

## Influence of polydentate ligands in the structure of dinuclear vanadium compounds\*

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**Abstract:** A review discussing general structural features of oxygen-bridged dinuclear vanadium(IV and/or V) complexes is presented, covering those that have been characterized by single-crystal X-ray diffraction. Many of these compounds contain functional Schiff bases or amines as ligands, this work illustrating the high propensity of the V center to increase its coordination number via dimerization of two tetra- or penta-coordinate monomers, if the steric and electronic control exerted by the ligands allows it. We also report the synthesis and characterization by single-crystal X-ray diffraction of two new dinuclear complexes:  $[\{V^VO[Sal(R,R\text{-chen})]\}_2(\mu_2\text{-O})_2]$  and  $[\{V^VO[mvan(S,S\text{-chen})]\}_2(\mu_2\text{-O})_2]$ . The complexes contain tridentate ligands with O-phenolate, N-imine, and N-amine coordination to the V<sup>V</sup> center. The molecular structures of these compounds demonstrate that they form dinuclear species in the solid state with a  $\{OV^V(\mu_2\text{-O})_2V^VO\}$  core.

**Keywords:** vanadium; dinuclear complexes; review; chiral Schiff bases; salen ligands; X-ray diffraction.

### INTRODUCTION

A variety of V complexes have been introduced as structural and/or functional models for biologically active V compounds [1]. Schiff-base complexes with imine donor groups, and reduced Schiff-base complexes containing amine donor groups are specific subfamilies within this group.

We report the synthesis and characterization by single-crystal X-ray diffraction of two new dinuclear V<sup>V</sup> complexes containing chiral Schiff-base ligands of sal<sub>2</sub>en-type. These compounds were prepared starting from  $[V^{IV}O(sal_2en)]$ -type complexes, but upon partial hydrolysis of the ligand and air oxidation of the V<sup>IV</sup>O unit dinuclear complexes containing tridentate ligands with O-phenolate, N-imine and N-amine coordination to V<sup>V</sup> centers were obtained.

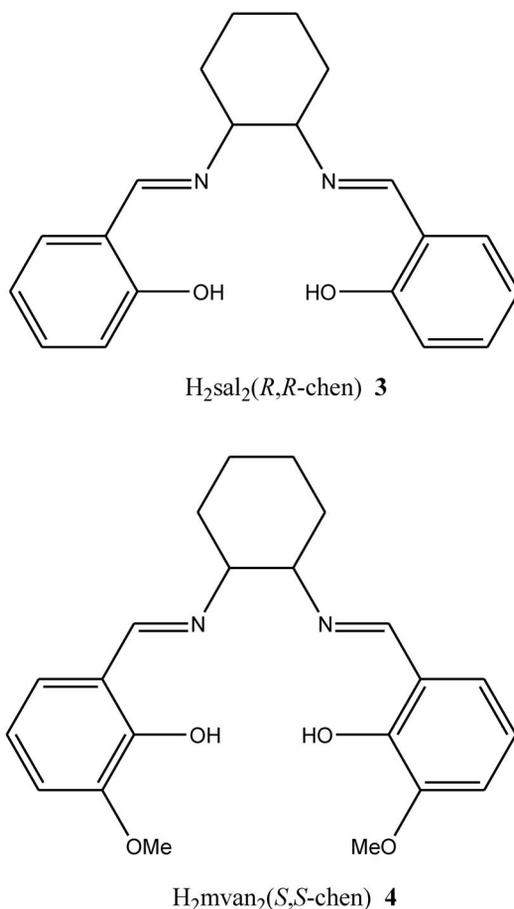
The influence of polydentate ligands in the structure of dinuclear V<sup>V</sup> compounds is very important. For this review, we have selected all structures of dinuclear V compounds with ligands acting as tridentate or tetradentate with V<sub>2</sub>O<sub>3</sub> and V<sub>2</sub>O<sub>4</sub> cores from the Cambridge Structural Database and compare their structures with the two dinuclear compounds now reported.

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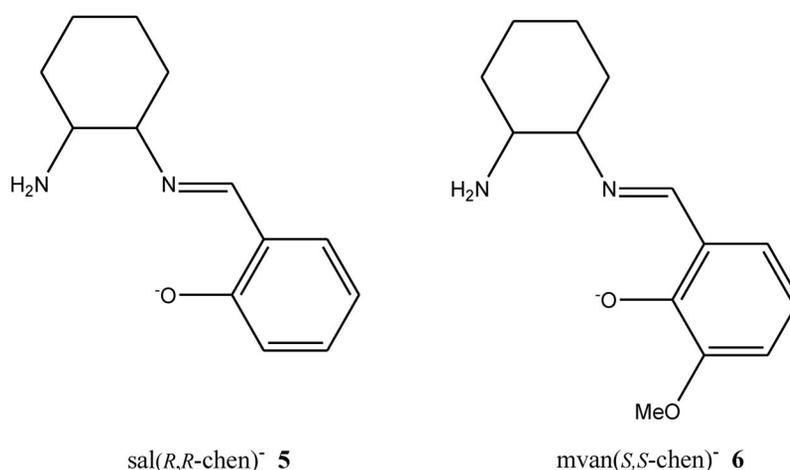
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**EXPERIMENTAL SECTION**

