Supplementary Data

Synthesis, Single Crystal X-ray Structure, Spectroscopy and Substitution Behavior of Niobium(V) Complexes Activated by Chloranilate as Bidentate Ligand

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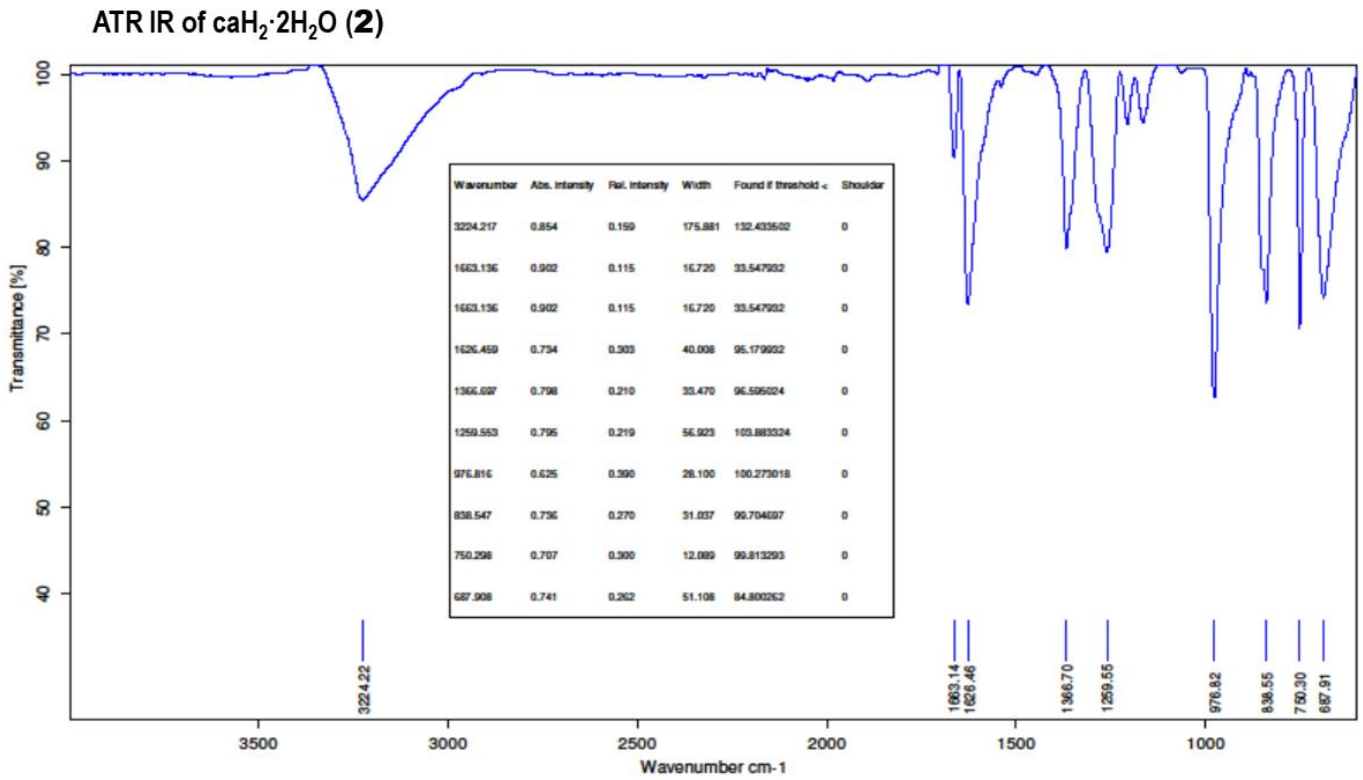
Table S1. Selected bond lengths within the chloranilic acid/ chloroanilate ligand in(caH_2)·$2H_2O$ (**2**), (Et_4N)*cis*-$[NbO(ca)_2(H_2O)OPPh_3]$·$3H_2O$·THF (**5**) and $(Et_4N)_4[Nb_4O_4(ca)_2(\mu^2\text{-}O)_2Cl_8]$·$2CH_3CN$ (**6**).

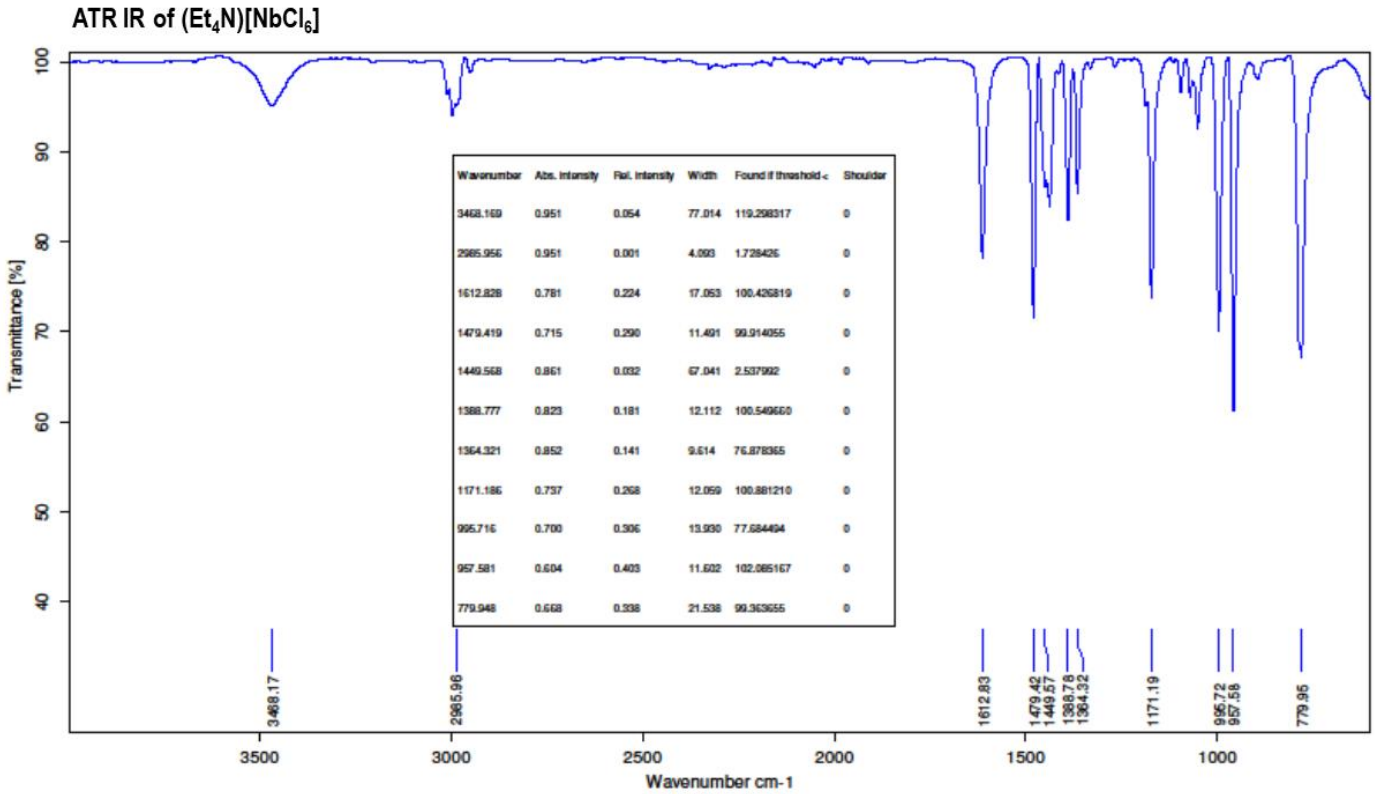
Bond lengths (Å)						
	2	**(º)**	**5**	**(º)**	**6**	**(º)**
C-O	C1-O1	1.2256(15)	C1-O1	1.316(3)	C6b-O3b	1.269(12)
	C1i-O1i	1.2256(15)	C2-O2	1.314(3)	C1b-O2b	1.237(12)
			C1a-O1a	1.278(5)	C4b-O5b	1.248(12)
			C2a-O2a	1.288(5)	C3b-O4b	1.279(12)
		1.226		1.299		1.258
C=O	C2-O2	1.3173(14)	C4-O4	1.301(4)	C6a-O3a	1.241(12)
	C2i-O2i	1.3173(14)	C5-O5	1.285(4)	C1a-O2a	1.278(12)
			C4a-O4a	1.227(5)	C4a-O5a	1.278(12)
			C5a-O5a	1.224(5)	C3a-O4a	1.253(12)
		1.317		1.259		1.263
C-Cl	C3-Cl1	1.7186(12)	C3-Cl1	1.799(2)	C2b-Cl3b	1.747(10)
	C3i-Cl1i	1.7186(12)	C3a-Cl1a	1.725(5)	C5b-Cl4b	1.724(10)
			C6-Cl2	1.782(2)	C2a-Cl3a	1.713(10)
			C6a-Cl2a	1.728(4)	C5a-Cl4a	1.728(10)
		1.719		1.759		1.728
Bond angles (º)						
	2	**(º)**	**5**	**(º)**	**6**	**(º)**
			O1-C1-C2	115.2(2)	O3a-C6a-C1a	115.9(8)
O-C-**C**$_{MC}$	O1 C1 C2	118.15(11)	O1a-C1a-C2a	113.7(3)	O3b-C6b-C1b	114.7(8)
			O2-C2-C1	114.5(2)	O2a-C1a-C6a	115.1(8)
			O2a-C2a-C1a	113.2(3)	O2b-C1b-C6b	115.5(8)
			O5-C5-C4	119.7(2)	O5a-C4a-C3a	116.3(8)
			O5a-C5a-C4a	116.3(4)	O5b-C4b-C3b	116.5(9)
			O4-C4-C5	120.8(2)	O4a-C3a-C4a	114.7(8)
			O4a-C4a-C5a	117.4(4)	O4b-C3b-C4b	114.2(9)
				116.35		115.36
			O2-C2-C3	125.3(2)	O2a-C1a-C2a	125.5(9)
O-C-**C**$_{Out}$	O2 C2 C3	122.05(11)	O2a-C2a-C3a	125.6(4)	O2b-C1b-C2b	125.8(9)
			O1-C1-C6	124.1(2)	O5b-C4b-C5b	123.6(10)
			O1a-C1a-C6a	125.9(4)	O5a-C4a-C5a	124.4(9)
			O4-C4-C3	118.6(2)	O4a-C3a-C2a	124.7(9)
			O4a-C4a-C3a	124.6(4)	O4b-C3b-C2b	127.2(10)
			O5-C5-C6	120.2(2)	O3a-C6a-C5a	124.9(9)
			O5a-C5a-C6a	125.6(4)	O3b-C6b-C5b	126.0(9)
				123.74		125.26
			C1a-C6a-Cl2a	120.4(3)	C6b-C5b-Cl4b	120.2(8)
C-C-**Cl**$_{Out}$	C2 C3 Cl1	121.12(9)	C1-C6-Cl2	121.02(15)	C6a-C5a-Cl4a	117.8(7)
			C2-C3-Cl1	117.48(15)	C1a-C2a-Cl3a	120.2(8)
			C2a-C3a-Cl1a	120.7(3)	C1b-C2b-Cl3b	118.1(7)
			C4-C3-Cl1	122.47(15)	C3b-C2b-Cl3b	118.9(8)
			C4a-C3a-Cl1a	118.4(3)	C3a-C2a-Cl3a	119.5(7)
			C5-C6-Cl2	121.02(15)	C4a-C5a-Cl4a	121.0(7)
			C5a-C6a-Cl2a	118.1(3)	C4b-C5b-Cl4b	119.1(8)
				119.95		119.35
			C3-C4-C5	120.0	C2b-C3b-C4b	118.6(9)
C-C-C	C3 C2 C1	120.18(10)	C3a-C4a-C5a	118.1(4)	C2a-C3a-C4a	120.5(8)

C6-C5-C4	120.0	C5a-C4a-C3a	119.3(8)
C6a-C5a-C4a	118.1(4)	C5b-C4b-C3b	119.8(9)
C6-C1-C2	120.0	C5a-C6a-C1a	119.2(8)
C6a-C1a-C2a	120.4(4)	C5b-C6b-C1b	119.3(9)
C1-C6-C5	120.0	C6b-C5b-C4b	120.6(9)
C1a-C6a-C5a	121.4(4)	C4a-C5a-C6a	121.2(9)
C2-C3-C4	120.0	C1a-C2a-C3a	120.2(9)
C2a-C3a-C4a	120.9(4)	C3b-C2b-C1b	122.9(9)
C3-C2-C1	120.0	C2a-C1a-C6a	119.4(8)
C3a-C2a-C1a	121.1(4)	C2b-C1b-C6b	118.7(9)
	120.0		119.98



Wavenumber	Abs. Intensity	Rel. Intensity	Width	Found if threshold <	Shoulder
3224.217	0.854	0.159	175.881	132.433502	0
1663.136	0.902	0.115	16.720	33.547932	0
1663.136	0.902	0.115	16.720	33.547932	0
1626.459	0.734	0.303	40.008	95.179932	0
1366.697	0.798	0.210	33.470	96.595024	0
1259.553	0.795	0.219	56.923	103.883324	0
976.816	0.625	0.390	28.100	100.273018	0
838.547	0.756	0.270	31.037	99.704697	0
750.298	0.707	0.300	12.089	99.813293	0
687.908	0.741	0.262	51.108	84.800262	0

Figure S1 ATR Infrared spectrum of caH2.H2O.



Wavenumber	Abs. intensity	Rel. intensity	Width	Found if threshold <	Shoulder
3468.169	0.951	0.054	77.014	119.298317	0
2985.956	0.951	0.001	4.093	1.728426	0
1612.828	0.781	0.224	17.053	100.426819	0
1479.419	0.715	0.290	11.491	99.914055	0
1449.568	0.861	0.032	67.041	2.537992	0
1388.777	0.823	0.181	12.112	100.549660	0
1364.321	0.852	0.141	9.614	76.878365	0
1171.186	0.757	0.268	12.059	100.881210	0
995.716	0.700	0.306	13.930	77.684494	0
957.581	0.604	0.403	11.602	102.085167	0
779.948	0.668	0.338	21.538	99.363655	0

Figure S2 ATR Infrared spectrum of $(Et_4N)[NbCl_6]$ (1).

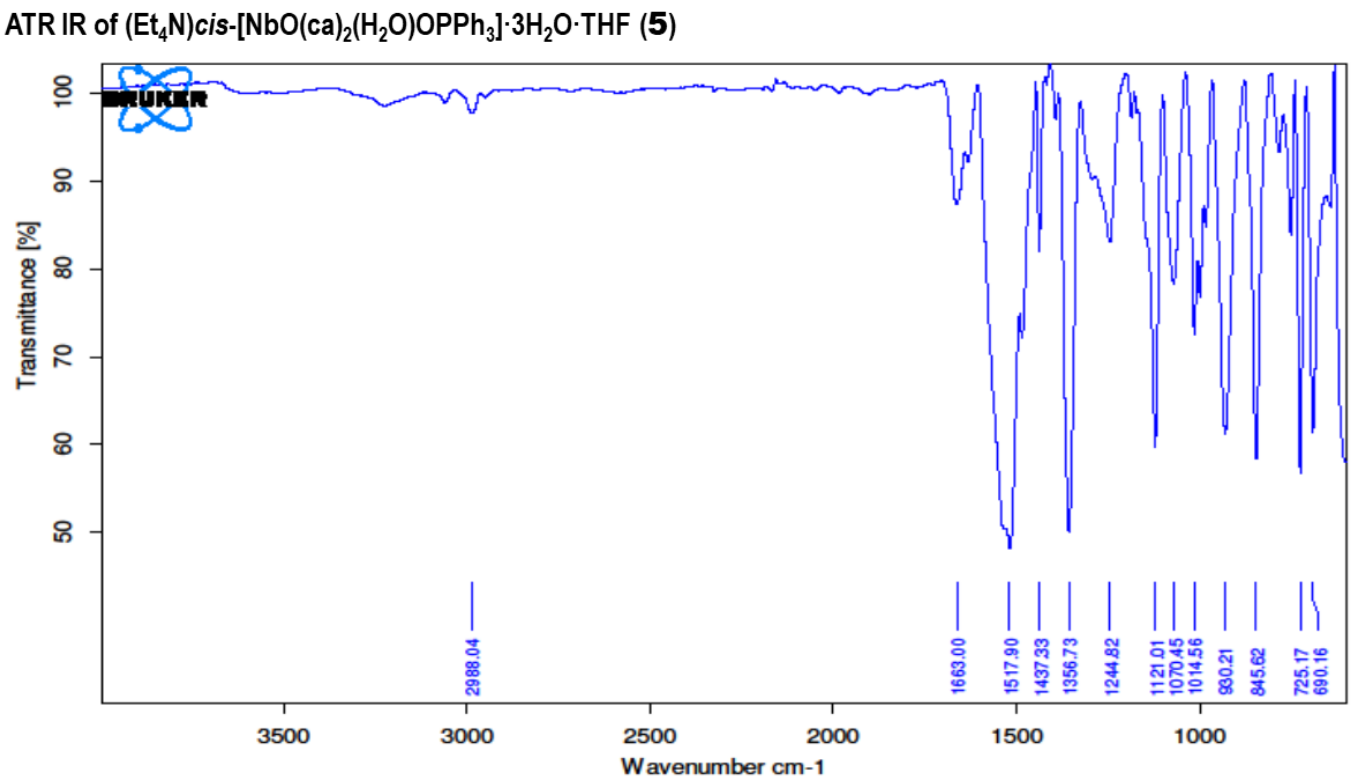
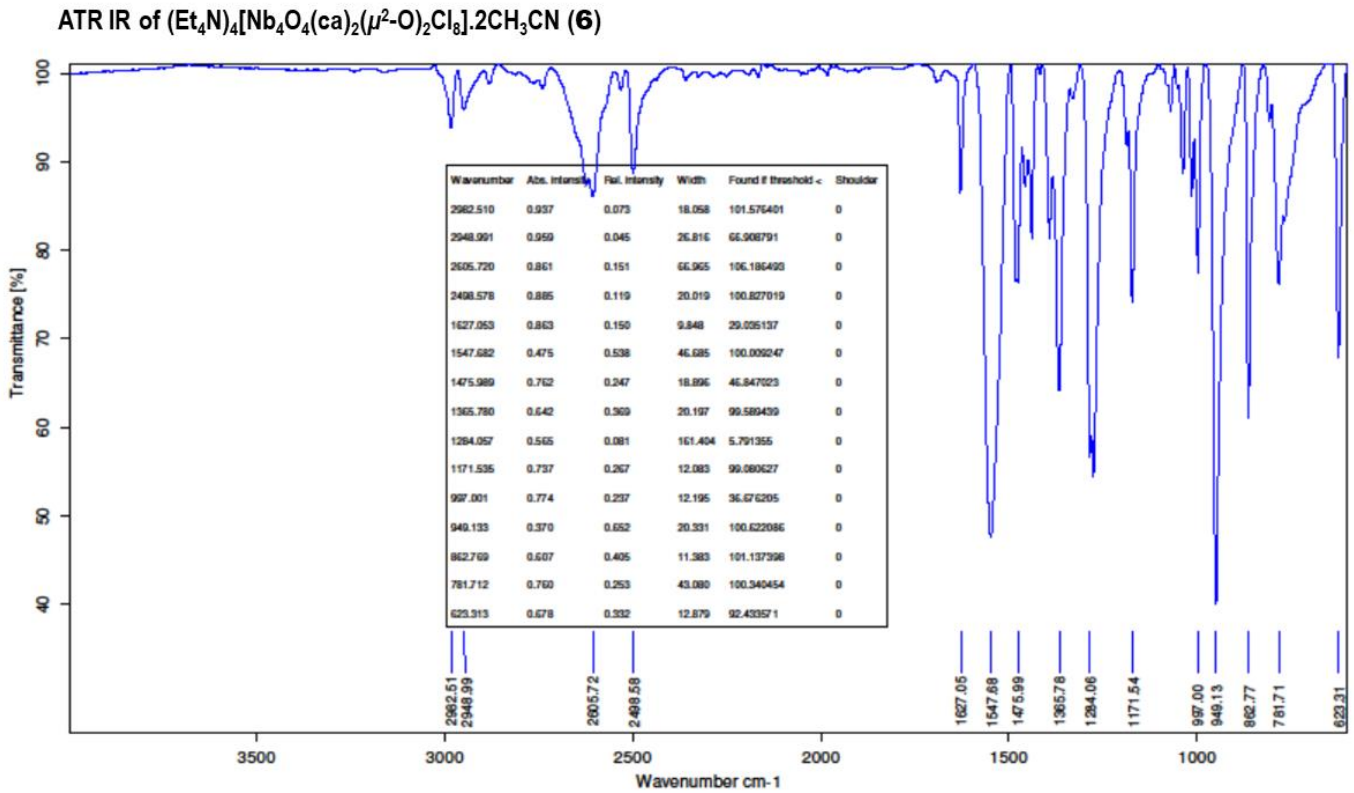


