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Journal Name

ARTICLE

Non-oxido divanadium(IV) and divanadium(V) thiolate complexes with a new type of chalcogenide bridging motif
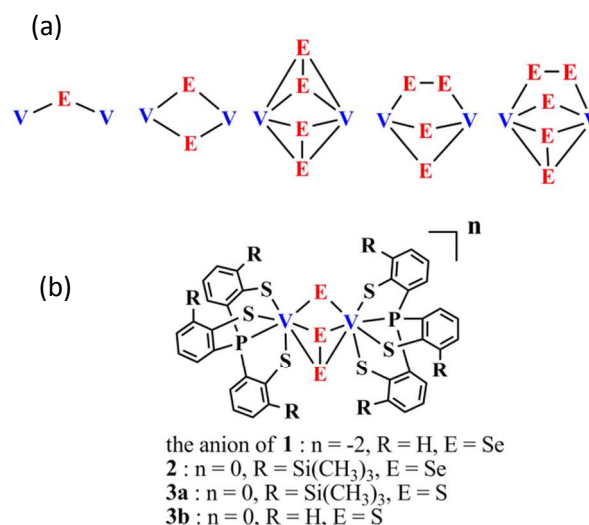
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In our effort to study vanadium chalcogenide chemistry, we have synthesized and characterized a class of non-oxido divanadium(IV) and divanadium(V) complexes with chalcogenide and dichalcogenide as bridges. All structures consist of a similar divanadium motif, in which two metal centers are bridged by one μ-chalcogenide and one μ-η^2:η^2-dichalcogenide, forming a $V_2(\mu$-E)(μ-η^2:η^2-E$_2$) (E = S or Se) core structure. These compounds are $[V^{IV}_2(PS3)_2(\mu$-Se$_2$)(μ-Se)][PPh$_4$]$_2$ (**1**), $[V^V_2(PS3'')_2(\mu$-Se$_2$)(μ-Se)]$ (**2**), $[V^V_2(PS3'')_2(\mu$-S$_2$)(μ-S)]$ (**3a**) and $[V^V_2(PS3)_2(\mu$-S$_2$)(μ-S)]$ (**3b**) ($[PS3]^{3-}$ = P(C$_6$H$_4$-2-S)$_3$ and $[PS3'']^{3-}$ = P(C$_6$H$_3$-3-SiMe$_3$-2-S)$_3$). Compound **1** exhibits a diamagnetic behavior, indicating a strong antiferromagnetic coupling between two d^1 centers. Compounds **2** and **3a**-**b** have the highest oxidation states in vanadium ions (+5/+5) among those reported divanadium chalcogenide clusters. The work demonstrates that high-valent divanadium chalcogenide clusters can be obtained with the activation of elemental chalcogens by low-valent vanadium ion.

Introduction

Vanadium chalcogenide chemistry receives much attention based on its relevance in biological systems, industrial application, and catalysis.[1-4] V-nitrogenase catalyzes biological nitrogen fixation and has also been found recently to have a CO reducing capacity. The structure is not resolved by X-ray crystallography, but the active site (FeVco) is proposed to contain a Fe$_7$VS$_9$ cluster via comparison with the characterization of Mo-nitrogenase.[5, 6] In addition, studies of vanadium-sulfur chemistry have been conducted to realize vanadium-based applications of hydrodesulfurization (HDS) catalysts in fuel refining processes and, conversely, for intentions to understand the transformation for vanadium impurity removal in crude oil.[7] Stemming from their oxophilic nature, high-valent vanadium ions (V^{IV} and V^V) tend to produce complexes that contain V=O moiety with hard-donor (such as N/O) co-ligands. It is for this reason that work done in high-valent vanadium-sulfur chemistry is especially difficult. Moreover, it is less feasible to isolate stable V^V-thiolate complexes because the redox conversion often occurs between V^V species and thiol groups.[8-12] Thus, reported non-oxido high-valent vanadium complexes are relatively rare compared to oxido ones. With respect to divanadium complexes, a recent

