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Supporting information

Expansion of Sodalite-Type Metal-Organic Frameworks with Heterometallic Metal-Oxo Cluster and Its Cation Exchange Property

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1. Materials and Methods

All reagents were purchased commercially and used without further purification. Elemental analyses (C, H and N) were performed on a Perkin–Elmer 2400 CHN elemental analyzer and (V, Na, Cu) PLASMA – SPEC (I) ICP atomicemission spectrometer. The IR spectra were obtained on an Alpha Centaurt FTIR spectrometer in the 400–4000cm^{-1} region with a KBr pellet. The TGA were performed on a Perkin – Elmer TGA7 instrument with a heating rate of 10 °C min^{-1}. UV-Vis absorption spectra were obtained using a VARIAN Cary 500 scan UV-Vis NIR spectrophotometer. The PXPD were recorded on a Rigaku D/Max-2500 diffractometer. XPS were recorded on a Thermo ESCALAB 250 spectrometer with an AlKα (1486.6 eV) achromatic X-ray source.

2. Synthesis

Synthesis of **1**: The mixture of NH_4VO_3 (0.20 mmol, 0.046 g), 1,3,5 – H_3BTC (0.60 mmol, 0.12 g), Na_2CO_3 (0.20 mmol, 0.04 g) TMA (0.20 mL), ethanol (3ml) and DMF (3.0 mL) was sealed in a Teflon – lined autoclave and heated at 160 °C for 5 days, followed by slow cooling to room temperature with a cooling rate of 2 °C h^{-1}. After being washed with DMF several times, the crystals of **1** were collected as dark blue block crystals with a yield of about 46% (based on V). Elem Anal calcd: V, 11.01%; Na, 4.96 %; C, 42.83 %; H, 3.81 %; N, 4.54 %. Found: V, 11.17 %; Na, 4.79 %: C, 42.94 %; H, 3.69 %; N, 4.66 %.

Synthesis of **2**: The mixture of NH_4VO_3 (0.20 mmol, 0.046 g), 1,3,5 – H_3BTC (0.80 mmol, 0.16 g), Li_2CO_3 (0.20 mmol, 0.014 g), TMAOH (0.20 ml), MeOH (1ml) and DMF (6 mL) was sealed in a Teflon – lined autoclave and heated at 160 °C for 5 days,

followed by slow cooling to room temperature with a cooling rate of 2 °Ch^{-1}. After being washing with DMF several times, the crystals of **2** were collected as blue block crystals with a yield of about 65 % (based on V). Elem Anal calcd: V, 7.16 %; Li, 0.97 %; C, 50.71%; H, 5.95 %; N, 5.91 %. Found: V, 7.02 %; Li, 0.84 %; C, 50.83 %; H, 5.89 %; N, 6.12 %.

3. X-Ray crystallography study

The crystallographic data of **1** and **2** were performed on a Rigaku R-AXIS RAPID IP diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation (λ = 0.71073 Å). The crystal data were solved by the direct method and refined by the full–matrix least–squares method on F^2, using the SHELXTL–97 crystallographic software package.[1] All non – hydrogen atoms were refined anisotropically. In the refinement, the restraint command 'isor' was employed to restrain the oxygen atoms so as to avoid the ADP and NPD problems on them. This command leads to the restraint number 12 for the compound **2**. In compound **1**, it was difficult to locate and resolve guest molecules as the crystal was comprised of highly disordered solvent, thus the SQUEEZE routine of PLATON was applied to remove the contributions to the scattering from the solvent molecules. The reported refinements are of the guest-free structures using the *.hkl files produced using the SQUEEZE routine.[2]

_platon_squeeze_void_nr

_platon_squeeze_void_average_x

_platon_squeeze_void_average_y

_platon_squeeze_void_average_z

_platon_squeeze_void_volume

_platon_squeeze_void_count_electrons

1	0.000	0.000	0.000	636.4	14.4
2	-0.010	0.485	-0.012	3234.6	73.1
3	0.333	0.667	0.667	637.2	14.5
4	0.667	0.333	0.333	637.1	14.5

_platon_squeeze_details

1 G. M. Sheldrick, *SHELXL97*, Program for Crystal Structure Refinement, University of Göttingen: Göttingen, Germany, 1997.

2 (a) A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7; (b) A. C. Sudik, A. R. Millward, N. W. Ockwig, A. P. Côté, J. Kim, O. M. Yaghi, *J. Am. Chem. Soc.*, 2005, **127**, 7110.

4. General Process of Cation Exchange Experiments.

100mg crystals of compounds **1** and **2** were soaked in 0.5mL, 0.1mol/L $CuCl_2$ acetone solution for 24 h, and enclosing the glass container (solution A). The blank experiment (with only 0.1mol/L $CuCl_2$ acetone solution) was taken up in another same glass container for 24 h (solution B). 24 h later, compare the colour of the two solution, and take the UV spectrum of the two solution. The cyrstals after cation exchange was washed with acetone for times, and taken up the PXRD, XPS and ICP-AES test. The PXRD data was compared with the data before cation exchange and cyrstal data simulative PXRD, and it shows that the main structure of the compound being cation exchange before and after was not changed.

