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Review

Coordination asymmetry in μ-oxido divanadium complexes: Development of synthetic protocols

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ABSTRACT

This brief review deals with the development of a general protocol for the synthesis of μ-oxido divanadium(V) compounds $[LOV^{V}\text{-}(\mu\text{-}O)\text{-}V^{V}O(Salen)]$ (L = L^{1}–L^{5}) (**1**–**5**) incorporating coordination asymmetry. One of the vanadium centers in these compounds has an octahedral environment, completed by tetradentate Salen ligand, while the other center has a square pyramidal geometry, made up of tridentate biprotic Schiff-base ligands ($H_{2}L^{1-5}$) with ONO (**1**–**3**) and ONS (**4**, **5**) type donor combinations. Single crystal X-ray diffraction, ESI-MS, and multi-nuclear NMR (^{1}H and ^{51}V) spectroscopy have been used extensively for the characterization of these compounds. The $V_{2}O_{3}$ core in these compounds, save **3**, has a rare type of twist-angular structure. The V(1)···V(2) separations (3.7921(7)–3.3084(6) Å) are by far the largest in these compounds compared to their peers containing a $V_{2}O_{3}$ core. The molecules retain their unsymmetrical binuclear structures also in solution as established by NMR spectroscopy. The mixed-oxidation

Abbreviations: ^{1}H NMR, proton nuclear magnetic resonance; ^{51}V NMR, vanadium nuclear magnetic resonance; EPR, electron paramagnetic resonance; ESI-MS, electrospray ionization mass spectrometry; CV, cyclic voltammetry; DPV, differential pulse voltammetry; NPV, normal pulse voltammetry; H_{2}Salen, *N*,*N*′-Bis(salicylidine)-1,2-diaminoethane; H_{2}bihyat, 2,6-bis[hydroxy(methyl)amino]-4-morpholino-1,3,5-triazine; Hhyta, 4-[hydroxy(methyl)amino]-N-methyl-6-morpholino-4-yl-1,3,5-triazin-2-amine; Hhyto, [4-hydroxy(methyl)amino]-6-morpholino-4-yl-triazin-2(1H)-one; Hacac, acetyl acetone; Im, imidazole; H_{3}nta, nitrilotriacetic acid; BzIm, benzimidazole; DMSO, dimethylsulfoxide; LMCT, ligand to metal charge transfer; HOMO, highest occupied molecular orbital; LUMO, lowest unoccupied molecular orbital.

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NMR
EPR
Electrochemistry

compound (ImH)[L^4OV^{IV}-(μ-O)-V^VOL^5] **7** containing two dissimilar ligands has a V_2O_3 core with a *syn*-angular structure and exhibits crystallographically imposed mirror symmetry due to static disorder. In solution of donor solvents, this angular core structure changes into a linear one (*anti*-linear) by accepting solvents in to the vacant coordination site of the metal centers. Finally, the protocol for the synthesis of heterobimetallic compounds with vanadium(V) and Re(VII) combination flanked by a single μ-oxido bridge has been developed in which the precursor complexes [$V^{IV}OL^{6,7}$] ($H_2L^{6,7}$ are Salen type of ligands) are allowed to oxidize aerially in the presence of added perrhenate anion. The oxidized [$V^VOL^{6,7}$]$^+$ species hold the ReO_4^- anion in the vacant coordination site of the metal ion, *trans* to the terminal oxido group, thus generating the V^V–O–Re^{VII} moiety in the heterobimetallic compounds (**9** and **10**). Both X-ray crystallography and ^{1}H NMR spectroscopy have been used to establish the identities of these compounds. In compound **9**, the Re(1)–O(11)–V(1) bridge angle is barely linear (170.2(3)°) with a Re···V separation of 3.9647(9) Å. The redox behavior of **9** and **10** are quite interesting, each undergoing two reductions both in the positive potential range at $E_{1/2}$ = 0.59 and 0.16 V vs. Ag/AgCl reference and have single-electron stoichiometry, confirmed by constant potential coulometry.

1. Introduction

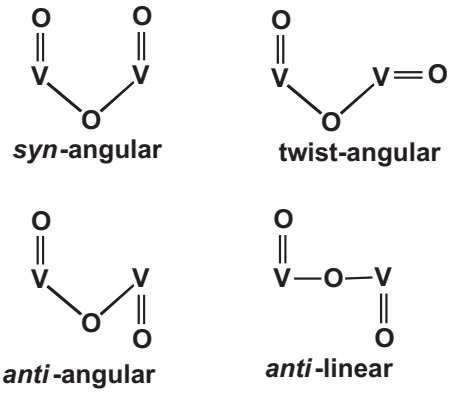
Binuclear metal complexes connected by a μ-oxido bridge are gaining increasing attention in contemporary coordination chemistry research. Such compounds with ancillary bridging ligand(s) (viz. carboxylates, etc.) play a crucial role in biological systems during dioxygen activation by a host of metalloenzymes, namely, methane monooxygenase, Δ^9-desaturase, ribonucleotide reductase and so forth [1–5]. These enzymes containing homo ($Fe^{II/IV}$, $Fe^{II/IV}$) and heterobinuclear (Fe^{II}/Cu^{II}) active sites are capable of activating dioxygen molecule by a variety of complex mechanisms involving a putative μ-hydroxo species as a key intermediate, responsible for the oxidation of organic substrates [6–12]. Such efficient use of μ-oxido species as catalyst by mother nature in biological system has made the chemists interested to use similar species as effective catalysts [13,14].

Interestingly, the lack of symmetry in the coordination environment of binuclear active sites of many metalloenzymes is an important structural feature that plays the crucial role in the mechanism of substrate activation [15–17]. Ligands providing donor atoms and coordination number asymmetry in tandem thus contribute effectively in the synthesis of biomimetic model compounds for replication of the structure and function of metallobiosites [18]. Moreover, such unsymmetrical bimetallic compounds have also attracted considerable attention, mainly because of their catalytic properties [19].

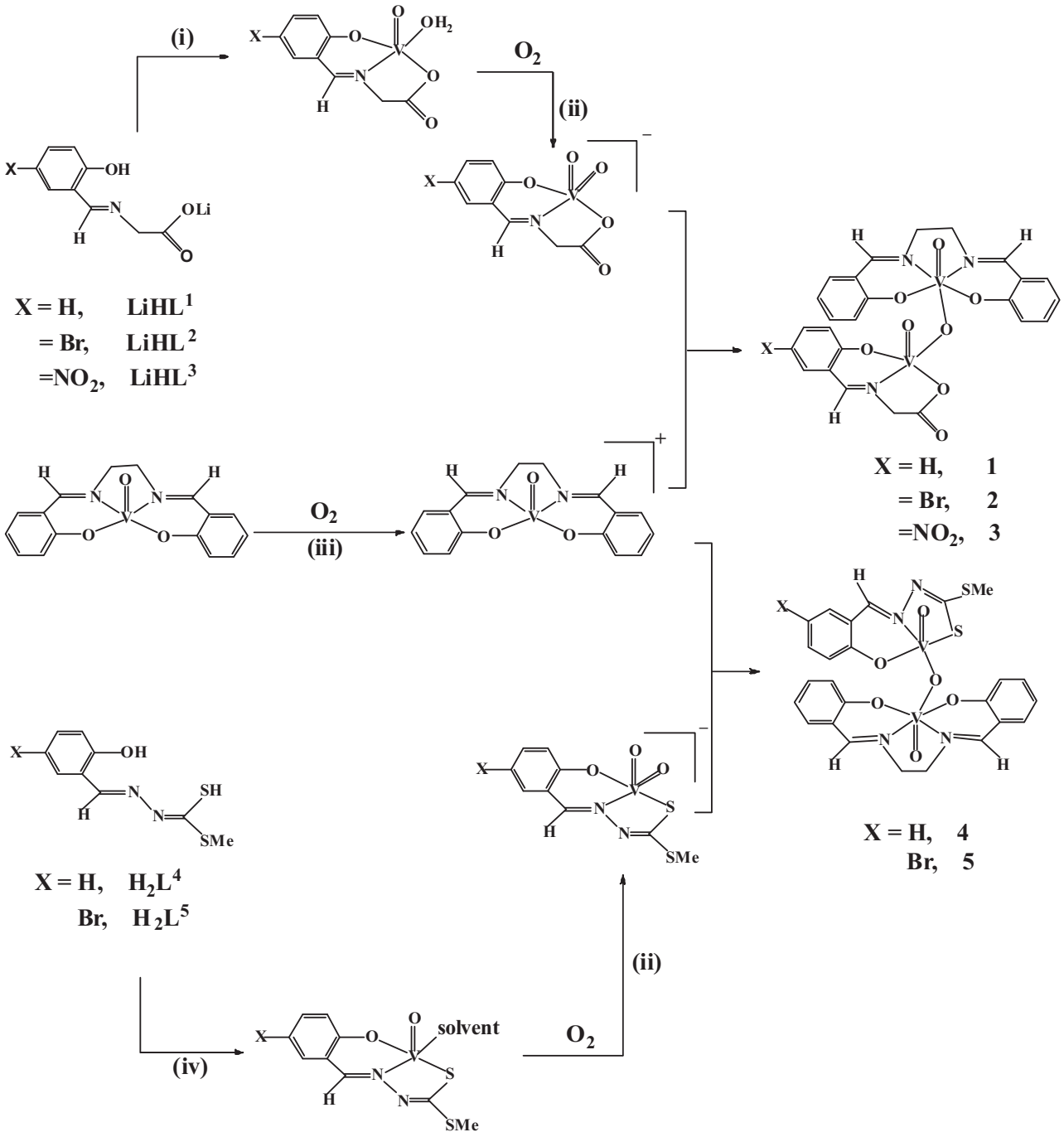
Vanadium is a versatile bio-essential element [20] capable of existing in a wide range of oxidation states spanning between 3− and 5+, that advances the usefulness of this element in the biological milieu. Current focus of considerable breadth and attention in the coordination chemistry of vanadium has been the subject of extensive research, stimulated by the potential pharmacological effects such as action against diabetes [20–27] and cancer [28–30], regulation of the proliferation and differentiation of osteoblast like cells in culture [31–33], the stimulation of phosphomutases and isomerases as well as the ability of vanadium in the inhibition of sodium potassium ATPase enzymes [34] provide great impetus in vanadate-phosphate analogy [27]. Moreover, the role of certain vanadium compounds as efficient catalysts attests the applicability of this metal ion in bulk industrial productions, viz., the use of oxovanadium compounds in asymmetric synthesis [35–40], in C–C bond formation as well as C–C, C–O and C–H bond cleavages [41–45], involvement as an intermediate in hydrosulfurization of crude oils [46], oxidative halogenation and selective epoxidation of unsaturated hydrocarbons and allyl alcohols [41,47]. Furthermore, the recent advancements in pyridine-2,6-dicarboxylate based vanadium compounds as potential material for bio-fuels have stimulated interest within scientific community to look more on to this metal ion [48,49]. Another important aspect of vanadium-based compounds that covers a vast domain is associated with the oxidation of hydrocarbon by vanadium oxides [50] and the significant development of a new class of multi-functional materials known as polyoxovanadates [51,52].

