblanc, H. Vilter, J.-B. Fournier, L. Delage, P. Potin, E. Rebuffet, G. Michel, P.L. Solari, M.C. Feiters, M. Czjzek, Coord. Chem. Rev. 301 (2015) 134–146;

b) M. Nicolai, G. Gonçalves, F. Natalio, M. Humanes, J. Inorg. Biochem. 105 (2011) 887-893.

[5] a) X. Zhao, X. Chen, J. Li, J. Chen, G. Sheng, F. Niu, D. Qu, Y. Huo, H. Zhu, Z. You, Polyhedron 97 (2015) 268–272;

b) E. Halevas, O. Tsave, M.P. Yavropoulou, A. Hatzidimitriou, J.G. Yovos, V. Psycharis, C. Gabriel, A. Salifoglou, J. Inorg. Biochem. 147 (2015) 99–115.

[6] a) U. Saha, T.K. Si, P.K. Nandi, K.K. Mukherjea, Inorg. Chem. Commun. 38 (2013) 43-46;

b) J. Pranczk, D. Wyrzykowski, D. Jacewicz, A. Sikorski, A. Tesmar, L. Chmurzyński, Polyhedron 100 (2015) 74–81.

[7] a) Y. Kurt, B. İlhan-Ceylan, M. Açıkgöz, E. Tüzün, G. Atun, B. Ülküseven, Polyhedron 65 (2013) 67–72;

b) J. Krzystek, A. Ozarowski, J. Telser, D.C. Crans, Coord. Chem. Rev. 301–302 (2015) 123– 133.

[8] a) M.R. Maurya, M. Kumar, A. Kumar, J.C. Pessoa, Dalton Trans. (2008) 4220-4232;

b) D. Sanna, P. Buglyó, A.I. Tomaz, J.C. Pessoa, S, Borović, G. Micera, E. Garribba, Dalton Trans. 41 (2012) 12824–12838.

[9] A.S. Ceccato, A. Neves, M.A. Brito, S.M. Drechsel, A.S. Mangrich, R. Werner, W. Haase, A.J. Bortoluzzi, J. Chem. Soc., Dalton Trans. (2000) 1573–1577.

[10] a) J. Pasán, J. Sanchiz, Ó. Fabelo, L. Cañadillas-Delgado, M. Déniz, P. Díaz-Gallifa, C.
 Martínez-Benito, F. Lloret, M. Julvee, C. Ruiz-Pérez, CrystEngComm 16 (2014) 8106–8118;

b) R. Bikas, H. Hosseini-Monfared, M. Korabik, M.S. Krawczyk, T. Lis, Polyhedron 81 (2014) 282–289.

[11] a) A. Ghisolfi, K.Y. Monakhov, R. Pattacini, P. Braunstein, X. López, C. Graaf, M. Speldrich, J. Leusen, H. Schilder, P. Kögerler, Dalton Trans. 43 (2014) 7847–7859;

b) R. Bikas, H. Hosseini-Monfared, G. Zoppellaro, R. Herchel, J. Tucek, A.M. Owczarzak, M. Kubicki, R. Zboril, Dalton Trans. 42 (2013) 2803–2812.

[12] a) E. Ruiz, P. Alemany, S. Alvarez, J. Cano, Inorg. Chem. 36 (1997) 3683–3688;

- b) M. Velayutham, B. Varghese, S. Subramanian, Inorg. Chem. 37 (1998) 1336–1340;
- c) A.S. Ceccato, A. Neves, M.A. Brito, S.M. Drechsel, A.S. Mangrich, R. Werner, W. Haase, A.J. Bortoluzzi, J. Chem. Soc., Dalton Trans., 2000, 1573-1577;
- d) D. Venegas-Yazigi, K. Muñoz, M. Saldías, K.V. Barra, A. Vega, V. Paredes-García, C.J. Gómez-García, E.L. Fur, W. Cañón-Mancisidor, E. Spodine, Inorg. Chim. Acta, 395 (2013) 176-180.
- [13] a) D. Venegas-Yazigia, D. Aravenab, E. Spodineb, E. Ruizd, S. Alvarez, Coord. Chem. Rev. 254 (2010) 2086–2095;

b) A.J. Mota, E. Colacio, J.-P. Costes, F. Dahan, Polyhedron 63 (2013) 127–132;

c) H. Hosseini-Monfared, R. Bikas, R. Szymczak, P. Aleshkevych, A.M. Owczarzak, M. Kubicki, Polyhedron 63 (2013) 74–82.