The chiral Schiff-base compounds  $H_2sal_2(R,R\text{-chen})$  **3** and  $H_2mvan_2(S,S\text{-chen})$  **4** (see Fig. 1) were prepared following a literature procedure [2] by reaction of the appropriate *o*-hydroxyaldehyde with the optically active diamine (2:1) in methanol. Compound **3** or **4** (1 equiv) was dissolved in MeOH, 1.1 equiv of  $VOCl_2$  (50 % aqueous solution) were added and the pH was adjusted to 7 with NaOH 1 M. Some time later, an oxovanadium(IV) complex precipitated, either  $[V^{IV}O\{sal_2(R,R\text{-chen})\}]$  or  $[V^{IV}O\{mvan_2(S,S\text{-chen})\}]$ , which was filtered, washed with MeOH, water, and dried under vacuum. These  $V^{IV}O$  complexes were dissolved in dimethylformamide (DMF) and were left under air. After slow and partial evaporation of the solvent, which took ca. 5 weeks, both solutions became yellow, and light green needles formed in the case of **1** (yield ca. 10 %), and yellow needles in the case of **2** (yield ca. 5 %), which were then separated for single-crystal X-ray diffraction studies. The compounds were found to be dinuclear complexes containing the tridentate ligands **5** or **6**, respectively (see Fig. 2). In the IR, the  $\nu(V=O)$  and  $\nu(C=N)$  are at 936 and 1651  $cm^{-1}$  for **1** and 928 and 1634  $cm^{-1}$  for **2**, respectively.



**Fig. 1** The chiral Schiff-base compounds  $H_2sal_2(R,R\text{-chen})$  **3** and  $H_2mvan_2(S,S\text{-chen})$  **4** used as starting materials for the synthesis of the  $V^{IV}$  complexes precursors of **1** and **2**.



**Fig. 2** Tridentate ligands *sal*(*R,R*-*chen*)<sup>-</sup> **5** and *mvan*(*S,S*-*chen*)<sup>-</sup> **6** found in the molecular structures of **1** and **2**, respectively.

### X-ray crystal structure determination

The 3D X-ray data for **1** and **2** were collected on a Bruker Kappa X8Apex CCD diffractometer by the  $\phi$ - $\omega$  scan method. The data were collected at low temperature. Reflections were measured from a hemisphere of data collected of frames each covering  $0.3^\circ$  in  $\omega$ . Of the 12 371 in **1** and 6764 in **2** reflections measured, all of which were corrected for Lorentz and polarization effects, and for absorption by semi-empirical methods based on symmetry-equivalent and repeated reflections, 4787 in **1** and 4490 in **2** independent reflections exceeded the significance level  $|F|/\sigma(|F|) > 4.0$ . Complex scattering factors were taken from the program package SHELXTL [3]. The structures were solved by direct methods and refined by full-matrix least-squares methods on  $F^2$ . The non-hydrogen atoms were refined with anisotropic thermal parameters in all cases. The hydrogen atoms were included in calculated positions and refined by using a riding mode for all the atoms in **1** (except for N1, C6, C7, and C14, which were left to refine freely), and were also included in calculated positions in all cases in **2** (except for N1, C7, and C20, which were left to refine freely). For **1** and **2**, the absolute configuration of the chiral centers was also established by refinement of the enantiomorph polarity parameter [ $x = -0.01(3)$  for **1** and  $0.98(3)$  for **2**] [4]. A final difference Fourier map showed no residual density outside:  $0.489, -0.741 \text{ e.}\text{\AA}^{-3}$  in **1** and  $0.501, -0.543 \text{ e.}\text{\AA}^{-3}$  in **2**. CCDC 700858 (for **1**) and 700859 (for **2**) contain the supplementary crystallographic data for this paper. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via <[www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif)>. Crystal data and details on data collection and refinement are summarized in Table 1.

**Table 1** Crystal data and structure refinement for **1** and **2**.

	<b>1</b>	<b>2</b>
Formula	C <sub>26</sub> H <sub>34</sub> N <sub>4</sub> O <sub>6</sub> V <sub>2</sub>	C <sub>28</sub> H <sub>38</sub> N <sub>4</sub> O <sub>8</sub> V <sub>2</sub>
<i>M</i> <sub>r</sub>	600.45	660.50
<i>T</i> [K]	100(2)	100(2)
λ, Å [Mo, K <sub>α</sub> ]	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	P2 <sub>1</sub>	P1
<i>a</i> [Å]	8.9787(9)	7.3583(10)
<i>b</i> [Å]	12.3991(12)	7.8797(10)
<i>c</i> [Å]	11.9723(12)	12.8270(17)
α [°]	90	72.932(2)
β [°]	103.657(2)	82.466(2)
γ [°]	90	83.366(2)
<i>Z</i>	2	1
Volume [Å <sup>3</sup> ]	1295.2(2)	702.50(16)
ρ <sub>calcd</sub> [gcm <sup>-3</sup> ]	1.540	1.561
μ mm <sup>-1</sup>	0.771	0.724
Reflections measured	12371	6764
Independent reflections <sup>b</sup>	4787	4490
R(int)	0.0382	0.0168
Goodness-of-fit on F <sup>2</sup>	1.039	1.161
R <sub>1</sub> <sup>c</sup>	0.0399	0.0282
wR <sub>2</sub> (all data) <sup>c</sup>	0.1087	0.0931

<sup>a</sup>The structures were solved using the SHELXS Program for Crystal Structure Determination [3a] and refined with SHELXL Program for Crystal Structure Refinement [3b].