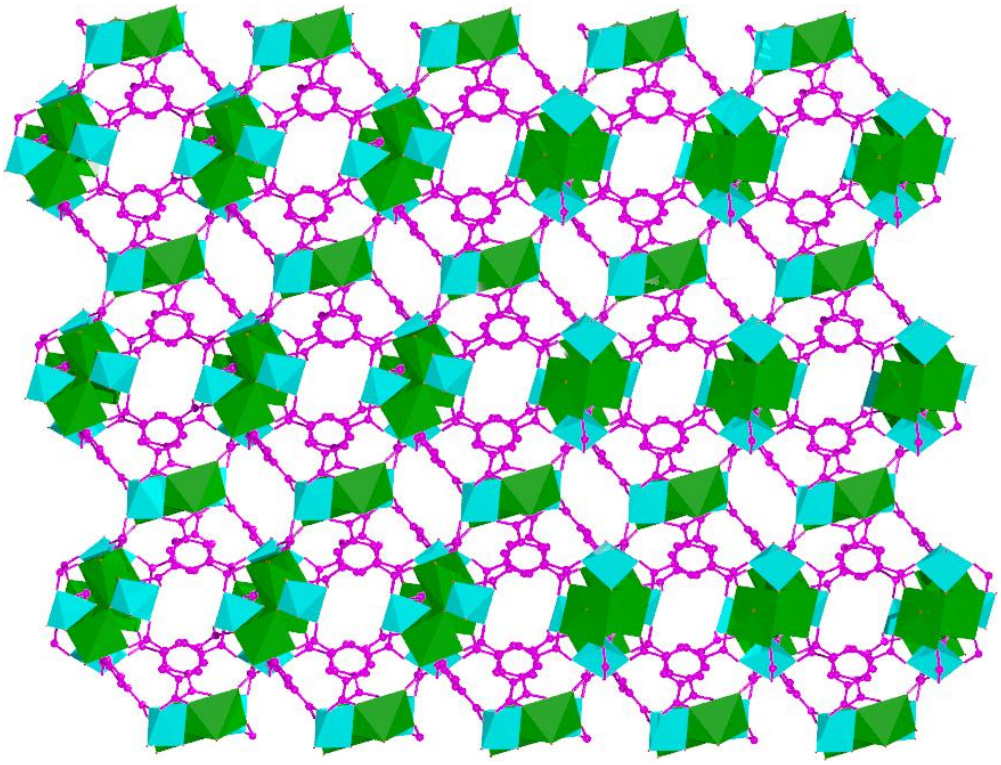


Fig. S1 Ball-and-stick and polyhedron view of the 3D framework of **1**. (blue octahedron, {VO_6}; green octahedron, {NaO_6}; red ball, O atom; pink ball, C atom.)

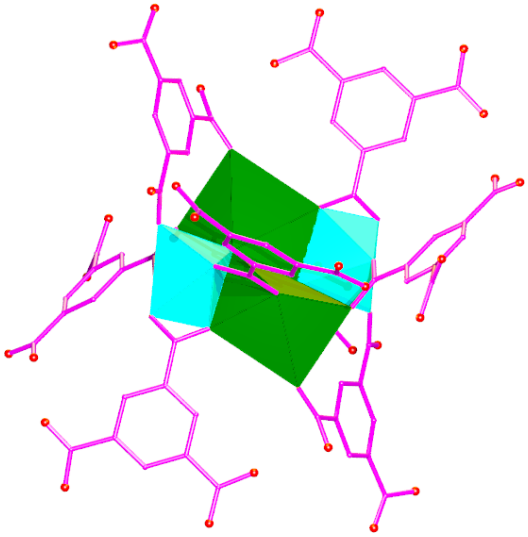


Fig. S2 Ball-and-stick and polyhedron view of the structural unit of **1**. (blue octahedron, {VO_6}; green octahedron, {NaO_6}; red ball, O atom; pink ball, C atom.)

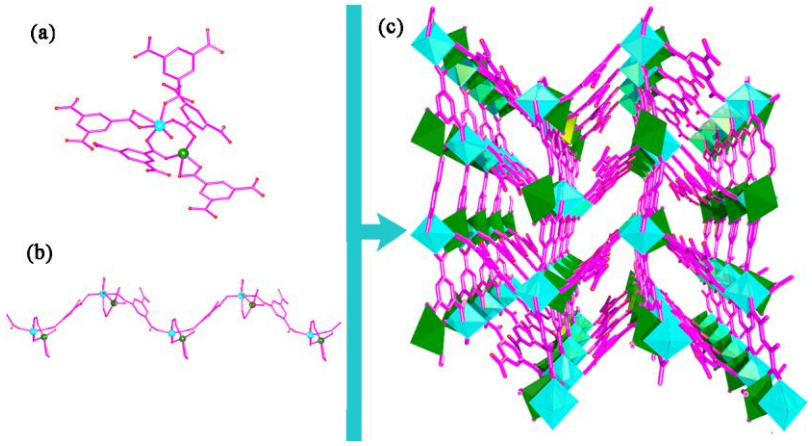


Fig. S3 (a) View of the connectivity patterns in **2**; (b) ball-and-stick view of the sinusoidal-chain in **2**; (c) view of the 3D framework of **2**. Color codes:blue octahedron, {VO_6}; green octahedron, {NaO_6}; red ball, O atom; pink ball, C atom.

