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Supplementary Information

Vanadium-Lithium Alkoxides: Synthesis, Structure, Spectroscopic Characterisation and Accidental Degradation of Silicone Grease

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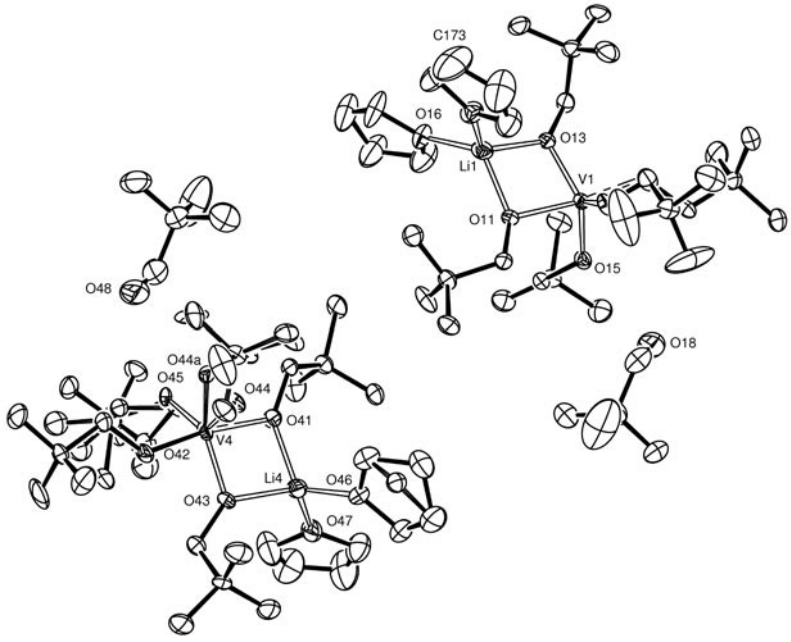

Figure S1. View of the asymmetric unit of $[V(ONep)_3(\mu\text{-}ONep)_2Li(thf)_2]\cdot NepOH$ (**2**). Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

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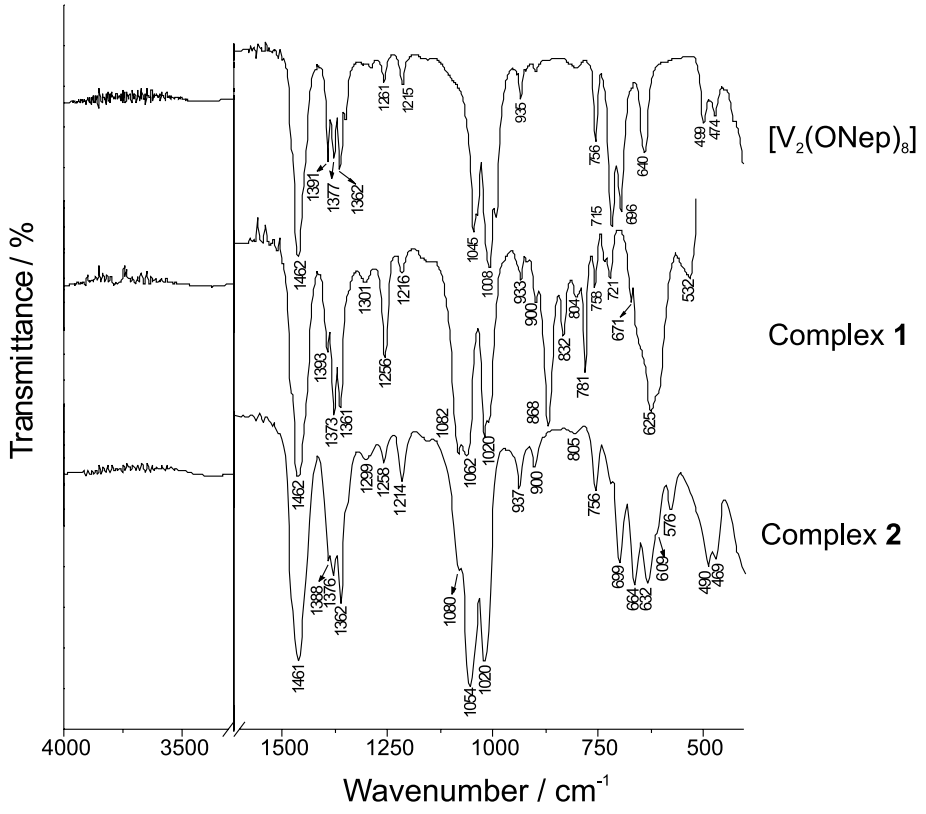

Figure S2. FTIR spectra (Nujol mull) of the $[V_2(\mu\text{-ONep})_2(ONep)_6]$ starting material and of the heterometal alkoxides **1** and **2**.