Several methodologies have been reported in the literature to synthesize unsymmetrical binuclear compounds. Few such approaches [13,53–56] involve targeted synthesis of unsupported oxido bridged (both homo and hetero nuclear) complexes. Unfortunately, none of these methods are useful for the synthesis of μ-oxido divanadium(V) compounds. Nevertheless, in the literature at least thirty structurally characterized μ-oxido divanadium compounds containing a $V_2O_3^{n+}$ (n = 4, 3 and 2) core have been reported [57,58]. All these compounds have symmetrical structures involving identical ligand molecule(s) attached to both the metal centers [46,59–83]. When these compounds have octahedral vanadium centers [59–70], the majority of these have a linear V–O–V bridge with the terminal oxido groups in mutually trans positions (*anti*-linear structure) [71]. On the other hand, when the vanadium centers have square pyramidal geometry [46,71–83], the terminal and bridging oxido atoms have diverse range of arrangements, from *anti*-linear [81,82] to *syn*-angular [46,71–73] through *anti*-angular [58,74–80] and twist angular [57,58,83] structures (see Scheme 1). Very recently Kabanos and co-workers [20b] have reported a divanadium(V) compound with ligand asymmetry following a protocol based on serendipity.

In this review we would like to summarize the work related to the synthesis and characterization of μ-oxido divanadium compounds containing $[V_2O_3]^{n+}$ (n = 4 and 3) cores where asymmetry plays an important role. Most of these works have been done in Authors' laboratory. Appropriate discussions have been also made to compare how asymmetry has influenced the steric configuration



Scheme 1. Possible configurations of the bridging and terminal oxygen atoms in $[V_2O_3]^{n+}$ (n = 4, 3, and 2) cores, present in the μ-oxido divanadium complexes. Reprinted with permission from [71], Copyright American Chemical Society.



Scheme 2. Conditions: (i) $VOSO_4 \cdot 3H_2O$, ethanol, stir; (ii) cation-assisted aerial oxidation; (iii) anion-assisted aerial oxidation in CH_3CN; (iv) $VO(acac)_2$, CH_3CN, reflux. Reprinted with permission from [58], Copyright American Chemical Society.

and electronic structure of the V_2O_3 core relative to their symmetric peers. Sincere attempts have been made to make the literature search as exhaustive as possible to include the work carried out during the last thirty years.

2. Introducing ligand asymmetry to the isovalent $[V^V_2O_3]^{4+}$ core: designing suitable strategy

A new protocol has been developed in recent years that led to the efficient synthesis of μ-oxido divanadium(V) compounds with a hitherto unknown unsymmetrical combination of ligands involving an octahedral and a square pyramidal vanadium(V) center tied together by a single μ-oxido bridge [57,58]. In order to achieve that, $[V^{IV}O(Salen)]$ (H_2Salen = *N*,*N*′-bis(salicylidene)-1,2-diaminoethane) has been used as a precursor to generate the octahedral vanadium(V) site because this compound in solution is aerially oxidized to $[V^VO(Salen)]^+$ in the occurrence of added anions, viz. ClO_4^-, BF_4^-, etc. [84,85]. To access the square pyramidal vanadium(V) centers, various tridentate biprotic Schiff base ligands based on amino acids or dithicarbazate have been employed. These ligands are capable of generating square pyramidal *cis*-dioxo anionic species $[LV^VO_2]^-$ in solution when the ligands are refluxed with $[VO(acac)_2]$ in acetonitrile in the presence of an added cation [86–88]. In the actual procedure as outlined in Scheme 2, stoichiometric amounts of $[V^{IV}O(Salen)]$,

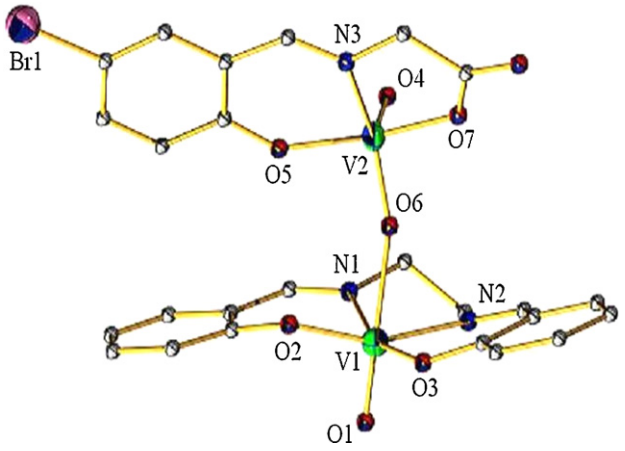


Fig. 1. Perspective view (ball and stick) and atom-numbering scheme for **2**. Hydrogen atoms have been omitted for clarity.
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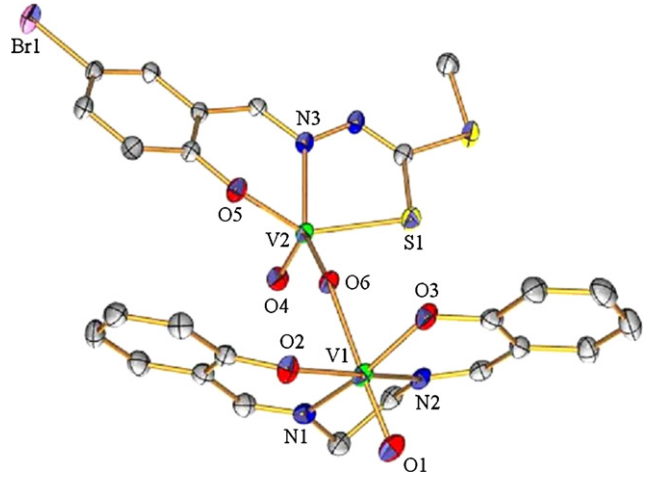

Fig. 2. Perspective view (ball and stick) and atom-numbering scheme for **5**. Hydrogen atoms have been omitted for clarity.
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H_2L [Lithium-*N*-(2-hydroxyphenyl)methyleneaminoacetate ($LiHL^1$), Lithium-*N*-(5-bromo-2-hydroxyphenyl) methyleneaminoacetate ($LiHL^2$) and Lithium-*N*-(2-hydroxy-5-nitrophenyl)methyleneaminoacetate ($LiHL^3$), *S*-methyl-3-(2-hydroxyphenyl)methylenedithiocarbazate (H_2L^4) and *S*-methyl-3-(5-bromo-2-hydroxyphenyl)methylenedithiocarbazate (H_2L^5)] and [$VO(acac)_2$] (1:1:1 mol ratio) were refluxed together in acetonitrile and subsequently exposed to atmospheric oxygen to get both $[V^VO(Salen)]^+$ and $[LVO_2]^-$ species together, thus allowing the anionic species to be accommodated in to the vacant coordination site of $[V^VO(Salen)]^+$ to generate the desired products as brown crystalline solids. The formation of $[V^VO(Salen)]^+$ is believed to be favored here by the anion $[LVO_2]^-$ assisted aerial oxidation of $[V^{IV}O(Salen)]$ [84,85], while that of $[LVO_2]^-$ is facilitated by the cation $[V^VO(Salen)]^+$ assisted aerial oxidation of the putative solvated species $[LV^{IV}O(solvent)]$ [86–88].

2.1. Probing the structures in the solid-state

2.1.1. X-ray crystallography

Molecular structures and atom labeling schemes for **2** and **5** are shown in Figs. 1 and 2 as representative classes of the unsymmetrical compounds. The two halves of these molecules, bridged by an oxygen atom O(6), have different coordination geometry for the vanadium centers. The coordination environment around V(1) in both the structures is distorted octahedral. Four donor atoms O(2), O(3), N(1) and N(2) from the Salen moiety occupy the basal plane while the apical positions are taken up by the terminal O(1) and the bridging O(6) oxygen atoms. The coordination geometry around V(2), on the other hand, is distorted square pyramidal. In compound **2**, the three donor atoms O(5), N(3), and O(7) from the tridentate amino acid-based ONO ligand along with the bridging oxido atom O(6) complete the equatorial plane around V(2) while the apical site is taken up by the terminal oxido atom O(4). In compound **5**, however, the basal positions around V(2) are taken up by S(1), N(3), and O(5) donors all coming from the tridentate dithiocarbazate-based ligand along with the bridging oxygen atom O(6).

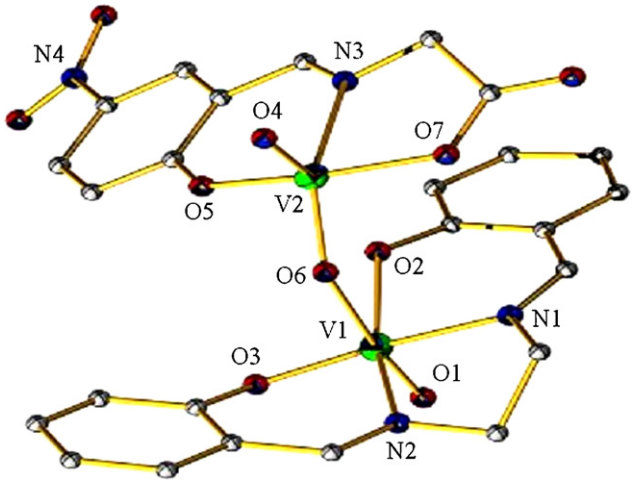

Fig. 3. Perspective view (ball and stick) and atom-numbering scheme for **3**. Hydrogen atoms have been omitted for clarity.
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Of particular interest in the structures of compounds **2**–**5** are the conformations of the V_2O_3 core, which are susceptible to the steric requirements of the attached ligands as well as to the coordination geometry of the participating vanadium centers [46,57–83]. In the present series of unsymmetrical compounds, the bridge angles V(1)–O(6)–V(2) for **2**, **4** and **5** have values in the range 166.20(9)°–157.79(16)°, in between those expected for symmetrical divanadium(V) compounds with octahedral (180°) [64–68] and square pyramidal (ca. 145°) vanadium centers [46,71–73]. The V_2O_3 core in these compounds has a rare *twist*-angular structure [57,58,83], a conformation intermediate between the regular *anti*-linear and *syn*-angular modes. An exception to this general trend in structure is, however, noticed in the structure of **3** (Fig. 3) where the V(1)–O(6)–V(2) bridge angle is 117.92(8)°, sufficiently lower than the values observed with rest of the compounds as described above. Also the basal planes around V(1) and V(2) in **3** are almost parallel as judged by the small dihedral angle (10.44°) between them while in the rest of the compounds, the concerned planes are nearly orthogonal with dihedral angels 75.63°, 80.81°, and 81.79° for **2**, **4**, and **5**, respectively. A clear manifestation of these differences in structural parameters is evident from the torsion angle O(1)–V(1)···V(2)–O(4) (Fig. 4), which is −178.35° for **3**, much larger than the values −38.87°, −50.59°, and 33.20° observed with the rest of the compounds. All these have led to the natural conclusion that the $V_2O_3^{4+}$ core in **3** is structurally different from the rest of the molecules in this series and has an *anti*-angular structure as displayed in Figs. 3 and 4.