[14] a) K. Takano, Y. Sunatsuki, M. Kojima, I. Kinoshita, T. Shibahara, Inorg. Chim. Acta, 2009, 362, 3201–3207;

b) V.A. Tuskaev, N.A. Kolosov, D.A. Kurmaev, S.C. Gagieva, V.N. Khrustalev, N.S. Ikonnikov, N.N. Efimov, E.A. Ugolkova, V.V. Minin, B.M. Bulychev, J. Organomet. Chem. 798 (2015) 393–400.

- [15] A. Sarkar, A.R. Paital, R.A. Khan, F. Arjmand, V. Bertolasi, C. Mathonière, R. Cléracf, D. Ray, Dalton Trans. 42 (2013) 12495–12506.
- [16] a) P.K. Nanda, V. Bertolasi, G. Aromi, D. Ray, Polyhedron 28 (2009) 987–993;
- b) D.Fe. Back, G.M. Oliveira, L.A. Fontana, A. Neves, B.A. Iglesias, T.P. Camargo, P.T. Campos, J.P. Vargas, Inorg. Chim. Acta 428 (2015) 163–169.
- [17] G.M. Sheldrick, Acta Cryst. A64 (2008) 112–122.
- [18] G.M. Sheldrick, *SHELXS/L-97, Programs for Crystal Structure Determination*, University of Gottingen, (1997) Gottingen, Germany.
- [19] K. Brandenburg, H.P. Gbr, Diamond (Version 3.2d), *Crystal and Molecular Structure Visualization*, Crystal Impact, (2009) Bonn, Germany.
- [20] a) M.J. Frisch, Gaussian 09 (Revision A.02), Gaussian. Inc., (2009) Wallinford, CT;
- b) A. Scheafer, C. Huber, R. Ahlrichs, J. Chem. Phys. 100 (1994) 5829-5835;
- c) A. Rodríguez-Fortea, P. Alemany, S. Alvarez, E. Ruiz, Eur. J. Inorg. Chem. (2004) 143–153.

[21] a) E. Ruiz, J. Cano, S. Alvarez, P. Alemany, J. Comp. Chem. 20 (1999) 1391–1400;