Table S1. Molecular dimensions for $[V_6Li_{10}O_8(ONep)_{14}\{OSi(Me)_2(ONep)\}_2]\cdot C_6H_{14}$ (**1**). Bond lengths are in Ångstroms, angles in degrees. Standard deviations are in parentheses

(a) About the vanadium atoms			
V(1)...V(2)	2.8430(13)	V(2)...V(3)	2.8998(13)
V(1)...V(3)	2.9075(13)	Li(1)...V(3)	2.896(10)
V(1)...Li(1)	2.850(10)	Li(2)...V(3)	2.991(10)
V(1)...Li(4)	2.739(9)	Li(3)...V(3)	2.875(9)
Li(2)...V(2)	2.847(11)	Li(4)...V(3')	3.020(9)
Li(5)...V(2)	2.761(9)	Li(5)...V(3')	3.055(9)
O(13)-V(2)-O(15)	84.51(15)	O(23)-V(2)-O(21)	104.97(16)
O(13)-V(2)-O(21)	88.22(16)	O(22)-V(2)-O(15)	81.86(15)
O(13)-V(2)-O(22)	130.31(15)	O(23)-V(2)-O(15)	89.36(15)
O(23)-V(2)-O(13)	109.32(15)	O(21)-V(2)-O(22)	93.37(15)
O(21)-V(2)-O(15)	165.44(14)	O(23)-V(2)-O(22)	118.02(16)
(b) About the lithium atoms			
Li(1)...Li(2)	2.569(15)	Li(2)...Li(3)	2.797(15)
Li(1)...Li(3)	2.682(13)	Li(4)-O(11)	1.902(10)
Li(2)-O(15)	1.931(11)	Li(4)-O(13)	2.034(10)
Li(2)-O(22)	1.940(12)	Li(4)-O(23')	1.993(9)
Li(2)-O(33)	2.418(11)	Li(4)-O(32')	2.056(10)
Li(2)-O(44)	1.899(12)	Li(4)...Li(5)	2.628(13)
O(15)-Li(2)-O(22)	83.4(5)	O(11)-Li(4)-O(13)	83.3(4)
O(15)-Li(2)-O(33)	80.0(4)	O(11)-Li(4)-O(23')	113.6(5)
O(44)-Li(2)-O(15)	98.6(5)	O(11)-Li(4)-O(32')	156.3(5)
O(22)-Li(2)-O(33)	112.8(5)	O(23')-Li(4)-O(13)	122.8(4)
O(44)-Li(2)-O(22)	158.0(6)	O(13)-Li(4)-O(32')	97.4(4)
O(44)-Li(2)-O(33)	89.0(4)	O(23')-Li(4)-O(32')	86.1(4)
(c) In the ligands			
Si(4)-C(42)	1.843(6)	Si(4)-C(43)	1.866(6)
Li(4)-O(11)-V(1)	91.6(3)	V(3)-O(33)-Li(2)	86.0(3)
Li(1)-O(12)-V(1)	96.6(3)	Li(3)-O(33)-V(3)	96.5(3)
V(1)-O(14)-V(3)	97.09(15)	Li(3)-O(33)-Li(2)	79.4(4)
V(1)-O(14)-Li(5')	150.6(3)	O(41)-Si(4)-C(42)	109.1(2)
Li(5')-O(14)-V(3)	93.5(3)	O(41)-Si(4)-C(43)	108.8(3)
V(2)-O(21)-Li(5)	92.8(3)	O(44)-Si(4)-O(41)	101.35(19)
V(2)-O(22)-Li(2)	94.9(3)	C(42)-Si(4)-C(43)	107.7(3)
V(2)-O(23)-V(3)	97.66(15)	O(44)-Si(4)-C(42)	114.8(2)
V(2)-O(23)-Li(4')	146.0(3)	O(44)-Si(4)-C(43)	114.8(3)
Li(4')-O(23)-V(3)	93.5(3)	Li(2)-O(44)-Li(1)	83.8(5)
V(3)-O(31)-Li(1)	89.3(3)	Li(1)-O(44)-Li(3)	84.6(4)
Li(3)-O(31)-V(3)	94.3(3)	Si(4)-O(41)-Li(3)	88.7(3)
Li(3)-O(31)-Li(1)	82.0(4)	Si(4)-O(44)-Li(1)	133.7(4)
V(3)-O(32)-Li(4')	96.3(3)	Li(2)-O(44)-Li(3)	90.6(4)
V(3)-O(32)-Li(5')	99.3(3)	Si(4)-O(44)-Li(2)	142.3(4)
Li(5')-O(32)-Li(4')	80.5(4)	Si(4)-O(44)-Li(3)	96.1(3)