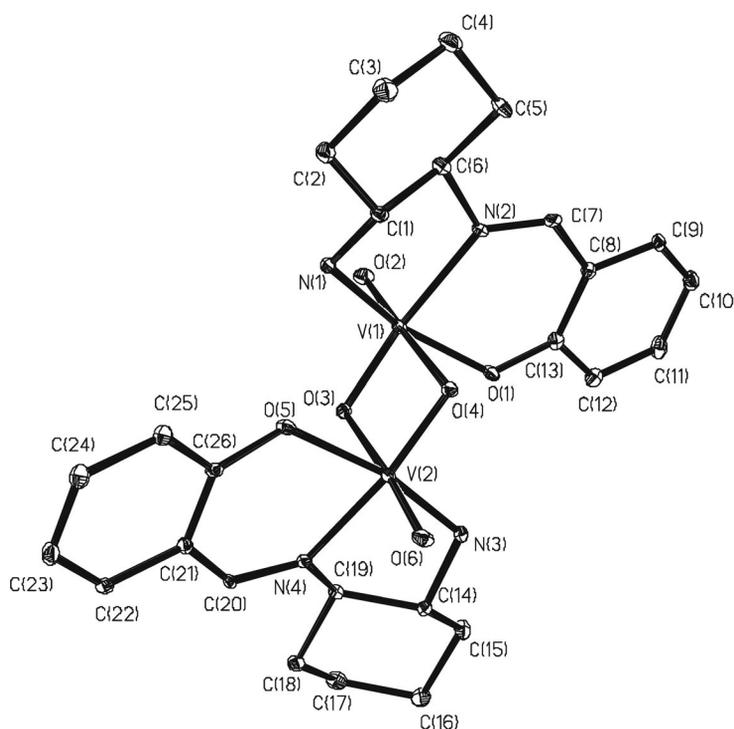
<sup>b</sup>*I* > 2 (*I*).

<sup>c</sup>R<sub>1</sub> = Σ|F<sub>o</sub> - F<sub>c</sub>| / Σ|F<sub>o</sub>|, wR<sub>2</sub> = {Σ[w(|F<sub>o</sub>|<sup>2</sup> - F<sub>c</sub>|<sup>2</sup>)<sup>2</sup>] / Σ[w(F<sub>o</sub><sup>4</sup>)]<sup>1/2</sup>.

## RESULTS AND DISCUSSION

Although the initial mixtures contained the V<sup>IV</sup> complexes of the Schiff-base ligands, in the case of compounds **1** and **2**, V<sup>V</sup> complexes containing the half Schiff-base monoanionic ligands **5** and **6** were obtained, where one of the imine bonds hydrolyzed [5]. Imines are susceptible to hydrolysis in aqueous media. In the present case, some water was present in the V<sup>IV</sup>-salen compounds used as starting materials, and could also have been introduced through the long contact of the solutions with air. One of the imine bonds of the ligand hydrolyzed, giving rise to a tridentate ligand containing one O-phenolate, one N-imine, and one primary N-amine donor atoms. The oxidation of V<sup>IV</sup> was probably due to diffusion of air into the solution. The resulting [(VOL)<sub>2</sub>(μ<sub>2</sub>-O)<sub>2</sub>] complexes contain the tridentate ligands **5** and **6**, two oxovanadium(V) units and two bridging O atoms, the molecular structures here reported showing they are dinuclear complexes in the solid state with a V<sub>2</sub>O<sub>4</sub> core.

**Molecular structure of [(V<sup>V</sup>O(sal(R,R-chen)))<sub>2</sub>(μ<sub>2</sub>-O)<sub>2</sub>] (**1**):** Complex **1**, containing the tridentate sal(R,R-chen)<sup>-</sup> ligand **5**, resulted from slow crystallization of a solution containing the parent V<sup>IV</sup> complex [V<sup>IV</sup>O{sal<sub>2</sub>(R,R-chen)}], and corresponds to the dinuclear compound shown in Fig. 3. (Table S1, in the Supplementary Information, includes selected bond lengths and angles.) The structure demonstrates that each V<sup>V</sup> center is six-coordinated with terminal oxygen atoms (O2 and O6) and two bridging oxygen atoms (O3 and O4). The V1–O2 and V2–O6 bonds have typical V=O distances of 1.614(3) and 1.610(3) Å, respectively, while the other two O atoms, O3 and O4, are involved in the bridge between the V1 and V2 atoms. O3 is strongly coordinated to V1 [V1–O3, 1.679(2) Å], O4 to V2

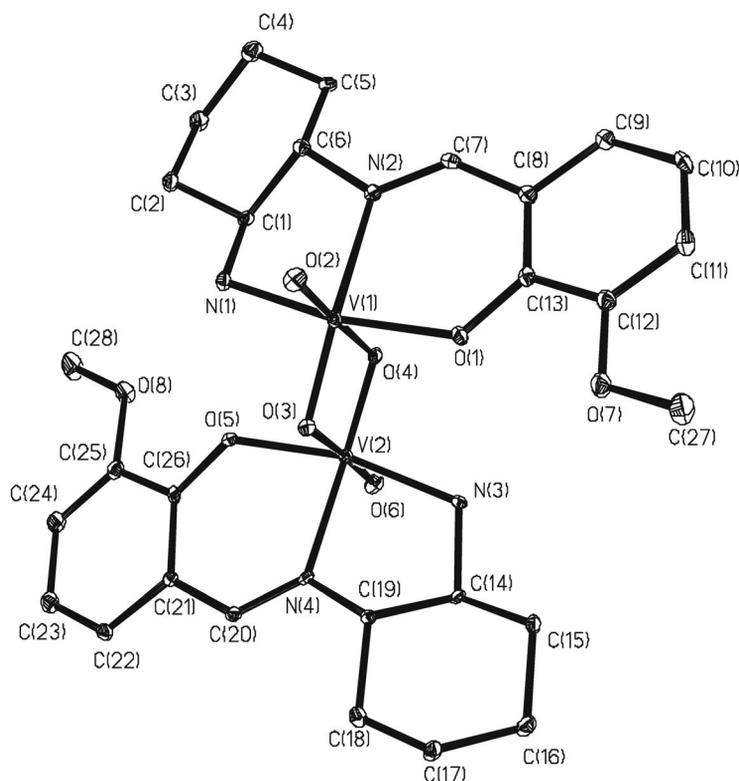


**Fig. 3** ORTEP diagram drawn at the 30 % probability level depicting the molecular structure of  $[\{VO[\text{sal}(R,R\text{-chen})]\}_2(\mu_2\text{-O})_2]$  **1** showing the atomic numbering scheme. The hydrogen atoms are omitted for simplicity.

