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Supporting Information for

Non-oxido divanadium(IV) and divanadium(V) thiolate complexes with a new type of chalcogenide bridging motif

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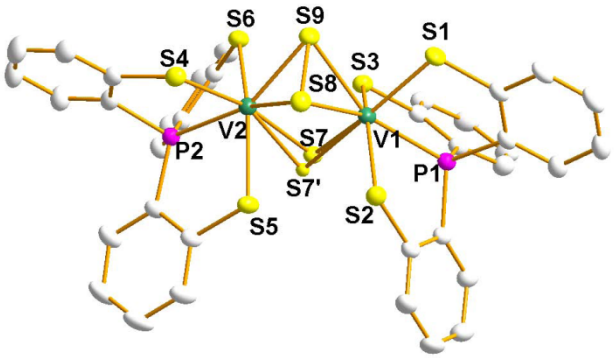

Figure S1. ORTEP diagram of $[V_2(PS3)_2(\mu\text{-}S_2)(\mu\text{-}S)]\cdot THF\cdot CH_3CN$ (**3b**$\cdot THF\cdot 2CH_3CN$) shown with 35% thermal ellipsoids. H atoms and solvate molecules are omitted for clarity.

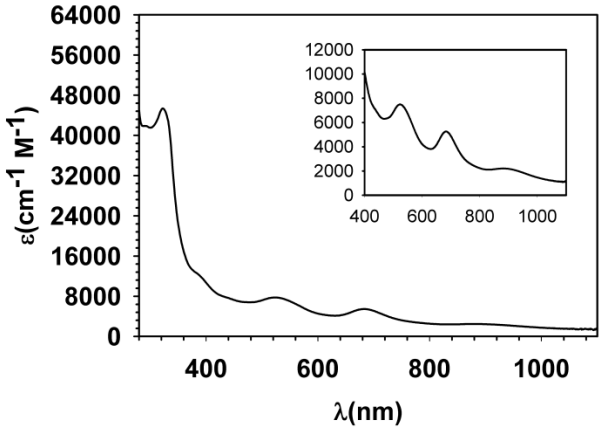

Figure S2. UV-Vis-NIR spectra of compound **1** in DMF (2.1 X 10^{-5} M); inset 8.4 X 10^{-5} M.

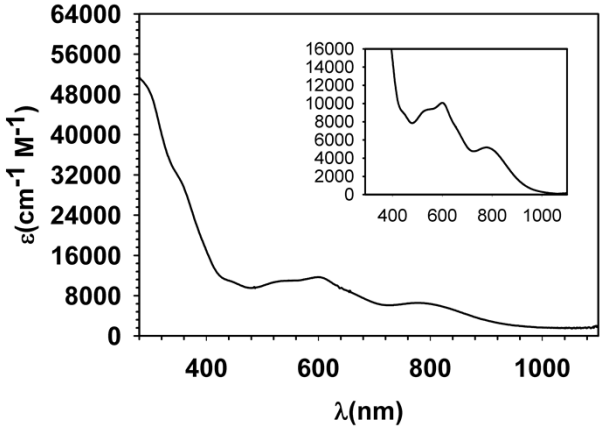

Figure S3. UV-Vis-NIR spectra of compound **2** in CH_2Cl_2 (1.2 X 10^{-5} M); inset (1.6 X 10^{-5} M).