Figure S3 ATR Infrared spectrum of (Et$_4$N)*cis*-[NbO(ca)$_2$(H$_2$O)OPPh$_3$]·3H$_2$O·THF (5).



Wavenumber	Abs. Intensity	Rel. Intensity	Width	Found if threshold <	Shoulder
2962.510	0.937	0.073	18.058	101.576401	0
2948.991	0.959	0.045	26.816	66.908791	0
2605.720	0.861	0.151	66.965	106.186493	0
2498.578	0.885	0.119	20.019	100.827019	0
1627.053	0.863	0.150	9.848	29.035137	0
1547.682	0.475	0.538	46.685	100.009247	0
1475.989	0.762	0.247	18.896	46.847023	0
1365.780	0.642	0.369	20.197	99.589439	0
1284.057	0.565	0.081	161.404	5.791355	0
1171.535	0.737	0.267	12.083	99.080527	0
997.001	0.774	0.237	12.195	36.676205	0
949.133	0.370	0.652	20.331	100.622086	0
862.769	0.607	0.405	11.383	101.137398	0
781.712	0.760	0.253	43.080	100.340454	0
623.313	0.678	0.332	12.879	92.43357	0

Figure S4 ATR Infrared spectrum of $(Et_4N)_4[Nb_4O_4(ca)_2(\mu^2\text{-}O)_2Cl_8].2CH_3CN$ (6).

^{1}H NMR of $caH_2 \cdot 2H_2O$ (**2**) in DMSO-d6

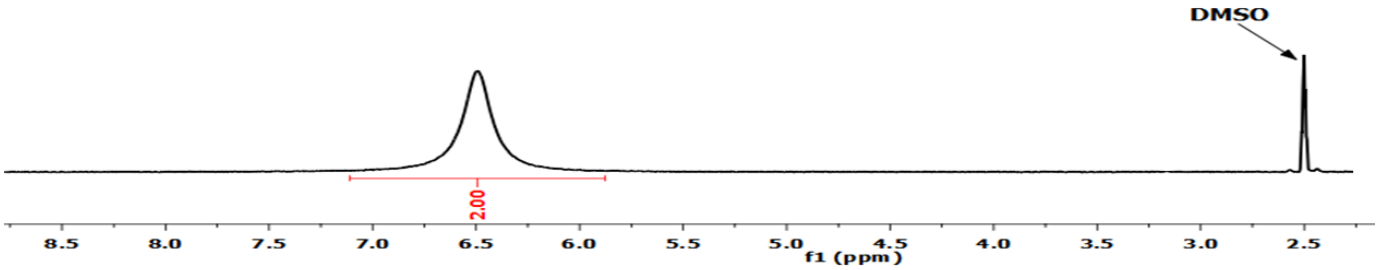


Figure S5 H-1 NMR spectrum of $caH_2.H_2O$ (2) in DMSO-d6.

^{1}H NMR of $OPPh_3$ in MeCN-d3

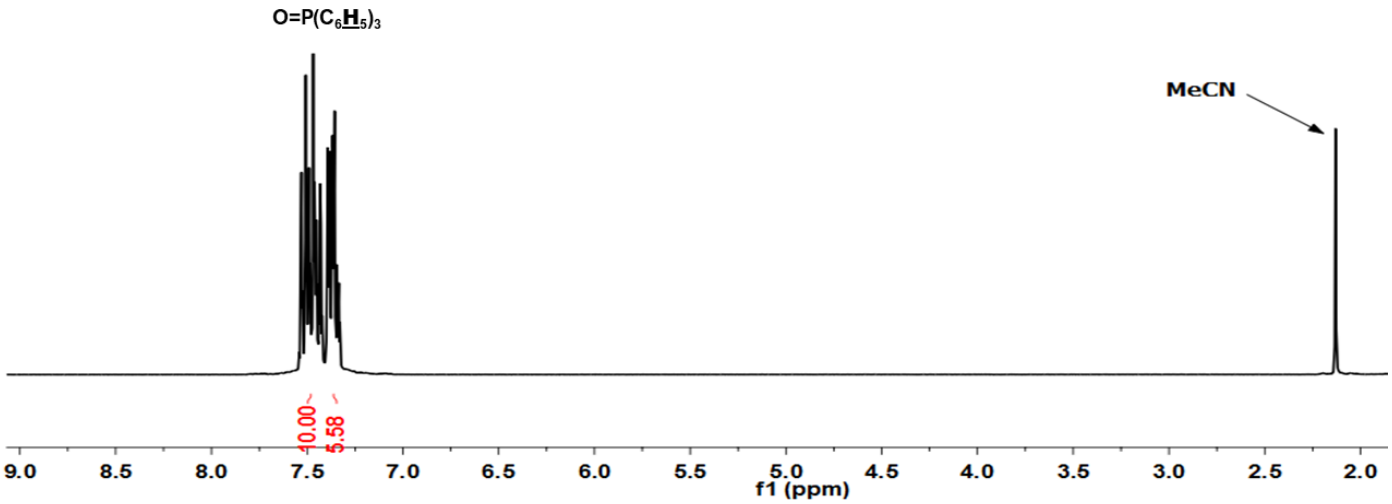


Figure S6 H-1 NMR spectrum of triphenylphosphine oxide in DMSO-d6.

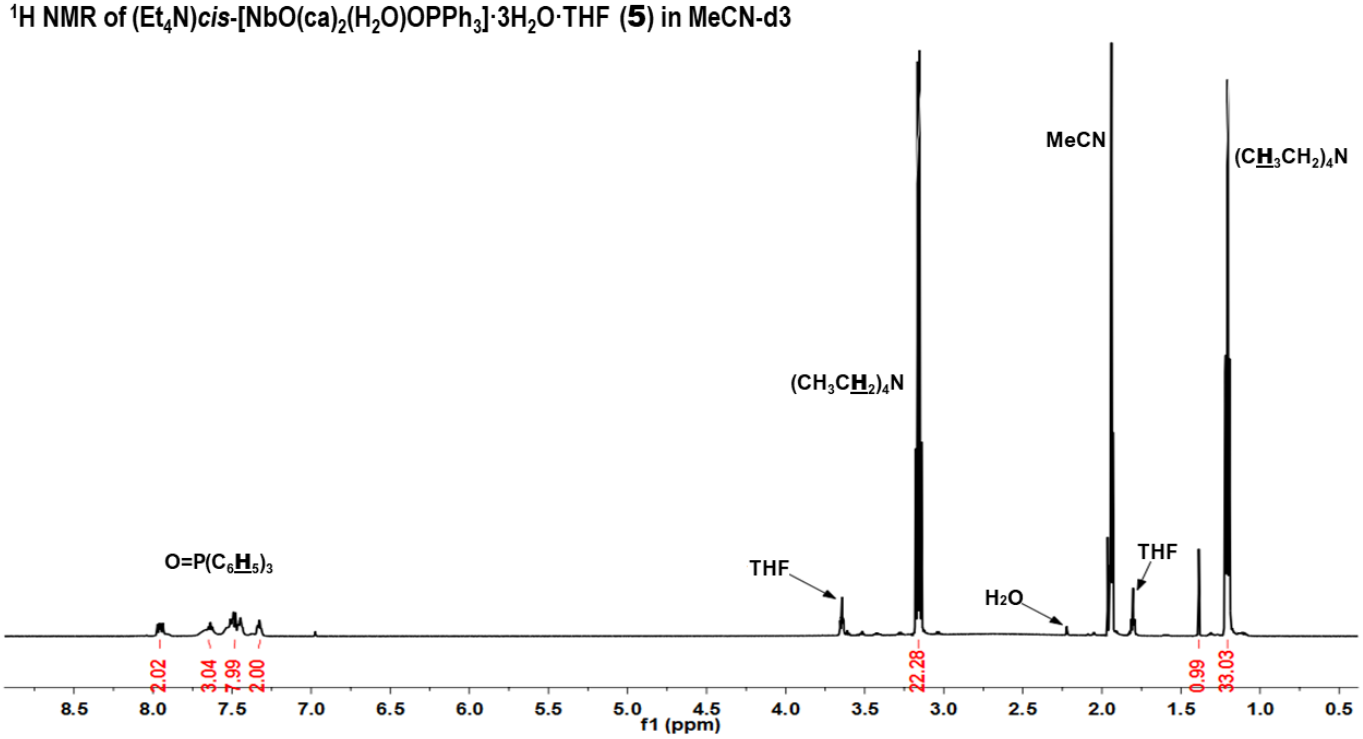


Figure S7 H-1 NMR spectrum of (Et$_4$N)*cis*-[NbO(ca)$_2$(H$_2$O)OPPh$_3$]·3H$_2$O·THF (5) in DMSO-d6.

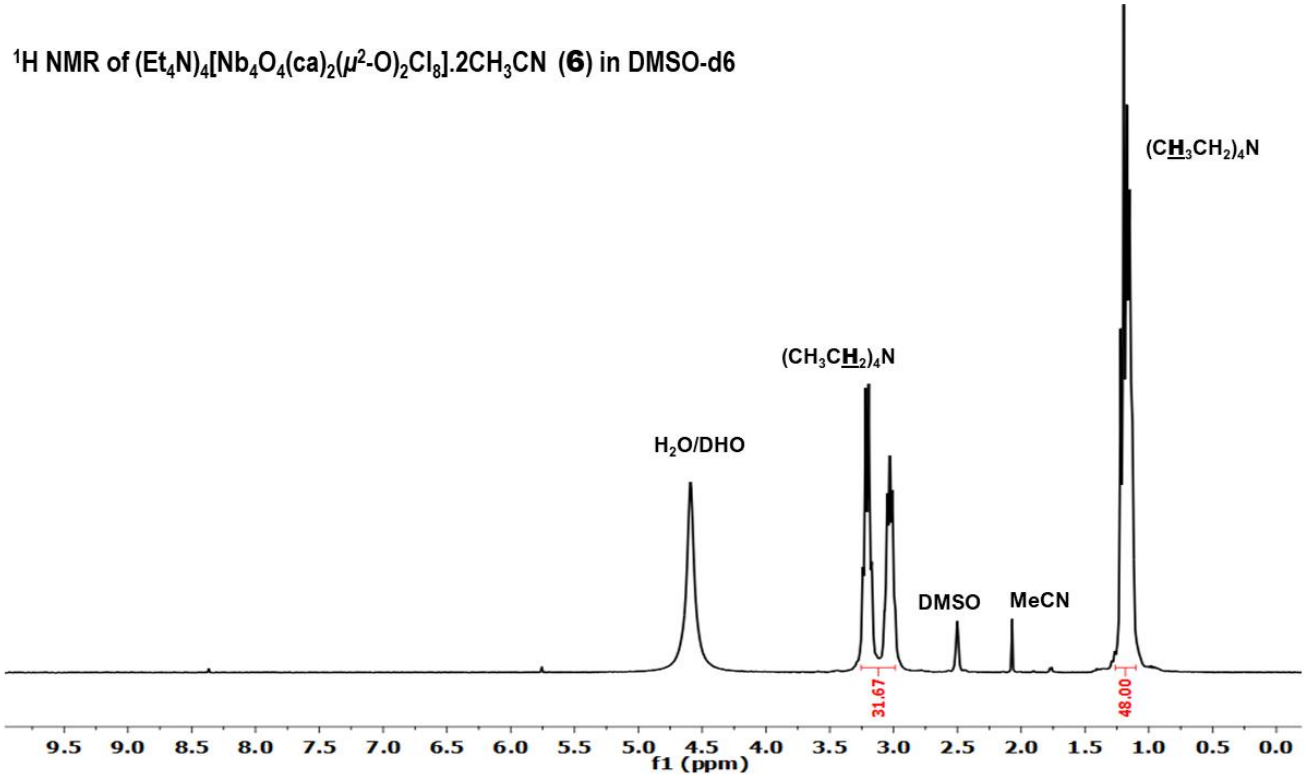


Figure S8 H-1 NMR spectrum $(Et_4N)_4[Nb_4O_4(ca)_2(\mu^2\text{-}O)_2Cl_8].2CH_3CN$ (6) in DMSO-d6.

^{13}C NMR of $(Et_4N)[NbCl_6]$ in DMSO-d6

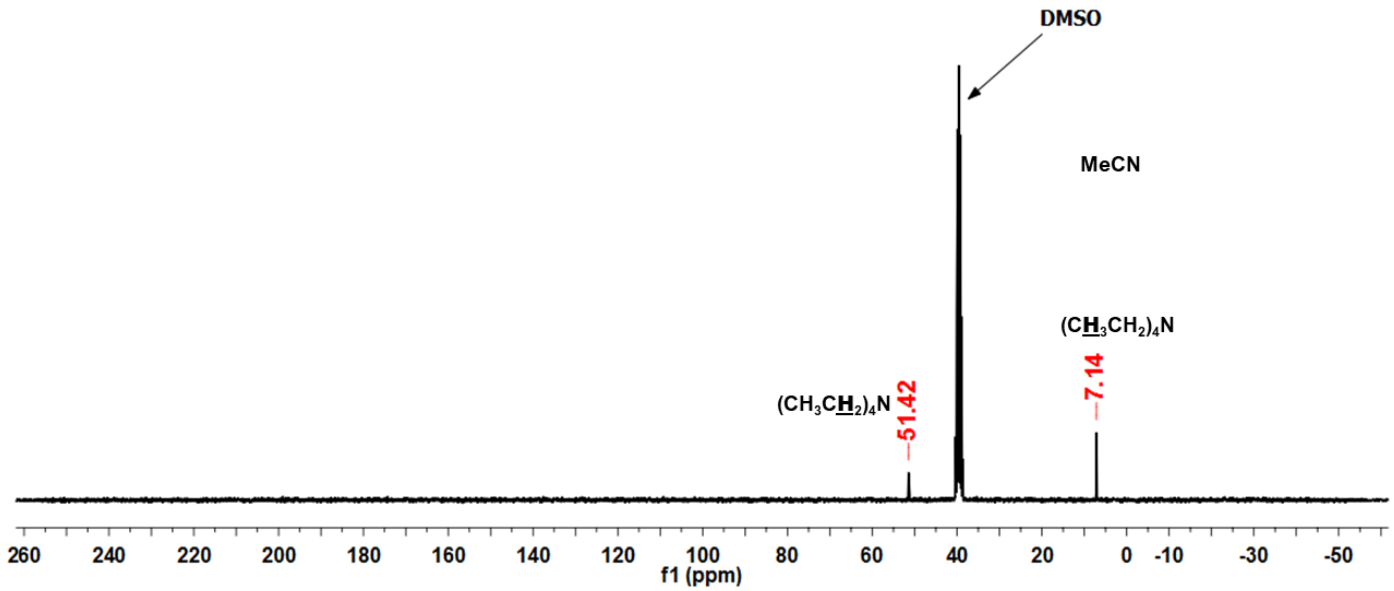


Figure S9 C-13 NMR spectrum of $(Et_4N)[NbCl_6]$ (1) in DMSO-d6.