Cambridge Structural Database (CSD) search indicates that approximately two hundred non-oxido divanadium complexes exist; these are far fewer than for oxido divandium ones (around 1600~1700 examples).[13] Particularly, examples of

the anion of **1** : n = -2, R = H, E = Se
2 : n = 0, R = Si(CH$_3$)$_3$, E = Se
3a : n = 0, R = Si(CH$_3$)$_3$, E = S
3b : n = 0, R = H, E = S

non-oxido divanadium cores containing chalcogenide bridges

Figure 1. Reported core motifs of divanadium chalcogenide clusters (a). Divanadium chalcogenide clusters reported in this communication (b).

are extremely limited.[1, 2, 4, 14] Among this group, the bridging motifs that are structurally characterized can be classified as $V_2(\mu\text{-E})$, $V_2(\mu\text{-E})_2$, $V_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-E}_2)_2$, $V_2(\mu\text{-E})_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-E}_2)$ $V_2(\mu\text{-E})(\mu\text{-}\eta^1\text{:}\eta^1\text{-E}_2)(\mu\text{-}\eta^2\text{:}\eta^2\text{-E}_2)$ (E = S or Se) (Figure 1a). At this work, we report several non-oxido divanadium complexes with chalcogenide and dichalcogenide as bridges. To the best of our knowledge, the bridging mode, $M_2(\mu\text{-E})(\mu\text{-}\eta^2\text{:}\eta^2\text{-E}_2)$ (E = S or Se), has only been seen in dimolybdenum and ditungsten compounds,[15-18] but has not been reported in divanadium chalcogenide chemistry. These compounds are $[V^{IV}_2(PS3)_2(\mu\text{-Se}_2)(\mu\text{-Se})][PPh_4]_2$ (**1**), $[V^V_2(PS3'')_2(\mu\text{-Se}_2)(\mu\text{-Se})]$ (**2**), $[V^V_2(PS3'')_2(\mu\text{-S}_2)(\mu\text{-S})]$ (**3a**) and $[V^V_2(PS3)_2(\mu\text{-S}_2)(\mu\text{-S})]$ (**3b**) ($[PS3]^{3-} = P(C_6H_4\text{-2-S})_3$ and $[PS3'']^{3-} = P(C_6H_3\text{-3-SiMe}_3\text{-2-S})_3$), as shown in Figure 1b. Notably, divanadium ions in **2** and **3a-b** have their highest oxidation states (+5/+5) among those reported divanadium chalcogenide clusters, where the common oxidation states are +4/+4 with the exception of a delocalized +4/+5 mixed-valence species, $[V_2(S_2CNR_2)_4(\mu\text{-S}_2)_2]^+$.[19]

Results and discussion

Synthesis

The reaction of $VCl_3(THF)_3$ and PS3 in CH_3CN, followed by the addition of 1.5 equivalent moles of Se gave a reddish-purple solution. Adding $[PPh_4]Br$ dissolved in CH_3CN and ether led to the precipitation of $\mathbf{1}\cdot0.25THF\cdot3CH_3CN$ in crystalline form. (41 % yield based on $VCl_3(THF)_3$). Complex **2** was obtained from the reaction of $VCl_3(THF)_3$, PS3'' and Se powder in THF/methanol. The resulting mixture was filtered and air was added to the filtrate, followed by layering methanol to produce a dark bluish-purple crystalline solid of $\mathbf{2}\cdot2THF$ (27% based on $VCl_3(THF)_3$). Compound **3a** was synthesized from the reaction of S_8 with a mixture of $VCl_3(THF)_3$ and PS3'' in THF, followed by the addition of $[FeCp_2][PF_6]$. The resulting purple solution was layered by methanol to give the crystalline solid of $\mathbf{3a}\cdot2THF\cdot2CH_3OH\cdot H_2O$ (54% based on $VCl_3(THF)_3$). The same synthetic protocol was applied for the isolation of compound $\mathbf{3b}\cdot THF\cdot2CH_3CN$ (47% yield).