Another important structural feature of these compounds that warrants mention is the trans location of the bridging oxygen atom O(6) relative to the terminal oxo-atom O(1) attached to the octa-

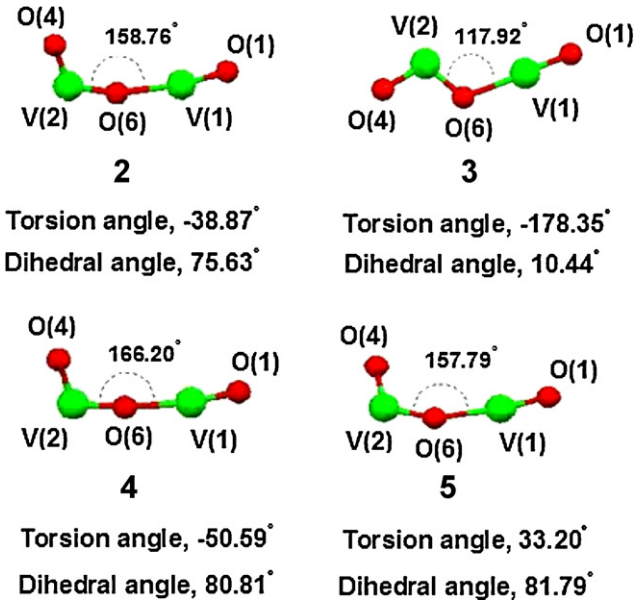

Fig. 4. Relative orientations of the bridging [O(6)] and the terminal oxygen atoms [O(1) and O(4)] of the $V_2O_3^{4+}$ cores, found in **2–5**. The torsion angles represent the angles included within O(1)–V(1)···V(2)–O(4), and the dihedral angles indicate the angles between the least-squares equatorial planes surrounding the vanadium centers V(1) and V(2).
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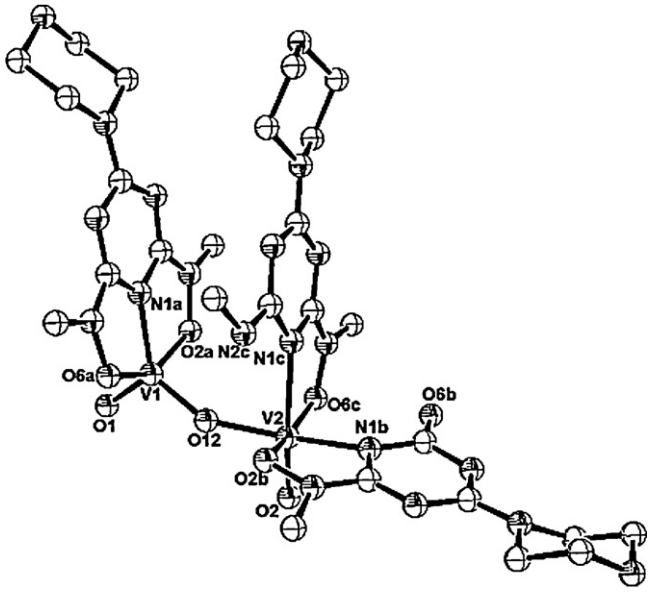

Fig. 5. Perspective view (ball and stick) and atom-numbering scheme for **6.** Hydrogen atoms have been omitted for clarity.
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hedral vanadium center V(1). Such a trans conformation is unique in vanadium compounds containing $V_2O_3^{n+}$ core. Technically, the V(1)–O(6) distances (2.140(3)–2.177(1) Å) in these compounds are significantly enlarged because of the trans labilizing influence of the terminal oxido atom O(1), compared to the other bridging distances V(2)–O(6) [1.6504–1.6548 Å]. In effect, the enlarged V(1)···V(2) separations in **2–5** [3.7921(7)–3.3084(6) Å] are by far the largest among their peers (divanadium compounds containing a V_2O_3 core) reported to date in the literature.

The only other unsymmetrical μ-oxido divanadium(V) compound [(bihyat)V^{V}O–(μ-O)–OV^{V}(hyta)(hyto)]·3H_2O **6** reported by Kabanos and co-workers [20b] has a *syn*-angular structure as displayed in Fig. 5. One of the vanadium centers V1 in this compound has a distorted square pyramidal geometry, completed by the tridentate bis (hydroxylamino) ligand H_2bihyat along with the oxido ligands O1 and O12, while the other metal center V2 has an octahedral geometry consisting of two bidentate ligands Hhyta and Hhito, both generated in solution due to vanadium-induced decomposition of the parent H_2bihyat ligand in water. The presence of two bidentate ligands instead of a tetradentate one as observed in compounds **1–5**, makes interesting difference in the structure of **6** [20b]. Thus the torsion angle between the two V=O_t bonds in **6** is significantly smaller (−1.6°), resulting in a *syn*-angular conformation of the V_2O_3 core. Also, the V–O_b distance in the octahedral core in **6** is much shorter (V2–O12, 1.927(3) Å) compared to the corresponding distances in **1–5**, due to the trans labilizing influence of the terminal oxido ligands in the later complexes. The remaining bridging distance V1–O12 (1.771(3) Å) on the other hand is elongated compared to the corresponding distances observed in **1–5**. All these modulate the V1–O12–V2 bridge angle (151.50(17)°) and V1···V2 separation (3.526 Å) in **6** to an intermediate level between those observed in compounds **2**, **4**, **5** (with twist-angular structure) and **3** (with trans-angular structure).

2.1.2. FT-IR spectroscopy

IR spectra of the binuclear complexes (**1–5**), taken as KBr pellets, contain all the important bands of the coordinated pair of ligands. These include a couple of strong bands at ca. 1620 and 1600 cm^{-1} region due to ν(C=N) stretching modes of the coordinated Schiff base moieties [46,71,86–89]. The carboxylate part of the complexes **1–3** also exhibits a pair of strong bands at ca. 1690–1660 and 1350–1330 cm^{-1} ranges, considered to be the signature for the ν_{asym}(COO) and ν_{sym}(COO) vibrations, respectively, as expected for an unidentate carboxylato group with normally large $\Delta\nu$ separation (ca. 350 cm^{-1}) [58]. In addition, a couple of strong bands appearing in the 948–964 and 903–916 cm^{-1} regions provide signature for the terminal V=O_t stretching, corresponding to the individual vanadium centers of the binuclear species (**1–5**). The μ-oxido bridge which connects the vanadium centers together offer a moderately strong antisymmetric bridge vibrations observed in the region 816–822 cm^{-1} [57,58,86].

2.2. Probing the structures in solution

2.2.1. Mass spectroscopy

ESI-MS spectroscopic data (in the positive ion mode) for the isovalent divanadium(V) compounds have been recorded in acetonitrile solution. The compounds display their respective molecular ion peak due to the [M + H^+] ionic species ([M–H_2O + H^+] for **3**). In Figs. 6a and 7a are displayed the isotope distribution patterns for the molecular ion peaks for two representative compounds **1** and **4,** respectively with two different types of tridentate ligands (ONO vs. ONS). Corresponding simulation patterns are displayed in the adjoining Figs. 6b and 7b, respectively. Similar results are also obtained with rest of the compounds, thus providing support in favor of the proposed compositions in solution involving coordination asymmetry.

2.2.2. ^{1}H NMR spectroscopy

^{1}H NMR spectra of the unsymmetrical compounds have been measured in DMSO-d_6, and the results are in conformity with their proposed compositions (see Tables 1 and 2). The spectroscopic profiles of **1** and **5** are displayed in Figs. 8 and 9, respectively, as representatives for each set of complexes along with their plausible interpretations. Spectrum of **1** contains two singlets at 9.37 and 8.68 ppm (in 2:1 intensity ratio), corresponding to the presence of two different types of azomethyne moieties in the molecule.

Table 1
^{1}H NMR spectroscopic data (δ, ppm)[a] for aminoacid-based isovalent μ-oxido divanadium(V) complexes (**1**–**3**) in DMSO-d_6 at 293 K.

1		**2**		**3**		Assignments
9.37 s	2H	9.39 s	2H	9.35 s	2H	H(7), H(7′)
8.68 s	1H	8.66 s	1H	8.88 s	1H	H(15)
7.99 (7.35) d	2H	8.11–7.70 m	4H	7.98 (7.56) d	2H	H(5), H(5′)
7.83 (7.39) t	2H			7.83 (7.57) t	2H	H(4), H(4′)
7.44 (7.65) d	1H	7.63 s	1H	8.51 (2.88) d	1H	H(13)
7.37 (7.62) t	1H	7.45(8.07) d	1H	8.18 (2.79) dd	1H	H(11)
7.26 (7.36) t	2H	7.16 brs	2H	7.27 (7.41) t	2H	H(3), H(3′)
7.14 (8.13) d	2H	6.98(7.99) d	2H	7.14 (8.22) d	2H	H(2), H(2′)
6.76–6.69 m	2H	6.68(8.31) d	1H	6.85 (9.30) d	1H	H(10), H(12)[b]
4.49 s	2H	4.50 s	2H	4.60 s	2H	H(16)
4.45, 4.22 (6.57) q	4H	4.20 brs	4H	4.44, 4.19 (6.42) q	4H	H(8), H(8′)

[a] Chemical shifts (δ) relative to internal TMS. Protons labels are as in the insets in Fig. 8. s, singlet; d, doublet; t, triplet; dd, double-doublet; q, AB quartet. Values in the parentheses represent coupling constants (J in Hz).
[b] H(12) proton is absent in cases of **2** and **3**.

Table 2
^{1}H NMR spectroscopic data (δ, ppm)[a] for dithicarbazate-based isovalent μ-oxido divanadium(V) complexes (**4**, **5**) in DMSO-d_6 at 293 K.

4		**5**		Assignments
9.35 s	2H	9.36 s	2H	H(7), H(7′)
8.98 s	1H	9.00 s	1H	H(15)
7.97 (6.82) d	2H	7.98 (7.31) d	2H	H(5), H(5′)
7.81 (6.94) t	2H	7.84 (7.54) t	2H	H(4), H(4′)
7.61 (7.58) d	1H	7.85 s	1H	H(13)
7.38 (7.59) t	1H	7.48 (2.55) dd	1H	H(11)
7.25 (6.91) t	2H	7.28 (7.18) t	2H	H(3), H(3′)
7.13 (7.81) d	2H	7.16 (8.10) d	2H	H(2), H(2′)
6.86–6.77 m	2H	6.76 (8.86) d	1H	H(12)[b], H(10)
4.42, 4.21 (5.63) q	4H	4.43, 4.20 (5.89) q	4H	H(8), H(8′)
2.49 s	3H	2.52 s	3H	H(17)

[a] Chemical shifts (δ) relative to internal TMS. Protons labels are as in insets in Fig. 9. s, singlet; d, doublet; t, triplet; dd, double doublet; q, AB quartet. Values in the parentheses represent coupling constants (J in Hz).
[b] H(12) proton is absent in case of **5**.