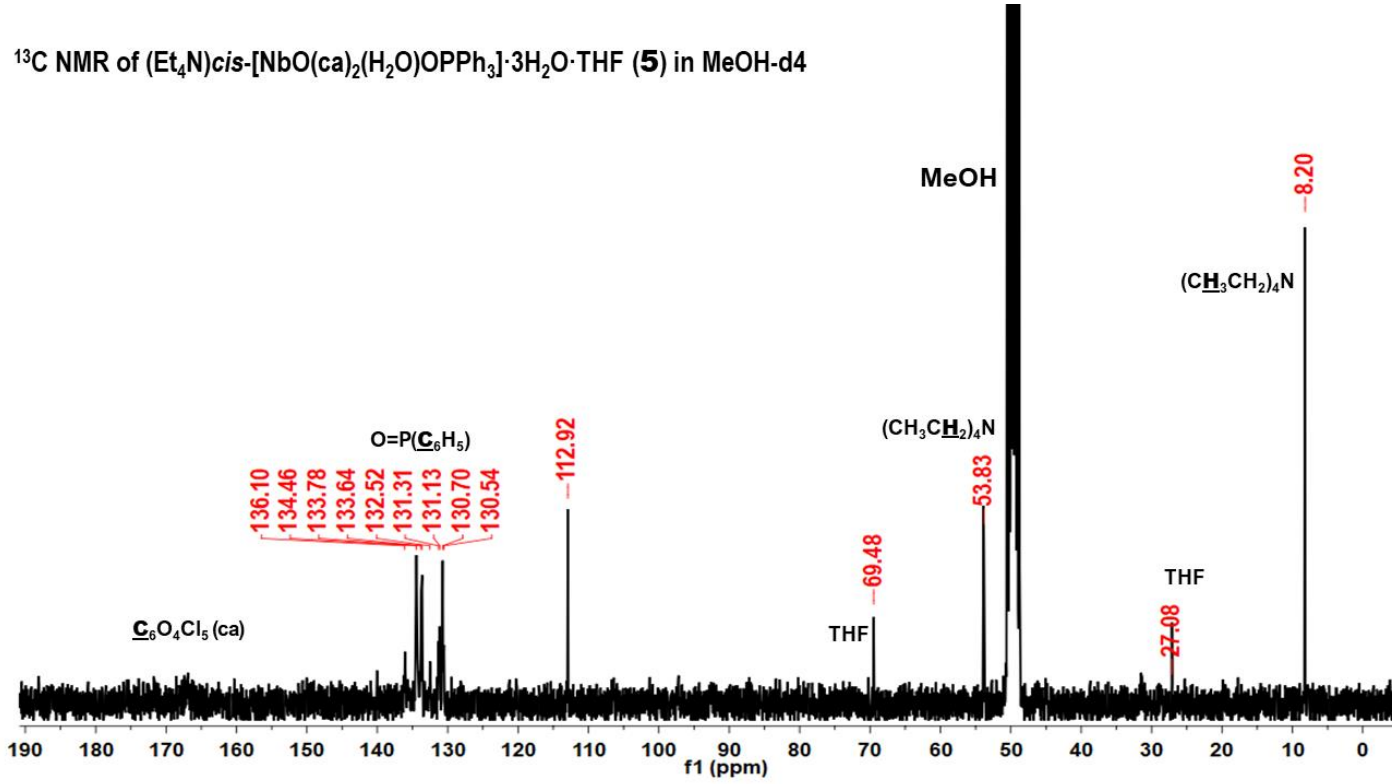


Figure S10 C-13 NMR spectrum of (Et4N)*cis*-[NbO(ca)2(H2O)OPPh3]·3H2O·THF (5) in DMSO-d6.

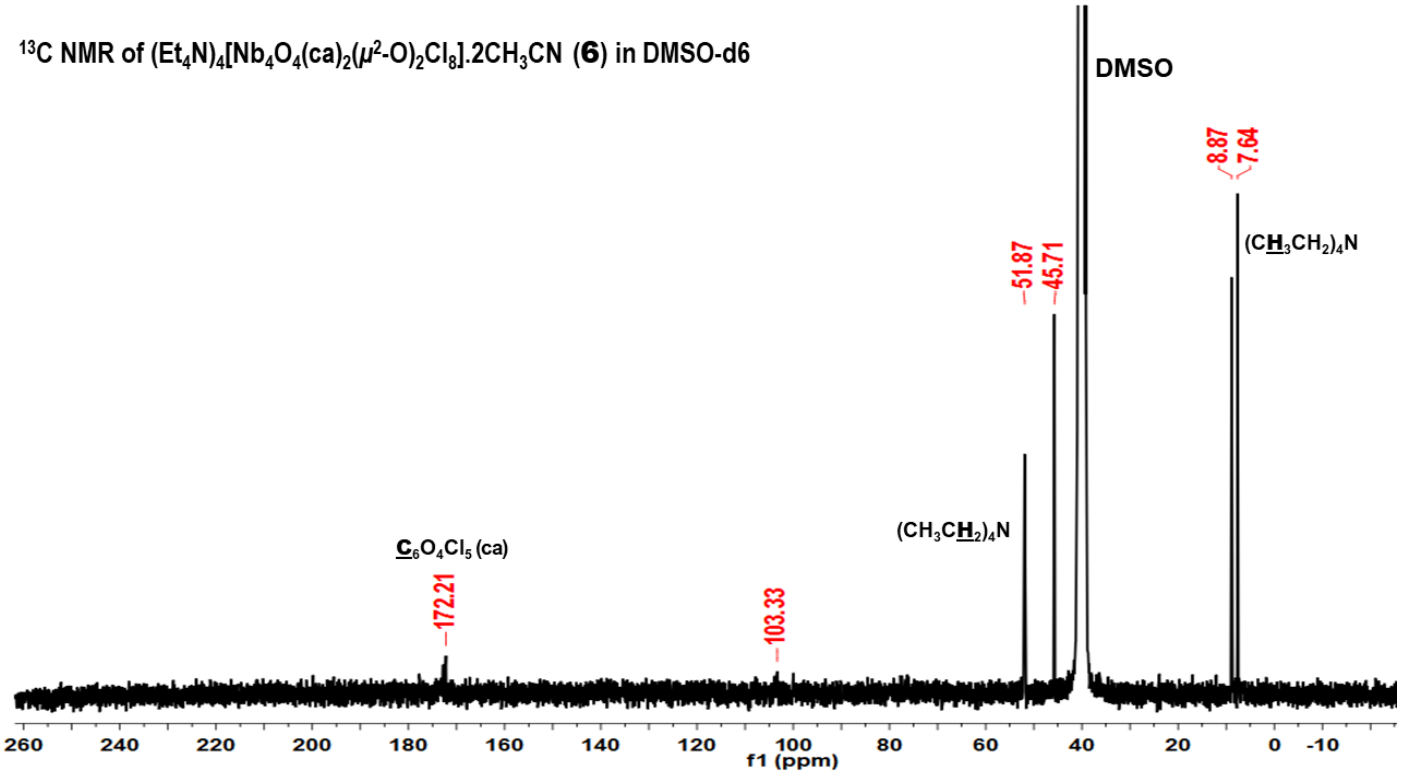


Figure S11 C-13 NMR spectrum of $(Et_4N)_4[Nb_4O_4(ca)_2(\mu^2\text{-}O)_2Cl_8].2CH_3CN$ (6) in DMSO-d6.

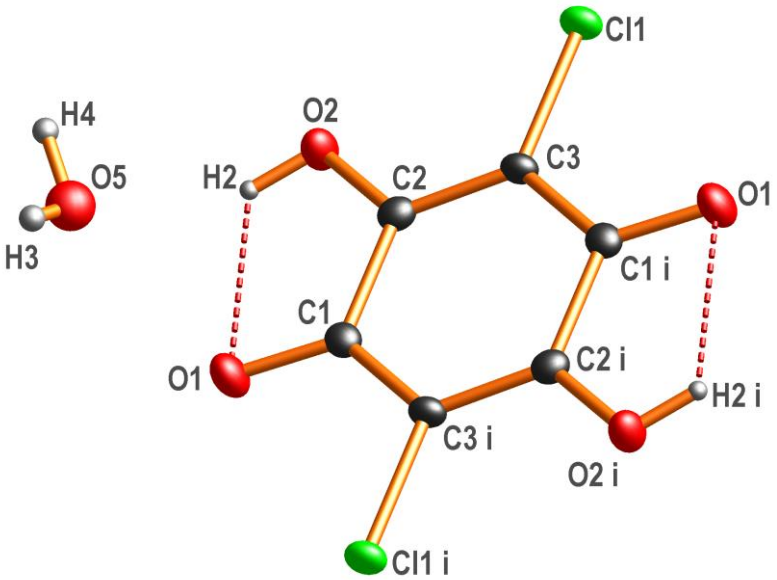


Figure S12 DIAMOND[10] view of ½(caH$_2$)·H$_2$O (2) with atom numbering system shown and thermal ellipsoids drawn at a 50% probability displacement. Atoms generated by symmetry are indicated by lower case roman numerals corresponding to the symmetry operator (i) 1-x, -y, -z.

Note: Numbering of atoms in (2) in Supplementary Materials, Figs A13-15 below, are chronologically and *not* always as in manuscript.

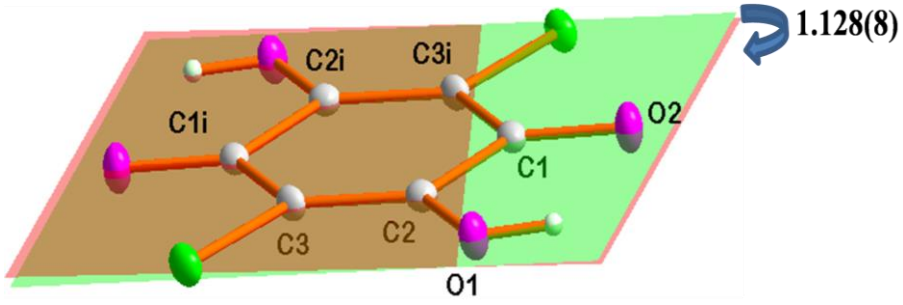


Figure S13 Representation of the plane passing through the four atoms O1, C2, C1 and O2 (plane 1, green) and the plane passing through the six atoms of chloranilic acid ring C1, C2, C3, C1i, C2i, and C3i (plane 2, pink). The solvated water molecule is omitted for clarity.

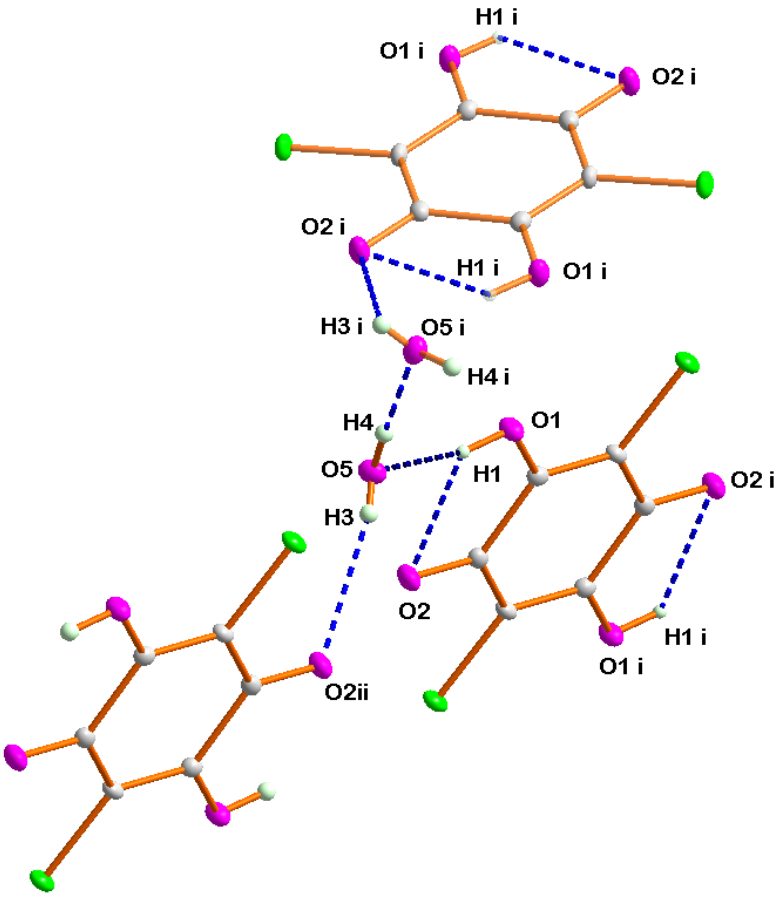


Figure S14 Inter-and intramolecular interactions of ½(caH$_2$)·H$_2$O (2). The blue dashed lines indicate O-H···O hydrogen bonds. [Symmetry codes: -x, -y, -z, x, ½ - y, z + ½].

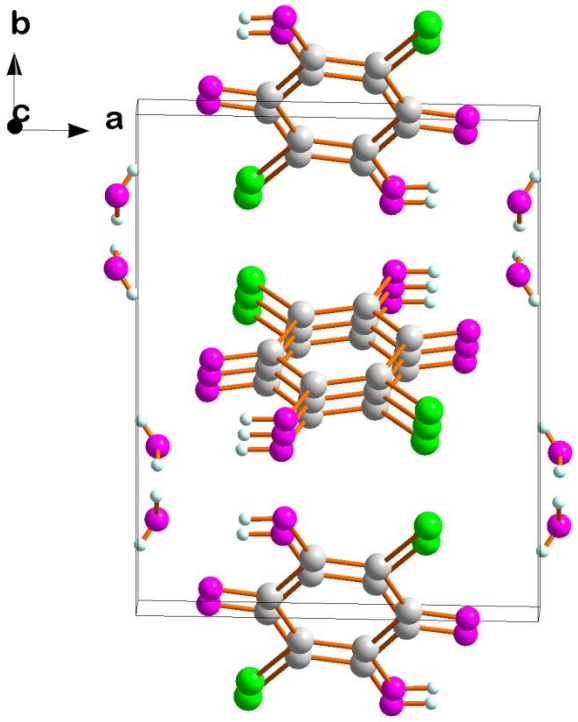


Figure S15 Unit cell for ½(caH$_2$)·H$_2$O (2) showing π-π stacking interactions along the c-axis.

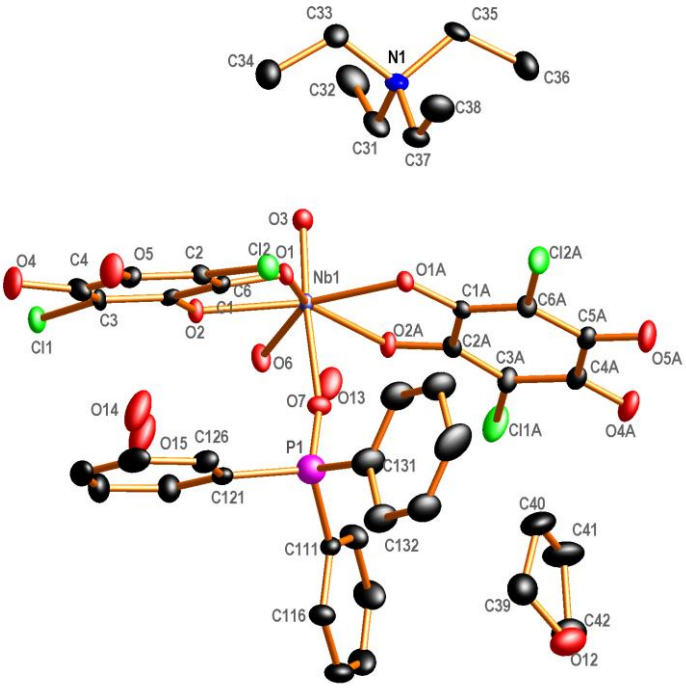


Figure S16 Molecular structure of *cis*-[NbO(ca)$_2$(H$_2$O)OPPh$_3$] (5a) with atom numbering system shown and the thermal ellipsoids drawn at a 50% probability level. Cation, hydrogen atoms and solvated molecules are omitted for clarity.

Note: Numbering of atoms in (5) in Supplementary Materials, Figs A17-A23 below, are chronologically and *not* always as in manuscript.

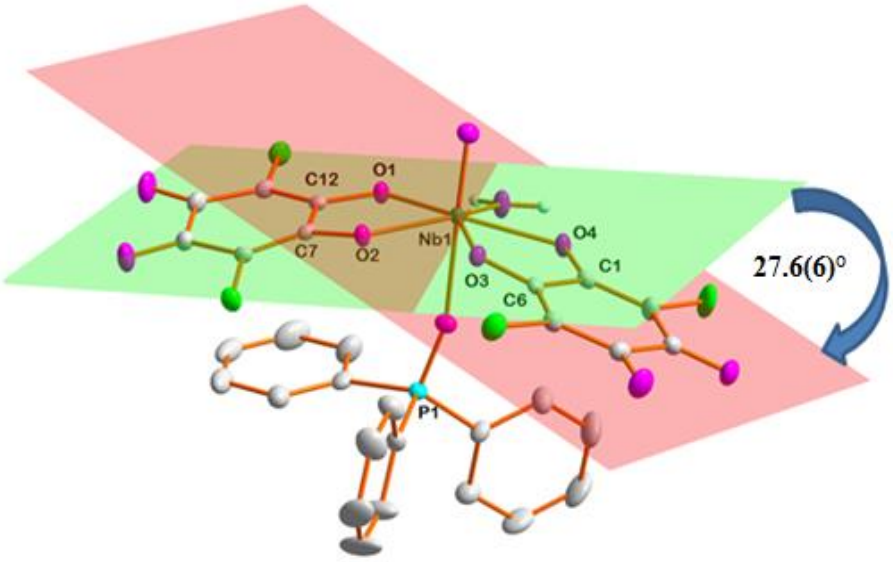


Figure S17 Representation of planes through *cis*-[NbO(ca)$_2$(H$_2$O)OPPh$_3$]. (5a). Plane 1 (green) passing through the five membered ring of chloranilate ligand in O1, C12, C7 and O2 and plane 2 (pink) passing through the five membered ring of chloranilate ligand (ca) in O3, C6, C1 and O4. H-atoms, counter ions and solvated molecules are omitted for clarity.