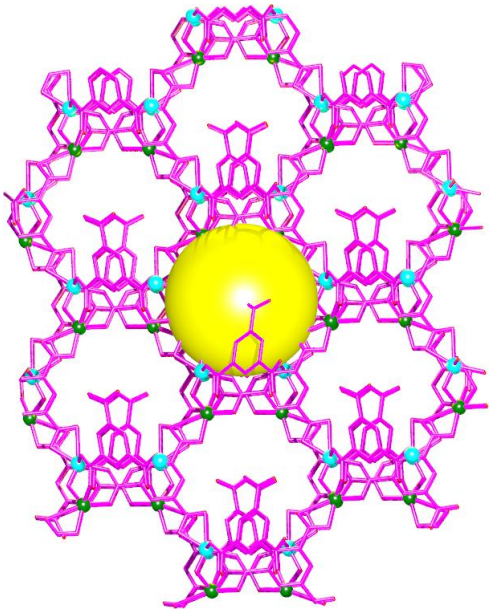


Fig. S4 Ball-and-stick view of the 3D framework of **2**. (blue ball, V atom; green ball, Na atom; red ball, O atom; pink ball, C atom.)

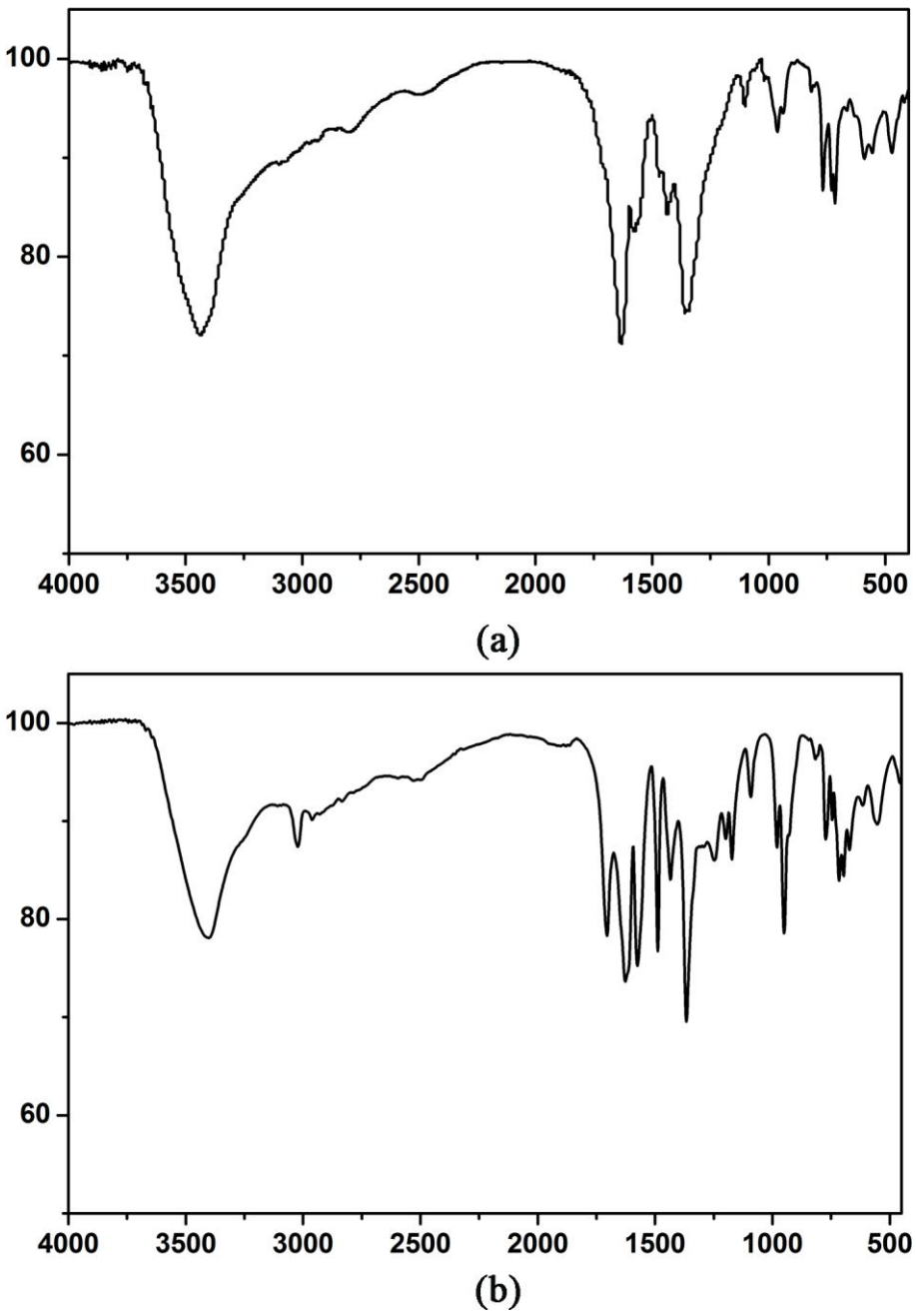


Fig. S5 IR spectra of (a) compound **1** and (b) **2.**

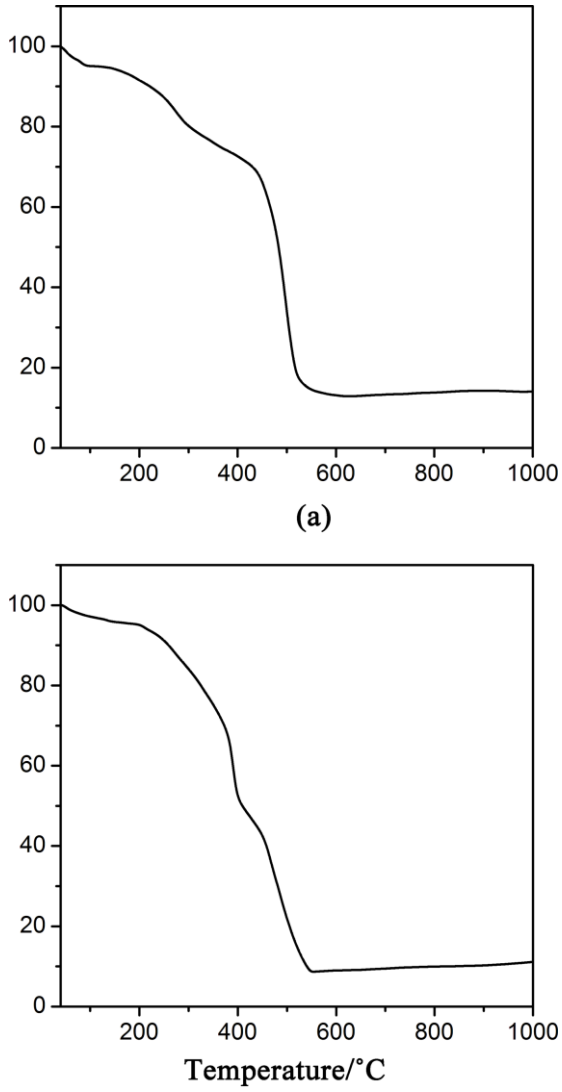


Fig. S6 TG curve of (a) compounds **1** and (b) **2**. The TG curve of **1** displays two continuous weight loss processes. The weight loss 85.2 % in total (calcd: 81.4 %) is attributed to the loss of DMF molecules, TMA molecules and BTC ligands. The TG curve of **2** shows three weight loss stages occurring at 200 – 350, 360 – 400 and 420 – 550 ˚C, respectively. The weight loss 91.1% in total (calcd: 90.1 %) is attributed to the loss of Tetramethylammonium cations and BTC ligands.

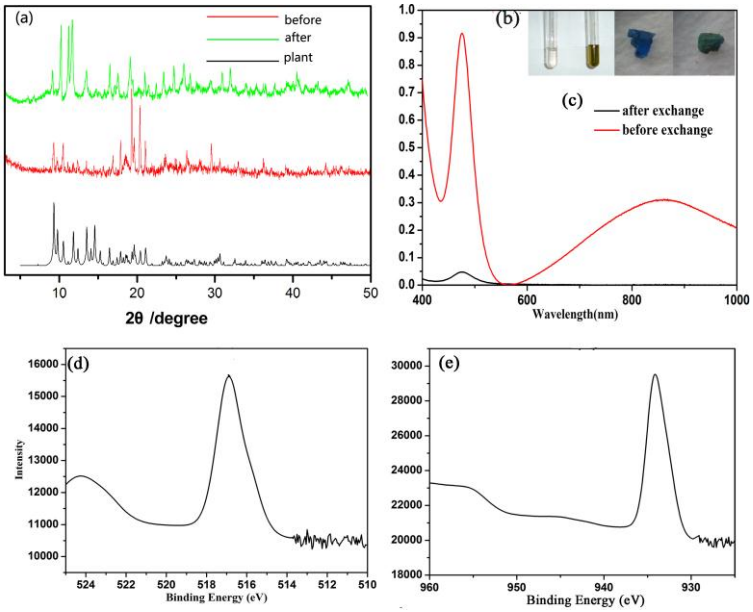
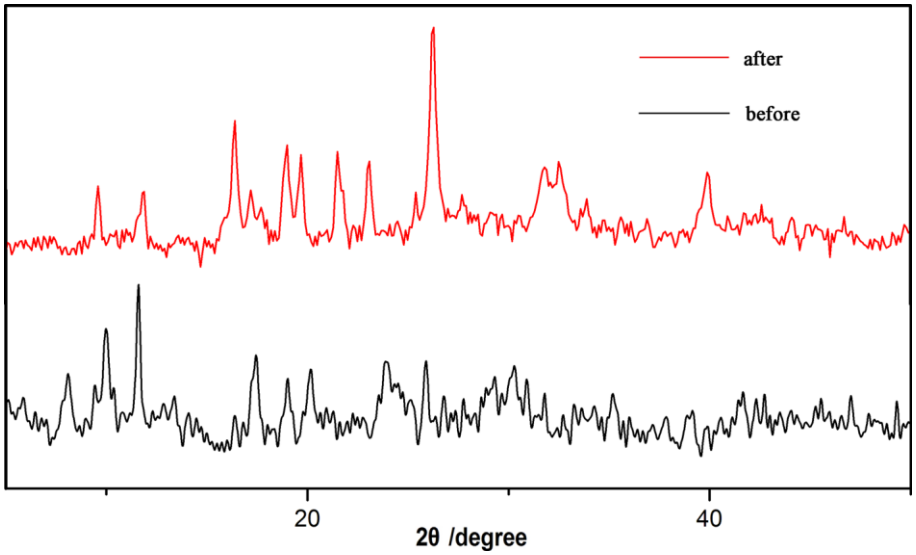
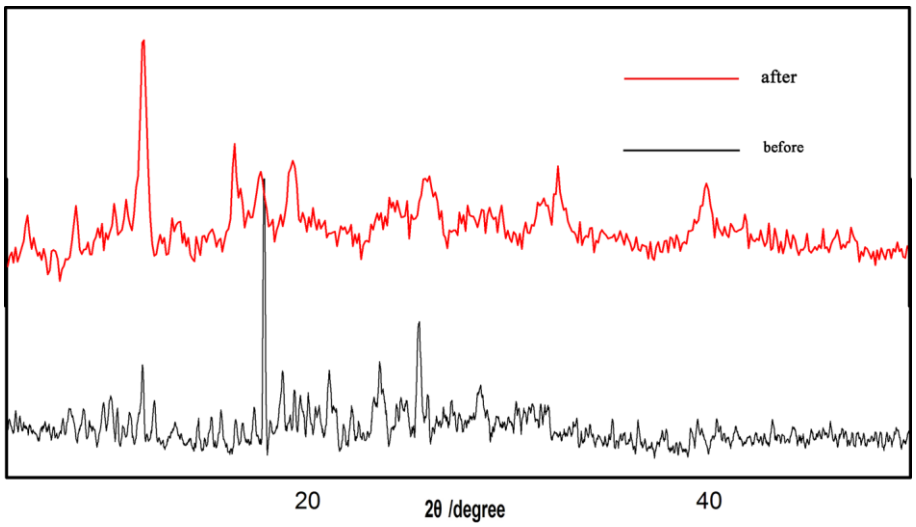