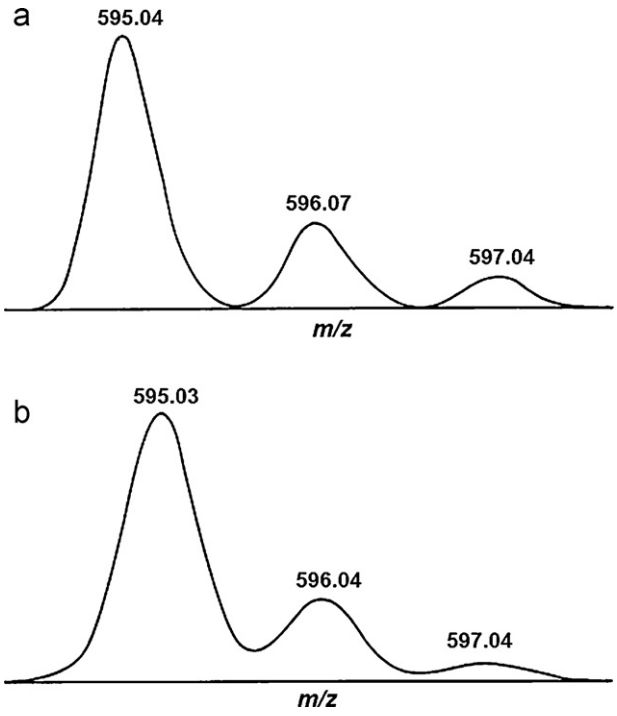

Fig. 6. Molecular ion peak in the ESI mass spectrum (positive) for complex **1** in acetonitrile with (a) observed and (b) simulated isotopic distributions.
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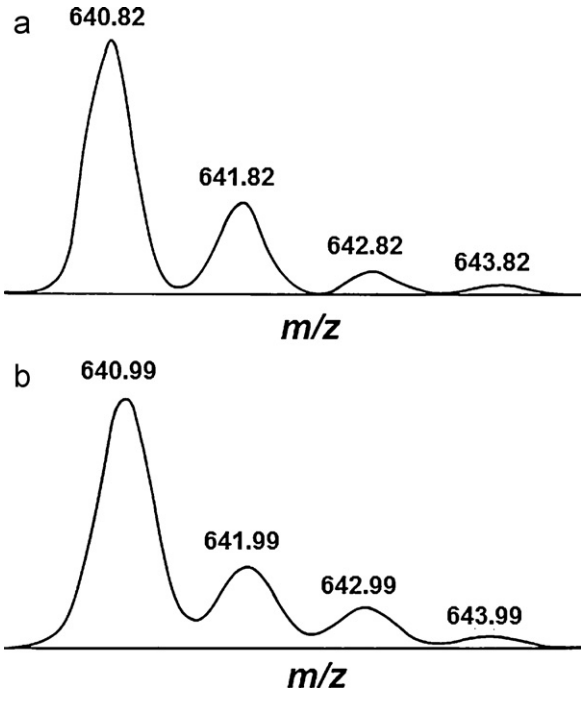

Fig. 7. Molecular ion peak in the ESI mass spectrum (positive) for complex **4** in acetonitrile with (a) observed and (b) simulated isotopic distributions.
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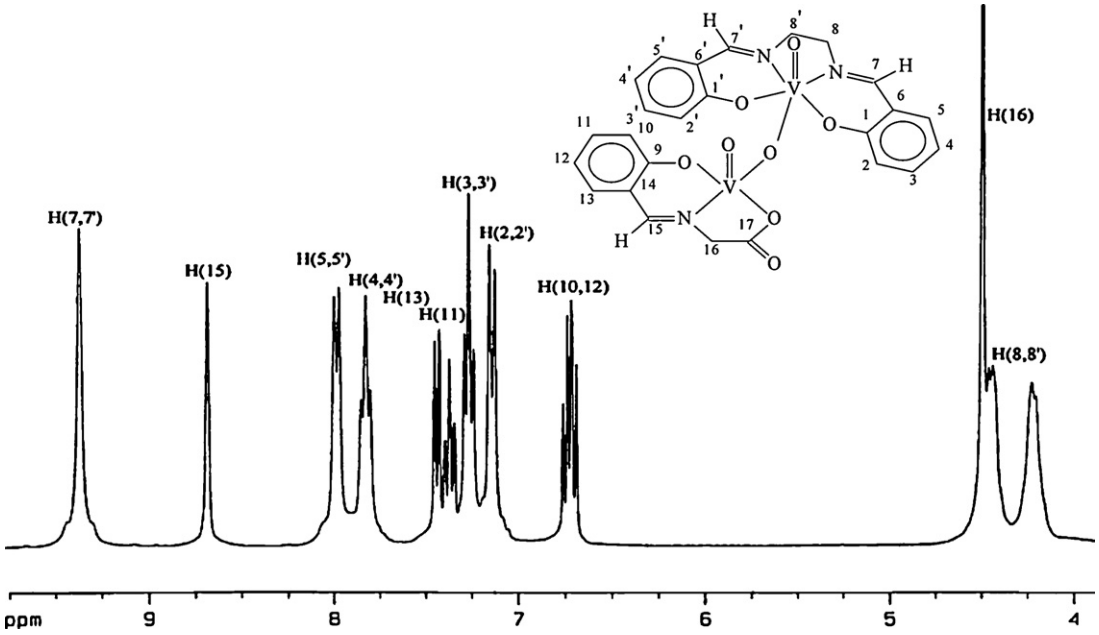

Fig. 8. ^{1}H NMR spectrum of compound **1** in DMSO-d_6 at 293 K.
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Similar signals in **5** appear at 9.36 and 9.00 ppm, respectively. All the aromatic protons in **1** show up in the 8.0–6.5 ppm region (8.0–6.75 ppm range in **5**) with expected splitting patterns. Of particular interest here is the appearance of a triplet pattern at 7.37 ppm (J = 7.62 Hz) due to the H(11) proton in the spectrum of **1**. Substitution of nitro- and bromo- at C(12) in **3** and **5**, respectively, make the same H(11) proton to appear (Fig. 9) as a pair of doublets at 7.50 and 7.47 ppm (8.20 and 8.17 ppm for **3**) due to *ortho-meta* coupling. Observance of small J values of 2.79 and 2.55 Hz for **3** and in **5**, respectively, provides an indication in favor of such weak coupling. The ethylenic protons H(8) and H(8′) are diastereotopic in these complexes due to the rigidity of the metal-bound bridge-head moiety in the coordinated Salen part and appear as an AB spin system with δ_A = 4.45 and δ_B = 4.22 ppm (J_{AB} = 6.57 Hz) in **1**. A sharp singlet at 4.49 ppm is characteristic of the H(16) protons of the amino acid part in **1**. All these and the remaining signals along with their observed splitting patterns are in conformity with the presence of asymmetric ligand environments around the vanadium(V) centers in **1**–**5**, as exist in solution.

2.2.3. ^{51}V NMR spectroscopy

^{51}V NMR spectroscopy is a useful analytical technique to clarify structural information in diamagnetic vanadium compounds [90–95]. ^{51}V NMR has the potential to sense the change that occurs at the vanadium nucleus due to coordination of the ligand(s) [90,96]. Literature has noticed significant upfield shifts in signal positions which are normal for ^{51}V NMR [57,58,71,89,90,94,97–100]. However, unusual downfield chemical shifts in ^{51}V NMR spectroscopy are also observed [101–103]. Thus chemical shifts in ^{51}V NMR nicely demonstrate the molecular orbital pictures and electronic distributions surrounding the vanadium centers. In other words, it gives us an idea about the HOMO–LUMO energy gap in a diamagnetic vanadium complex.

To understand more about their solution structures, ^{51}V NMR spectra of **1–5** have been measured in DMSO-d_6 solution at room temperature. Almost identical features are obtained in all the cases. Spectra of **1** and **5** are displayed in Fig. 10 as representatives for each type of complexes. Two sharp signals are obtained in each spectrum, both in the negative region of the chemical shift. In the case of **1**, a very sharp peak (peak I), appears at −533 ppm which is more likely due to [$V^{V}OL^{1}$] moiety [71] while the other peak, moderately sharp in appearance (peak II), shows up at −574 ppm arising from the [$V^{V}O$(Salen)] part of the compound [89,100]. Corresponding signals in the spectrum of **5** appear at −466 and −574 ppm, respectively.

Thus, a change in the donor atoms set from ONO to ONS set in the tridentate ligand system around the square pyramidal vanadium(V) center (V2) generates a remarkable downfield shift (by ca. 70 ppm) of the corresponding ^{51}V NMR signal. Changing the donor site from a hard oxygen atom to a soft sulfur donor, the HOMO–LUMO energy separations in the complexes **4** and **5** decreases resulting in lower excitation energy for the LMCT transition that influences the shielding parameter, σ, at the vanadium nucleus [90,102,104] and hence the corresponding ^{51}V NMR signal. However, as expected, the signal due to the [$V^{V}O$(Salen)] moiety remains unchanged at −574 ppm in both compounds. The results from ^{51}V NMR spectroscopic study again are in compliance with the asymmetric ligand environments around the vanadium centers in **1**–**5** when present in solution.

2.3. Electrochemical and EPR spectroscopic studies

Voltammetric features of **1** and **4**, each representing a typical group of compounds are displayed in Figs. 11 and 12, respectively. The data obtained are summarized in Table 3. The voltammogram of **1** includes a couple of reduction processes involving a reversible process at $(E_{1/2})_I$ = 0.45 V (process A) and an irreversible process at E_{pc} = −1.48 V (process B), all potentials are vs. Ag/AgCl reference. In addition to the processes A and B, the voltammogram of **4** also includes a third redox process (process C) at $(E_{1/2})_{II}$ = −1.74 V. All these are reduction processes as indicated by steady-state voltammetry (using an ultramicro electrode, 10 μM in diameter) and involve an identical number of electron(s), established by normal pulse voltammetry (NPV), also shown in Figs. 11 and 12.