Structural description

The structures of compounds **1**, **2**, **3a** and **3b** were determined by X-ray crystallography. Their ORTEP diagrams are shown in Figure 2 (**1**, **2** and **3a**) and Figure S1 (**3b**). The selected bond distances are summarized in Table 1. All structures consist of a similar divanadium motif, in which two metal centers are bridged by one μ-chalcogenide and one $\mu\text{-}\eta^2\text{:}\eta^2$-dichalcogenide, forming a $V_2(\mu\text{-E})(\mu\text{-}\eta^2\text{:}\eta^2\text{-E}_2)$ core structure (E = Se for **1** and **2**; S for **3a** and **3b**). The coordination sphere of each metal center is completed by one tetradentate *tris*(benzenethiolato)phosphine ligand. The geometry adopted in each vanadium center can be described as a distorted pentagonal bipyramid with μ-E and one S-donor of title ligand in axial positions (Figure 2). Other donor atoms including
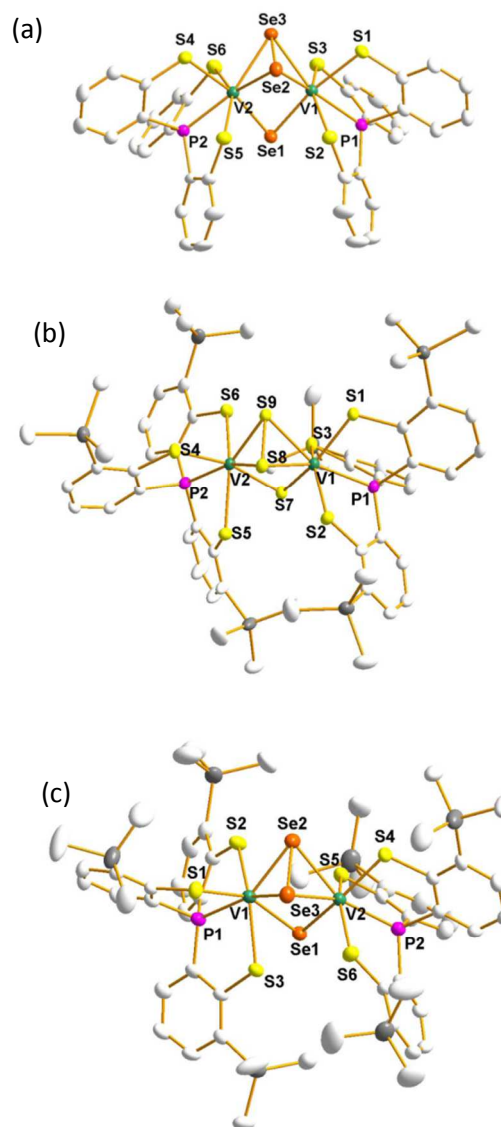

Figure 2. Thermal ellipsoid plots (35% probability) of $\mathbf{1}\cdot0.25THF\cdot3CH_3CN$ (a), $\mathbf{2}\cdot2THF$ (b) and $\mathbf{3a}\cdot2THF\cdot2CH_3OH\cdot H_2O$ (c). The cations, solvent molecules and H atoms are omitted for clarity.

$\mu\text{-}\eta^2\text{-E}_2$, two thiolato groups and one phosphine atom of PS3 ligand are in the equatorial plane. The distortion from an ideal pentagonal bipyramid is large in divanadium(V) complexes **2**, **3a** and **3b**. The geometries of two dinuclear centers can be viewed as two pentagonal bipyramids that share a triangular face composed of three bridging chalcogenide atoms. The dihedral angles between equatorial planes of two pentagonal bipyramids are 88.5, 83.5, 85.4 and 85.8 degree for **1**, **2**, **3a** and **3b**, respectively. If the $\mu\text{-}\eta^2\text{-E}_2$ ligand is considered to occupy a single vertex, all structures can be alternatively viewed as a distorted bi-octahedrons sharing an edge. The V-V distances for **1**, **2**, **3a** and **3b** are 2.909 Å, 3.081 Å, 3.017 Å and 2.901 Å, respectively. The separation between the two metal centers found in divanadium(IV) complexes is slightly shorter than that in divanadium(V) when the bridging atoms are the same (**1** versus **2**). In divanadium(V) complexes, the V-V