Fig. S7 (a) The PXRD patterns of compound **2**; (b) the comparison of the solution before and after cation exchange and the visual observation of Cu^{II} uptake into single crystals of **2**; (c) UV spectra of the solution before and after cation exchange; (d) XPS of V(IV) in **2** after cation exchange; (e) XPS of Cu (II) in **2** after cation exchange.



(a)



(b)

Fig. S8 The PXRD patterns after and before adsorption of (a) compound **1** and (b) compound **2.**

Table S1. Selected bond lengths (Å) for compound **1**.

V(1)-O(5)	1.5988(14)	V(1)-O(3)	1.9385(14)
V(1)-O(6)#1	1.9836(14)	V(1)-O(8)#2	2.0048(14)
V(1)-O(2)	2.0808(14)	V(1)-O(4)	2.2836(14)
V(1)-C(2)	2.527(2)	V(1)-Na(1)#3	3.4097(10)
Na(1)-O(7)#4	2.3044(17)	Na(1)-O(9)#2	2.3082(18)
Na(1)-O(1)#5	2.3433(17)	Na(1)-O(2)#3	2.4678(16)
Na(1)-O(5)	2.5674(17)	Na(1)-O(5)#3	2.8131(17)
Na(1)-V(1)#3	3.4097(10)	C(1)-C(5)	1.386(3)
C(1)-C(4)	1.387(3)	C(2)-O(4)	1.247(2)
C(2)-O(2)	1.278(2)	C(2)-C(5)	1.488(3)
C(3)-C(4)	1.391(3)	C(3)-C(11)	1.393(3)
C(4)-C(12)	1.500(3)	C(5)-C(10)	1.387(3)
C(6)-O(1)	1.227(2)	C(6)-O(3)	1.290(2)
C(6)-C(8)	1.506(3)	C(7)-C(8)#5	1.379(3)
C(7)-C(8)	1.393(3)	C(8)-C(7)#6	1.379(3)
C(9)-O(7)	1.231(2)	C(9)-O(6)	1.278(2)
C(9)-C(11)	1.497(3)	C(10)-C(11)	1.390(3)
C(12)-O(9)	1.225(2)	C(12)-O(8)	1.280(2)
O(1)-Na(1)#6	2.3433(17)	O(2)-Na(1)#3	2.4678(16)
O(5)-Na(1)#3	2.8131(17)	O(6)-V(1)#7	1.9837(14)
O(7)-Na(1)#8	2.3044(17)	O(8)-V(1)#9	2.0048(14)
O(9)-Na(1)#9	2.3082(18)		

Table S2. Selected bond angles (°) for compound **1**.

O(5)-V(1)-O(3)	110.70(7)	O(5)-V(1)-O(6)#1	99.67(7)
O(3)-V(1)-O(6)#1	85.02(6)	O(5)-V(1)-O(8)#2	100.41(7)
O(3)-V(1)-O(8)#2	87.29(6)	O(6)#1-V(1)-O(8)#2	159.92(6)
O(5)-V(1)-O(2)	96.21(6)	O(3)-V(1)-O(2)	153.09(6)
O(6)#1-V(1)-O(2)	90.61(6)	O(8)#2-V(1)-O(2)	87.89(6)
O(5)-V(1)-O(4)	155.71(6)	O(3)-V(1)-O(4)	93.44(5)
O(6)#1-V(1)-O(4)	84.55(6)	O(8)#2-V(1)-O(4)	77.41(6)
O(2)-V(1)-O(4)	59.68(5)	O(5)-V(1)-C(2)	126.25(7)
O(3)-V(1)-C(2)	122.93(6)	O(6)#1-V(1)-C(2)	88.79(6)
O(8)#2-V(1)-C(2)	79.89(6)	O(2)-V(1)-C(2)	30.26(6)
O(4)-V(1)-C(2)	29.50(6)	O(5)-V(1)-Na(1)#3	54.90(5)
O(3)-V(1)-Na(1)#3	156.33(5)	O(6)#1-V(1)-Na(1)#3	79.91(4)
O(8)#2-V(1)-Na(1)#3	112.57(5)	O(2)-V(1)-Na(1)#3	45.95(4)
O(4)-V(1)-Na(1)#3	103.10(4)	C(2)-V(1)-Na(1)#3	75.14(5)
O(7)#4-Na(1)-O(9)#2	92.63(7)	O(7)#4-Na(1)-O(1)#5	110.85(7)
O(9)#2-Na(1)-O(1)#5	86.65(6)	O(7)#4-Na(1)-O(2)#3	82.77(6)
O(9)#2-Na(1)-O(2)#3	175.39(6)	O(1)#5-Na(1)-O(2)#3	95.10(6)
O(7)#4-Na(1)-O(5)	132.75(7)	O(9)#2-Na(1)-O(5)	74.66(5)