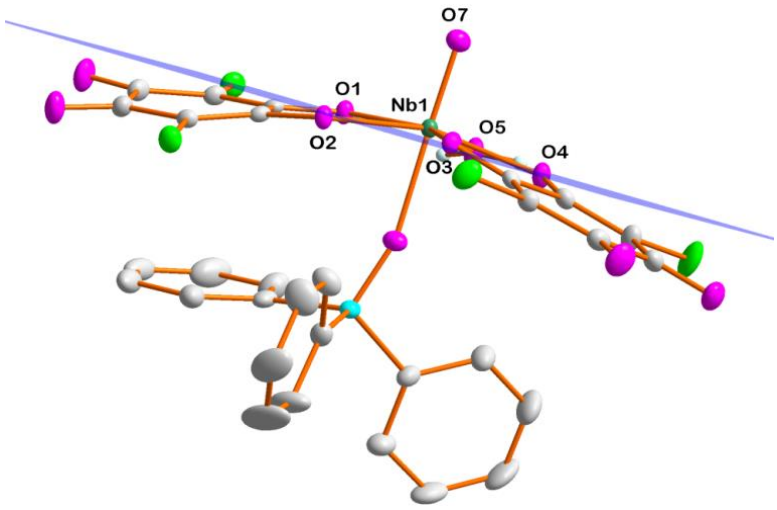


Figure S18 Representation of *cis*-[NbO(ca)$_2$(H$_2$O)OPPh$_3$] (5a). The blue plane constructed through the five oxygen atoms O1, O2, O3, O4 and O5 illustrates the distance between the plane and O7. H-atoms, counter ions and solvated molecules are omitted for clarity.

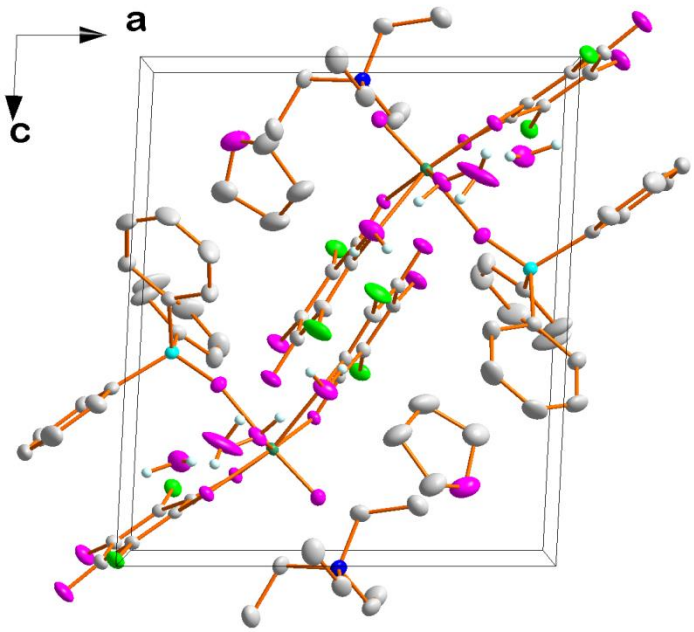


Figure S19 Packing diagram of *cis*-(Et$_4$N)[NbO(ca)$_2$(H$_2$O)OPPh$_3$].3H$_2$O.THF (**5**) showing two molecular formula per unit cell along b-axis. H-atoms are omitted for clarity.

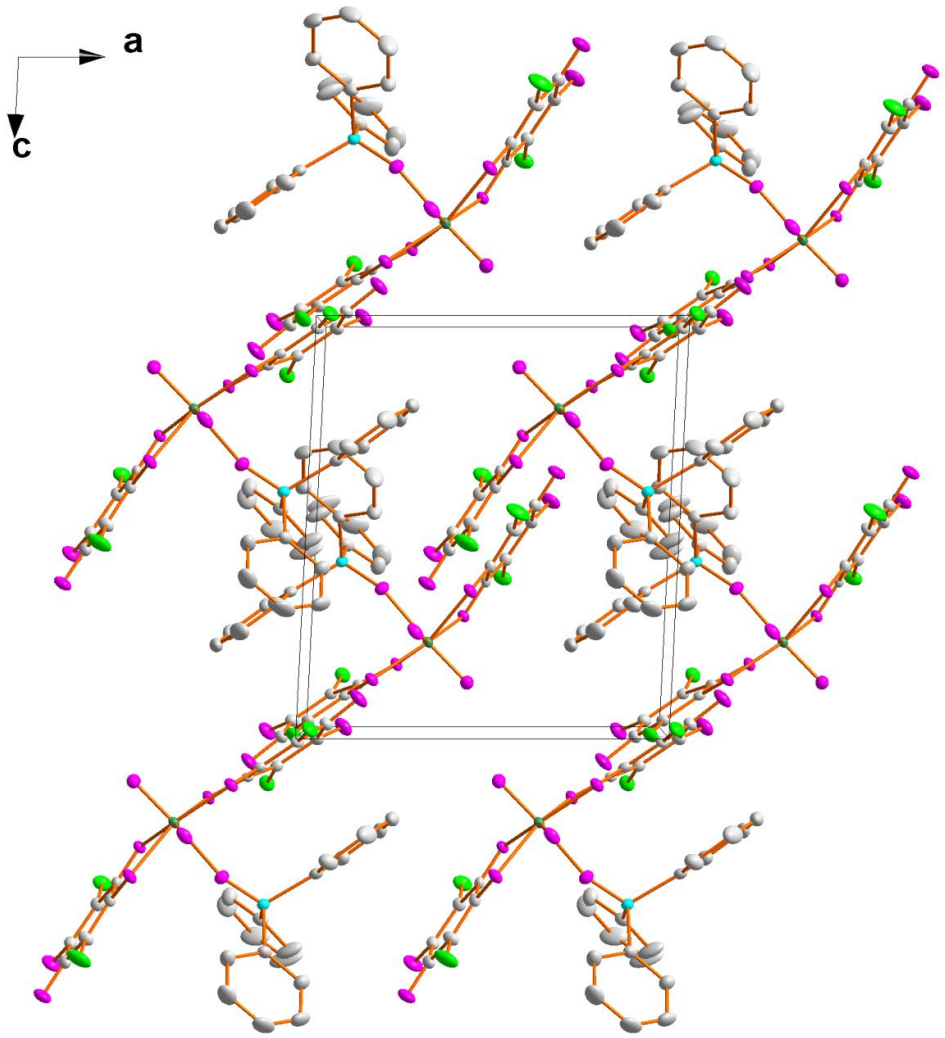


Figure S20 Expanded packing diagram of *cis*-[NbO(ca)$_2$(H$_2$O)OPPh$_3$] (5a) showing extended wing-like orientation chain head to tail π- π stacking interactions along the b-axis. H-atoms, counter ions and solvated molecules are omitted for clarity.

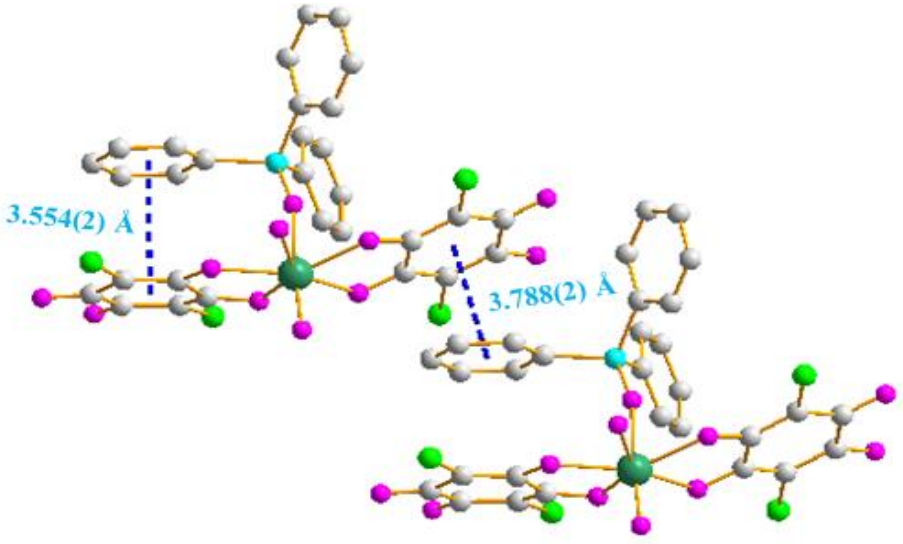


Figure S21 Extended structure of *cis*-[NbO(ca)$_2$(H$_2$O)OPPh$_3$] (5a) showing head to tail packing interaction along the b-axis. The thick blue dashed lines indicate π-π stacking interactions [centroid-centroid distance = 3.554(2) and 3.788(2) Å, -1+x, y, z] between a phenyl ring on the OPPh$_3$ and coordinated chloranilate (ca) ligands. H-atoms, counter ions and solvated molecules are omitted for clarity.

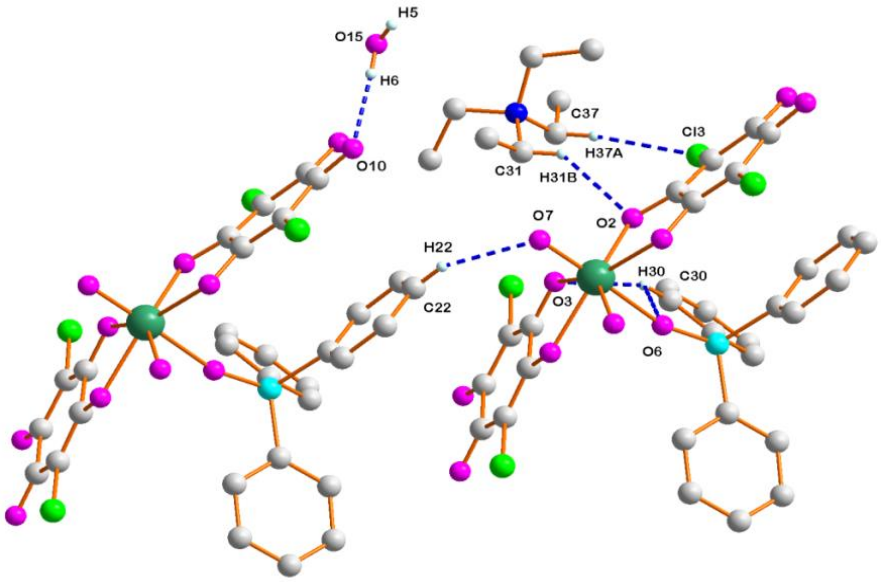


Figure S22 Extended structure of (Et_4N)*cis*-[$NbO(ca)_2(H_2O)OPPh_3$].3H_2O.THF (**5**) showing the intra- and intermolecular interactions. The blue dashed lines indicate O-H...O, C-H...O and C-H...Cl hydrogen-bonds.

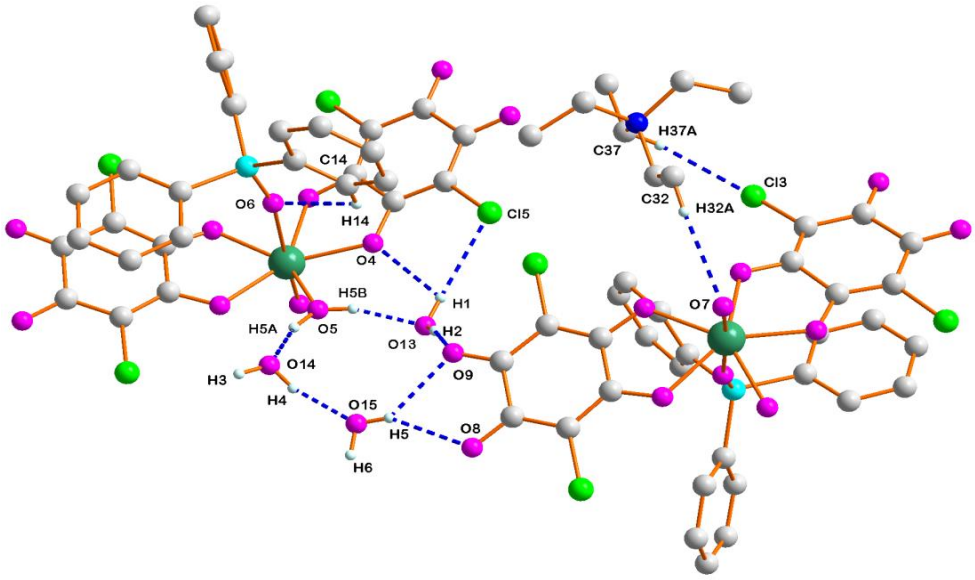


Figure S23 Extended structure of (Et_4N)*cis*-[$NbO(ca)_2(H_2O)OPPh_3$].3H_2O.THF (**5**) showing blue dashed lines, indicating different triangle and v-shaped bifurcated hydrogen-bonds found between its symmetry-generated molecules. The rest of the hydrogen atoms are omitted for clarity.

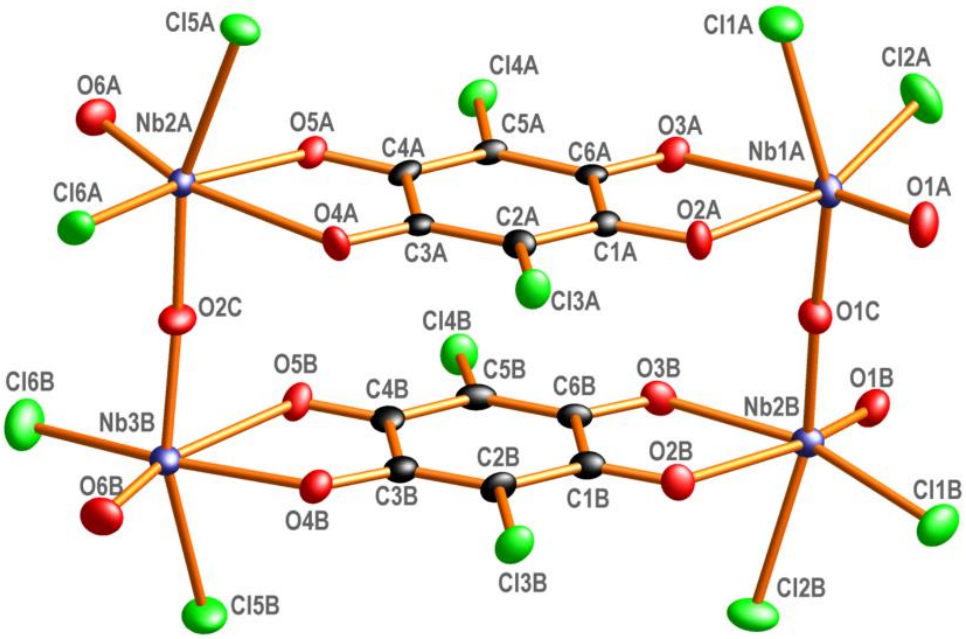


Figure S24 Tetranuclear structure of the $[Nb_4O_4(ca)_2(\mu^2\text{-}O)_2Cl_8]$ anion of (6a) with hydrogen atoms, counter ions, and solvated molecules omitted for clarity.

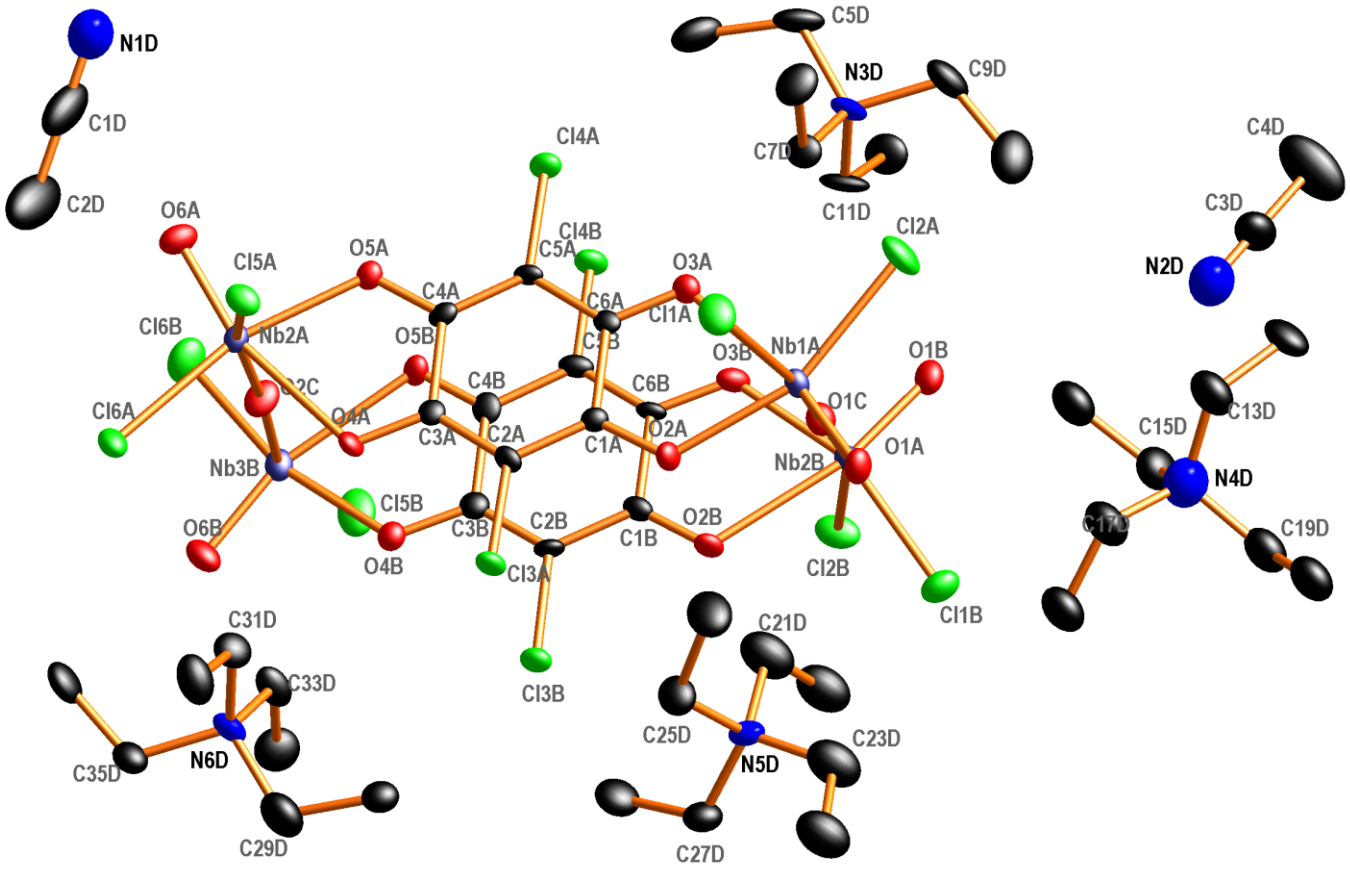


Figure S25 Tetranuclear structure of $(Et_4N)_4[Nb_4O_4(ca)_2(\mu^2\text{-}O)_2Cl_8].2CH_3CN$ (**6**) showing the atom numbering. Thermal ellipsoids are drawn at the 50% probability level and only hydrogen atoms are omitted for clarity.