distance is slightly longer when selenide atoms act as bridges compared to sulfide donors (**2** versus **3a** and **3b**). However, the discrepancy in V-V distance is generally not significant with the change of metal oxidation state and the bridging atom. The separation of two vanadium ions for reported divanadium chalcogenide complexes spreads along a range of 2.6~3.0 Å, depending on bridging type and geometry.[7] In addition, the intermetallic interaction also plays a key factor.[20] The V-V distances (2.909-3.017 Å) in complexes **1-3b** comply with this range. The distance of 2.909 Å between two V^{IV} centers in **1** is longer than those reported cases that have metal-metal bonding interaction.[7, 20] [[(Me3Si)$_2$N]$_2$V]$_2$(μ-S)$_2$ has been confirmed by theoretic calculation to have a metal-metal bond, but the V-V distance (2.86 Å) is relatively long.[20] Thus, a further investigation by calculation is needed to provide conclusive information regarding the intermetallic bonding interaction in **1**.[7, 20] The Se-Se distances in μ-η^2-Se$_2$ ligand (2.302(2) Å and

2.264(1) Å for **1** and **2**, respectively**)** are comparable to those in the reported divanadium(IV) complexes with μ-η^2-Se$_2$ as bridges.[21] The S-S distances of 2.012(2) Å and 2.010(1) Å for **3a** and **3b**, respectively, are within the range of metal bound disulfide.[22] In comparison with structural parameters for two [V$_2$(μ-Se)(μ-Se$_2$)]$^{2-/0}$ analogues, the average V-S$_{PS3}$ distance (2.490 Å) is longer in **1** than that in **2** (2.407 Å). However, the average V-(μ-Se) is shorter in **1** (2.388 Å) than that in **2** (2.510 Å). Compounds **3a** and **3b** have an average V-S$_{PS3}$ distances of 2.387 Å and 2.380 Å, respectively, close to those in **2**. The bond valence sum calculation supports that the oxidation states of two vanadium ions in **1** are closer to +4 (4.233 and 4.329); those in **2** have relatively higher values (4.596 and 4.572).[23] The calculation also confirms +5 oxidation states of vanadium ions in **3a** and **3b** (4.938 and 4.846 for **3a**; 4.756 and 5.104 for**3b**).

Table 1 Selected bond distances (Å) for **1**, **2**, **3a**, **3b**

	1 · 0.25THF · 3CH$_3$CN	**2** · 2THF	**3a** · 2THF · 2CH$_3$OH · H$_2$O	**3b** · THF · 2CH$_3$CN
V-V	2.909(2)	3.081(2)	3.017(2)	2.901(1)
V1-P1	2.391(2)	2.374(2)	2.400(3)	2.400(1)
V2-P2	2.366(3)	2.377(2)	2.383(3)	2.388(1)
V1-S1	2.466(3)	2.330(2)	2.317(2)	2.332(1)
V1-S2	2.527(2)	2.377(2)	2.357(1)	2.339(1)
V1-S3	2.461(3)	2.515(4)	2.488(1)	2.490(1)
V2-S4	2.460(3)	2.326(3)	2.322(2)	2.331(1)
V2-S5	2.552(3)	2.518(2)	2.480(2)	2.413(1)
V2-S6	2.476(2)	2.375(2)	2.360(1)	2.386(1)
V-(μ-E)	2.392(2)	2.507(2)	2.387(4)	2.346(1)
	2.384(2)	2.513(1)	2.431(3)	2.404(2)
	2.557(2)	2.523(1)	2.365(2)	2.374(1)
V-(μ-E2)	2.553(2)	2.560(1)	2.426(3)	2.412(1)
	2.514(2)	2.560(1)	2.439(4)	2.409(1)
	2.556(2)	2.527(1)	2.377(3)	2.388(1)
E-E	2.302(2)	2.264(1)	2.012(2)	2.010(1)