O(1)#5-Na(1)-O(5)	113.48(6)	O(2)#3-Na(1)-O(5)	108.40(6)
O(7)#4-Na(1)-O(5)#3	76.65(6)	O(9)#2-Na(1)-O(5)#3	116.31(6)
O(1)#5-Na(1)-O(5)#3	156.04(6)	O(2)#3-Na(1)-O(5)#3	62.56(5)
O(5)-Na(1)-O(5)#3	69.60(5)	O(7)#4-Na(1)-V(1)#3	68.30(5)
O(9)#2-Na(1)-V(1)#3	140.33(5)	O(1)#5-Na(1)-V(1)#3	132.13(5)
O(2)#3-Na(1)-V(1)#3	37.30(3)	O(5)-Na(1)-V(1)#3	92.79(4)
O(5)#3-Na(1)-V(1)#3	27.71(3)	C(5)-C(1)-C(4)	120.99(19)
O(4)-C(2)-O(2)	119.27(18)	O(4)-C(2)-C(5)	120.61(18)
O(2)-C(2)-C(5)	120.08(18)	O(4)-C(2)-V(1)	64.36(10)
O(2)-C(2)-V(1)	55.15(9)	C(5)-C(2)-V(1)	171.65(15)
C(4)-C(3)-C(11)	120.78(19)	C(1)-C(4)-C(3)	118.78(19)
C(1)-C(4)-C(12)	119.15(18)	C(3)-C(4)-C(12)	122.05(18)
C(1)-C(5)-C(10)	119.73(18)	C(1)-C(5)-C(2)	119.22(18)
C(10)-C(5)-C(2)	121.04(18)	O(1)-C(6)-O(3)	124.58(18)
O(1)-C(6)-C(8)	120.38(18)	O(3)-C(6)-C(8)	114.93(17)
C(8)#5-C(7)-C(8)	120.72(19)	C(7)#6-C(8)-C(7)	119.28(19)
C(7)#6-C(8)-C(6)	119.90(17)	C(7)-C(8)-C(6)	120.63(18)
O(7)-C(9)-O(6)	125.53(19)	O(7)-C(9)-C(11)	120.05(18)
O(6)-C(9)-C(11)	114.41(18)	C(5)-C(10)-C(11)	120.08(19)
C(10)-C(11)-C(3)	119.48(18)	C(10)-C(11)-C(9)	120.60(18)
C(3)-C(11)-C(9)	119.90(18)	O(9)-C(12)-O(8)	125.6(2)
O(9)-C(12)-C(4)	119.27(19)	O(8)-C(12)-C(4)	115.13(17)
C(6)-O(1)-Na(1)#6	151.66(14)	C(2)-O(2)-V(1)	94.59(11)
C(2)-O(2)-Na(1)#3	158.62(13)	V(1)-O(2)-Na(1)#3	96.75(5)
C(6)-O(3)-V(1	141.02(13)	C(2)-O(4)-V(1)	86.14(12)
V(1)-O(5)-Na(1)	135.82(8)	V(1)-O(5)-Na(1)#3	97.38(6)
Na(1)-O(5)-Na(1)#3	110.40(5)	C(9)-O(6)-V(1)#7	130.94(13)
C(9)-O(7)-Na(1)#8	134.15(14)	C(12)-O(8)-V(1)#9	128.73(13)
C(12)-O(9)-Na(1)#9	137.11(16)		

Table S3. Selected bond lengths (Å) for compound **2**.

V(1)-O(3)	1.600(3)	V(1)-O(5)	1.967(3)
V(1)-O(4)#2	1.996(3)	V(1)-O(11)#1	1.996(3)
V(1)-O(2)	2.089(3)	V(1)-O(1)	2.404(3)
V(1)-C(1)	2.574(5)	V(1)-Li(1)	3.043(8)
Li(1)-O(6)#3	1.904(8)	Li(1)-O(10)#1	1.965(9)
Li(1)-O(9)#2	1.976(9)	Li(1)-O(3)	2.075(9)
Li(1)-C(8)#3	2.553(9)	Li(1)-O(7)#3	2.661(9)
Li(1)-C(18)#2	2.769(10)	O(1)-C(1)	1.238(5)
O(2)-C(1)	1.273(5)	O(4)-C(18)	1.285(5)
O(4)-V(1)#4	1.996(3)	O(5)-C(13)	1.290(5)
O(6)-C(8)	1.256(6)	O(6)-Li(1)#5	1.904(8)
O(7)-C(8)	1.231(6)	O(7)-Li(1)#5	2.661(9)
O(8)-C(13)	1.224(5)	O(9)-C(18)	1.240(5)