Electrochemical behavior of [VO(Salen)] is well documented [105–107]. Taking hints from those studies, one can consider processes A and B in **1** to be restricted to the [VO(Salen)] part of the compound. Process A is believed to be originating from

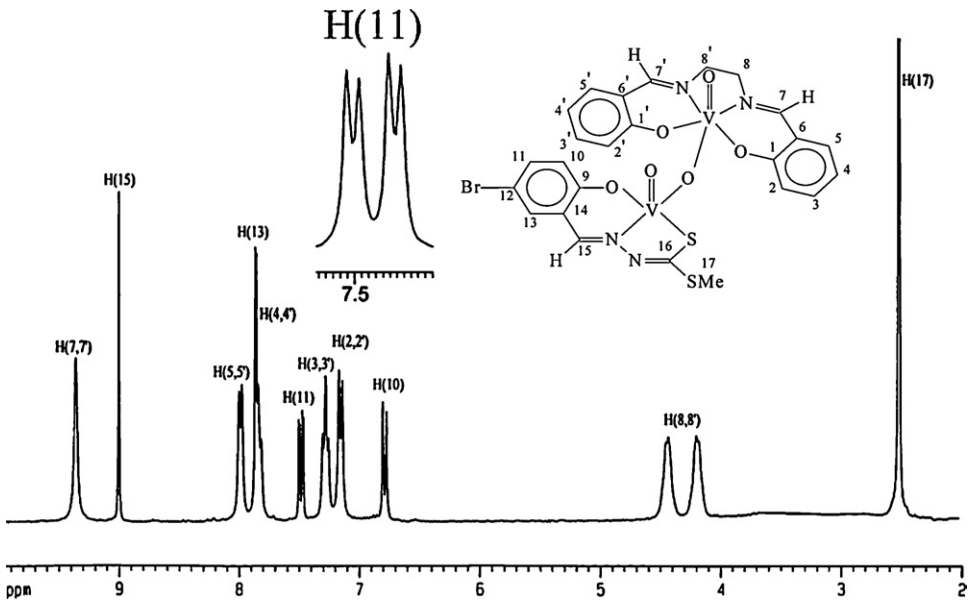


Fig. 9. ^{1}H NMR spectrum of compound **5** in DMSO-d_6 at 293 K. The inset shows the appearance of the H(11) proton as a pair of doublets due to *ortho-meta* coupling. Reprinted with permission from [58], Copyright American Chemical Society.

Table 3
Electrochemical data of **1–5** from the cyclic voltammetry experiments[a].

Compound	Process A				Process B	Process C	
	$(E^b_{1/2})_I$ (V)	ΔE^c_p (mV)	i_{pc}/i_{pa}	n	E_{pc} (V)	$(E_{1/2}{}^b)_{II}$ (V)	$\Delta E_p{}^c$ (mV)
1	0.45	73	1.00	0.98 ± 0.05	−1.48		
2	0.44	62	0.90		−1.49		
3	0.42	66	0.99		−1.52		
4	0.42	69	0.99	1 ± 0.1	−1.5	−1.74	110
5	0.43	71	0.99		−1.55	−1.83	125

[a] All potentials vs. Ag/AgCl reference.
[b] $E_{1/2}$ values calculated using the formula 0.5 ($E_{pc} + E_{pa}$) with data obtained from cyclic voltammetry.
[c] $\Delta E_p = E_{pa} - E_{pc}$ at a scan rate of 100 mV s^{-1}.

$[VO(Salen)]^{1+/0}$ couple, process B on the other hand is due to a $[V(Salen)]^{2+/1+}$ electron-transfer, presumably involving a putative nonoxido vanadium species. The quasi-reversible process observed at −1.74 V (process C) for **4** appears to involve the reduction of $[L^4V^VO]$ part of $[\mathbf{4}]^-$ as confirmed by control experiment [58]. Electron-stoichiometry for process A of both **1** and **4** has been confirmed by constant potential coulometric experiments with platinum-gauze working electrode. Results are in conformity with a single-electron stoichiometry for this process as shown by Eq. (1).

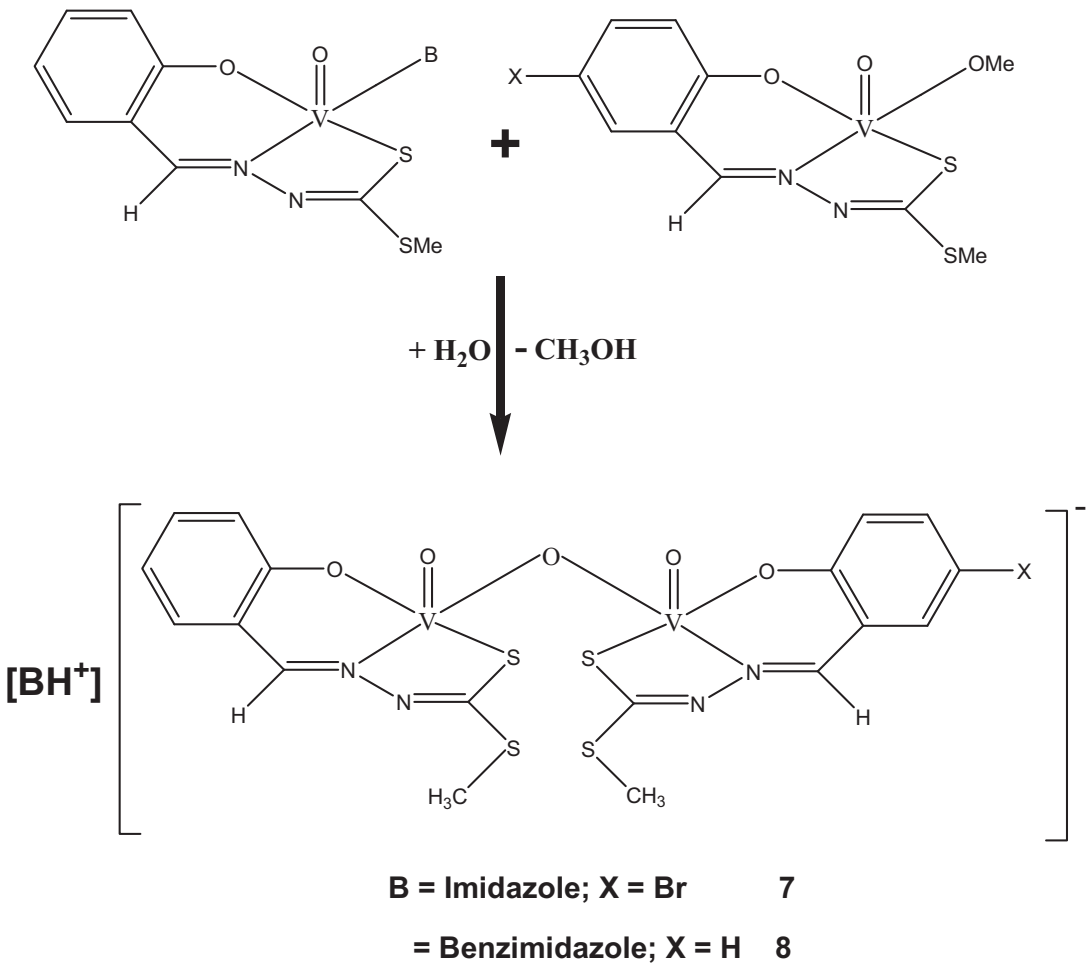
$$[L^{1-5}OV^V\text{–}(\mu\text{-}O)\text{–}V^VO(Salen)]^0 \underset{(E_{1/2})_I}{\overset{+e}{\rightleftharpoons}} [L^{1-5}OV^V\text{–}(\mu\text{-}O)\text{–}V^{IV}O(Salen)]^{1-} \quad (1)$$

EPR spectra of the catholyte solutions obtained after coulometric reduction of **1** and **5** have been recorded at room temperature and are displayed in Fig. 13. The spectra in both the cases feature an 8-line profile (^{51}V, $I = 7/2$) with $\langle g \rangle = 1.991$ and $\langle A \rangle = 89 \times 10^{-4}$ cm^{-1} for **1**. Corresponding values are 1.990 and 88×10^{-4} cm^{-1} for **5**. In the absence of any mononuclear vanadium(IV) species in solution, the observed $\langle A \rangle$ values for the catholyte solutions of **1** and **5** provide clear indication of the trapped-valence nature of the reduced mixed-valence μ-oxido divanadium(IV/V) species $[\mathbf{1–5}]^{1-}$ in the time-scale of EPR spectroscopy [66]. The unpaired electron is therefore localized on one of the vanadium centers, preferably on the [VO(Salen)] part, indicating class A character, according to the Robin–Day classification of mixed-valence compounds [108].

3. Introducing ligand asymmetry in to the mixed-oxidation $[V^{IV/V}_2O_3]^{3+}$ core: looking for a strategy

3.1. Synthetic protocol

Among the various types of mixed-oxidation vanadium compounds reported thus far, binuclear oxovanadium(IV/V) species containing a $[V_2O_3]^{3+}$ core represent the largest class because of their favorable thermodynamic stability and ease of formation from the constituent $[V^{IV}O]^{2+}$ and $[V^VO_2]^+$ ions [109]. Nishizawa et al. was the first to report the crystal structure of a (μ-oxido)divanadium(IV/V) compound $(NH_4)_3[V_2O_3(nta)_2]\cdot 3H_2O$, prepared by the metathesis of the constituent $[V^VO_2(nta)]^{2-}$ and $[V^{IV}O(nta)]^{1-}$ anions [59]. The molecule has a linear V–O–V bridge with terminal oxido-groups in mutually trans positions. Since then, many other dioxidovanadium(IV/V) compounds have been reported, showing diversity in their electronic and molecular structures [46,60,64,65,67,71,72,83]. One thing is, however, common to all these structures. They all have identical ligand molecules attached to the individual vanadium centers. In an earlier communication [46], it was reported that a homoleptic anionic mixed-oxidation compound $(BzImH)[L^4OV^{IV}\text{–}(\mu\text{-}O)\text{–}V^VOL^4]$ can be prepared following the Nishizawa's methodology by allowing the constituent precursor compounds $[L^4OV^V(OCH_3)]$ and $[L^4OV^{IV}(BzIm)]$ to react in acetonitrile in 1:1 molar ratio. This



Scheme 3. Synthetic protocol for the preparation of mixed-oxidation divanadium(IV/V) compound containing $[V_2O_3]^{3+}$ core with ligand asymmetry. Reprinted with permission from [71], Copyright American Chemical Society.

synthesis protocol has been successfully modified and applied to introduce ligand asymmetry for the first time in to a mixed-oxidation divanadium(IV/V) compound containing $[V_2O_3]^{3+}$ core when precursor compounds $[L^4OV^{IV}(Im)]$ and $[L^5OV^{V}(OCH_3)]$ with two dissimilar ligands are allowed to react to get the compound $(ImH)[L^4OV^{IV}–(\mu\text{-}O)–V^{V}OL^5]$ **7** as shown in Scheme 3.

3.1.1. Crystal structure

Molecular structure and the atom numbering scheme for the mixed-oxidation compound **7** is displayed in Fig. 14. Interestingly, the anion in **7** possesses crystallographic mirror symmetry with the bridging oxygen atom O(1) residing on the mirror plane. This indicates an apparent equivalence of the two LOV halves in the unsymmetrical anion due to statistical distribution of the molecular forms $[L^4OV–(\mu\text{-}O)–VOL^5]^{1-}$ and $[L^5OV^{IV}–(\mu\text{-}O)–V^{V}OL^4]^{1-}$ appearing in pairs in the crystal lattice (Fig. 15). Individual molecules in this pair are connected by intermolecular hydrogen bonds [71]. The molecule has a bent V–O–V (149.7(4)°) bridge with a *syn*-angular $[V_2O_3]^{3+}$ core structure (Scheme 1) [71]. In a similar albeit homoleptic anion $[L^4OV–(\mu\text{-}O)–VOL^4]^{1-}$ in **8** (Scheme 3) reported earlier [46], the two vanadium atoms are crystallographically nonequivalent, while in the heteroleptic anion $[L^4OV–(\mu\text{-}O)–VOL^5]^{1-}$ of **7** due to the dimerization process as discussed above, the positions of the two vanadium centers are averaged. The bridging V–O_b distance 1.801(2) Å observed in each half of **7** is actually the arithmetic mean of two unequal V-O_b distances observed in **8**. Similar averaging also holds true for the V–O(3) distances in **7**.