Note: Numbering of atoms in (6) in Supplementary Materials, Figs A26-A30 below, are chronologically and *not* always as in manuscript.

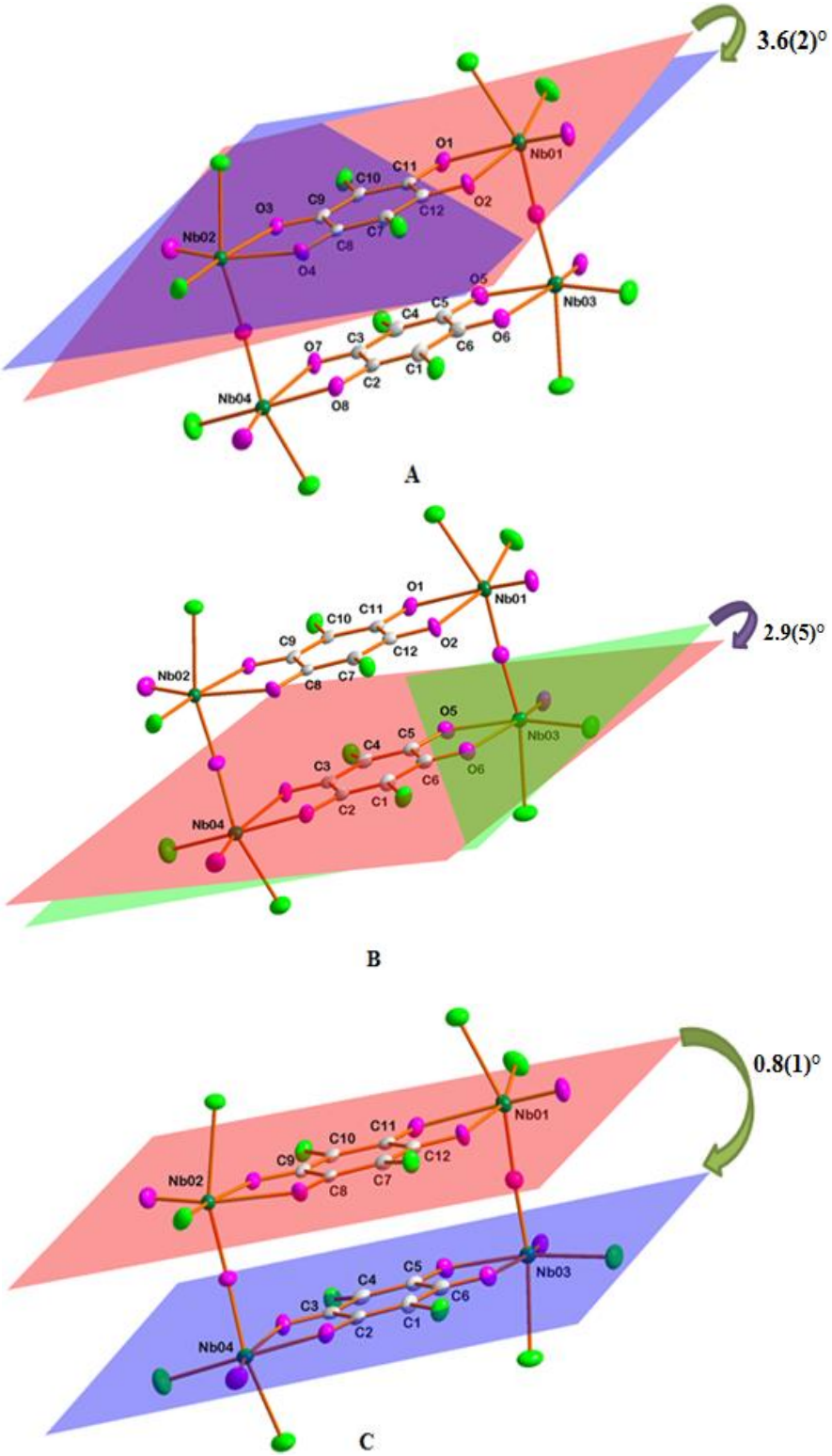


Figure S26 Representation of the planes through $[Nb_4O_4(ca)_2(\mu^2\text{-}O)_2Cl_8]$ (6a), (**A**) plane 1 (red) passing through the five-membered ring of μ-chloranilate in O1, C11, C12, O2 and Nb01 and plane 2 (blue) passing through the μ-chloranilate ring of C7-C12; **(B)** plane 1 (red) passing through the five membered ring of μ-chloranilate in O5, C5, C6, O6 and Nb03 and plane 2 (green) passing through the μ-chloranilate ring of C1-C6; (**C**) plane 1 (red) passing through the top of the μ-chloranilate ring of C7-C12 and plane 2 (blue) passing through the bottom of μ-chloranilate ring of C1-C6. The counter ion, solvated diacetonitrile molecules and H-atoms are omitted for clarity.

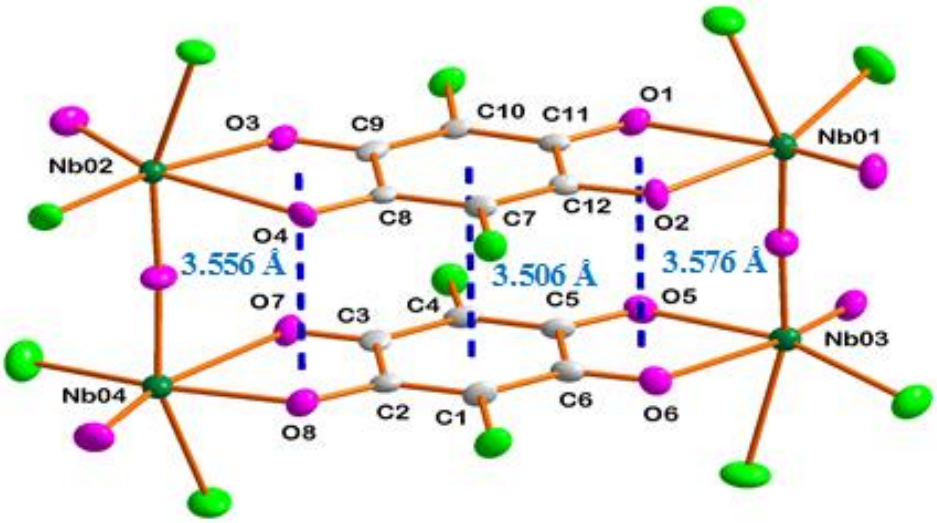


Figure S27 Tetranuclear structure of $[Nb_4O_4(ca)_2(\mu^2\text{-}O)_2Cl_8]$ (6a) anion of with the thick blue dashed lines indicating π-π stacking interactions between the μ-chloranilate rings (C7-C12 and C1-C6) and five membered rings of μ-chloranilate ligands (Nb02, O3, C9, C8, and O4 and Nb04, O7, C3, C2, and O8 and as well as Nb01, O2, C12, C11, and O1 and Nb03, O6, C6, C5, and O5). Hydrogen atoms, counter ions and solvated molecules are omitted for clarity.

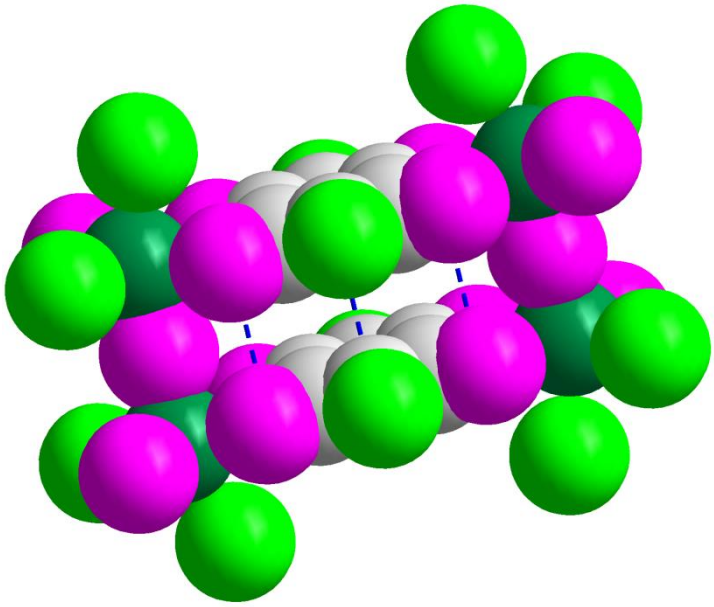


Figure S28 Tetranuclear structure of $[Nb_4O_4(ca)_2(\mu_2\text{-}O)_2Cl_8]$ (6a) with space filling, the thick blue dashed lines indicating π-π stacking interactions between the μ-chloranilate rings (C7-C12 and C1-C6) and five membered rings of μ-chloranilate ligands (Nb02, O3, C9, C8, and O4 and Nb04, O7, C3, C2, and O8 and as well as Nb01, O2, C12, C11, and O1 and Nb03, O6, C6, C5, and O5) (Figure 5.14). Thermal ellipsoids are drawn at the 50% probability level and with the van der Waal distance of 1.25 Å. Hydrogen atoms, counter ions and solvated molecules are omitted for clarity.

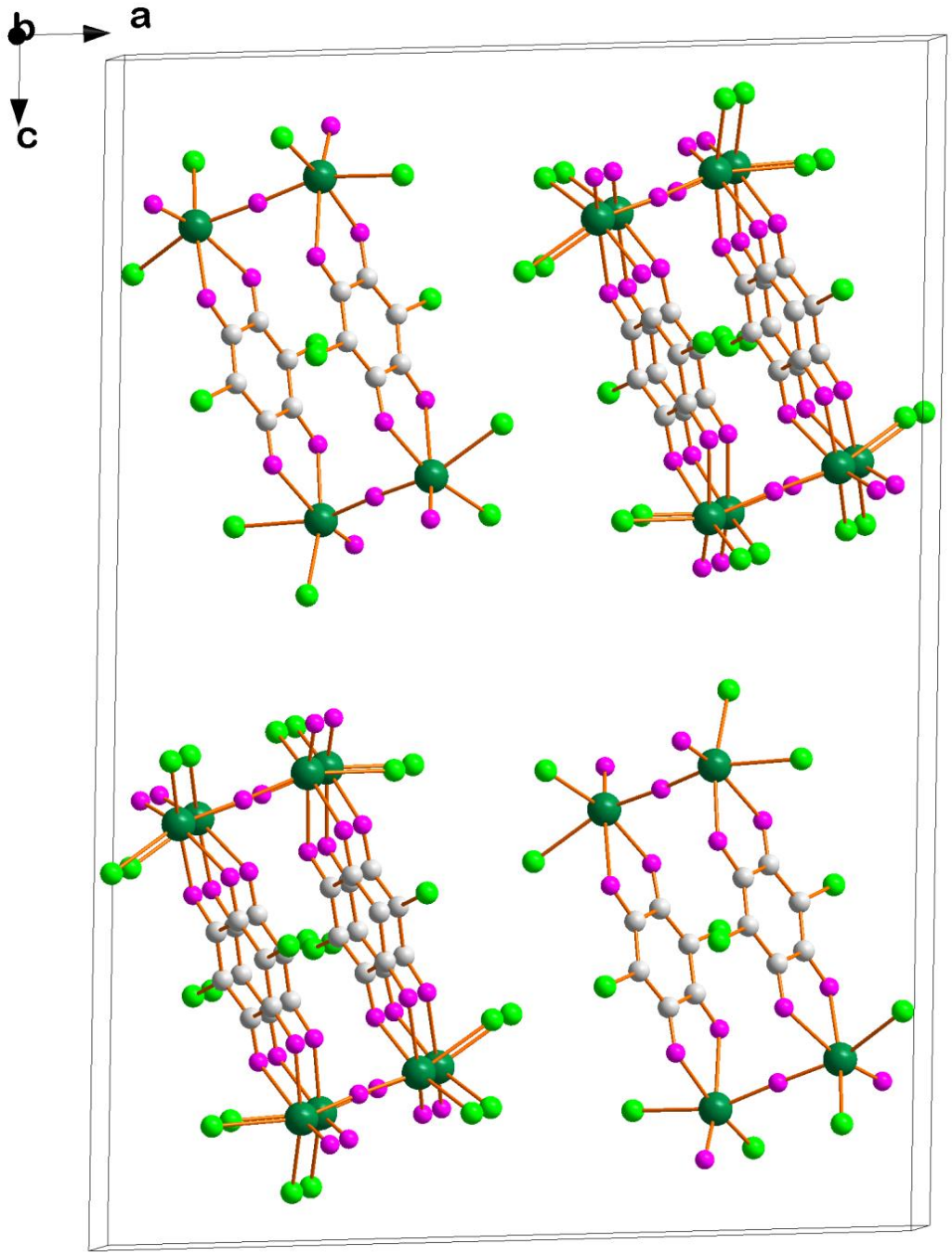


Figure S29 Tetranuclear structure of $[Nb_4O_4(ca)_2(\mu^2\text{-}O)_2Cl_8]$ of (6a) showing sheet like crystal packing along the b-axis. H-atoms, counter ions and solvated molecules are omitted for clarity.

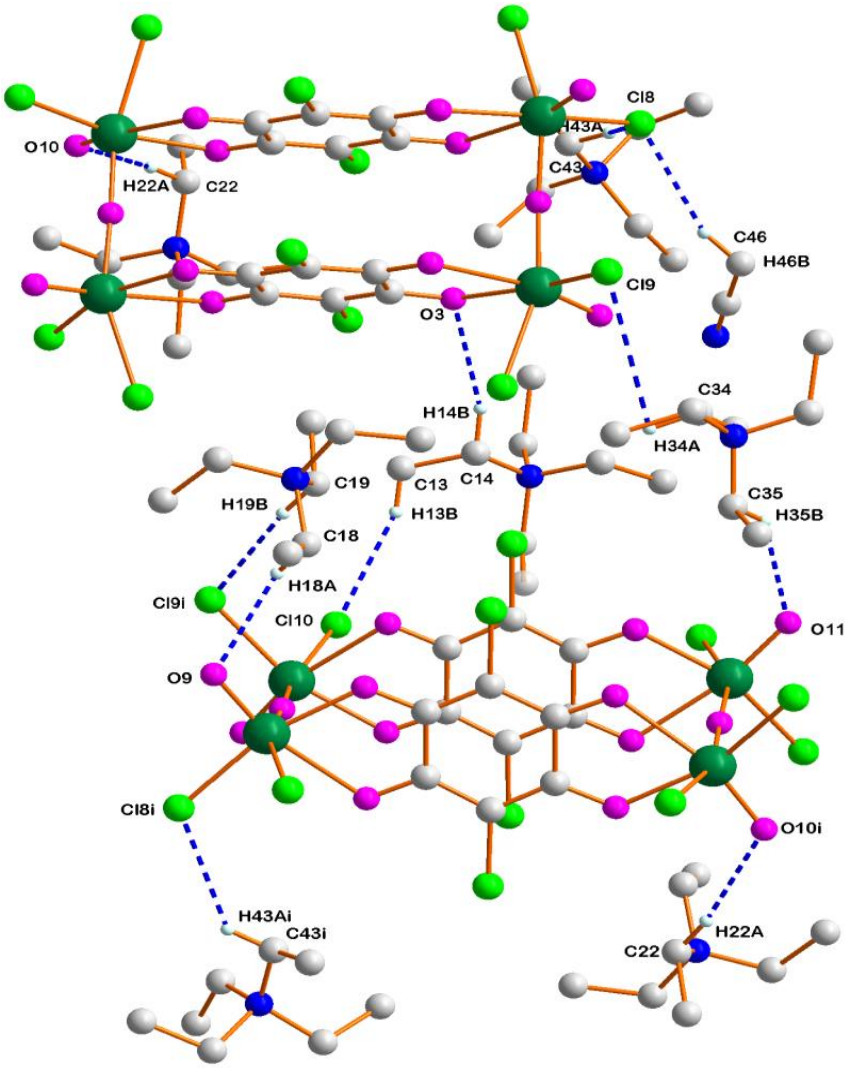


Figure S30 Tetranuclear structure of $(Et_4N)_4[Nb_4O_4(ca)_2(\mu^2\text{-}O)_2Cl_8].2CH_3CN$ (**6**) showing the intra- and intermolecular interactions. The blue dashed lines indicate C-H...O and C-H...Cl extended halogen and hydrogen-bonds found between its symmetry-generated molecules. The rest of the hydrogen atoms, counter ions and solvated molecules are omitted for clarity.

Table S2 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for ½(caH₂)·H₂O (1). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atoms	x	y	z	U(eq)
Cl1	7186.6(3)	1424.3(3)	5045.5(6)	13.56(10)
O2	3630.8(11)	1584.2(9)	3145.6(18)	14.3(2)
O1	1811.3(10)	289.7(9)	-1121.2(18)	15.8(2)
C1	3275.0(14)	143.0(11)	-683(2)	11.1(2)
C2	4338.0(14)	840.8(12)	1693(2)	11.1(2)
C3	5954.4(14)	676.2(11)	2301(2)	10.8(2)
O8	503.5(11)	1844.3(10)	2608.8(19)	15.6(2)

Table S3 Bond lengths (Å) and angles (°) for ½(caH₂)·H₂O (1).