O(9)-Li(1)#4	1.976(9)	O(10)-C(11)	1.242(5)
O(10)-Li(1)#6	1.965(9)	O(11)-C(11)	1.272(5)
O(11)-V(1)#6	1.996(3)	O(12)-C(21)	1.240(7)
O(13)-C(21)	1.230(6)	C(1)-C(2)	1.514(6)
C(2)-C(7)	1.379(6)	C(2)-C(3)	1.397(6)
C(3)-C(4)	1.398(6)	C(25)-N(3)	1.471(7)
C(4)-C(5)	1.385(6)	C(4)-C(8)	1.518(6)
C(5)-C(6)	1.391(6)	C(9)-C(20)	1.391(6)
C(6)-C(7)	1.394(6)	C(6)-C(18)	1.497(6)
C(12)-C(29)	1.379(6)	C(8)-Li(1)#5	2.553(9)
C(14)-N(2)	1.462(8)	C(9)-C(19)	1.397(6)
C(15)-N(1)	1.462(9)	C(10)-N(1)	1.493(8)
C(16)-N(2)	1.489(9)	C(11)-C(29)	1.506(6)
C(18)-Li(1)#4	2.769(10)	C(12)-C(20)	1.395(6)
C(17)-N(2)	1.502(8)	C(13)-C(20)	1.512(6)
C(19)-C(21)	1.534(6)	C(19)-C(30)	1.392(6)
C(28)-N(2)	1.452(8)	C(22)-N(1)	1.425(10)
C(26)-N(3)	1.505(6)	C(23)-N(1)	1.439(9)
C(27)-N(3)	1.472(7)	C(24)-N(3)	1.486(6)
C(29)-C(30)	1.401(6)		

Table S4. Selected bond angles (°) for compound **2**.

O(3)-V(1)-O(5)	104.30(14)	O(3)-V(1)-O(4)#1	103.18(14)
O(5)-V(1)-O(4)#1	86.52(13)	O(3)-V(1)-O(11)#2	104.03(15)
O(5)-V(1)-O(11)#2	151.56(13)	O(4)#1-V(1)-O(11)#2	84.72(14)
O(3)-V(1)-O(2)	95.75(14)	O(5)-V(1)-O(2)	92.83(12)
O(4)#2-V(1)-O(2)	160.63(12)	O(11)#1-V(1)-O(2)	86.75(12)
O(3)-V(1)-O(1)	153.30(14)	O(5)-V(1)-O(1)	79.56(12)
O(4)#2-V(1)-O(1)	103.43(12)	O(11)#1-V(1)-O(1)	76.28(13)
O(2)-V(1)-O(1)	57.54(12)	O(3)-V(1)-C(1)	124.86(15)
O(5)-V(1)-C(1)	89.04(13)	O(4)#2-V(1)-C(1)	131.25(13)
O(11)#1-V(1)-C(1)	76.77(13)	O(2)-V(1)-C(1)	29.41(12)
O(1)-V(1)-C(1)	28.53(12)	O(3)-V(1)-Li(1)	39.48(19)
O(5)-V(1)-Li(1)	125.80(19)	O(4)#2-V(1)-Li(1)	72.67(19)
O(11)#1-V(1)-Li(1)	76.83(19)	O(2)-V(1)-Li(1)	122.06(19)
O(1)-V(1)-Li(1)	153.07(19)	C(1)-V(1)-Li(1)	141.7(2)
O(6)#3-Li(1)-O(10)#1	129.4(5)	O(6)#3-Li(1)-O(9)#2	105.4(4)
O(10)#2-Li(1)-O(9)#2	95.6(4)	O(6)#3-Li(1)-O(3)	120.2(4)
O(10)#1-Li(1)-O(3)	102.0(4)	O(9)#2-Li(1)-O(3)	96.3(4)
O(6)#3-Li(1)-C(8)#3	28.23(19)	O(10)#1-Li(1)-C(8)#3	123.2(4)
O(9)#2-Li(1)-C(8)#3	131.7(4)	O(3)-Li(1)-C(8)#3	101.7(4)
O(6)#3-Li(1)-O(7)#3	55.1(2)	O(10)#1-Li(1)-O(7)#3	105.4(4)
O(9)#2-Li(1)-O(7)#3	157.7(4)	O(3)-Li(1)-O(7)#3	86.9(3)
C(8)#3-Li(1)-O(7)#3	27.20(16)	O(6)#3-Li(1)-C(18)#2	128.9(4)