3.1.2. EPR spectroscopy

For mixed-oxidation divanadium(IV/V) compounds, EPR spectroscopy provides an useful diagnostic tool to understand the state of delocalization of the unpaired electron. Observation of a 15-line profile (^{51}V, $I = 7/2$) (Fig. 16) gives a clear indication of the odd electron being interacted with both the participating vanadium centers [46,59,64,65,83], while an 8-line pattern, also observed in some cases [67], indicates a valence-trapped situation for the odd electron on the time-scale of EPR spectroscopy. Spectra of **7** in acetonitrile/toluene (1:2, v/v) solution at variable temperature are shown in Fig. 16. The asymmetric distortion observed in the 15-line spectrum at room temperature (Fig. 16a, $\langle g \rangle = 1.987$ and $\langle A \rangle_{15} = 44.8 \times 10^{-4}\ cm^{-1}$) has been explained as due to a solvent dependent equilibrium process shown by Eq. (2). Compound **7** with square pyramidal vanadium centers when dissolved in a coordinating solvent like acetonitrile, may add up two molecules of solvent (S) to generate a species having octahedral vanadium centers with a concomitant change in the $[V_2O_3]^{3+}$ core structure from a *syn*-angular to an *anti*-linear mode (Scheme 1). The linear V–O–V bridge allows effective interactions between the d_{xy} metal orbitals via the $p\pi$ orbital of the bridging oxido atom [110]. On the other hand, a valence-trapped situation is normally encountered in molecules with a *syn*-angular core due to poor overlap of the symmetry-constrained d_{xy} metal orbitals [46]. Both these species in equilibrium are EPR active but magnetically inequivalent due to the differences in their $[V_2O_3]$ core structures. The spectroscopic features observed at room temperature appear to arise from the superposition of the EPR spectra of two closely related species present

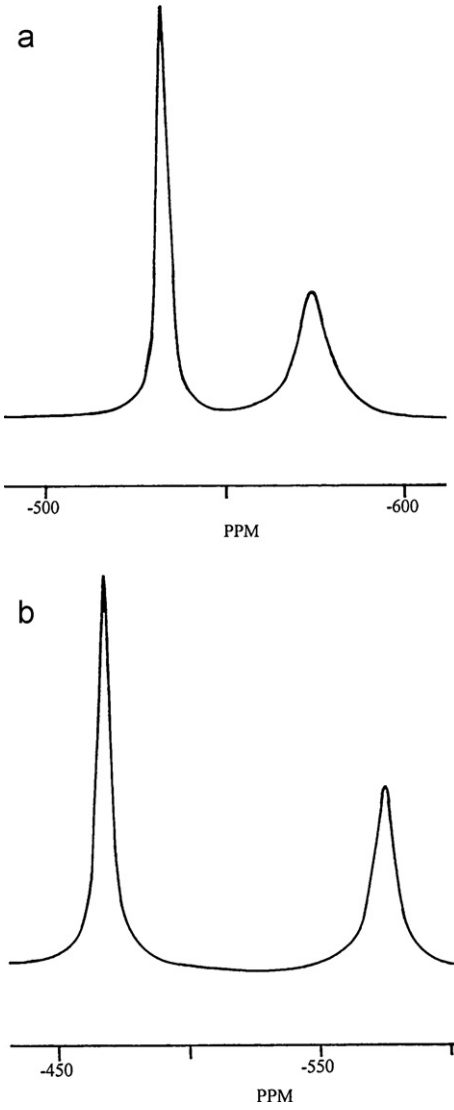


Fig. 10. ^{51}V NMR spectra of the complexes (a) **1** and (b) **5** in DMSO-d_6 solution at room temperature showing retention of binuclear structures in solution.
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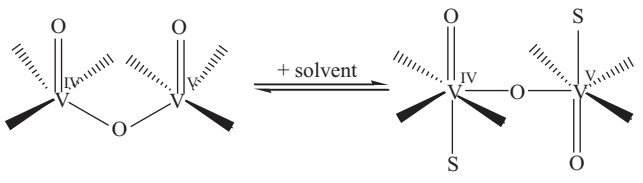
in equilibrium. As the temperature is lowered, the equilibrium is likely to be shifted more to the right-hand side. The spectrum at 240 K (Fig. 16b) appears to have a more clear 15-line feature with some degree of broadening still there due to slower tumbling of the molecules at the prevailing lower temperature. On further lowering of the temperature, the intramolecular thermal electron-transfer rate (k_{th}) decreases, resulting in a spectroscopic coalescence from a 15-line to an 8-line feature at 220 K (Fig. 16c) due to thermal trapping of the odd electron at one of the vanadium centers.



(2)

To test the validity of the proposed solvation hypothesis, the EPR spectrum of **7** was further examined in neat toluene and propylene carbonate as non-coordinating solvents. In each case a clear 8-line pattern at $\langle g \rangle = 1.97$ with $\langle A \rangle_8 = 89 \times 10^{-4}\,cm^{-1}$ is obtained at room temperature.

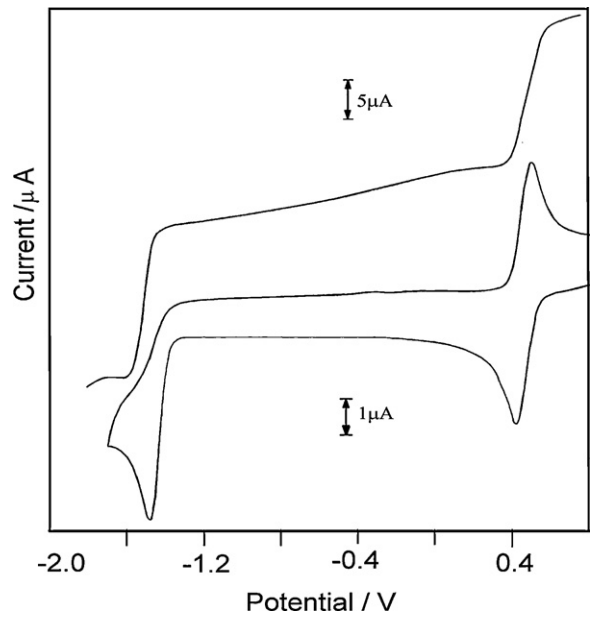


Fig. 11. Cyclic and normal pulse voltammograms of **1** in DMSO (0.1 M TBAP) at room temperature using a platinum-disk working electrode; scan rate 100 mV s^{-1} and potentials vs. Ag/AgCl.
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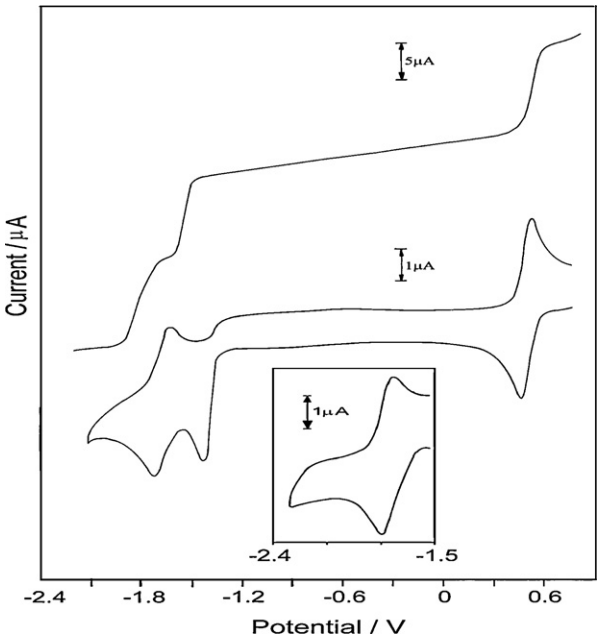

Fig. 12. Cyclic and normal pulse voltammograms of **4** in DMSO; potentials vs. Ag/AgCl, 0.1 M TBAP at a platinum working electrode, scan rate 100 mV s^{-1}. The inset shows a lone quasi-reversible process for the mononuclear vanadium(V) compound [$L^4VO(OCH_3)$] at an identical experimental condition.
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4. Introducing metal asymmetry in to the V–O–V core: making V–O–M scaffold

4.1. Synthetic protocol

The chemistry of hetrobimetallic systems involving M–O–M′ framework has received increasing importance in recent years because of their interesting properties arising out of the cooperative influence of two dissimilar metal ions held together in a close prox-

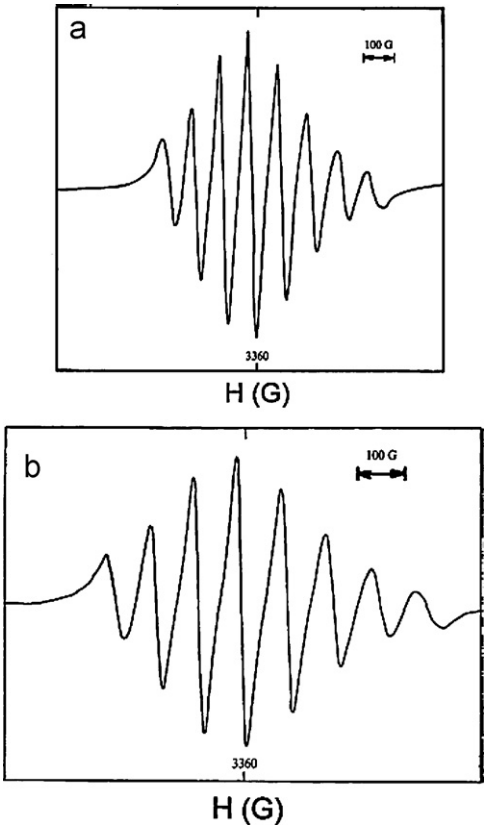

Fig. 13. The X-band EPR spectra at room temperature of the catholyte solutions (in DMSO), generated electrochemically by coulometric reduction of compounds (a) **1** and (b) **5** (E_w set at 0.2 V vs. Ag/AgCl).
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imity [5,13,14,19,56,111–131]. Such asymmetry is often prevalent in many metalloenzymes that catalyze some of the fundamental reactions in Biology [16,18,53,132,133]. These serve as an impetus for chemists to synthesize prototypes of catalysts involving two

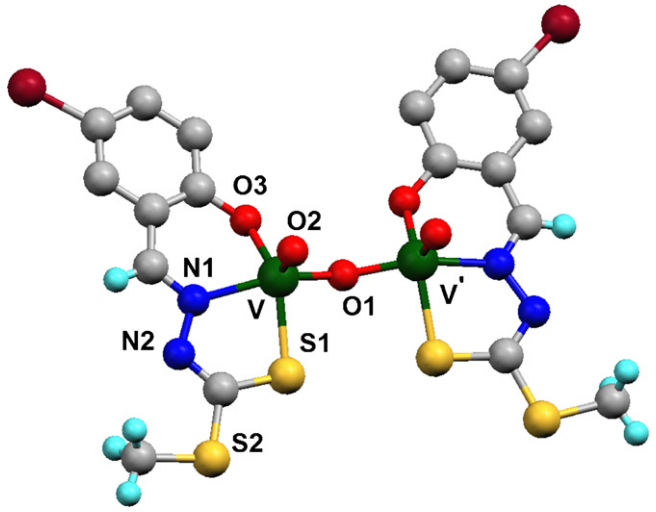

Fig. 14. Molecular structure of **7** showing the atom-labeling scheme. The atom with a prime symbol is symmetry related. Imidazolium cation and hydrogen atoms attached to the aromatic rings are omitted for clarity.
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different metal centers, the idea being that such a system will be more efficient than the one involving the individual metal centers. To our knowledge, only one such compound with vanadium (containing V(V)–O–Cr(III) bridge) has been reported [124] with no crystallographic confirmation of the proposed structure.