- b) E. Ruiz, A. Rodriguez-Fortea, J. Cano, S. Alvarez, P. Alemany, J. Comput. Chem. 24 (2003) 982–989.
- [22] a) D.L. Pavia, G.M. Lampman, G.S. Kriz, *Introduction to Spectroscopy*, third ed. (2001) Thomson Learning, Albany, NY, USA;
- b) M. Ghorbanloo, R. Bikas, G. Małecki, Inorg. Chim. Acta 445 (2016) 8-16;
- c) N. Noshiranzadeh, R. Bikas, K. Slepokura, M. Shaabani, T. Lis, J. Fluorine Chem. 160 (2014) 34–40.
- [23] a) K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Sixth Ed., John Wiley & Sons, Inc. (2009) Hoboken, New Jersey.
- b) M.A. Kamyabi, F. Soleymani-Bonoti, R. Bikas, H. Hosseini-Monfared, N. Arshadi, M. Siczek, T. Lis, Phys. Chem. Chem. Phys. 17 (2015) 32161–32172;
- c) R. Bikas, H. Hosseini-Monfared, L. Sieroń, A. Gutiérrez, J. Coord. Chem. 66 (2013) 4023-4031.
- [24] a) R.T. Conley, Infrared Spectroscopy, Allyn & Bacon (1966) Boston.
- b) R. Bikas, P. Aleshkevych, H. Hosseini-Monfared, J. Sanchiz, R. Szymczak, T. Lis, Dalton Trans. 44 (2015) 1782–1789;
- c) R. Bikas, N. Noshiranzadeh, L. Sieroń, H. Hosseini-Monfared, J.M. Barandiaran, T. Lis, J. Alonso, Inorg. Chem. Commun. 67 (2016) 85–89.
- [25] a) H. Hosseini-Monfared, R. Bikas, P. Mahboubi-Anarjan, S.W. Ng, E.R.T. Tiekink, Z. Anorg. Allg. Chem. 640 (2014) 243–248;
- b) N. Noshiranzadeh, R. Bikas, M. Emami, M. Siczek, T. Lis, Polyhedron 111 (2016) 167-172;
- c) N. Noshiranzadeh, M. Mayeli, R. Bikas, K. Slepokura, T. Lis, Transit. Met. Chem. 39 (2014) 33–39;
- d) R. Bikas, M. Ghorbanloo, S. Jafari, V. Eigner, M. Dusek, Inorg. Chim. Acta 453 (2016) 78–85.
- [26] a) R. Bikas, H. Hosseini-Monfared, P. Aleshkevych, R. Szymczak, M. Siczek, T. Lis, Polyhedron 88 (2015) 48–56;
- b) N. Noshiranzadeh, M. Emami, R. Bikas, K. Slepokura, T. Lis, Polyhedron 72 (2014) 56-65;
- c) N. Noshiranzadeh, A. Heidari, F. Haghi, R. Bikas, T. Lis, J. Mol. Struct. 1128 (2017)391–399.

- [27] D.F. Back, G.M. Oliveira, L.A. Fontana, A. Neves, B.A. Iglesias, T.P. Camargo, P.T. Campos, J.P. Vargas, Inorg. Chim. Acta 428 (2015) 163–169.
- [28] a) K. Ooms, T. Polenova, A.-M. Shough, D.J. Doren, M.J. Nash, R.F. Lobo, J. Phys. Chem. C 113 (2009) 10477–10484;
- b) S. Gupta, N. Khanijo, A. Mansingh, J. Non-Cryst. Solids 181 (1995) 58-63.
- [29] W. Plass, Angew. Chem. Int. Ed. 35 (1996) 627-631.
- [30] a) A. Rodríguez-Fortea, P. Alemany, S. Alvarez, E. Ruiz, Eur. J. Inorg. Chem. (2004) 143– 153;
- b) S.L. Castro, M.E. Cass, F.J. Hollander, S.L. Bartley, Inorg. Chem. 34 (1995) 466-472;
- c) Y. Sun, M. Melchior, D.A. Summers, R.C. Thompson, S.J. Rettig, C. Orvig, Inorg. Chem. 37 (1998) 3119–3121;
- d) A.S. Ceccato, A. Neves, M.A. Brito, S.M. Drechsel, A.S. Mangrich, R. Werner, W. Haase, A.J. Bortoluzzi, J. Chem. Soc., Dalton Trans. (2000) 1573–1577.
- [31] M.I. Khan, Y.-D. Chang, Q. Chen, J. Salta, Y.-S. Lee, C.J. O'Connor, J. Zubieta, Inorg. Chem. 33 (1994) 6340–6350.
- [32] W. Plass, Inorg. Chem. 36 (1997) 2200–2205.

[33] O. Kahn, Molecular Magnetism, (1993) VCH, New York.

Tables/Schemes/Figures caption

Table 1. Crystallographic data of 1

Table 2. Selected geometrical parameters (Å, °) for complex 1

 Table 3. Selected hydrogen bonding interactions in the crystal package of complex 1

Scheme 1. Synthesis pathway of H₃L and complex 1

Scheme 2. Possible structures of $[VO(\mu-OR)_2VO]^{2+}$ cores described by W. Plass [28]

Fig. 1. (a) Molecular structure of complex $[V_2(O)_2(L)(\mu$ -OCH₃)] ·CH₃OH (1); (b) Coordination environment around vanadium atoms in complex 1

Fig. 2. Powder experimental EPR spectra multiplied by temperature (ν =9.4 GHz). The inset shows enlarged low-field part of spectra.