Symmetry transformations used to generate equivalent atoms: ' : 1-x, 1-y, 1-z

Table S2. Selected molecular dimensions for one of the two independent [$V(ONep)_3(\mu\text{-}ONep)_2Li(thf)_2$] molecules in the crystals of complex **2**. Bond lengths are in Ångstroms, angles in degrees. Standard deviations are in parentheses

Bond lengths involving the vanadium and lithium atoms			
V(4)-O(41)	1.932(3)	V(4)-O(44)	1.810(8)
V(4)-O(42)	1.863(3)	V(4)-O(45)	1.70(2)
V(4)-O(43)	1.863(3)	V(4)...Li(4)	2.882(9)
Li(4)-O(41)	1.900(9)	Li(4)-O(46)	1.962(10)
Li(4)-O(43)	1.935(9)	Li(4)-O(47)	1.965(10)
Bond angles about the vanadium and lithium atoms			
O(42)-V(4)-O(41)	170.77(16)	O(44)-V(4)-O(42)	95.7(2)
O(43)-V(4)-O(41)	82.10(14)	O(45)-V(4)-O(42)	87.5(5)
O(44)-V(4)-O(41)	83.6(3)	O(44)-V(4)-O(43)	108.9(4)
O(45)-V(4)-O(41)	100.6(5)	O(45)-V(4)-O(43)	128.3(5)
O(42)-V(4)-O(43)	89.46(14)	O(45)-V(4)-O(44)	122.7(6)
O(41)-Li(4)-O(43)	81.1(4)	O(43)-Li(4)-O(47)	111.2(5)
O(41)-Li(4)-O(46)	111.0(5)	O(46)-Li(4)-O(47)	105.6(4)
O(41)-Li(4)-O(47)	124.6(5)	Li(4)-O(41)-V(4)	97.5(3)
O(43)-Li(4)-O(46)	123.3(5)	V(4)-O(43)-Li(4)	98.7(3)

*Additional notes on the solid state structure of [$V(ONep)_3(\mu\text{-}ONep)_2Li(thf)_2$]·NepOH (Complex **2**)*

There are two independent V-Li complex molecules and two solvent (neopentanol) molecules in the crystal. One of the complex molecules shows disorder in three of its ligands, *viz* the NpO ligands of O(44) and O(45), and the thf ligand of O(46); these have all been resolved. In the thf ligand, one methylene group is disordered over two sites, giving alternative 'flaps' to the envelope conformations of this ligand. There are two distinct arrangements of the ligand of O(44), shown coordinated to V(4) through O(44) and O(44A); the central carbon atom of each, C(442) and C(44B), is common to both orientations and has been refined with coordinates and thermal parameters tied for the two atoms. The ONp ligand of O(45) is similar except that three orientations have been resolved for this ligand; the central atoms of all three, C(452), C(45B) and C(45Z), share common coordinates and thermal parameters; the O atoms, O(45A) and O(45X), of two of the ligands also share sites, and the methyl group carbon atoms C(455) and C(45D), of the ligands of O(45) and O(45A), are shared by the third ligand, of O(45X).

No hydroxyl hydrogen atoms have been located on any of the ONep ligands or discrete solvent molecules/anions. Considering vanadium(IV) and Li^+ in the complexes, to balance charges, the separate small ONep units must be neopentanol molecules, with hydroxyl H atoms that cannot be seen at the present resolution level. Assuming that the discrete molecules are NepOH, there are suitable acceptor groups for hydrogen bond formation between O(18)-H and O(15), and between O(48)-H and either O(44A) or O(45); the O···O distances are 2.844, 2.986 and 3.007 Å respectively, and the corresponding C-O···O angles are 104.6, 109.2 and 86.0 ° (Figure S1). The oxidation state +IV of the transition metal in **2** is further supported by the EPR studies described in the manuscript.