[V2–O4, 1.669(2) Å]. Atom O4 is weakly associated with V1 [V1–O4, 2.335(3) Å] and O3 with V2 [V2–O3, 2.302(3) Å]. The remaining three coordination sites are occupied by the phenolate O atoms [V1–O1, 1.926(3) Å, and V2–O5, 1.927(3) Å], imine N atoms [V1–N2, 2.186(3) Å, and V2–N4, 2.154(3) Å] and primary amine N atoms [V1–N1, 2.144(3) Å, and V2–N3, 2.126(3) Å], the bond lengths being similar to those reported for other V<sup>V</sup>-salen compounds. The V–V distance is 3.1122(7) Å, and the O2–V1–O3 and O6–V2–O4 angles are, 105.86(14)° and 106.44(14)°, respectively, also similar to those observed in other compounds [6].

Within the possible configurations for the  $[VO(\mu_2\text{-OR})_2VO]^{2+}$  core in complexes consisting of two edge-sharing octahedrally coordinated oxovanadium centers, we classify this core in compound **1** as *anti*-coplanar [7].

**Molecular structure of  $[\{V^V O[S,S\text{-mvan}(\text{chen})]\}_2(\mu_2\text{-O})_2]$  (**2**):** Complex **2**, containing the tridentate *mvan*(*S,S*-chen)<sup>–</sup> ligand **6**, resulted from slow crystallization of a solution containing the parent V<sup>IV</sup> complex  $[V^{IV}O\{mvan(S,S\text{-chen})_2\}]$ , and corresponds to the dinuclear compound shown in Fig. 4. Each unit contains two tridentate *mvan*(chen)<sup>–</sup> ligands **6**, and its molecular structure is shown in Fig. 4. (Table S1, in the Supplementary Information, includes selected bond lengths and angles). The structure demonstrates that each V<sup>V</sup> center is six-coordinated with a terminal oxygen atom (O2 and O6) and two bridging oxygen atoms (O3 and O4). The V1–O2 and V2–O6 bonds have typical V=O distances of 1.622(3) and 1.623(3) Å, respectively, while the other two O atoms, O3 and O4, are involved in the bridge between the V1 and V2 atoms. O3 is strongly bound to V1 [V1–O3, 1.667(2) Å] and O4 to V2 [V2–O4, 1.663(2) Å]. Atom O4 is weakly associated with V1 [V1–O4, 2.409(3) Å] and O3 with V2 [V2–O3, 2.437(3) Å]. The remaining three coordination sites are occupied by the phenolate O atoms [V1–O1, 1.915(3) Å, and V2–O5, 1.915(3) Å], imine N atoms [V1–N2, 2.183(3) Å, and V2–N4, 2.171(3) Å], and primary amine N atoms [V1–N1, 2.131(3) Å, and V2–N3, 2.127(3) Å], the bond



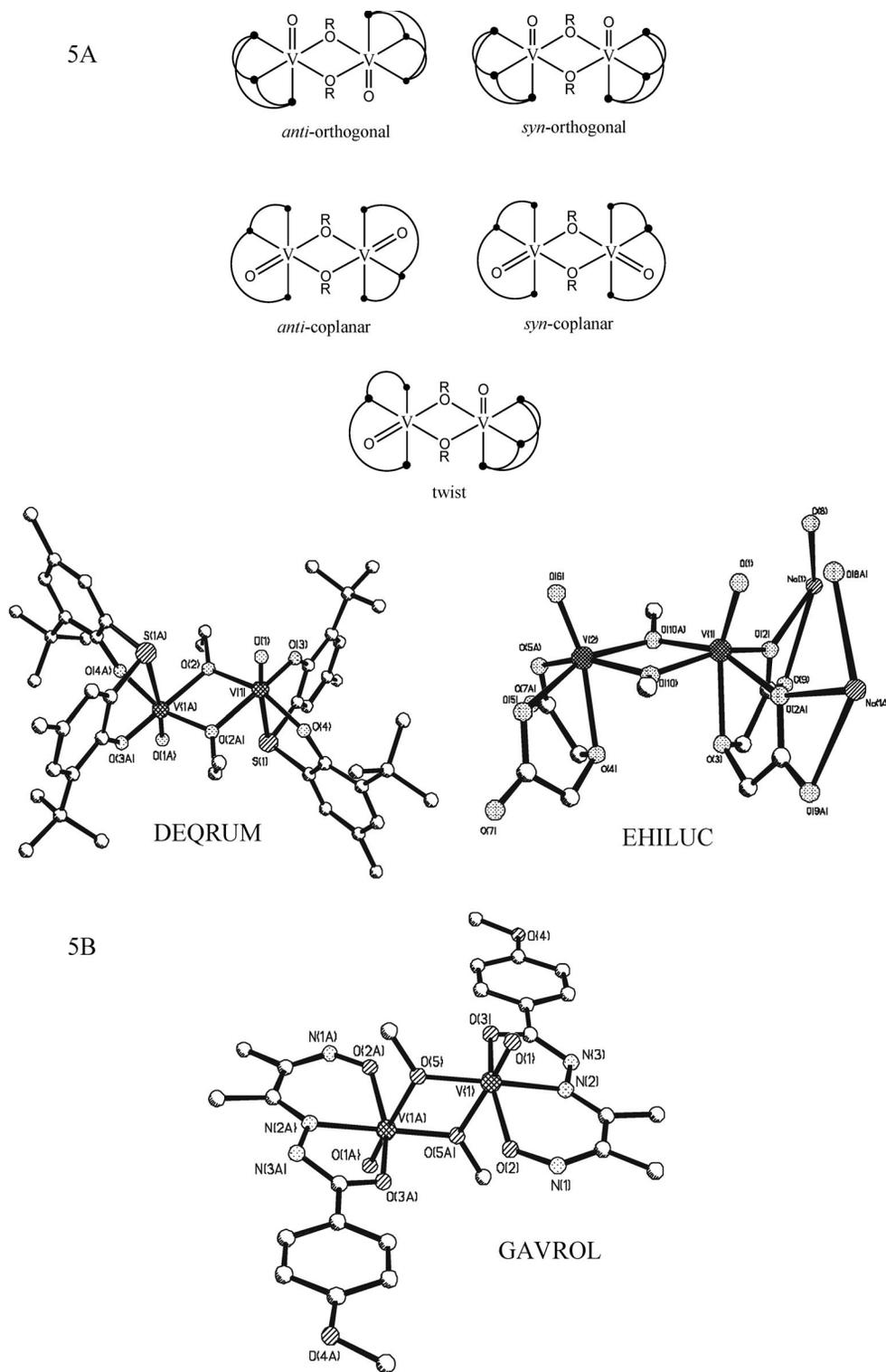
**Fig. 4** ORTEP diagram drawn at the 30 % probability level depicting the molecular structure of  $[\{\text{VO}[\text{mvan}(\text{S},\text{S}\text{-schen})]\}_2(\mu_2\text{-O})_2]$  **2** showing the atomic numbering scheme. The hydrogen atoms are omitted for simplicity.