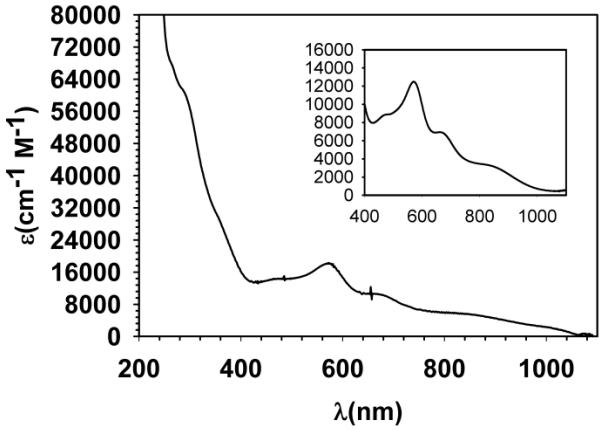

Figure S4. UV-Vis-NIR spectra of compound **3a** in CH_2Cl_2 (4.9 X 10^{-6} M); inset (9.9 X 10^{-6} M)**.**

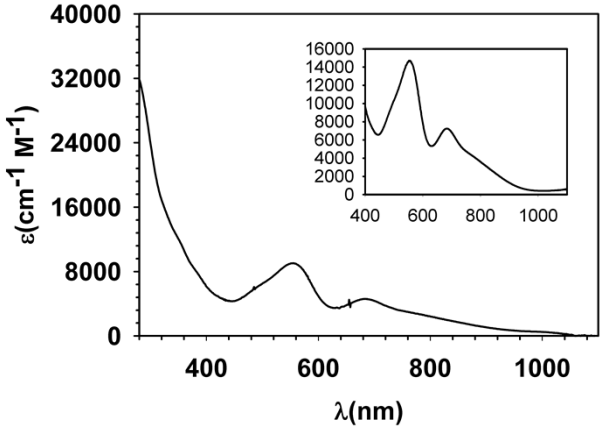

Figure S5. UV-Vis-NIR spectra of **3b** in CH_2Cl_2 (2.8 X 10^{-5} M) ; inset (1.3 X 10^{-4}M).