Atoms	Distance (Å)	Atoms	Angle (°)
Cl1-C3	1.7186(12)	O1-C1-C2	118.15(11)
O2-C2	1.3173(14)	O1-C1-C3^{i}	123.73(11)
O1-C1	1.2256(15)	C3^{i}-C1-C2	118.11(10)
C1-C2	1.5104(16)	O2-C2-C1	117.75(10)
C1-C3^{i}	1.4532(16)	O2-C2-C3	122.05(11)
C2-C3	1.3508(17)	C3-C2-C1	120.18(10)
		C1^{i}-C3-Cl1	117.19(9)
		C2-C3-Cl1	121.12(9)
		C2-C3-C1^{1}	121.69(10)

Symmetry code: (i) 1-X,-Y,-Z

Table S4 Anisotropic displacement parameters ($Å^2$ x 10^3) for ½(caH₂)·H₂O (1). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + \ldots + 2\,h\,k\,a^*\,b^*\,U^{12}]$.

Atoms	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl1	13.43(16)	15.96(16)	10.21(15)	-3.0(1)	0.89(11)	-3.51(10)
O2	11.3(4)	17.1(4)	14.7(4)	-5.1(3)	3.6(3)	0.0(3)
O1	10.7(4)	19.0(5)	16.9(5)	-3.3(4)	1.9(3)	0.4(3)
C1	12.3(6)	10.4(5)	10.4(5)	1.5(4)	2.1(4)	-1.5(4)
C2	13.7(6)	10.1(5)	9.7(5)	0.3(4)	3.3(4)	-1.1(4)
C3	12.1(5)	11.2(5)	8.3(5)	-1.2(4)	1.3(4)	-2.5(4)
O8	13.8(4)	17.6(5)	16.7(5)	-3.0(4)	6.2(4)	-1.9(4)

Table S5(a) Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for ½(caH$_2$)·H$_2$O (1).

Atoms	x	y	z	U(eq)
H2	2628.58	1576.79	2486.34	21
H8A	440(20)	2200(20)	4050(30)	42(6)
H8B	-70(20)	1167(16)	2370(40)	38(6)

(b) General hydrogen-bond distances (Å) and angles (°) of ½(caH$_2$)·H$_2$O (1).

D-H…A	d(D-H) (Å)	D(H…A) (Å)	d(D…A) (Å)	D-H…A (°)
O1-H1…O5	0.82	1.87	2.632(2)	154
O1-H1…O2	0.82	2.25	2.703(2)	115
O5-H4…O5i	0.91(4)	1.99(4)	2.898(2)	178(3)
O5-H3…O2ii	0.62(4)	2.33(4)	2.938(2)	167(5)

Symmetry code: (i) x, ½ - y, z + ½ (ii) -x, -y, -z,

Table S6 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for (Et_4N) *cis*-[$NbO(ca)_2(H_2O)OPPh_3$]·$3H_2O$·THF (5). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atoms	x	y	z	U(eq)
Nb1	3333.6(3)	1029.4(2)	7858.9(2)	11.15(8)
Cl1A	5690.6(14)	2002.4(7)	4622.7(10)	33.5(3)
Cl1	-289.0(10)	1956.1(6)	10139.8(9)	20.5(2)
P1	789.1(10)	598.2(6)	5857.5(8)	14.8(2)
O1A	4293(3)	85.2(16)	7222(2)	14.1(5)
O3	4486(3)	1140.2(17)	8863(2)	19.2(6)
O1	2460(3)	65.4(16)	8428(2)	14.4(5)
O7	1966(3)	807.8(16)	6525(2)	18.3(6)
O2A	4454(3)	1407.4(16)	6581(2)	16.6(6)
O5A	6611(4)	-760.5(19)	4344(3)	28.3(8)
N1	4935(4)	-1856(2)	9729(3)	20.7(8)
O4	-1546(3)	547(2)	10851(3)	27.8(7)
O5	-1135(3)	-841.4(19)	10125(3)	28.6(8)
O12	2060(5)	38(2)	1437(3)	45.1(11)
C3A	5590(4)	1098(3)	5062(3)	19.2(8)
O6	2976(3)	2166.9(17)	7583(3)	20.8(6)
O2	1805(3)	1381.1(16)	8781(2)	15.1(6)
O4A	6728(3)	632(2)	3637(3)	26.6(7)
C111	667(4)	1216(2)	4741(3)	19.0(9)
C4A	6172(4)	528(2)	4462(3)	17.8(8)
C131	882(6)	-355(3)	5445(4)	33.1(5)
C122	-949(5)	1411(3)	6928(4)	31.0(11)
C124	-2636(5)	893(4)	7941(4)	39.4(16)
C126	-1291(5)	85(3)	6957(4)	25.8(10)
C6A	5416(4)	-422(2)	5808(3)	16.1(8)
C35	6312(4)	-2125(3)	9779(4)	25.1(10)
C34	3131(5)	-1716(3)	11021(4)	33.4(11)
C115	-409(6)	1697(4)	3145(4)	36.7(13)
C32	5555(6)	-502(3)	10106(5)	37.9(13)
C2	1090(2)	868.9(11)	9199(2)	13.1(8)
C3	57(2)	1004.4(12)	9827(2)	16.5(7)
C4	-692(2)	417.6(16)	10156(2)	24.9(10)
C5	-408(2)	-304.7(13)	9856(2)	20.5(8)
C6	624(3)	-440.2(11)	9228(2)	15.1(8)
C1	1373(2)	146.6(13)	8900(2)	15.1(8)
C31	4840(5)	-1042(3)	9392(4)	29.4(11)
C112	1655(5)	1721(3)	4615(4)	28.0(10)
C5A	6083(4)	-288(2)	4868(3)	17.8(8)
C39	1852(7)	-146(4)	2491(5)	48.1(16)
C136	1793(6)	-805(3)	5973(4)	33.1(5)
C2A	4988(4)	934(2)	5977(3)	15.0(8)
C113	1599(6)	2209(3)	3764(5)	37.7(13)
C42	2819(7)	696(4)	1504(5)	43.1(14)
C135	1871(6)	-1546(3)	5728(4)	33.1(5)

C36	6970(5)	-2116(4)	8728(5)	35.6(12)
C37	4105(5)	-2285(3)	8916(4)	28.4(10)
C121	-623(4)	695(3)	6603(3)	20.4(9)
C116	-383(5)	1211(3)	4005(4)	25.7(10)
C1A	4883(4)	148(2)	6359(3)	13.2(7)
C114	578(6)	2197(4)	3041(4)	40.4(14)
C41	3719(7)	636(5)	2492(5)	53.5(17)
C125	-2304(5)	190(4)	7633(4)	36.9(13)
C123	-1980(6)	1499(4)	7586(5)	41.3(15)
C133	150(6)	-1414(3)	4424(4)	33.1(5)
C38	4029(6)	-3118(3)	9092(5)	37.6(13)
C40	3098(8)	-14(5)	3114(5)	57(2)
C132	43(6)	-656(3)	4674(4)	33.1(5)
C134	1058(7)	-1850(3)	4945(5)	45.0(16)
Cl2A	5352.8(11)	-1322.2(6)	6276.6(9)	23.7(2)
Cl2	920.6(10)	-1346.4(6)	8725.1(8)	20.1(2)
C33	4484(5)	-1961(3)	10852(4)	24.9(10)
O13	4550(4)	3027.5(19)	6609(3)	30.5(8)
O14	1161(5)	3051(2)	8074(4)	45.9(8)
O15	2192(5)	4382(3)	7703(3)	45.9(8)

Table S7 Bond lengths (Å) and angles (°) for (Et_4N)*cis*-[$NbO(ca)_2(H_2O)OPPh_3$]·$3H_2O$·THF (5).

Atoms	Distance (Å)	Atoms	Angle (°)
Nb1-O1A	2.149(3)	O1A-Nb1-O7	82.55(11)
Nb1-O3	1.718(3)	O3-Nb1-O1A	92.39(13)
Nb1-O1	2.103(3)	O3-Nb1-O1	98.46(13)
Nb1-O7	2.192(3)	O3-Nb1-O7	174.93(13)
Nb1-O2A	2.145(3)	O3-Nb1-O2A	97.15(13)
Nb1-O6	2.108(3)	O3-Nb1-O6	96.99(14)
Nb1-O2	2.116(3)	O3-Nb1-O2	94.89(13)
Cl1A-C3A	1.725(5)	O1-Nb1-O1A	72.07(11)
Cl1-C3	1.799(2)	O1-Nb1-O7	80.31(11)
P1-O7	1.506(3)	O1-Nb1-O2A	141.15(11)
P1-C111	1.792(4)	O1-Nb1-O6	141.38(12)
P1-C131	1.797(5)	O1-Nb1-O2	73.07(11)
P1-C121	1.796(5)	O2A-Nb1-O1A	71.93(11)
O1A-C1A	1.278(5)	O2A-Nb1-O7	81.03(12)
O1-C1	1.316(3)	O6-Nb1-O1A	142.17(11)
O2A-C2A	1.288(5)	O6-Nb1-O7	86.89(12)
O5A-C5A	1.224(5)	O6-Nb1-O2A	70.57(11)
N1-C35	1.520(6)	O6-Nb1-O2	70.52(11)
N1-C31	1.527(6)	O2-Nb1-O1A	145.06(11)
N1-C37	1.521(6)	O2-Nb1-O7	89.47(12)
N1-C33	1.522(6)	O2-Nb1-O2A	140.32(12)
O4-C4	1.301(4)	O7-P1-C111	107.95(19)
O5-C5	1.285(4)	O7-P1-C131	110.3(2)
O12-C39	1.394(8)	O7-P1-C121	110.86(19)
O12-C42	1.427(8)	C111-P1-C131	111.7(2)
C3A-C4A	1.428(6)	C111-P1-C121	108.6(2)
C3A-C2A	1.370(5)	C121-P1-C131	107.5(3)
O2-C2	1.314(3)	C1A-O1A-Nb1	119.9(3)
O4A-C4A	1.227(5)	C1-O1-Nb1	117.4(2)
C111-C112	1.391(7)	P1-O7-Nb1	163.9(2)
C111-C116	1.405(6)	C2A-O2A-Nb1	120.0(3)
C4A-C5A	1.559(6)	C35-N1-C31	111.5(4)
C131-C136	1.396(8)	C35-N1-C37	112.2(4)
C131-C132	1.388(7)	C35-N1-C33	104.8(3)
C122-C121	1.400(7)	C37-N1-C31	105.8(4)
C122-C123	1.399(7)	C37-N1-C33	111.7(4)
C124-C125	1.374(10)	C33-N1-C31	110.9(4)
C124-C123	1.375(10)	C39-O12-C42	104.6(5)
C126-C121	1.387(7)	C4A-C3A-Cl1A	118.4(3)
C126-C125	1.402(7)	C2A-C3A-Cl1A	120.7(3)
C6A-C5A	1.422(6)	C2A-C3A-C4A	120.9(4)
C6A-C1A	1.372(6)	C2-O2-Nb1	118.0(2)
C6A-Cl2A	1.728(4)	C112-C111-P1	118.0(3)
C35-C36	1.520(7)	C112-C111-C116	119.5(4)
C34-C33	1.508(7)	C116-C111-P1	122.6(4)
C115-C116	1.391(7)	C3A-C4A-C5A	118.1(4)
C115-C114	1.382(9)	O4A-C4A-C3A	124.6(4)

C32-C31	1.501(8)	O4A-C4A-C5A	117.4(4)
C2-C3	1.39	C136-C131-P1	117.5(4)
C2-C1	1.39	C132-C131-P1	122.3(4)
C3-C4	1.39	C132-C131-C136	120.1(5)
C4-C5	1.39	C123-C122-C121	118.8(5)
C5-C6	1.39	C125-C124-C123	120.2(5)
C6-C1	1.39	C121-C126-C125	119.7(5)
C6-Cl2	1.782(2)	C5A-C6A-Cl2A	118.1(3)
C112-C113	1.385(7)	C1A-C6A-C5A	121.4(4)
C39-C40	1.509(10)	C1A-C6A-Cl2A	120.4(3)
C136-C135	1.373(7)	N1-C35-C36	115.3(4)
C2A-C1A	1.499(6)	C114-C115-C116	119.8(5)
C113-C114	1.371(9)	O2-C2-C3	125.3(2)
C42-C41	1.528(8)	O2-C2-C1	114.5(2)
C135-C134	1.385(8)	C3-C2-C1	120.0
C37-C38	1.519(8)	C2-C3-Cl1	117.48(15)
C41-C40	1.566(12)	C4-C3-Cl1	122.47(15)
C133-C132	1.406(7)	C4-C3-C2	120.0
C133-C134	1.375(9)	O4-C4-C3	118.6(2)
		O4-C4-C5	120.8(2)
		C3-C4-C5	120.0
		O5-C5-C4	119.7(2)
		O5-C5-C6	120.2(2)
		C6-C5-C4	120.0
		C5-C6-Cl2	121.02(15)
		C1-C6-C5	120.0
		C1-C6-Cl2	118.71(15)
		O1-C1-C2	115.2(2)
		O1-C1-C6	124.1(2)
		C6-C1-C2	120.0
		C32-C31-N1	115.6(4)
		C113-C112-C111	119.9(5)
		O5A-C5A-C4A	116.3(4)
		O5A-C5A-C6A	125.6(4)
		C6A-C5A-C4A	118.1(4)
		O12-C39-C40	106.7(6)
		C135-C136-C131	120.3(5)
		O2A-C2A-C3A	125.6(4)
		O2A-C2A-C1A	113.2(3)
		C3A-C2A-C1A	121.1(4)
		C114-C113-C112	120.5(5)
		O12-C42-C41	108.0(5)
		C136-C135-C134	120.2(6)
		C38-C37-N1	115.8(4)
		C122-C121P1	117.4(4)
		C126-C121-P1	122.0(4)
		C126-C121-C122	120.1(4)
		C115-C116-C111	119.7(5)
		O1A-C1A-C6A	125.9(4)
		O1A-C1A-C2A	113.7(3)
		C6A-C1A-C2A	120.4(4)
		C113-C114-C115	120.7(5)
		C42-C41-C40	101.9(6)
		C124-C125-C126	120.3(5)

	C124-C123-C122	120.9(6)
	C134-C133-C132	120.5(5)
	C39-C40-C41	103.1(5)
	C131-C132-C133	118.8(5)
	C133-C134-C135	120.2(5)
	C34-C33-N1	115.4(4)

Table S8 Anisotropic displacement parameters (Å² x 10³) for (Et_4N)*cis*-[$NbO(ca)_2(H_2O)OPPh_3$]·3H_2O· THF (5). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + \ldots + 2 h k a^* b^* U^{12}]$.

Atoms	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Nb1	11.07(14)	9.73(14)	12.85(14)	-0.70(13)	2.78(10)	-0.40(14)
Cl1A	53.1(8)	18.6(5)	30.5(6)	4.0(5)	21.9(6)	-6.5(5)
Cl1	22.9(5)	15.9(5)	23.4(5)	-3.8(4)	7.1(4)	3.5(4)
P1	14.4(5)	16.5(5)	13.5(4)	0.5(4)	-0.6(4)	-0.1(4)
O1A	13.9(13)	11.8(13)	16.9(14)	0.4(11)	3.6(11)	0.9(11)
O3	17.9(13)	20.3(17)	19.4(13)	-3.1(12)	1.1(11)	0.3(12)
O1	12.0(13)	13.4(13)	18.3(14)	0.9(11)	5.4(11)	0.9(10)
O7	19.5(15)	15.6(14)	19.2(14)	0.5(11)	-3.6(12)	-0.7(11)
O2A	17.3(14)	14.0(14)	19.4(14)	-1.3(11)	9.2(11)	-1.8(11)
O5A	34.0(19)	25.5(18)	26.7(17)	-5.3(14)	14.2(14)	4.3(15)
N1	22.1(19)	22.6(19)	17.2(18)	6.6(15)	-0.8(14)	4.8(15)
O4	26.5(17)	29.8(18)	28.8(17)	1.5(14)	18.7(14)	-1.9(14)
O5	29.1(18)	22.9(17)	35.3(19)	-0.2(14)	16.5(15)	-9.9(14)
O12	61(3)	41(2)	32(2)	-2.9(18)	-9(2)	6(2)
C3A	24.2(19)	13.1(19)	21.0(18)	-1.1(17)	6.8(15)	-1.7(18)
O6	23.5(16)	11.9(14)	27.9(16)	4.5(12)	12.0(13)	2.3(12)
O2	14.6(14)	12.0(13)	19.2(14)	-0.9(11)	7.6(11)	-1.1(11)
O4A	29.4(18)	30.9(18)	20.6(15)	-3.9(14)	12.3(13)	-6.9(15)
C111	19(2)	24(2)	14.4(17)	3.1(14)	1.3(15)	4.3(15)
C4A	16.6(19)	20(2)	17.1(18)	-3.4(16)	2.6(15)	-4.7(16)
C131	42.3(13)	23.7(12)	32.4(12)	-4.3(9)	-6.5(10)	-6.9(10)
C122	32(3)	34(3)	28(3)	1(2)	7(2)	8(2)
C124	17(2)	78(5)	24(2)	-2(3)	2.8(17)	8(3)
C126	21(2)	37(3)	20(2)	5.7(19)	1.0(17)	-5(2)
C6A	17.5(19)	11.7(18)	19.4(19)	-0.1(15)	2.7(15)	-0.9(15)
C35	19(2)	30(2)	26(2)	7.7(19)	-2.7(17)	9.1(18)
C34	33(3)	36(3)	32(3)	4(2)	9(2)	5(2)
C115	35(3)	51(3)	24(2)	5(2)	-7(2)	14(3)
C32	38(3)	23(3)	53(3)	7(2)	2(3)	3(2)
C2	13.6(17)	16(2)	9.8(15)	0.2(13)	-1.0(13)	-4.0(13)
C3	16.0(16)	17.2(17)	16.5(16)	-5.5(19)	2.7(13)	6.4(19)
C4	16(2)	33(3)	26(2)	10.5(19)	4.4(17)	3.7(18)
C5	18(2)	27(2)	16.2(19)	3.5(17)	3.3(15)	-0.5(18)
C6	14.3(18)	12.5(18)	18.6(19)	1.8(15)	0.7(15)	-0.7(15)
C1	14.9(18)	19(2)	10.9(17)	-0.4(15)	1.0(14)	0.1(15)
C31	28(2)	25(2)	36(3)	13(2)	6(2)	10(2)
C112	21(2)	32(3)	31(3)	10(2)	1.6(19)	-1.5(19)
C5A	17.3(19)	19(2)	17.3(19)	-3.8(16)	2.2(15)	-2.3(16)
C39	51(4)	54(4)	40(3)	-1(3)	3(3)	17(3)
C136	42.3(13)	23.7(12)	32.4(12)	-4.3(9)	-6.5(10)	-6.9(10)
C2A	11.4(16)	14(2)	19.2(17)	-2.6(15)	1.2(13)	-2.7(15)
C113	33(3)	40(3)	40(3)	21(2)	9(2)	0(2)
C42	49(4)	41(3)	38(3)	-7(3)	-10(3)	2(3)
C135	42.3(13)	23.7(12)	32.4(12)	-4.3(9)	-6.5(10)	-6.9(10)
C36	27(3)	44(3)	37(3)	7(2)	8(2)	9(2)