lengths again being similar to those reported for other  $\text{V}^{\text{V}}$ -salen compounds. The V–V distance is 3.2307(7) Å and the O2–V1–O3 and O6–V2–O4 angles are, 107.06(13)° and 107.89(14)°, respectively, also similar to those observed in other compounds [6], and in compound **1**.

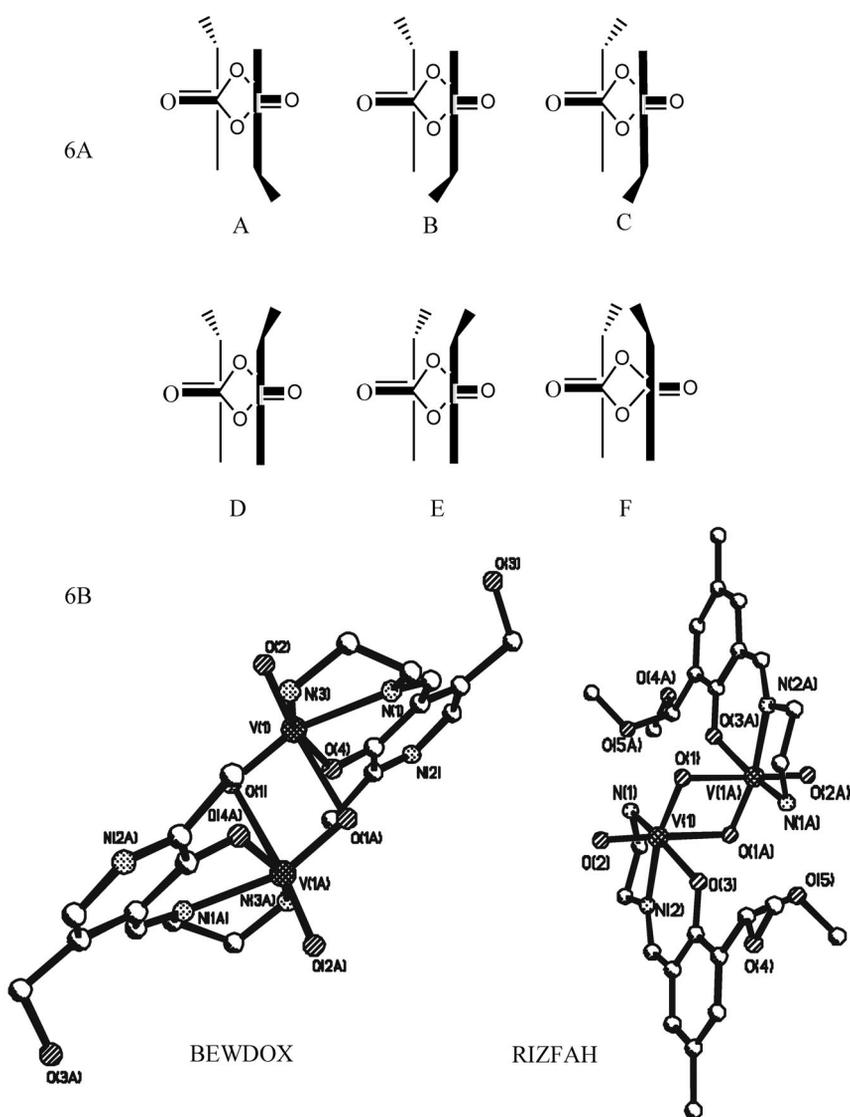
The possible configurations of a  $[\text{VO}(\mu_2\text{-OR})_2\text{VO}]^{2+}$  core in complexes consisting of two edge-sharing octahedral  $\text{V}^{\text{IV}}\text{O}$  centers are shown in Fig. 5a. The configuration is classified according to the orientation of the V=O groups with respect to the plane defined by the two V centers and the two bridging oxygen atoms (*syn*, *anti*), and with the facial or equatorial disposition of the tridentate ligands (*orthogonal*, *coplanar*, *twist*) [7]. This classification can be applied to compounds with the  $[\text{VO}(\mu_2\text{-OR})_2\text{VO}]^{n+}$  core ( $n = 1, 2, \text{ or } 3$ ) [8]. A few examples are shown in Fig. 5b.