In a bid to introduce asymmetry for getting molecule with V–O–M core, the methodology developed to introduce ligand asymmetry (Scheme 2) has been suitably modified as depicted in Scheme 4 [88a]. Thus [V^{IV}O(Salen)] and its analogs when oxidized aerially in a THF/acetonitrile solvent combination in the presence of added ReO_4^- anion, yield the products (**9** and **10**) obtained in the form of brownish-green crystalline solid with the perrhenate anion accommodated in the coordination sphere of vanadium(V), trans to the terminal oxido group as confirmed by X-ray crystallography.

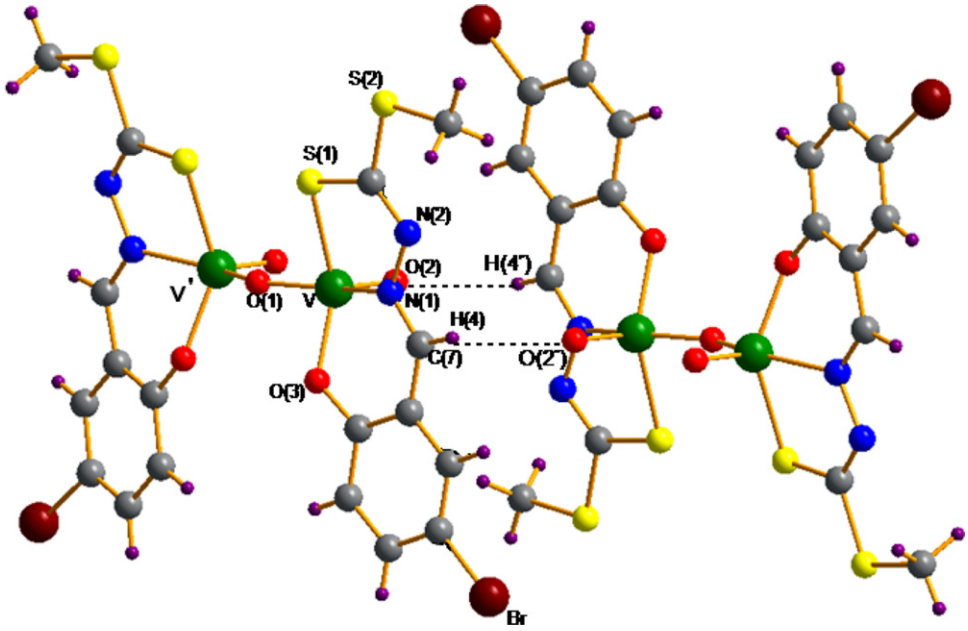

Fig. 15. Perspective view of structure of the dimeric form of the anion of **7** showing hydrogen bonds between O(2) and H(4)′: C(7)′–H(4)′···O(2); 2.503(4) Å, 145.2(4)°. Counterion and solvent molecules are omitted for clarity.
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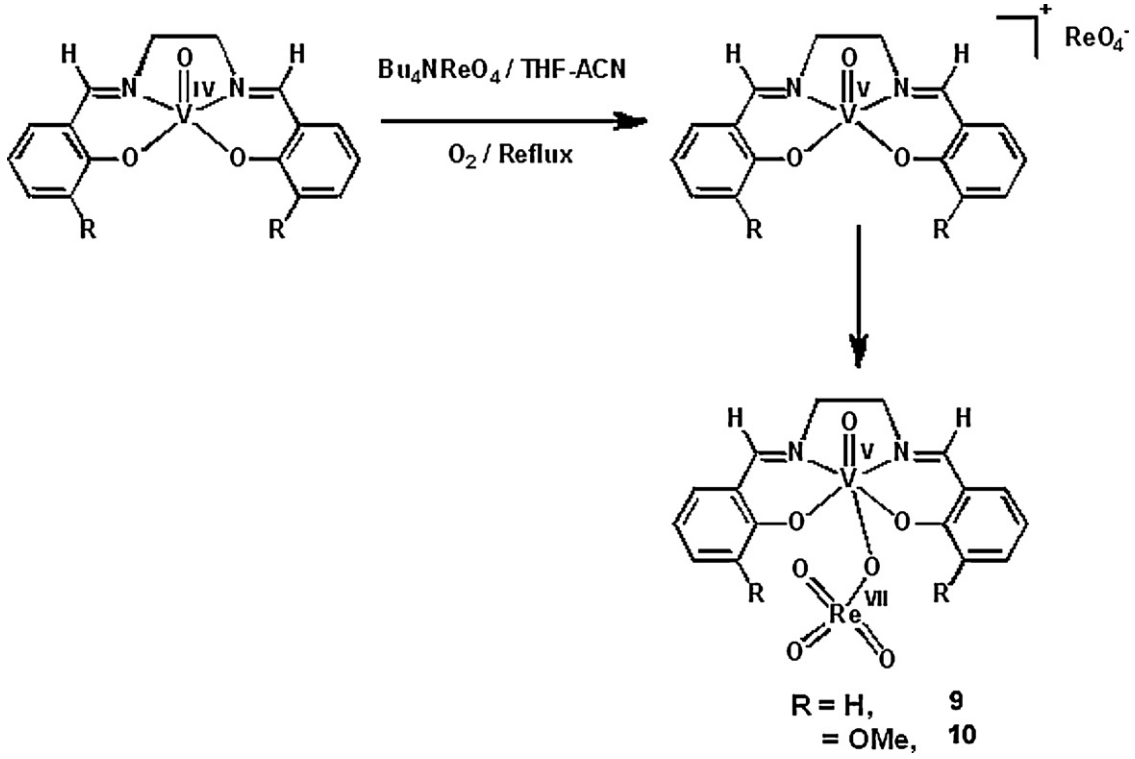

Scheme 4. Synthetic strategy for the preparation of unsupported μ-oxido asymmetric vanadium(V)-rhenium(VII) complexes.
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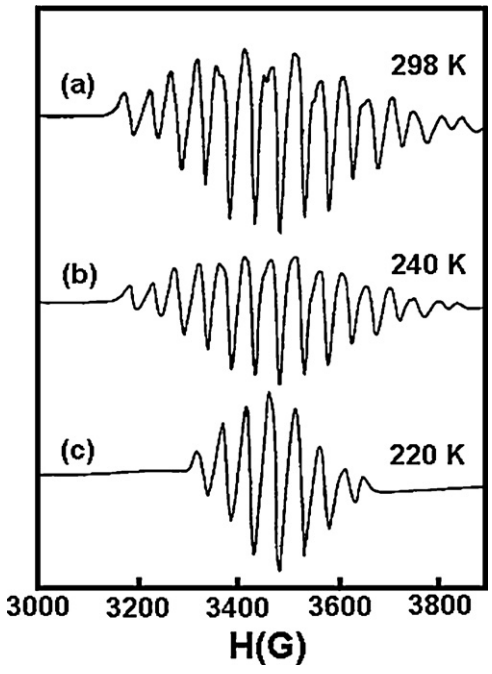

Fig. 16. X-band EPR spectra of **7** in CH_3CN/toluene (1:2, v/v) solution at variable temperatures.
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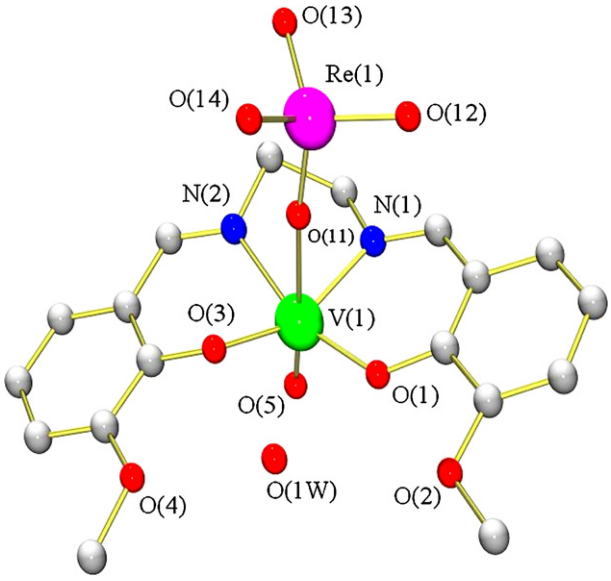

Fig. 17. Ball-and-stick diagram and atom-numbering scheme of the asymmetric binuclear complex $[L^7OV(\mu\text{-}O)ReO_3]$ **10**. The hydrogen atoms have been omitted for clarity.
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4.1.1. X-ray crystallography

The perspective view of the heterobinuclear compound **10** is displayed in Fig. 17. The molecule contains a bridging oxygen atom O(11) that links the vanadium(V) and rhenium(VII) centers and provides a heretofore unknown example of a single μ-oxido bridged vanadium(V)–rhenium(VII) compound. The Re–O distances (1.703(5)–1.736(4) Å) and the O–Re–O bond angles (108.5(2)–110.1(2)°) indicate an almost ideal tetrahedral geometry around the rhenium center. The V···Re separation is 3.9647(9) Å. The V(1)–O(11)–Re angle is 170.2(3)° and the V(1)–O(11) bond length (2.243(4) Å) shows distinct elongation compared to the relevant distances in the basal plane owing to the trans labilizing influence of the terminal oxido group.