C37	25(2)	35(3)	25(2)	3(2)	-5.1(19)	8(2)
C121	15(2)	32(2)	13.9(19)	1.9(17)	-1.3(15)	2.5(18)
C116	22(2)	32(3)	23(2)	3.8(17)	-2.7(17)	2.0(17)
C1A	10.7(17)	13.4(18)	15.5(18)	1.4(15)	0.6(14)	-0.7(14)
C114	42(3)	52(4)	29(3)	20(3)	11(2)	17(3)
C41	58(4)	63(4)	37(3)	-1(3)	-21(3)	2(4)
C125	18(2)	65(4)	27(3)	12(3)	0(2)	-10(3)
C123	37(3)	58(4)	30(3)	-6(3)	6(2)	21(3)
C133	42.3(13)	23.7(12)	32.4(12)	-4.3(9)	-6.5(10)	-6.9(10)
C38	36(3)	37(3)	38(3)	-4(2)	-9(2)	-3(2)
C40	65(5)	81(6)	25(3)	5(3)	-8(3)	25(4)
C132	42.3(13)	23.7(12)	32.4(12)	-4.3(9)	-6.5(10)	-6.9(10)
C134	78(5)	22(3)	35(3)	-10(2)	2(3)	-12(3)
Cl2A	33.5(6)	13.6(4)	24.7(5)	-0.6(4)	7.8(4)	5.6(4)
Cl2	22.0(5)	12.9(4)	25.8(5)	-1.4(4)	4.6(4)	-1.7(4)
C33	29(2)	23(2)	23(2)	5.8(18)	2.8(19)	4.3(19)
O13	46(2)	16.2(16)	30.8(18)	4.8(13)	14.9(16)	-0.7(15)
O14	70(2)	35.5(16)	34.8(15)	-1.2(12)	27.1(15)	-0.8(15)
O15	70(2)	35.5(16)	34.8(15)	-1.2(12)	27.1(15)	-0.8(15)

Table S9 Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for (Et_4N)*cis*-[$NbO(ca)_2(H_2O)OPPh_3$]·$3H_2O$·THF (5).

Atoms	x	y	z	U(eq)
H6A	2379.48	2433.31	7815.08	31
H6B	3393.87	2459.41	7198.88	31
H122	-479.85	1830.61	6705.17	37
H124	-3321.52	960.66	8400.7	47
H126	-1064.29	-401.06	6742.64	31
H35A	6330.52	-2639.54	10058.03	30
H35B	6811.05	-1811.71	10294.08	30
H34A	2927.92	-1804.04	11762.52	50
H34B	3045.24	-1184.93	10859.8	50
H34C	2539.6	-1998.84	10549.42	50
H115	-1104.06	1686.07	2632.2	44
H32A	5436.49	2.57	9825.31	57
H32B	5228.73	-528.1	10822.77	57
H32C	6467.7	-626.04	10137.31	57
H31A	5162.17	-996.38	8667.93	35
H31B	3926.42	-898.69	9351.6	35
H112	2366.18	1730.93	5111.83	34
H39A	1593.01	-673.12	2544.47	58
H39B	1167.82	168.41	2769.11	58
H136	2361.64	-597.22	6503.08	40
H113	2272.44	2555.1	3680.51	45
H42A	2262.83	1138	1558.48	52
H42B	3319.39	748.07	859.63	52
H135	2484.31	-1851.43	6097.22	40
H36A	7848.89	-2297.92	8838.91	53
H36B	6502.63	-2437.08	8215.81	53
H36C	6984.3	-1607.29	8452.42	53
H37A	3227.02	-2079.3	8912.94	34
H37B	4435.38	-2195.84	8202.99	34
H116	-1072.66	876.73	4093.35	31
H114	550.36	2535.81	2461.1	49
H41A	3733.41	1101.7	2909.28	64
H41B	4600.09	510.67	2300.63	64
H125	-2761.32	-227.05	7878.17	44
H123	-2228.85	1983.59	7791.18	50
H133	-408.85	-1626.54	3890.19	40
H38A	3474.42	-3341.26	8530.3	56
H38B	4886.95	-3333.37	9074.19	56
H38C	3675.27	-3216.51	9786.08	56
H40A	3644.65	-463.14	3119.73	69
H40B	2947.82	131.96	3855.99	69
H132	-592.25	-355.93	4323.02	40
H134	1126.91	-2360.53	4767.37	54
H33A	4561.1	-2493.18	11039.36	30
H33B	5065.53	-1681.22	11349	30
H13A	4160.37	3349.87	6220.95	46

H13B	4893.1	2739.17	6169.72	46
H14A	1479.52	3477.43	7967.07	69
H14B	742.83	3104.13	8632.14	69
H15A	2024.99	4737.2	8109.61	380(160)
H15B	2576.69	4544.19	7203.1	160(60)

Table S10 Torsion angles (°) for (Et_4N)*cis*-[$NbO(ca)_2(H_2O)OPPh_3$]·$3H_2O$·THF (5).

Torsion angles	Angle (°)	Torsion angles	Angle (°)
Nb1-O1A-C1A-C6A	-172.6(3)	C2-C3-C4-O4	171.3(3)
Nb1-O1A-C1A-C2A	8.7(4)	C2-C3-C4-C5	0.0
Nb1-O1-C1-C2	-15.2(3)	C3-C2-C1-O1	-171.4(3)
Nb1-O1-C1-C6	173.79(14)	C3-C2-C1-C6	0.0
Nb1-O2A-C2A-C3A	171.4(3)	C3-C4-C5-O5	-177.1(3)
Nb1-O2A-C2A-C1A	-7.8(4)	C3-C4-C5-C6	0.0
Nb1-O2-C2-C3	179.63(15)	C4-C5-C6-C1	0.0
Nb1-O2-C2-C1	-5.3(3)	C4-C5-C6-Cl2	-173.9(2)
Cl1A-C3A-C4A-O4A	-1.3(6)	C5-C6-C1-O1	170.6(3)
Cl1A-C3A-C4A-C5A	179.7(3)	C5-C6-C1-C2	0.0
Cl1A-C3A-C2A-O2A	0.2(6)	C1-C2-C3-Cl1	-177.6(2)
Cl1A-C3A-C2A-C1A	179.3(3)	C1-C2-C3-C4	0.0
Cl1-C3-C4-O4	-11.2(3)	C31-N1-C35-C36	-62.9(6)
Cl1-C3-C4-C5	177.5(2)	C31-N1-C37-C38	-179.2(4)
P1-C111-C112-C113	-179.9(4)	C31-N1-C33-C34	58.3(6)
P1-C111-C116-C115	-179.0(4)	C112-C111-C116-C115	1.6(7)
P1-C131-C136-C135	176.9(5)	C112-C113-C114-C115	-0.2(9)
P1-C131-C132-C133	-177.7(4)	C5A-C6A-C1A-O1A	-178.3(4)
O7-P1-C111-C112	4.8(4)	C5A-C6A-C1A-C2A	0.3(6)
O7-P1-C111-C116	-174.7(4)	C39-O12-C42-C41	35.3(7)
O7-P1-C131-C136	15.2(5)	C136-C131-C132-C133	-1.4(9)
O7-P1-C131-C132	-168.4(5)	C136-C135-C134-C133	-1.4(10)
O7-P1-C121-C122	64.8(4)	C2A-C3A-C4A-O4A	-179.9(4)
O7-P1-C121-C126	-107.8(4)	C2A-C3A-C4A-C5A	1.1(6)
O2A-C2A-C1A-O1A	-0.6(5)	C42-O12-C39-C40	-41.0(7)
O2A-C2A-C1A-C6A	-179.3(4)	C42-C41-C40-C39	-8.3(7)
O4-C4-C5-O5	11.8(4)	C37-N1-C35-C36	55.6(6)
O4-C4-C5-C6	-171.1(3)	C37-N1-C31-C32	178.0(4)
O5-C5-C6-C1	177.1(3)	C37-N1-C33-C34	-59.5(5)
O5-C5-C6-Cl2	3.2(3)	C121-P1-O7-Nb1	24.5(8)
O12-C39-C40-C41	30.3(7)	C121-P1-C111-C112	125.0(4)
O12-C42-C41-C40	-15.4(7)	C121-P1-C111-C116	-54.5(4)
C3A-C4A-C5A-O5A	-178.9(4)	C121-P1-C131-C136	-105.8(5)
C3A-C4A-C5A-C6A	0.6(6)	C121-P1-C131-C132	70.6(5)
C3A-C2A-C1A-O1A	-179.8(4)	C121-C122-C123-C124	2.2(8)
C3A-C2A-C1A-C6A	1.4(6)	C121-C126-C125-C124	0.2(8)
O2-C2-C3-Cl1	-2.8(3)	C116-C111-C112-C113	-0.4(8)
O2-C2-C3-C4	174.9(3)	C116-C115-C114-C113	1.3(9)
O2-C2-C1-O1	13.2(3)	C1A-C6A-C5A-O5A	178.2(4)
O2-C2-C1-C6	-175.4(3)	C1A-C6A-C5A-C4A	-1.3(6)
O4A-C4A-C5A-O5A	2.1(6)	C114-C115-C116-C111	-2.0(8)
O4A-C4A-C5A-C6A	-178.5(4)	C125-C124-C123-C122	-1.4(8)
C111-P1-O7-Nb1	143.3(7)	C125-C126-C121-P1	173.1(4)
C111-P1-C131-C136	135.2(5)	C125-C126-C121-C122	0.7(7)
C111-P1-C131-C132	-48.4(6)	C123-C122-C121-P1	-174.6(4)
C111-P1-C121-C122	-53.6(4)	C123-C122-C121-C126	-1.8(8)
C111-P1-C121-C126	133.8(4)	C123-C124-C125-C126	0.2(8)
C111-C112-C113-C114	-0.3(9)	C132-C131-C136-C135	0.5(9)
C4A-C3A-C2A-O2A	178.8(4)	C132-C133-C134-C135	0.4(10)
C4A-C3A-C2A-C1A	-2.1(6)	C134-C133-C132-C131	1.0(9)

C131-P1-O7-Nb1	-94.4(7)	Cl2A-C6A-C5A-O5A	1.1(6)
C131-P1-C111-C112	-116.6(4)	Cl2A-C6A-C5A-C4A	-178.3(3)
C131-P1-C111-C116	63.9(5)	Cl2A-C6A-C1A-O1A	-1.3(6)
C131-P1-C121-C122	-174.6(4)	Cl2A-C6A-C1A-C2A	177.3(3)
C131-P1-C121-C126	12.8(5)	Cl2-C6-C1-O1	-15.4(3)
C131-C136-C135-C134	0.9(9)	Cl2-C6-C1-C2	174.0(2)
C35-N1-C31-C32	-59.8(6)	C33-N1-C35-C36	177.0(5)
C35-N1-C37-C38	59.0(6)	C33-N1-C31-C32	56.7(6)
C35-N1-C33-C34	178.8(4)	C33-N1-C37-C38	-58.4(6)

Table S11 General hydrogen-bond distances (Å) and angles (°) of (Et_4N)*cis*-[$NbO(ca)_2(H_2O)OPPh_3$]·$3H_2O$·THF (5).

Interactions	D-H…A	D-H(Å)	H…A (Å)	D…A (Å)	D-H…A (°)
I	O13-H1…Cl5	0.87(4)	2.52(4)	3.370(2)	166(3)
II	O13-H1…O4	0.87(4)	2.47(4)	2.921(3)	113(3)
III	O13-H2…O9[a]	0.86(4)	1.89(4)	2.739(3)	171(3)
IV	O14-H4…O15[a]	0.85(3)	1.85(3)	2.673(4)	165(5)
V	O15-H5…O8	0.81(3)	2.35(3)	3.062(3)	147(3)
VI	O15-H5…O9	0.81(3)	2.24(3)	2.922(3)	142(3)
VII	O5-H5A…O14	0.92(3)	1.69(3)	2.577(3)	163(3)
VIII	O5-H5B…O13	0.84(4)	2.79(4)	2.608(3)	165(4)
IX	O15-H6…O10[b]	0.85(4)	2.05(4)	2.890(3)	175(5)
X	C14-H14…O6	0.93	2.49	2.918(3)	108
XI	C18-H18…O8[c]	0.93	2.40	3.212(4)	145
XII	C22-H22…O7[c]	0.93	2.44	3.314(4)	157
XIII	C30-H30…O3	0.93	2.52	3.394(3)	156
XIV	C30-H30…O6	0.93	2.57	2.985(3)	108
XV	C31-H31B…O2[d]	0.97	2.57	3.374(4)	140
XVI	C33-H32A…O7[d]	0.96	2.57	3.500(4)	163
XVII	C32-H32B…O11[e]	0.96	2.56	3.522(4)	175
XVIII	C34-H34C…O12[f]	0.96	2.57	3.403(4)	146
XIX	C37-H37A…Cl3[d]	0.97	2.78	3.740(3)	172

Symmetry code: (a) -x+1, y+½, -z+1 (b), x+1, y, z - 1 (c), x-1, y, z (d), x, y+1, (e), x+1, y+1, z (f), -x+1, y+½, -z+2

Table S12 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $(Et_4N)_4[Nb_4O_4(ca)_2(\mu^2\text{-}O)_2Cl_8].2CH_3CN$ (6). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atoms	x	y	z	U(eq)
Nb2B	3987.7(4)	5243.7(9)	3566.7(3)	16.95(19)
Nb2A	1048.0(4)	6433.6(9)	1423.6(3)	16.09(19)
Nb1A	2451.9(4)	6477.5(9)	3963.3(3)	16.76(19)
Nb3B	2426.4(4)	4522.2(9)	1069.3(3)	19.4(2)
Cl4A	2413.0(11)	9003(2)	2476.4(8)	21.4(5)
Cl4B	3832.4(12)	7492(2)	2108.7(8)	23.6(5)
Cl3A	1148.2(12)	3799(2)	2901.4(8)	21.2(5)
Cl3B	2561.5(12)	2290(2)	2534.4(9)	23.0(5)
Cl5A	180.4(11)	7141(2)	1850.8(8)	22.0(5)
Cl6A	363.0(13)	4959(2)	1079.7(9)	26.7(6)
Cl1B	4057.1(13)	3652(3)	4102.3(9)	29.8(6)
Cl2B	4768.2(13)	4076(3)	3169.0(10)	30.0(6)
Cl1A	1423.8(13)	7479(3)	3964.9(10)	32.6(6)
Cl2A	2880.0(15)	8287(3)	4305.9(10)	34.5(7)
Cl5B	3498.1(13)	3793(3)	1026.8(11)	37.5(7)
Cl6B	2557.2(15)	5754(3)	445.3(10)	37.0(7)
O5A	1611(3)	7394(7)	1892(2)	17.1(14)
O4A	1163(3)	5178(7)	2059(2)	18.7(14)
O2A	1982(3)	5374(7)	3480(2)	19.9(15)
O3A	2462(3)	7565(7)	3297(2)	20.4(15)
O5B	2990(3)	5912(7)	1548(2)	19.1(14)
O3B	3823(4)	6139(7)	2962(2)	21.2(15)
O4B	2496(3)	3733(7)	1701(2)	20.1(15)
O2B	3327(3)	3968(7)	3116(2)	18.0(14)
O1B	4482(4)	6368(8)	3765(2)	25.9(16)
N6D	707(4)	1242(8)	1686(3)	21.7(18)
N5D	1321(4)	1902(8)	4334(3)	21.4(18)
O1A	2355(4)	5480(8)	4385(2)	25.5(16)
O6B	2047(4)	3247(8)	851(3)	29.9(18)
O1C	3221(3)	5878(7)	3753(2)	22.4(15)
O6A	1024(4)	7682(8)	1069(3)	27.0(17)
O2C	1755(3)	5524(8)	1260(2)	25.4(16)
N3D	4360(4)	9880(8)	3267(3)	22.7(19)
C1A	1879(4)	5767(9)	3097(3)	14.3(17)
C5A	2074(4)	7571(9)	2578(3)	13.8(17)
C2A	1528(4)	5160(9)	2784(3)	15.5(18)
C5B	3446(4)	6141(9)	2242(3)	17.9(19)
C4A	1728(4)	6964(9)	2269(3)	14.6(18)
C3A	1459(4)	5679(9)	2367(3)	14.5(18)
C1B	3228(4)	4365(9)	2747(3)	16.7(18)
C6A	2172(4)	7048(9)	2995(3)	13.5(17)
C4B	3085(4)	5500(10)	1919(3)	17.6(19)
C6B	3522(4)	5644(9)	2649(3)	13.5(17)
C30D	937(5)	511(11)	2459(4)	28(2)

C2B	2881(4)	3752(9)	2420(3)	16.5(18)
C7D	3709(5)	9368(11)	3331(4)	25(2)
C11D	4736(5)	8800(9)	3095(4)	21(2)
C12D	5397(5)	9124(13)	3014(5)	36(3)
C35D	429(6)	727(11)	1264(4)	29(2)
N4D	3748(7)	5521(15)	5599(5)	59(2)
C28D	1378(7)	807(13)	3598(4)	39(3)
C8D	3243(5)	10347(13)	3485(4)	34(3)
C3B	2804(5)	4222(10)	2017(3)	18.4(19)
C36D	361(6)	1644(13)	898(4)	36(3)
C33D	1360(5)	1739(12)	1617(4)	30(3)
C1D	1404(9)	9167(18)	202(5)	55(5)
C9D	4651(6)	10384(13)	3681(4)	38(3)
C6D	4069(7)	10691(13)	2514(4)	39(3)
C31D	342(6)	2363(12)	1845(4)	29(2)
C5D	4336(6)	10992(11)	2962(4)	33(3)
C27D	1386(6)	686(11)	4085(4)	32(3)
C10D	4741(7)	9422(16)	4032(5)	48(4)
C29D	726(8)	150(15)	2006(5)	50.8(15)
C14D	4203(7)	7549(13)	5907(5)	43(3)
C25D	681(6)	2421(13)	4224(4)	34(3)
C23D	1394(8)	1622(17)	4805(5)	53(2)
C34D	1817(6)	804(14)	1446(4)	40(3)
C17D	3120(7)	4962(15)	5458(6)	50.8(15)
N1D	1476(7)	10210(16)	287(5)	59(2)
C19D	4095(7)	4672(16)	5915(5)	50.8(15)
C21D	1791(7)	2891(16)	4203(6)	53(2)
C32D	-320(6)	2043(15)	1953(4)	42(3)
N2D	5212(7)	7986(15)	4991(5)	59(2)
C15D	4186(8)	5574(15)	5225(5)	47(4)
C18D	3100(7)	3740(15)	5252(5)	50.8(15)
C2D	1308(12)	7886(19)	100(5)	76(7)
C26D	501(7)	3609(15)	4462(5)	48(4)
C3D	5625(8)	8649(15)	5028(5)	50(4)
C24D	918(8)	745(16)	4992(6)	53(2)
C4D	6158(8)	9490(20)	5077(7)	79(7)
C13D	3643(7)	6794(15)	5764(6)	50.8(15)
C22D	2443(7)	2404(16)	4229(6)	53(2)
C20D	3764(7)	4431(16)	6341(5)	50.8(15)
C16D	3925(7)	6367(16)	4852(5)	50.8(15)

Table S13 Bond lengths (Å) and angles (°) for $(Et_4N)_4[Nb_4O_4(ca)_2(\mu^2\text{-}O)_2Cl_8]\cdot 2CH_3CN$ (6).