An additional type of isomerism is possible considering the bound ligands in a dinuclear structure. Three types of isomers may form with an antiparallel orientation with phenolate moieties arranged on opposite sides of the  $\text{V}_2\text{O}_4$  cores (A–C in Fig. 6A) [9], and two examples are depicted in Fig. 6B. Three other sets (D–F in Fig. 6A) have a parallel orientation. Each of the three sets within a parallel/antiparallel group is distinguishable by the R groups, which may have *syn* or *anti* conformations. The R groups (–OCH<sub>3</sub> in RIZFAH) are *syn* when located on the same ligand face as the terminal oxo group of the core, and the R groups (–CH<sub>2</sub>OH in BEWDOX) are *anti* when located on the opposite face.

There are many oxo-bridged dinuclear vanadium(IV and/or V) complexes whose structure has been determined by X-ray diffraction [10,11], although those involving the  $\text{OV}^{\text{V}}(\mu_2\text{-O})\text{V}^{\text{IV}}\text{O}$  unit are relatively rare [12]. In those containing mixed-valence V atoms {a  $\text{OV}^{\text{V}}(\mu_2\text{-O})\text{V}^{\text{IV}}\text{O}$  unit}, several different configurations are possible for the bridging and terminal oxygen atoms in the  $[\text{V}_2\text{O}_3]^{3+}$  core (see



**Fig. 5** (A) Possible configurations of a  $[\text{VO}(\mu_2\text{-OR})_2\text{VO}]^{2+}$  core [7]; (B) molecular structures of DEQRUM (*anti-orthogonal*) [25], EHILUC (*syn-orthogonal*) [26] and GAVROL (*anti-coplanar*) [22a].



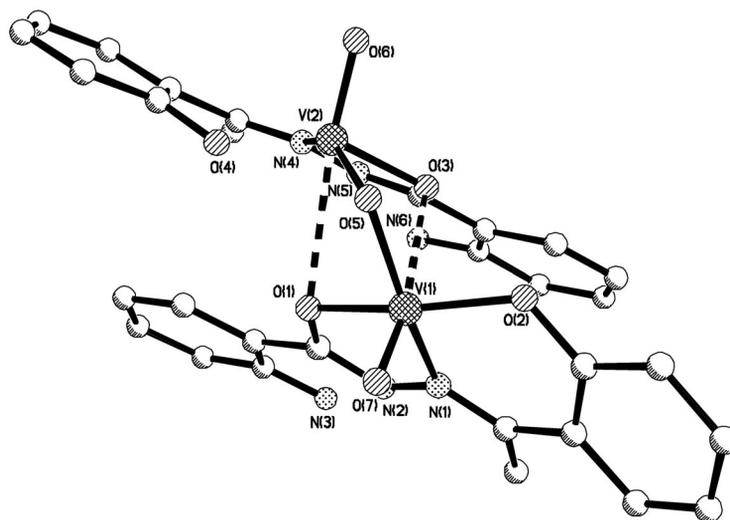
**Fig. 6** (A) Different isomers around the  $V_2O_4$  core. The three sets of isomers may form with antiparallel orientation (A–C), and the other three sets with a parallel orientation (D–F). Each of the three sets within a parallel/antiparallel group is distinguished by functional groups (R) which may have *syn* or *anti* conformations [9]; (B) molecular structures of BEWDOX (antiparallel, type A-*anti*-coplanar) [5] and RIZFAH (antiparallel, type C-*anti*-coplanar) [27].

Fig. 7A) [13]. In our literature survey, we only found *anti*-linear, *twist*-angular, and *syn*-angular configurations (see Table S5), and Fig. 7B gives one example of a molecular structure for each of these  $V_2O_3$  configurations.

Within the structures containing tetradentate ligands only dinuclear compounds with *anti*-linear configuration have been described (see Table S3). Other examples with linear configurations in fact have a polymeric nature. All dinuclear V species found in the literature with *twist*-angular configuration present a short contact [14], which is considered as a weak bond involving another donor O atom coordinated to one of the V atoms; this normally implies a shorter V–V distance in the dinuclear species



(see Fig. 8) [15]. The ligands act as tridentate, and the V atoms are both in oxidation state V, except RETZUL [16], which is a mixed-valence complex generated in solution by electroreduction of the corresponding  $[V^V_2O_3]^{4+}$  congener (see Table S4).



**Fig. 8** Molecular structure of ODUBOE [15] with a short contact between the ketonic oxygen and V atoms.

Water molecules can block the second  $\mu_2$ -O bridge as found in complex  $[\{VO(\text{van-L-Ser})(\text{H}_2\text{O})\}_2(\mu_2\text{-O})]$  [12,17], but this effect can be exerted by the ligand itself when it acts as polydentate. Aroylhydrazones of *ortho*-hydroxy aldehydes, which provide a phenolic-OH, an imine-N, and an amide-O as binding groups, are very efficient in stabilizing high oxidation states of metals of the first transition series [18], and a family of dinuclear  $V^V$  complexes containing the  $OV^V(\mu_2\text{-O})V^VO$  core, with distorted square-pyramidal coordination geometry around the metal center, was reported by S. Pal et al., and an example is given in Fig. 9 [19]. With the *o*-*N*-salicylideneaminomethylphenol ligand, two square-pyramids are linked via an oxo-bridge [20]. In other cases, vanadate esterification with carbohydrates is obtained, with each V atom in a distorted trigonal-bipyramidal arrangement (an example is depicted in Fig. 10). In the case of *N*-salicylidene-*L*-valinate as ligand, a complex involving double (mixed) bridging by oxo-O and carboxylate-O was isolated, and this is one of the rare examples where two VO terminal groups make an angle near  $90^\circ$  (*twist*-angular configuration) [12]. In complexes with thiohydrazone ligands, the terminal O atoms are in the *syn* orientation, with a torsion angle close to  $0^\circ$  (configuration *syn*-linear) [11b]. In other cases, such as the neutral bis[oxovanadium(V)] complex  $[\{VO(\text{van-L-ser})(\text{H}_2\text{O})\}_2(\mu_2\text{-O})]$  [17] the two  $V=O$  units are between the *syn* and *anti* configurations, in a *twist*-angular configuration (see Fig. 11).