O(10)#1-Li(1)-C(18)#2	78.8(3)	O(9)#2-Li(1)-C(18)#2	23.53(16)
O(3)-Li(1)-C(18)#2	83.8(3)	C(8)#3-Li(1)-C(18)#2	154.6(4)
O(7)#3-Li(1)-C(18)#2	170.4(4)	O(6)#3-Li(1)-V(1)	149.1(4)
O(10)#1-Li(1)-V(1)	78.5(3)	O(9)#2-Li(1)-V(1)	81.3(3)
O(3)-Li(1)-V(1)	29.35(14)	C(8)#3-Li(1)-V(1)	129.9(4)
O(7)#3-Li(1)-V(1)	109.9(3)	C(18)#2-Li(1)-V(1)	62.04(19)
C(1)-O(1)-V(1)	83.4(3)	C(1)-O(2)-V(1)	96.9(3)
V(1)-O(3)-Li(1)	111.2(3)	C(18)-O(4)-V(1)#4	131.4(3)
C(13)-O(5)-V(1)	125.5(3)	C(8)-O(6)-Li(1)#5	106.0(4)
C(8)-O(7)-Li(1)#5	71.5(3)	C(18)-O(9)-Li(1)#4	116.9(4)
C(11)-O(10)-Li(1)#6	128.3(4)	C(11)-O(11)-V(1)#6	125.6(3)
O(1)-C(1)-O(2)	120.5(4)	O(1)-C(1)-C(2)	120.8(4)
O(2)-C(1)-C(2)	118.7(4)	O(1)-C(1)-V(1)	68.1(3)
O(2)-C(1)-V(1)	53.7(2)	C(2)-C(1)-V(1)	164.2(3)
C(7)-C(2)-C(3)	119.7(4)	C(7)-C(2)-C(1)	123.1(4)
C(3)-C(2)-C(1)	117.1(4)	C(4)-C(3)-C(2)	120.2(4)
C(5)-C(4)-C(3)	119.0(4)	C(19)-C(30)-C(29)	120.6(4)
C(3)-C(4)-C(8)	120.0(4)	C(5)-C(4)-C(8)	120.9(4)
C(5)-C(6)-C(7)	118.8(4)	C(4)-C(5)-C(6)	121.4(4)
C(7)-C(6)-C(18)	120.4(4)	C(5)-C(6)-C(18)	120.8(4)
O(7)-C(8)-O(6)	125.8(5)	C(2)-C(7)-C(6)	120.9(4)
O(6)-C(8)-C(4)	116.9(4)	O(7)-C(8)-C(4)	117.3(4)
O(6)-C(8)-Li(1)#5	45.8(3)	O(7)-C(8)-Li(1)#5	81.3(4)
C(20)-C(9)-C(19)	120.0(4)	C(4)-C(8)-Li(1)#5	159.1(4)
O(12)-C(21)-C(19)	116.6(5)	O(8)-C(13)-O(5)	124.8(4)
O(10)-C(11)-C(29)	118.5(4)	O(10)-C(11)-O(11)	124.3(4)
C(29)-C(12)-C(20)	120.8(4)	O(11)-C(11)-C(29)	117.2(4)
O(8)-C(13)-C(20)	119.7(4)	C(12)-C(29)-C(30)	119.3(4)
O(9)-C(18)-O(4)	125.6(4)	O(5)-C(13)-C(20)	115.4(4)
O(4)-C(18)-C(6)	115.5(4)	O(9)-C(18)-C(6)	118.9(4)
O(4)-C(18)-Li(1)#4	92.5(3)	O(9)-C(18)-Li(1)#4	39.5(3)
C(30)-C(19)-C(9)	119.5(4)	C(6)-C(18)-Li(1)#4	143.6(4)
C(9)-C(19)-C(21)	120.6(4)	C(30)-C(19)-C(21)	119.9(4)
C(9)-C(20)-C(13)	121.4(4)	C(9)-C(20)-C(12)	119.9(4)
O(13)-C(21)-O(12)	125.6(5)	C(12)-C(20)-C(13)	118.7(4)
C(12)-C(29)-C(11)	120.0(4)	O(13)-C(21)-C(19)	117.8(5)
C(27)-N(3)-C(26)	110.5(5)	C(30)-C(29)-C(11)	120.8(4)
C(24)-N(3)-C(26)	108.0(5)	C(25)-N(3)-C(26)	108.8(5)
C(22)-N(1)-C(15)	112.3(6)	C(22)-N(1)-C(23)	106.1(8)
C(22)-N(1)-C(10)	112.4(6)	C(23)-N(1)-C(15)	105.8(7)
C(15)-N(1)-C(10)	111.4(6)	C(23)-N(1)-C(10)	108.3(6)
C(28)-N(2)-C(16)	109.3(7)	C(28)-N(2)-C(14)	110.5(7)
C(28)-N(2)-C(17)	108.6(6)	C(14)-N(2)-C(16)	109.2(6)
C(16)-N(2)-C(17)	110.8(6)	C(14)-N(2)-C(17)	108.5(5)

C(27)-N(3)-C(24)	108.5(5)	C(27)-N(3)-C(25)	111.4(5)
C(25)-N(3)-C(24)	109.6(4)		

Symmetry transformations used to generate equivalent atoms: #1 -x-1/2,y+1/2,z+1/2; #2 x-1/2,-y-1/2,z; #3 x,y,z+1; #4 -x-1/2,y-1/2,z-1/2; #5 x,y,z-1; #6 x+1/2,-y-1/2,z

Table 1 Crystal data and structure refinements for compounds **1** and **2.**

Compounds	**1**	**2**
Empirical formula	$C_{16.50}H_{17.50}N_{1.50}NaO_{9.50}V$	$C_{30}H_{42}LiN_3O_{13}V$
M	462.75	710.55
Temperature/K	296(2) K	293(2) K
Crystal system	Hexagonal	Orthorhombic
Space group	*R-3*	*Pna21*
a/Å	20.463(4)	18.079(4)
b/ Å	20.463(4)	16.435(3)
c/ Å	27.880(7)	11.603(2)
α/°	90	90
β/°	90	90
γ/°	120	90
V/Å^3	10111(3)	3447.6(12)
Z	18	4
D_c/g cm^{-3}	1.368	1.369
Measured reflections	20457	28417
Independent reflections	5212	7671
Data/restraints/parameters	5212 / 0/ 208	7671 / 13 / 433
Goodness of fit *S*	0.903	1.004
Final *R* indicts [I >2σ(I)][a]	*R1*=0.0385	*R1=0.0609*
	wR2=0.0904	*wR2=0.1293*
R indices (all data)[b]	*R1*=0.0610	*R1=0.1045*
	wR2=0.0956	*wR2=0.1480*

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