Characterization

Compound **1** is highly air-sensitive in solution and displays a dark reddish purple color. Dissolving compounds **2**, **3a** and **3b** in solvent gives a deep purple color and the solutions are relatively less sensitive to the air compared to **1**. The electronic spectra all show intense absorption bands in 400-800 nm region associated with ligand to metal charge transition (Figures S2-S5). The intense purple color for these complexes in solution state is attributed to a characteristic absorption band around 500-600 nm. Compound **1** is a divanadium(IV) species, however, it exhibits a diamagnetic behaviour in both solid and solution states due to the strong coupling between two V^{IV} ions in the molecule. The SQUID measurement detects no magnetism at the temperature range 5-300 K. The ^{1}H, ^{31}P, ^{51}V and ^{77}Se NMR spectra all give well-resolved peaks (Figure S6); usually observed in those of diamagnetic species. The resonances of ^{1}H NMR are distributed between 0~10 ppm and there is no signal found at the paramagnetic region. The ^{31}P

NMR spectrum displays two peaks, 119 ppm and 23 ppm, associated with the phosphine atoms of PS3 ligand and the PPh$_4^+$ cation, respectively. The ^{51}V and ^{77}Se absorption bands are found at 1087 ppm and 430 ppm, respectively. The chemical shifts are comparable to those in **2**, a divanadium(V) analogue of **1**, (1027 ppm for ^{51}V and 421ppm for ^{77}Se). The strong coupling between two d^1 centers also appear in other divanadium(IV) complexes with *bis*(μ-sufido) or *bis*(μ-disulfido) as bridges.[20, 22] A theoretic calculation is needed to understand the magnetic interaction between two d^1 centers.[20] Compounds **2**, **3a** and **3b** all display diamagnetic behavior as expected for divanadium(V) species. The ^{51}V NMR spectra give the absorption peaks at 1027, 765, and 716 ppm, respectively. The ^{51}V nucleus in non-oxido vanadium complexes is generally deshielded (with respect to the standard, VOCl$_3$) and mostly displays resonance downfield. In contrast, the ^{51}V spectrum of oxido vanadium complexes gives resonance signal upfield, indicating a shielded ^{51}V nucleus.[22] The low shielding for ^{51}V nuclei in **1-3b** is consistent with other divanadium complexes

containing bridging chalcogenide and dichalcogenide groups, but much more deshielded than those binding with N/O donors.[24] The [51]V nuclei in [$V_2(\mu\text{-Se})(\mu\text{-Se}_2)$] complexes (**1** and **2**), are more effectively deshielded by ca. 300 ppm relative to those in [$V_2(\mu\text{-S})(\mu\text{-S}_2)$] complexes (**3a** and **3b**). This agrees with the trend reported in literatures that shielding decreases from sulfide to selenide.[25, 26] For example, divanadium(IV) complexes bridging by chalcogenide and dichalogenide groups, [$V_2(C_5Me_5)_2(\mu\text{-S})(\mu\text{-S}_2)(\mu\text{-O})$], [$V_2(C_5Me_5)_2(\mu\text{-Se})(\mu\text{-Se}_2)(\mu\text{-O})$] and [$V_2(C_5Me_5)_2(\mu\text{-Te})(\mu\text{-Te}_2)(\mu\text{-O})$], have [51]V chemical shifts of 1266 ppm, 1647 ppm and 2240 ppm, respectively.[27, 28] Interestingly, the cases also show 300-400 ppm deshielded when changing bridges from sulfide to selenide. It illustrates the similar trend between [$V_2(\mu\text{-Se})(\mu\text{-Se}_2)$] and [$V_2(\mu\text{-S})(\mu\text{-S}_2)$] complexes reported herein. In addition, the chemical shift does not vary dramatically with the change of oxidation state, i.e., **1** and **2** have very similar [51]V chemical shifts (1087 and 1027 ppm). The redox properties of these complexes were investigated by cyclic voltammogram (CV). The measurement of **1** gave a reversible peak at -0.742 V (vs. Fc/Fc$^+$) associated with oxidation process. The low redox potential of **1** reflects its high air-sensitivity. The CVs of **3a** and **3b** display quasi-reversible waves at -1.058 V and -0.804 V (vs. Fc/Fc$^+$), respectively, related to the reduction process. The measurement of compound **2** did not show any peak associated with reduction process. Overall, the spectroscopic characterizations of these complexes are consistent with the findings of their X-ray structures; this implies the dinuclear core motifs of these complexes, $V_2(\mu\text{-E})(\mu\text{-}\eta^2{:}\eta^2\text{-E}_2)$ (E = S or Se), found in solid state remains intact while dissolving in solution.