Tetradentate ligands can also determine the steric control on  $V^V$  coordination and form dinuclear complexes with only one O-bridging atom (see in Fig. 7b, PAQVEI). Two examples of such types of  $V^V$ -dinuclear species, which were prepared from salan-type ligands, have been recently obtained by our group [2]. A dinuclear V compound,  $[(V^VO_2)_2(\text{pyren})_2]$  [5], bearing a tridentate ligand was previously obtained. It presents an *anti*-coplanar configuration [5], and an antiparallel type A disposition [9] of the  $-\text{CH}_2\text{OH}$  groups of pyridoxal. The complex  $[\{V^VO[\text{pyr}(S,S\text{-chen})]\}_2(\mu\text{-O})_2]$  [21], also presents an *anti*-coplanar configuration but an antiparallel type C disposition of the  $-\text{CH}_2\text{OH}$  functional groups.

The structure of **2** (similar to the one obtained for **1**) can also be classified as *anti*-coplanar (see Fig. 5). The functional groups are in an intermediate situation with respect to *syn* or *anti* disposition (see

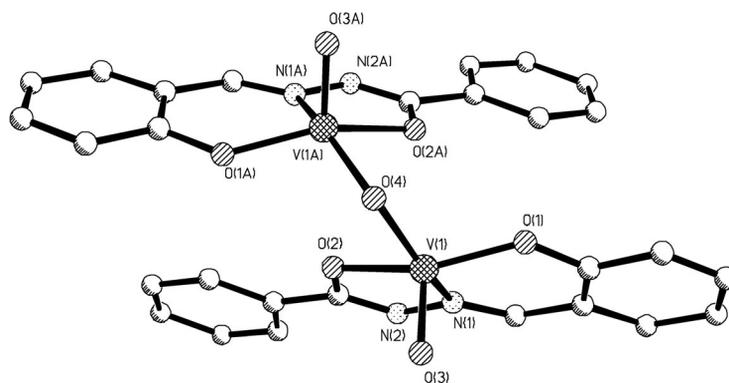


Fig. 9 Molecular structure of HAZFUJ01 [19].

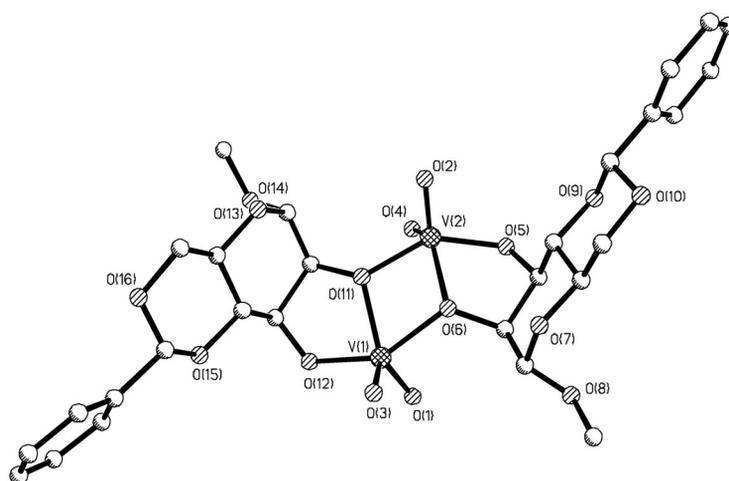


Fig. 10 Molecular structure of TOGQEL [29].

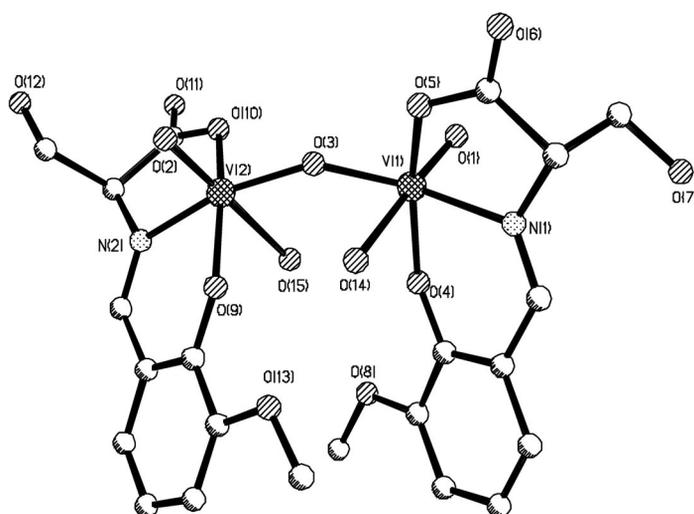
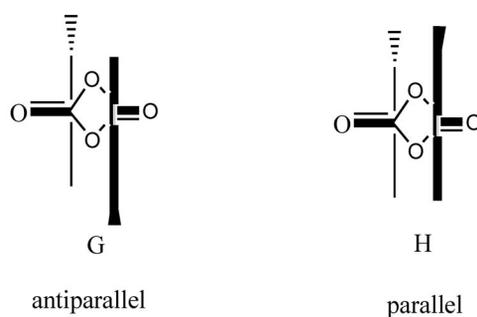


Fig. 11 Molecular structure of FIQFOA [30].



**Fig. 12** Intermediate situation of the functional groups according to the classification proposed by Pecoraro and coworkers [9].