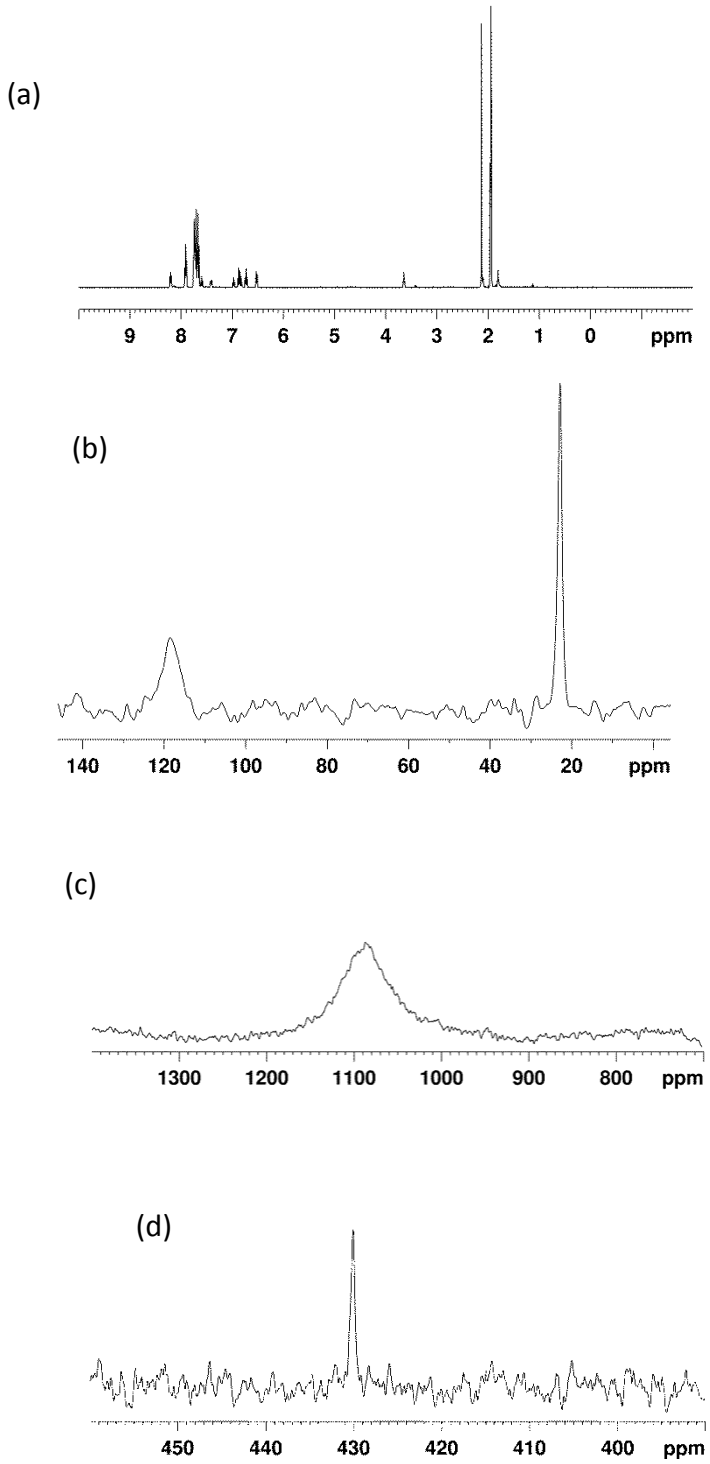

Figure S6. ^{1}H-NMR (a), ^{31}P-NMR (b), ^{51}V-NMR (c) and ^{77}Se-NMR (d) spectra of compound **1**. The first three spectra were measured in CD_3CN and the last was taken in d_6-DMSO.