Fig. 3. χT vs. *T* curve for powder of 1; the solid line corresponds to the calculated curves using eq. (1) with parameters J = -1.60(5) cm⁻¹, g = 1.985.

Fig. 4. Spin density plots of the HS (a) and the LS BS (b) states. Positive, blue; negative, green. Color code, C, gray, N, blue, Br, dark red, O, red.

Fig. 5. HOMO-1 (a) and HOMO (b) alpha orbitals of the HS state (iso val 0.075). The picture shows the d_{xy} oxidovanadium orbitals and their delocalization towards the p_y orbital of the methoxy-oxygen. Color code, C, gray, N, blue, Br, dark red, O, red.

Fig. 6. out-of-plane shift of the methyl group from the XZ plane of the vanadium(IV) octahedron, τ , in compound 1. The V=O bond is coloured in orange, the XZ plane is drawn in green.

Fig. 7. Magnetic coupling constant dependence as a function of the out-of-plane-shift of the methyl group, τ . Circles, simulated values; triangle, experimental value from magnetic susceptibility data.

Fig 8. SOMOs of the molecules simulated with $\tau = 0^{\circ}$ (a) and with $\tau = 60^{\circ}$ (b). It is evident that in the former case there is a good alignment of the orbitals for a maximum overlap, and in the case of $\tau = 60^{\circ}$ the p_y orbital is out of the best alignment for the maximum overlap.

Table 1. Crystallographic data of 1

Compound	Complex 1				
net formula	$C_{28}H_{27}Br_3N_4O_6V_2$ ·CH ₄ O				
$M_{\rm r}/{\rm g}~{\rm mol}^{-1}$	889.19				
crystal size/mm	$0.50 \times 0.29 \times 0.26$				
<i>T</i> /K	90				
Radiation	ΜοΚα				
Diffractometer	Xcalibur with CCD Ruby detector				
crystal system	monoclinic				
Crystal shape, color	Block, dark violet-red				
space group	P2 ₁				
a/Å	9.2556(18)				
b/Å	14.971(3)				
c/Å	12.082(2)				
α/°	90				
β/°	106.40(2)				
γ/°	90				
$V/Å^3$	1606.0(5)				
Ζ	2				
calc. density/g cm^{-3}	1.839				
μ/mm^{-1}	4.37				
F(000)	880				
θ range	2.8–31				
h,k,l	$-12 \rightarrow 13, -18 \rightarrow 21, -17 \rightarrow 17$				
R _{int}	0.022				
$R(F_{\rm obs})$	0.023				
$R_{\rm w}(F^2)$	0.041				
S	1.01				
hydrogen refinement	Mixed				
measured reflections	16090				
independent reflections	8629				
reflections with $I > 2\sigma(I)$	8183				
parameters	409				
restraints	1				
Max electron density/e $Å^{-3}$	0.40				
Min electron density/e $Å^{-3}$	-0.54				