Figs. 6 and 8), and we propose a new type of isomer with antiparallel type G orientation (see Fig. 12), as also found in other examples in the literature [22].

Examples involving Schiff-base derivatives are BIWCAL (penta-coordinated ligand, which does not include short contacts), EJUCIC (including short contacts), FIQFOA and TAWZAS (both with water completing the coordination sphere), KERDUG (complex structure) and TOZRIJ (including short contacts). See references in Table S1.

In Table 2, we summarize the general features of dinuclear V complexes with structure determined from single-crystal X-ray diffraction by considering three groups of compounds.

**Table 2** Selected structures of dinuclear V compounds with ligands acting as tridentate or tetradentate donors from the Cambridge Structural Database.

Group I. CSD codes of dinuclear V compounds with ligands acting as tetradentate donors	Group II. CSD codes of dinuclear V species with twist-angular configuration	Group III. CSD codes of mixed valence dinuclear V complexes with the $[V_2O_3]^{3+}$ core
AVNLAC	BIWCAL	AVNLAC
BUPCEU	EJUCIC	BECCIV
DAGWIR	FIQFOA	DAGWIR
FEKGUY	HAZFUJ	HOWWAR
HOWWAR	HAZFUJ01	JICLUC
JICLUC	HERCAI	MIZCON
LAGGEG	JUYKET	PAQVEI
MIZCON	KERDUG	PEHYEG
PAQVEI	KOHQED	RETZUL
PEHYEG	ODUBOE	ROCKID
ROCKID	PIKTIN	ROQBUU
SOCMIG	RETZUL	SOCMIG
ZUFJOZ	TAWZAS	TABMOZ
	TOZRIJ	XUMHUI

If the *anti* position with respect to  $V=O_t$  is occupied by an O atom (ketonic, carboxylic, phenolic...) of an available donor group of the ligand coordinated to the other V atom, the coordination sphere is completed with such a short contact. If such a donor group is not available the coordination sphere is completed by another O-bridging atom.

All structures found in the literature survey of dinuclear V complexes with ligands acting as tetradentate present an *anti*-linear configuration, and most of them are mixed-valence  $V^{IV}-O-V^V$  compounds (group I in Table 2; see also Table S3). The structures of complexes  $\{[V^V O(\text{sal}(\text{dpan}))]_2(\mu_2-O)\}$

and  $[\{V^VO[t\text{-Busal}(\text{chan})]\}_2(\mu_2\text{-O})]$  [2] are the first examples of dinuclear V complexes with tetradentate ligands with the  $O=V^V-O-V^V=O$  unit. They present a *twist*-angular configuration and with both V atoms in the oxidation state V.

With tripodal tertiary amines the nitrogen tripod atom is *anti* with respect to the  $O_l$  and the configuration is *anti*-linear. With tetradentate Schiff-base ligands, the *anti* position is often occupied by the O-bridging atom in polymeric structures (group I in Table 2; see also Table S3). In compounds  $[\{V^VO[\text{sal}(\text{dpan})]\}_2(\mu_2\text{-O})]$  and  $[\{V^VO[t\text{-Busal}(\text{chan})]\}_2(\mu_2\text{-O})]$  [2], the *anti* position is occupied by a secondary amine group and the *t*-butyl groups of the bulky ligand do not allow the *anti*-linear configuration.

All structures of dinuclear V species with *twist*-angular configuration found in the literature present a short contact involving another donor atom coordinated to one of the V atoms, resulting in a shorter V–V distance in the dinuclear species. The ligands act as tridentate and the V atoms are both in oxidation state V, except RETZUL [16], which is a mixed-valence complex generated in solution by electroreduction of the corresponding  $[V^V_2O_3]^{4+}$  complex (see group II in Table 2; see also Table S4).

The mixed-valence dinuclear V compounds found in the literature are compounds with the following patterns (see group III in Tables 2 and S5): (i) most of them are complexes with tertiary amines acting as ligands [6,10,11a]; (ii) some contain tridentate ligands with sulfur atoms [11c,13,23]; (iii) only one example was found with a Schiff-base derivative acting as tridentate ligand (it was crystallized from a sodium acetate-containing solution) [24].

We can conclude that if the crystallization conditions are not the main driving force, the steric and electronic requirements of the ligands are significant factors influencing the conformation of the cores in dinuclear V complexes and predictions on possible configurations can be made.

## CONCLUSIONS

The dinuclear structures containing the tridentate ligands illustrate the high propensity of the V center to increase its coordination number via dimerization of two pentacoordinated monomers if the steric control exerted by the ligands allows it. In several cases the original tetradentate Schiff-base ligands present in the mother solution either hydrolyze or decompose, allowing the formation of dinuclear species with tridentate ligands, one terminal oxo group and two bridging  $\mu$ -oxo groups. In this work, we report two new dinuclear  $V^V$  complexes with structure determined by single-crystal X-ray diffraction:  $[\{V^VO[\text{sal}(R,R\text{-chen})]\}_2(\mu_2\text{-O})_2]$  **1** and  $[\{V^VO[\text{mvan}(S,S\text{-chen})]\}_2(\mu_2\text{-O})_2]$  **2**. The complexes contain tridentate ligands, formed upon partial hydrolysis of either  $\text{sal}_2(R,R\text{-chen})$  (in the case of **1**) or of  $\text{mvan}_2(S,S\text{-chen})$  (in the case of **2**), with O-phenolate, N-imine, and N-amine coordination to the  $V^V$  center.

We also present a review discussing general structural features of O-bridged dinuclear vanadium(IV and/or V) complexes covering those that have been characterized by single-crystal X-ray diffraction encompassing the structures of **1** and **2** within the general features found.

## SUPPLEMENTARY INFORMATION

Tables S1–S5 are available online (doi:10.1351/PAC-CON-08-09-16).

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