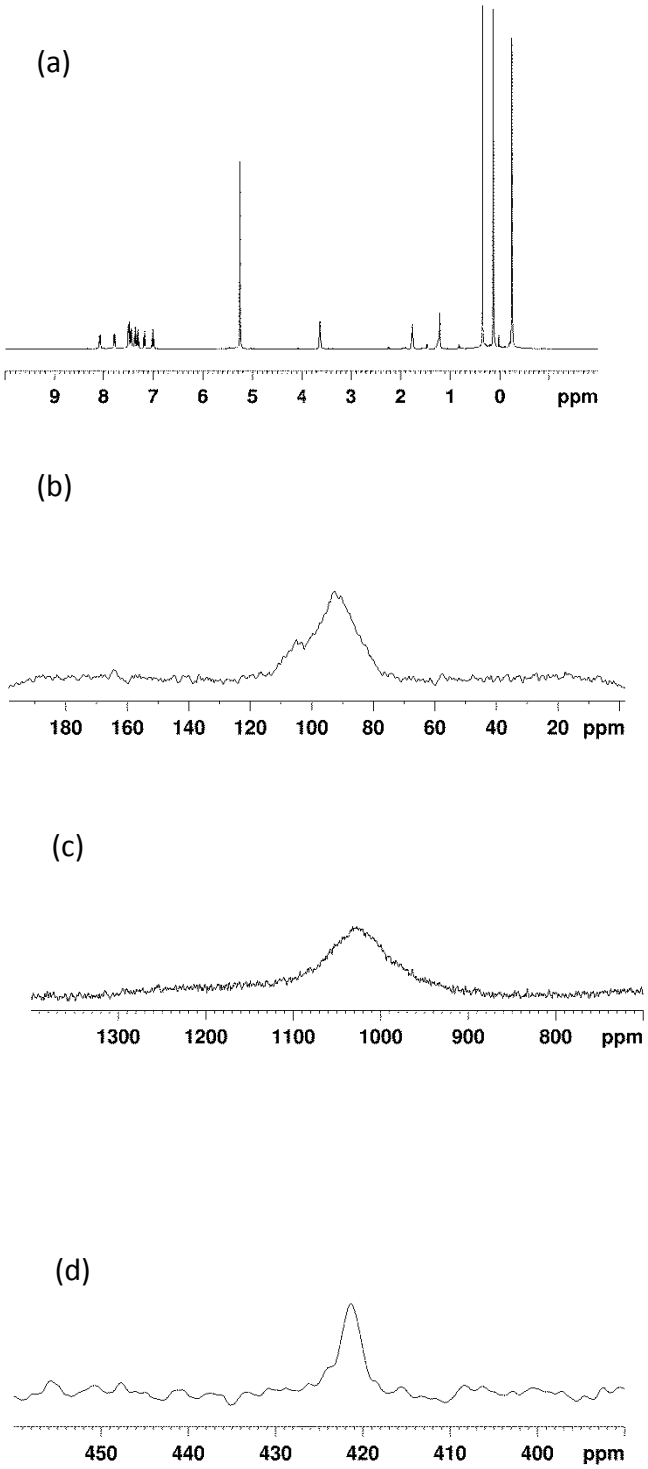

Figure S7. ^{1}H-NMR (a), ^{31}P-NMR (b), ^{51}V-NMR (c) and ^{77}Se-NMR (d) spectra of compound **2**. The spectra were measured in CD_2Cl_2.

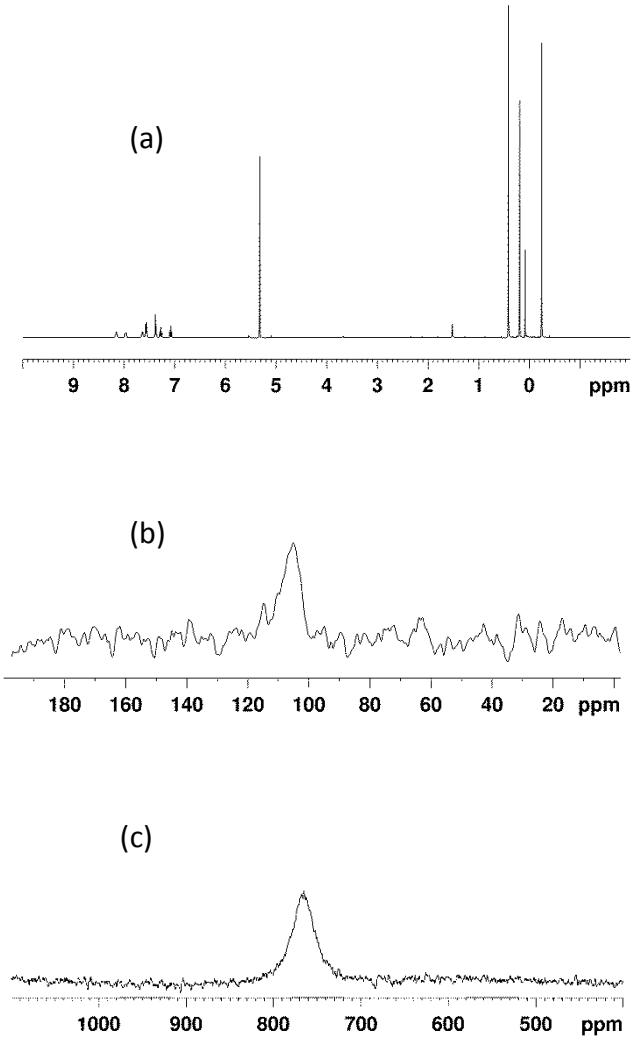

Figure S8. ^{1}H-NMR (a), ^{31}P-NMR (b), and ^{51}V-NMR (c) spectra of compound **3a**. The spectra were measured in CD_2Cl_2.