Experimental

All procedures were carried out under dinitrogen with standard Schlenk techniques or glove box. Air-sensitive compounds or reagents were weighed out inside a glove box with control of static electricity. Ligands, $H_3[PS3]$ and $H_3[PS3"]$,[29] as well as $VCl_3(THF)_3$[30] were synthesized according to the literature procedures. THF and ether were dried by distillation from Na/benzophenone. CH_3OH, CH_3CN, and CH_2Cl_2 were dried by distillation from CaH_2 and P_2O_5. Otherwise all starting materials were obtained commercially and used without further purification.

Elemental analyses were measured with Elemetar vario EL III. NMR spectra were obtained on a Bruker AMX500 and AMX400. The samples were prepared in a sealed NMR tube under nitrogen atmosphere. Electronic spectra were recorded with Hewlett Packard 8453 spectrophotometer at room temperature. Electrochemical studies were performed with a CHI 600A electrochemical analyzer. Cyclic voltammograms (CVs) were obtained at ambient temperature under N_2 atmosphere by using a three-component system consisting of a platinum disk working electrode, a platinum wire auxiliary electrode, and a $Ag/AgNO_3$ (0.01 M in CH_3CN) as the reference electrode. The experiments were performed in CH_2Cl_2 or CH_3CN by using 0.1 M tetrabutylammonium

tetrafluoroborate as the supporting electrolyte. The ferrocenium/ferrocene (Fc$^+$/Fc) couple was measured as an external standard.

Syntheses

[$V_2(PS3)_2(\mu\text{-Se}_2)(\mu\text{-Se})$][$PPh_4$]$_2$ (1)
One equivalent of $VCl_3(THF)_3$ (0.104g, 0.278 mmol) was added to an acetonitrile solution of $H_3[PS3]$ (0.100 g, 0.279 mmol) and 1.6 M n-BuLi (0.55 mL, 0.88 mmol) to generate a brown solution. The brown solution was added within 1.5 equivalent mole of Se to become a reddish-purple solution which was layer with [PPh_4]Br (0.120g, 0.286 mmol) in acetonitrile and ether to give a deep reddish-purple crystalline solid of **1**·0.25THF·3CH$_3$CN over a week period (0.105g , 0.058 mmol, ca. 41 % based on VCl_3(thf)$_3$). Anal. Calcd for $C_{88}H_{70}N_2P_4S_6Se_3V_2$ (**1**·2CH$_3$CN): C, 58.38; H, 3.90; N, 1.55; S, 10.63. Found: C, 58.06; H, 3.94; N, 1.66; S, 11.01. UV-Vis-NIR (DMF) λ_{max}, nm (ε, M^{-1}cm^{-1}): 322(4.5x10^4), 524(7.5x10^3), 683(5.3x10^3), 887(2.2x10^3)