Bond	Distance/Å	Bond	Angle/deg
V1-01	1.608(2)	O2A-V1-O2	2C 83.78(9)
V1–O2A	1.948(2)	O1M-V1-O	2C 75.98(8)
V1–O1M	1.981(2)	N1A-V1-O2	2C 87.81(9)
V1–O2C	2.157(2)	01–V1–N2A	A 91.33(10)
V1–N1A	2.073(3)	02A-V1-N2	2A 161.84(9)
V1-N2A	2.215(3)	O1M-V1-N	12A 92.57(9)
V2-O2	1.612(2)	N1A-V1-N2	2A 79.27(10)
V202B	1.951(2)	O2C-V1-N2	2A 81.43(9)
V2-01M	1.966(2)	O2-V2-O2H	3 101.66(11)
V2–O2C	2.164(2)	O2-V2-O1N	M 100.93(10)
V2-N1B	2.056(2)	O2B-V2-O	1M 92.91(9)
V2–N2B	2.222(3)	O2-V2-N1I	3 98.79(11)
		O2B-V2-N	1B 89.24(10)
Bond	Angle/deg	O1M-V2-N	1B 159.28(9)
V1-O1M-V2 108.49(9)		O2-V2-O20	C 170.37(10)
V1-02C-V	2 95.67(8)	O2B-V2-O2	2C 87.71(9)
O1-V1-O2	A 104.36(11)	01M-V2-0	2C 76.11(8)
01-V1-01	M 98.68(10)	N1B-V2-02	2C 83.40(9)
02A-V1-0	1M 94.00(9)	O2–V2–N2H	3 90.06(11)
O1-V1-N1.	A 96.59(11)	O2B-V2-N2	2B 164.63(9)
O2A-V1-N	1A 89.73(10)	O1M-V2-N	12B 94.60(10)
O1M-V1-N	11A 162.84(9)	N1B-V2-N2	2B 79.06(10)
O1-V1-O2	C 170.71(11)	O2C-V2-N2	2B 81.12(9)
01-V1-020	<u>C 170.71(11)</u>	02C-V2-N2	2B 81.12(9)
P			

Table 2. Selected geometrical parameters (Å, °) for complex 1

D-HA	D-H (Å)	H···A (Å)	D…A (Å)	$D-H\cdots A(deg)$
$C9A-H9A1\cdotsO2^{i}$	0.99	2.40	3.293(4)	149
C10A-H10A…O1	0.99	2.59	3.128(4)	114
$C8B-H8B2\cdotsO1^{ii}$	0.99	2.59	3.135(4)	115
C10B-H10D····O2	0.99	2.53	3.082(4)	115
$C7C-H7C\cdots O2M^{i}$	1.00	2.57	3.461(4)	149
O2 <i>M</i> −H2 <i>M</i> ···O2 <i>B</i>	0.84	2.13	2.934(3)	160
	-x+1, y=1/2, -			

Table 3. Selected hydrogen bonding interactions in the crystal package of complex 1





Scheme 2. Possible structures of $[VO(\mu-OR)_2VO]^{2+}$ cores described by W. Plass [28]



Fig. 1. (a) Molecular structure of complex $[V_2(O)_2(L)(\mu$ -OCH₃)] ·CH₃OH (1); (b) Coordination environment around vanadium atoms in complex 1



Fig. 2. Powder experimental EPR spectra multiplied by temperature (ν =9.4 GHz). The inset shows enlarged low-field part of spectra.



Fig. 3. χT vs. *T* curve for powder of **1**; the solid line corresponds to the calculated curves using eq. (1) with parameters J = -1.60(5) cm⁻¹, g = 1.985.



Fig. 4. Spin density plots of the HS (a) and the LS BS (b) states. Positive, blue; negative, green. Color code, C, gray, N, blue, Br, dark red, O, red.



(b)

Fig. 5. HOMO-1 (a) and HOMO (b) alpha orbitals of the HS state (iso val 0.075). The picture shows the d_{xy} oxidovanadium orbitals and their delocalization towards the p_y orbital of the methoxy-oxygen. Color code, C, gray, N, blue, Br, dark red, O, red.



Fig. 6. out-of-plane shift of the methyl group from the XZ plane of the vanadium(IV) octahedron, τ , in compound 1. The V=O bond is coloured in orange, the XZ plane is drawn in green.



Fig. 7. Magnetic coupling constant dependence as a function of the out-of-plane-shift of the methyl group, τ . Circles, simulated values; triangle, experimental value from magnetic susceptibility data.



Fig 8. SOMOs of the molecules simulated with $\tau = 0^{\circ}$ (a) and with $\tau = 60^{\circ}$ (b). It is evident that in the former case there is a good alignment of the orbitals for a maximum overlap, and in the case of $\tau = 60^{\circ}$ the p_y orbital is out of the best alignment for the maximum overlap.