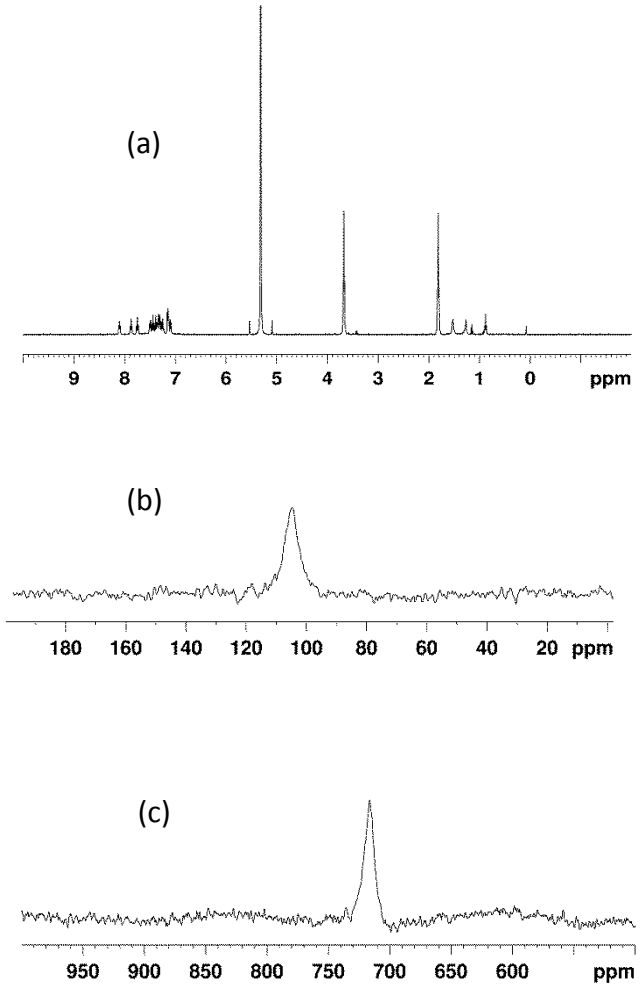

Figure S9. ^{1}H-NMR (a), ^{31}P-NMR (b), and ^{51}V-NMR (c) spectra of compound **3b**. The spectra were measured in CD_2Cl_2.

Table S1. X-ray Crystallographic Data for **1**, **2**, **3a**, **3b**.

Compound	**1** • $3CH_3CN$ • 0.25THF	**2**·THF	**3a**·$2CH_3OH$·2THF·H_2O	**3b**·$2CH_3CN$·THF
Chemical formula	$C_{91}H_{72}N_3O_{0.25}P_4S_6Se_3V_2$	$C_{58}H_{80}OP_2S_6Se_3Si_6V_2$	$C_{64}H_{98}O_5P_2S_9Si_6V_2$	$C_{44}H_{38}N_2OP_2S_9V_2$
Fw	1866.52	1554.82	1568.32	1063.12
T, K	150(2)	200(2)	150(2)	230(2)
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	P 2/c	P-1	P-1	$P2_1/n$
a,Å	23.551(19)	15.430(2)	14.3175(5)	18.842(2)
b,Å	13.683(11)	15.527(2)	16.3327(6)	12.4528(14)
c,Å	27.38(2)	17.671(2)	19.5112(7)	20.766(2)
α, deg	90	80.054(2)	81.827(2)	90
β, deg	99.212(14)	69.489(2)	88.006(2)	104.691(2)
γ, deg	90	77.016(2)	64.137(2)	90
V,Å	8710(12)	3843.3(9)	4062.0(3)	4713.2(9)
Z	4	2	2	4
D_{cala}/g cm^{-3}	1.423	1.328	1.282	1.501
μ(Mo-K$_\alpha$)/mm^{-1}	1.732	1.995	0.632	0.901
F(000)	3780	1562	3864	2174
Collected data	61983	45695	45567	35059
Unique data (R_{int})	21294(0.0750)	18526(0.0962)	14146 (0.0569)	11648(0.0304)
Refined parameters	996	678	773	543
$R_1{}^a(I>2\sigma(I))$	0.0578	0.0659	0.0617	0.0436
$_wR_2\,(I>2\sigma(I))$	0.1320	0.1654	0.1675	0.1287
GOF	1.035	0.974	1.076	1.023

$R_1 = \Sigma \| F_o| - |F_c\| / \Sigma |F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$; $w = 1/\sigma^2(|Fo|)$