[$V_2(PS3")_2(\mu\text{-Se}_2)(\mu\text{-Se})$] (2)
$H_3[PS3"]$ (0.100 g, 0.174 mmol) and CH_3ONa (0.028 g, 0.523 mmol) were dissolved in dry methanol. The solution was added to a THF solution of VCl_3(thf)$_3$ (0.065g, 0.174 mmol) to generate a brown solution, followed by the addition of 1.6 equivalents of Se. The generated reddish-purple solution was filtered with celite and the filtrate was exposed to the air for five minutes to cause the color of solution to change to a bluish-purple. The methanol was layered to give a dark bluish-purple crystalline solid of **2**·THF after two weeks (0.035g, 0.024 mmol, ca. 27 % based on VCl_3(thf)$_3$). Anal. Calcd for $C_{58}H_{80}OP_2S_6Se_3Si_6V_2$ (**2** · THF): C, 44.80; H, 5.19; S, 12.37. Found: C, 44.32; H, 5.26; S, 11.99. UV-Vis-NIR (CH_2Cl_2) λ_{max}, nm (ε, M^{-1}cm^{-1}): 557(9.4x10^3), 598(1.0x10^4), 775(5.2x10^3)

[$V_2(PS3")_2(\mu\text{-S}_2)(\mu\text{-S})$] (3a)
One equivalent of VCl_3(thf)$_3$ (0.200g, 0.535 mmol) was added to a THF solution of $H_3[PS3"]$ (0.308 g, 0.536 mmol) and 1.6 M n-BuLi (1.10 mL, 1.76 mmol) to generate an brown solution. Adding 1.6 equivalent mole of S_8 (0.027g, 0.856mmol) and 1.0 equivalent mole of [$FeCp_2$][PF_6] (0.177g, 0.535 mmol) to the reaction mixture gave a purple solution Layering methanol on top of the solution produced a dark purple crystalline solid of **3a**·2THF·2CH$_3$OH·H$_2$O [0.193g, 0.144 mmol, ca. 54 % based on VCl_3(thf)$_3$]. Anal. Calcd for $C_{54}H_{72}P_2S_9Si_6V_2$ (**3a**): C, 48.33; H, 5.41; S, 21.50. Found: C, 48.20; H, 5.33; S, 21.59. UV-Vis-NIR (CH_2Cl_2) λ_{max}, nm (ε, M^{-1}cm^{-1}): 571(1.2x10^4), 662(7.0x10^3).

[$V_2(PS3)_2(\mu\text{-S}_2)(\mu\text{-S})$] (3b)
One equivalent of VCl_3(thf)$_3$ (0.104g, 0.278 mmol) was added to a THF solution of $H_3[PS3]$ (0.100 g, 0.279 mmol) and 1.6 M n-BuLi (0.55 mL, 0.88 mmol) to generate a brown solution. Adding 1.6 equivalent mole of S_8 (0.014g, 0.444 mmol) and 1.0 equivalent mole of [$FeCp_2$][PF_6] (0.092g, 0.278mmol) to the reaction mixture gave a purple solution Layering acetonitrile

on top of the solution produced a dark purple crystalline solid of **3b**·THF·2CH$_3$CN [0.059g, 0.065 mmol, ca. 47 % based on VCl$_3$(thf)$_3$]. Anal. Calcd for C$_{42}$H$_{35}$ONP$_2$S$_9$V$_2$ (**3b**·2CH$_3$CN): C, 48.47; H, 3.05; S, 29.12. Found: C, 47.89; H, 3.58; S, 29.99. UV-Vis-NIR (CH$_2$Cl$_2$) λ_{max}, nm (ε, M^{-1}cm^{-1}): 552(1.5x10^4), 684(7.3x10^3)

X-ray crystallography

X-ray Crystallographic Data were collected by a Nonius Kappa diffractometer equipped with a CCD detector. Least-squares refinement of the positional and anisotropic thermal parameters for the contribution of all non-hydrogen atoms and fixed hydrogen atoms was based on F^2. A SADABS absorption correction was made.[31] The SHELXTL structural refinement program was employed.[32] All the non-hydrogen atoms were refined with anisotropic displacement factors. All the hydrogen atoms are calculated by using the riding model.