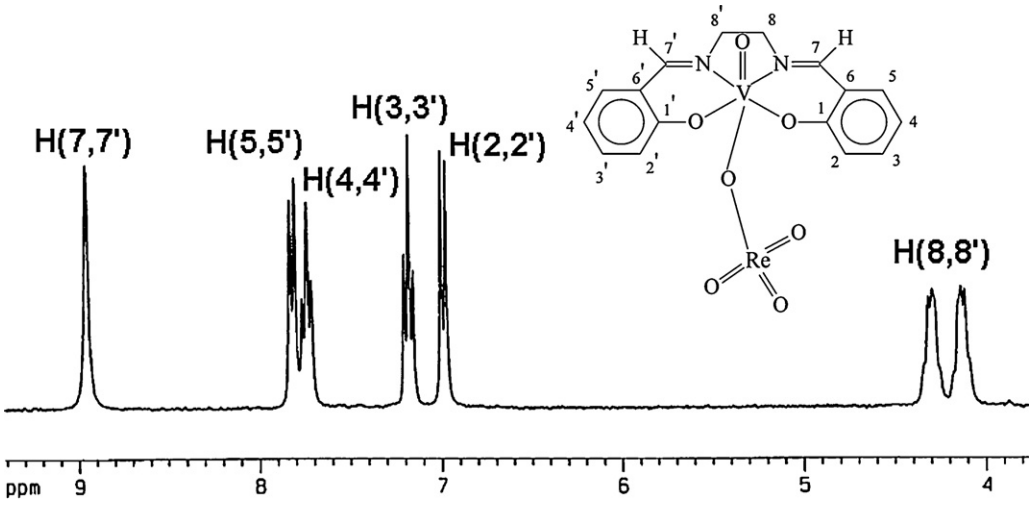

Fig. 18. ^{1}H NMR spectrum of compound **9** in acetonitrile-d_3 at room temperature showing the retention of the binuclear structure in solution.
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4.1.2. ^{1}H NMR spectroscopy

^{1}H NMR spectrum of **9** in acetonitrile-d_3 is displayed in Fig. 18. It involves a singlet at 8.96 ppm (9.02 in **10**) due to the azomethyne protons. All the aromatic protons in **9** appear in the 7.83–6.97 ppm region (7.43–7.18 ppm in **10**) with expected integration and splitting patterns. The ethylenic protons H(8) and H(8′) (Fig. 18) are diastereotopic in these complexes because of the anisochronous nature of the bridge-head protons in the coordinated Salen moiety and appear as AA′BB′spin system involving two multiplets centered at 4.30 and 4.12 ppm (4.42 and 4.20 ppm in **10**). A sharp singlet at 3.96 ppm is characteristic of the OCH_3 protons in **10**. Of particular interest, here is the position of the azomethyne protons. Because of the coordination of the ReO_4 moiety to the oxovanadium(V) center, the position of this singlet is shifted upfield to 8.96 ppm compared to what has been observed (9.35–9.39 ppm) in comparable compounds [88a]. The results are in conformity with the heterobinuclear structures in **9** and **10** remaining intact in acetonitrile solution. The compounds however slowly dissociate in DMSO solution as demonstrated by the slow increase in electrical conductivity of the original non-conducting solutions with the passage of time.

4.2. Electrochemical and EPR spectroscopic studies

Votammetric features of **9** and **10** are almost identical. Both CV and differential pulse voltammogram (DPV) of **9** are displayed in Fig. 19 as a representative example, showing two electrochemical responses at $(E_{1/2})_I = 0.59$ V (process I) and $(E_{1/2})_{II} = 0.16$ V (process II) (vs. Ag/AgCl reference) involving identical number of electrons. Based on these results as well as from NPV and constant potential coulometric experiments, the electrochemical processes observed with these compounds are consistent with two successive one-electron steps as shown by Eqs. (3) and (4).

$$\text{Process I}$$
$$[L^{6,7}OV^{V}\text{–}(\mu\text{-O})\text{–}Re^{VII}O_3]^{0} \underset{(E_{1/2})_I=0.59\,V}{\overset{+e^-}{\rightleftharpoons}} [L^{6,7}OV^{IV}\text{–}(\mu\text{-O})\text{–}Re^{VII}O_3]^{1-} \quad (3)$$

$$\text{Process II}$$
$$[L^{6,7}OV^{IV}\text{–}(\mu\text{-O})\text{–}Re^{VII}O_3]^{1-} \underset{(E_{1/2})_{II}=0.16\,V}{\overset{+e^-}{\rightleftharpoons}} [L^{6.7}OV^{IV}\text{–}(\mu\text{-O})\text{–}Re^{VII}O_3]^{2-} \quad (4)$$

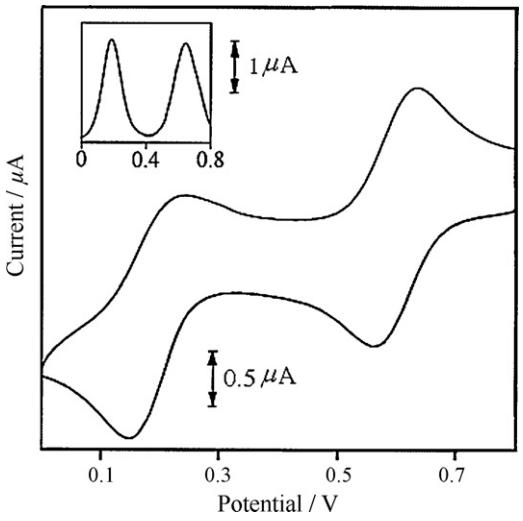

Fig. 19. Cyclic voltammogram of **9** in dichloromethane solution; potentials vs. Ag/AgCl, 0.1 M TBAP at a platinum electrode, scan rate 100 mV s^{-1}. The inset shows the differential pulse voltammogram establishing the involvement of same number of electron(s) for both processes I and II.
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The solution from the bulk electrolysis of **9** (process 1) has been further characterized by EPR spectroscopy (Fig. 20). The one-electron reduced species $[L^{6}V^{IV}O\text{–}(\mu\text{-O})\text{–}OReO_3]^{1-}$ in dichloromethane/toluene (1:10, v/v) solution at room temperature shows (Fig. 20, inset) an 8-line isotropic pattern ($\langle g\rangle$, 1.977; $\langle A\rangle$, 87×10^{-4} cm^{-1}) characteristic of an unpaired electron being coupled to the vanadium nuclear spin (^{51}V, $I = 7/2$). Interestingly, each of these spectroscopic lines again is split into a doublet because of the familiar 'two-line pattern' superhyperfine coupling [A (^{185,187}Re) = 20.7×10^{-4} cm^{-1}] from the attached rhenium center (^{185}Re, ^{187}Re, $I = 5/2$) [134]. In the frozen solution, however, the spectrum displayed well-resolved axial features with two sets of eight-line patterns. Some of these lines are distinctly split into doublets due to ^{185,187}Re superhyperfine coupling. The corresponding spin-Hamiltonian parameters are $g_\perp = 1.948$, $A_\perp = 153 \times 10^{-4}$ cm^{-1}, $g_\perp = 1.988$, $A_\perp = 53 \times 10^{-4}$ cm^{-1} and A (^{185}Re, ^{187}Re) = 20.7×10^{-4} cm^{-1}.

Confirmation of electron stoichiometry for process II is however, not possible due to the instability of the reduced

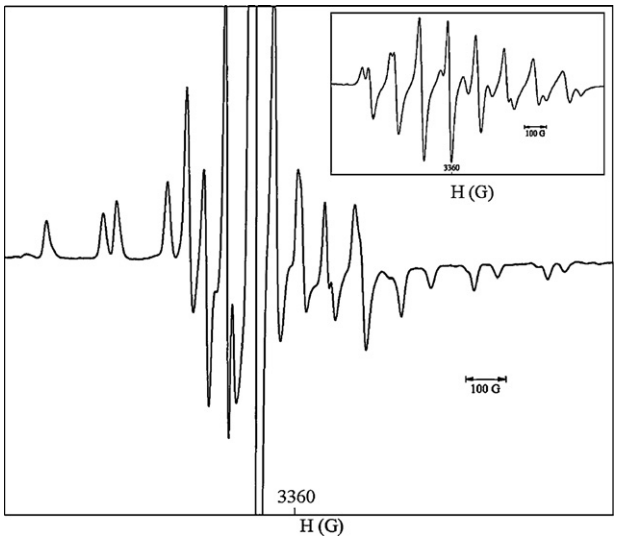

Fig. 20. The EPR spectrum at 77 K of the catholyte solutions (in dichloromethane/toluene, 1:10, v/v) generated electrochemically by coulometric reduction of compound **9** (E_w set at 0.2 V vs. Ag/AgCl). The inset shows an eight-line isotropic pattern at room temperature for the same compound under identical experimental conditions.
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$[L^{6,7}OV^{IV}–(\mu\text{-}O)–Re^{VI}O_3]^{2-}$ species in the required longer timescale of coulometric experiment.

5. Conclusion

Synthetic methodologies have been developed to introduce ligand asymmetry into the $[V_2O_3]^{n+}$ ($n = 4$ and 3) cores for the first time. Such asymmetry has intense influence on the steric and electronic environments around the vanadium centers. In a typical isovalent divanadium(V) compound (**1**–**5**), one of the vanadium centers has an octahedral coordination geometry, completed by the tetradentate N_2O_2 (Salen-based) ligand. The second vanadium center has a square pyramidal geometry made up with a tridentate biprotic Schiff-base ligand based on either amino acid part (**1**–**3**) or dithiocarbazate (**4**, **5**), providing ONO and ONS type donor set, respectively. All these compounds, save **3**, have closely similar structures (triclinic space group, *P*1-) with a rare type of twist-angular V_2O_3 core. Crystals of **3** on the other hand have a monoclinic space group ($P2_1/c$) with an *anti*-angular V_2O_3 core structure. The V(1)···V(2) separations are unprecedentedly larger in these compounds compared to their peers. The angularity in the structures of these V_2O_3 cores probably remain intact in solution and block all sorts of electronic communications between the participating vanadium centers as revealed from ^{51}V NMR, CV and EPR studies. The mixed oxidation compound (ImH)$[L^4OV^{IV}–(\mu\text{-}O)–V^VOL^5]$ **7** exhibits crystallographically imposed mirror symmetry due to static disorder which is quite unusual considering the *syn*-angular structure of its V_2O_3 core. This is due to the presence of a dimeric structure with bromine atom disordered over the two ligand sites (one-half occupancy). In solution however, they show solvent-dependent equilibrium involving two magnetically inequivalent structural forms of the divanadium(IV,V) compound, with *syn*-angular and *anti*-linear structures of the $[V_2O_3]^{3+}$ core. Finally, heterobinuclear compounds (**9** and **10**) containing V^V–O–Re^{VII} moiety have been synthesized using a similar strategy as developed for **1**–**5**. The V–O–Re bridge is almost linear (170.2(3)°) in these compounds and remains intact in acetonitrile or dichloromethane solution but undergoes dissociation in DMSO. In dichloromethane, both **9** and **10** undergo two one-electron reductions at $E_{1/2} = 0.59$ and 0.16 V vs. Ag/AgCl reference. In the first process, the reducing electron enters the vanadium(V) center and remains partially delocalized between the metal centers as evident from the EPR spectrum of $[9]^-$, involving ^{185,187}Re superhyperfine coupling.

6. Future perspective

Future work will be directed towards development of synthetic protocols for the synthesis of heterobimetallic compounds containing V-O-M cores, where M stands for various transition metal ions. Metal complexes with similar cores are expected to function as efficient catalyst to modulate various electron transfer reactions. The work is now in progress in the authors' laboratory to develop such methodology which will be addressed in their future publications.

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