Crystal data for **1**·0.25THF·3CH$_3$CN : CCDC-990544, C$_{91}$H$_{75}$N$_3$O$_{0.25}$P$_4$S$_6$Se$_3$V$_2$, M = 1869.63, Monoclinic, space group $P2/c$, a = 23.551(19) Å, b = 13.683(11) Å, c = 27.38(2) Å, α = 90°, β = 99.212(14)°, γ = 90°, V = 8710(12) Å^3, Z = 4, $d_{(calcd)}$ = 1.423 g/cm^3, T = 150(2) K, 61983 reflection collected, 21294 independent, R_{int} = 0.0750, R_1 = 0.0578, wR_2 = 0.1320 for all data.

Crystal data for **2**·2THF : CCDC-990546, C$_{62}$H$_{88}$O$_2$P$_2$S$_6$Se$_3$Si$_6$V$_2$, M = 1626.97, Triclinic, space group P-1, a = 15.430(2) Å, b = 15.527(2) Å, c = 17.671(2) Å, α =80.054(2)°, β = 69.489(2)°, γ = 77.016(2)°, V = 3843.3(9) Å^3, Z = 2, $d_{(calcd)}$ = 1.328 g /cm^3, T = 200(2) K, 45695 reflection collected, 18526 independent, R_{int} = 0.0962, R_1 = 0.0659, wR_2 = 0.1654 for all data.

Crystal data for **3a**·2THF·2CH$_3$OH·H$_2$O : CCDC-990547, C$_{64}$H$_{98}$O$_5$P$_2$S$_9$Si$_6$V$_2$, M = 1568.32, Triclinic, space group P-1, a = 14.3175(5) Å, b = 16.3327(6) Å, c = 19.5112(7) Å, α = 81.827(2)°, β = 88.006(2)°, γ = 64.137(2) °, V = 4062.0(3) Å^3, Z = 2, $d_{(calcd)}$ = 1.282 g /cm^3, T = 150(2) K, 45567 reflection collected, 14146 independent, R_{int} = 0.0569, R_1 = 0.0617, wR_2 = 0.1675 for all data.

Crystal data for **3b**·THF·2CH$_3$CN : CCDC-990545, C$_{44}$H$_{38}$N$_2$OP$_2$S$_9$V$_2$, M = 1063.12, Monoclinic, space group $P2_1/n$, a = 18.842(2) Å, b = 12.4528(14) Å, c = 10.766(2) Å, α = 90°, β = 104.691(2)°, γ = 90 °, V = 4713.2(9) Å^3, Z = 4, $d_{(calcd)}$ = 1.501 g /cm^3, T = 230(2) K, 35059 reflection collected, 11648 independent, R_{int} = 0.0304, R_1 = 0.0436, wR_2 = 0.1287 for all data.

Conclusions

With *tris*(benzenethiolato)phosphine and its derivatives as supporting ligands, we successfully isolated and characterized several divanadium(IV) and divanadium(V) complexes bridging by chalcogenide and dichalcogenide groups. The dinuclear core motif, V$_2$(μ-E)(μ- η^2: η^2-E$_2$) (E = S or Se), has never been reported in structurally characterized vanadium clusters. In particular, based on our knowledge, complexes **2**, **3a** and **3b** represent unprecedented examples of divanadium

chalcogenide clusters, in which two vanadium ions have the highest oxidation states (+5/+5). Obtaining these high-valent vanadium complexes was not accomplished via direct synthesis from the reaction of V^{IV} and V^V ions with supporting ligands. Rather, the divanadium(IV) complex (**1**) was formed through the reaction of VCl$_3$(THF)$_3$, PS3 ligand and selenium, where elemental chalcogen was activated by a V^{III} species. Lastly, further oxidation with external oxidants such as dioxygen and ferrocenium led to the formation of divanadium(V) compounds, **2** and **3a-b**, respectively.

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Notes and references

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† Electronic Supplementary Information (ESI) available: The ORTEP diagram of **3b**, The electronic spectra, The NMR spectra, X-ray structural parameters. See DOI: 10.1039/b000000x/

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