Atoms	Distance (Å)	Atoms	Angle (°)
Nb2B-Cl1B	2.383(3)	Cl1B-Nb2B-Cl2B	88.12(11)
Nb2B-Cl2B	2.469(3)	Cl1B-Nb2B-O2B	91.57(19)
Nb2B-O3B	2.132(7)	O3B-Nb2B-Cl1B	160.6(2)
Nb2B-O2B	2.390(7)	O3B-Nb2B-Cl2B	82.8(2)
Nb2B-O1B	1.705(8)	O3B-Nb2B-O2B	70.0(3)
Nb2B-O1C	1.900(8)	O2B-Nb2B-Cl2B	79.66(19)
Nb2A-Cl5A	2.459(3)	O1B-Nb2B-Cl1B	103.0(3)
Nb2A-Cl6A	2.386(3)	O1B-Nb2B-Cl2B	96.1(3)
Nb2A-O5A	2.129(7)	O1B-Nb2B-O3B	95.0(3)
Nb2A-O4A	2.398(7)	O1B-Nb2B-O2B	164.8(3)
Nb2A-O6A	1.731(8)	O1B-Nb2B-O1C	100.3(4)
Nb2A-O2C	1.896(7)	O1C-Nb2B-Cl1B	94.1(2)
Nb1A-Cl1A	2.464(3)	O1C-Nb2B-Cl2B	162.4(2)
Nb1A-Cl2A	2.376(3)	O1C-Nb2B-O3B	89.6(3)
Nb1A-O2A	2.139(7)	O1C-Nb2B-O2B	82.8(3)
Nb1A-O3A	2.381(7)	Cl6A-Nb2A-Cl5A	88.49(10)
Nb1A-O1A	1.711(8)	Cl6A-Nb2A-O4A	92.67(18)
Nb1A-O1C	1.919(8)	O5A-Nb2A-Cl5A	84.68(19)
Nb3B-Cl5B	2.450(3)	O5A-Nb2A-Cl6A	162.6(2)
Nb3B-Cl6B	2.375(3)	O5A-Nb2A-O4A	70.3(2)
Nb3B-O5B	2.402(7)	O4A-Nb2A-Cl5A	77.29(19)
Nb3B-O4B	2.142(7)	O6A-Nb2A-Cl5A	96.1(3)
Nb3B-O6B	1.716(8)	O6A-Nb2A-Cl6A	102.5(3)
Nb3B-O2C	1.914(7)	O6A-Nb2A-O5A	94.1(3)
Cl4A-C5A	1.728(9)	O6A-Nb2A-O4A	163.4(3)
Cl4B-C5B	1.724(10)	O6A-Nb2A-O2C	103.1(4)
Cl3A-C2A	1.713(10)	O2C-Nb2A-Cl5A	160.3(2)
Cl3B-C2B	1.747(10)	O2C-Nb2A-Cl6A	91.9(3)
O5A-C4A	1.278(12)	O2C-Nb2A-O5A	89.2(3)
O4A-C3A	1.253(12)	O2C-Nb2A-O4A	83.0(3)
O2A-C1A	1.278(11)	Cl2A-Nb1A-Cl1A	88.97(12)
O3A-C6A	1.241(12)	Cl2A-Nb1A-O3A	88.9(2)
O5B-C4B	1.248(12)	O2A-Nb1A-Cl1A	80.6(2)
O3B-C6B	1.269(12)	O2A-Nb1A-Cl2A	158.5(2)
O4B-C3B	1.279(12)	O2A-Nb1A-O3A	70.9(3)
O2B-C1B	1.237(12)	O3A-Nb1A-Cl1A	80.18(19)
N6D-C35D	1.528(14)	O1A-Nb1A-Cl1A	97.5(3)
N6D-C33D	1.530(13)	O1A-Nb1A-Cl2A	102.5(3)
N6D-C31D	1.525(14)	O1A-Nb1A-O2A	97.6(3)
N6D-C29D	1.532(19)	O1A-Nb1A-O3A	168.4(3)
N5D-C27D	1.521(15)	O1A-Nb1A-O1C	100.9(4)
N5D-C25D	1.517(14)	O1C-Nb1A-Cl1A	159.6(2)
N5D-C23D	1.501(19)	O1C-Nb1A-Cl2A	95.6(2)
N5D-C21D	1.531(18)	O1C-Nb1A-O2A	88.2(3)
N3D-C7D	1.528(13)	O1C-Nb1A-O3A	80.0(3)
N3D-C11D	1.519(13)	Cl6B-Nb3B-Cl5B	89.36(12)
N3D-C9D	1.514(15)	Cl6B-Nb3B-O5B	95.45(19)
N3D-C5D	1.520(15)	O5B-Nb3B-Cl5B	76.84(19)
C1A-C2A	1.375(13)	O4B-Nb3B-Cl5B	83.8(2)
C1A-C6A	1.543(13)	O4B-Nb3B-Cl6B	164.8(2)
C5A-C4A	1.362(13)	O4B-Nb3B-O5B	69.8(3)

C5A-C6A	1.424(13)	O6B-Nb3B-Cl5B	99.5(3)
C2A-C3A	1.417(14)	O6B-Nb3B-Cl6B	100.5(3)
C5B-C4B	1.426(14)	O6B-Nb3B-O5B	163.6(3)
C5B-C6B	1.379(14)	O6B-Nb3B-O4B	94.0(4)
C4A-C3A	1.524(13)	O6B-Nb3B-O2C	102.1(4)
C1B-C6B	1.539(13)	O2C-Nb3B-Cl5B	157.3(3)
C1B-C2B	1.405(14)	O2C-Nb3B-Cl6B	93.5(3)
C4B-C3B	1.527(14)	O2C-Nb3B-O5B	80.5(3)
C30D-C29D	1.520(19)	O2C-Nb3B-O4B	87.8(3)
C2B-C3B	1.359(14)	C4A-O5A-Nb2A	123.2(6)
C7D-C8D	1.541(16)	C3A-O4A-Nb2A	115.4(6)
C11D-C12D	1.499(14)	C1A-O2A-Nb1A	122.7(6)
C35D-C36D	1.507(18)	C6A-O3A-Nb1A	115.1(6)
N4D-C17D	1.53(2)	C4B-O5B-Nb3B	114.9(7)
N4D-C19D	1.52(2)	C6B-O3B-Nb2B	123.9(6)
N4D-C15D	1.53(2)	C3B-O4B-Nb3B	124.4(7)
N4D-C13D	1.47(2)	C1B-O2B-Nb2B	115.5(6)
C28D-C27D	1.525(18)	C35D-N6D-C33D	109.6(9)
C33D-C34D	1.514(19)	C35D-N6D-C29D	106.7(9)
C1D-N1D	1.15(2)	C33D-N6D-C29D	110.7(10)
C1D-C2D	1.42(3)	C31D-N6D-C35D	111.8(9)
C9D-C10D	1.51(2)	C31D-N6D-C33D	105.4(9)
C6D-C5D	1.52(2)	C31D-N6D-C29D	112.7(10)
C31D-C32D	1.521(17)	C27D-N5D-C21D	112.1(10)
C14D-C13D	1.505(19)	C25D-N5D-C27D	107.2(9)
C25D-C26D	1.528(19)	C25D-N5D-C21D	107.3(10)
C23D-C24D	1.52(2)	C23D-N5D-C27D	108.8(10)
C17D-C18D	1.45(2)	C23D-N5D-C25D	110.8(10)
C19D-C20D	1.55(2)	C23D-N5D-C21D	110.6(11)
C21D-C22D	1.50(2)	Nb2B-O1C-Nb1A	177.6(5)
N2D-C3D	1.14(2)	Nb2A-O2C-Nb3B	175.6(5)
C15D-C16D	1.53(2)	C11D-N3D-C7D	106.4(8)
C3D-C4D	1.46(2)	C11D-N3D-C5D	112.1(9)
		C9D-N3D-C7D	111.6(9)
		C9D-N3D-C11D	111.1(9)
		C9D-N3D-C5D	105.1(9)
		C5D-N3D-C7D	110.5(9)
		O2A-C1A-C2A	125.5(9)
		O2A-C1A-C6A	115.1(8)
		C2A-C1A-C6A	119.4(8)
		C4A-C5A-Cl4A	121.0(7)
		C4A-C5A-C6A	121.2(9)
		C6A-C5A-Cl4A	117.8(7)
		C1A-C2A-Cl3A	120.2(8)
		C1A-C2A-C3A	120.2(9)
		C3A-C2A-Cl3A	119.5(7)
		C4B-C5B-Cl4B	119.1(8)
		C6B-C5B-Cl4B	120.2(8)
		C6B-C5B-C4B	120.6(9)
		O5A-C4A-C5A	124.4(9)
		O5A-C4A-C3A	116.3(8)
		C5A-C4A-C3A	119.3(8)
		O4A-C3A-C2A	124.7(9)
		O4A-C3A-C4A	114.7(8)
		C2A-C3A-C4A	120.5(8)

	O2B-C1B-C6B	115.5(8)
	O2B-C1B-C2B	125.8(9)
	C2B-C1B-C6B	118.7(9)
	O3A-C6A-C1A	115.9(8)
	O3A-C6A-C5A	124.9(9)
	C5A-C6A-C1A	119.2(8)
	O5B-C4B-C5B	123.6(10)
	O5B-C4B-C3B	116.5(9)
	C5B-C4B-C3B	119.8(9)
	O3B-C6B-C5B	126.0(9)
	O3B-C6B-C1B	114.7(8)
	C5B-C6B-C1B	119.3(9)
	C1B-C2B-Cl3B	118.1(7)
	C3B-C2B-Cl3B	118.9(8)
	C3B-C2B-C1B	122.9(9)
	N3D-C7D-C8D	114.5(10)
	C12D-C11D-N3D	114.2(9)
	C36D-C35D-N6D	116.3(10)
	C19D-N4D-C17D	111.3(13)
	C19D-N4D-C15D	102.4(13)
	C15D-N4D-C17D	111.2(13)
	C13D-N4D-C17D	108.2(14)
	C13D-N4D-C19D	113.6(13)
	C13D-N4D-C15D	110.0(13)
	O4B-C3B-C4B	114.2(9)
	O4B-C3B-C2B	127.2(10)
	C2B-C3B-C4B	118.6(9)
	C34D-C33D-N6D	116.0(10)
	N1D-C1D-C2D	179(2)
	C10D-C9D-N3D	114.6(11)
	C32D-C31D-N6D	113.5(11)
	N3D-C5D-C6D	114.3(10)
	N5D-C27D-C28D	116.1(10)
	C30D-C29D-N6D	114.4(11)
	N5D-C25D-C26D	116.0(11)
	N5D-C23D-C24D	116.8(13)
	C18D-C17D-N4D	119.1(15)
	N4D-C19D-C20D	115.1(14)
	C22D-C21D-N5D	112.2(14)
	C16D-C15D-N4D	112.3(14)
	N2D-C3D-C4D	180(2)
	N4D-C13D-C14D	117.7(14)

Table S14 Anisotropic displacement parameters ($Å^2$ x 10^3) for $(Et_4N)_4[Nb_4O_4(ca)_2(\mu^2\text{-}O)_2Cl_8]\cdot 2CH_3CN$ (6). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + \ldots + 2\ h\ k\ a^*\ b^*\ U^{12}]$.

Atoms	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Nb2B	15.8(4)	14.3(4)	20.7(4)	-0.7(3)	0.3(3)	-2.6(3)
Nb2A	15.4(4)	18.3(4)	14.4(4)	0.8(3)	0.2(3)	1.8(3)
Nb1A	14.9(4)	19.8(4)	15.5(4)	-0.9(3)	-0.2(3)	-4.4(3)
Nb3B	15.6(4)	23.3(5)	19.3(4)	-1.9(4)	0.4(3)	3.3(3)
Cl4A	16.9(11)	17.0(11)	30.1(13)	5.7(9)	-2.3(9)	-5.9(9)
Cl4B	28.6(13)	16.6(11)	25.6(12)	3.9(9)	0.6(10)	-9.2(10)
Cl3A	25.3(12)	14.5(11)	23.8(12)	2.4(9)	-1.9(9)	-9.4(9)
Cl3B	21.9(12)	15.1(11)	31.5(13)	3.3(10)	-5.1(10)	-6.5(9)
Cl5A	16.2(11)	22.2(12)	27.9(12)	-5.1(10)	4.7(9)	-1.0(9)
Cl6A	30.1(13)	18.2(12)	30.8(14)	-6.1(10)	-10.3(11)	2.2(10)
Cl1B	29.7(14)	26.6(14)	33.2(14)	11.7(11)	1.0(11)	-0.7(11)
Cl2B	20.4(12)	24.9(13)	45.4(16)	-4.6(12)	11.9(11)	-0.5(10)
Cl1A	23.8(13)	37.9(16)	36.2(15)	-7.6(13)	1.6(11)	6.7(12)
Cl2A	40.7(16)	32.7(16)	30.2(14)	-13.6(12)	2.2(12)	-15.9(13)
Cl5B	21.9(13)	50.2(19)	40.1(16)	-8.2(14)	-1.0(11)	13.6(13)
Cl6B	33.7(15)	49.4(19)	27.9(14)	11.4(13)	3.5(11)	-3.5(14)
O5A	12(3)	20(4)	19(3)	3(3)	-1(3)	-1(3)
O4A	27(4)	14(3)	15(3)	-4(3)	-3(3)	-4(3)
O2A	27(4)	20(4)	13(3)	1(3)	-3(3)	-5(3)
O3A	16(3)	20(4)	25(4)	2(3)	-4(3)	-3(3)
O5B	14(3)	23(4)	20(3)	5(3)	-4(3)	-5(3)
O3B	27(4)	14(3)	22(4)	1(3)	4(3)	-4(3)
O4B	18(3)	20(4)	22(4)	2(3)	-3(3)	0(3)
O2B	20(3)	14(3)	20(3)	2(3)	2(3)	-8(3)
O1B	23(4)	28(4)	27(4)	1(3)	-7(3)	2(3)
N6D	20(4)	18(4)	27(5)	-7(4)	2(3)	-6(3)
N5D	18(4)	15(4)	32(5)	4(4)	3(3)	2(3)
O1A	27(4)	31(4)	18(4)	5(3)	-4(3)	-7(3)
O6B	30(4)	22(4)	37(5)	-9(3)	-6(3)	-2(3)
O1C	21(4)	25(4)	21(4)	-2(3)	0(3)	-1(3)
O6A	32(4)	22(4)	27(4)	7(3)	5(3)	2(3)
O2C	20(4)	31(4)	25(4)	2(3)	5(3)	9(3)
N3D	23(4)	12(4)	33(5)	-4(4)	2(4)	-7(3)
C1A	11(4)	14(4)	17(4)	1(3)	3(3)	0(3)
C5A	8(4)	10(4)	23(5)	2(3)	2(3)	-2(3)
C2A	9(4)	16(4)	22(5)	-3(4)	0(3)	-3(3)
C5B	13(4)	12(4)	29(5)	0(4)	6(4)	-1(3)
C4A	8(4)	15(4)	21(5)	5(4)	2(3)	2(3)
C3A	11(4)	15(4)	18(4)	-1(3)	2(3)	4(3)
C1B	11(4)	14(4)	25(5)	-2(4)	1(3)	-2(3)
C6A	8(4)	12(4)	20(4)	-2(3)	2(3)	2(3)
C4B	8(4)	23(5)	22(5)	-2(4)	2(3)	4(4)
C6B	11(4)	8(4)	22(5)	0(3)	4(3)	-3(3)
C30D	27(6)	23(6)	34(6)	1(5)	1(5)	2(5)
C2B	17(4)	9(4)	24(5)	5(4)	1(4)	-3(3)

C7D	12(4)	27(6)	34(6)	0(5)	4(4)	0(4)
C11D	23(5)	5(4)	35(6)	-1(4)	8(4)	-3(4)
C12D	15(5)	39(7)	53(8)	4(6)	2(5)	-5(5)
C35D	29(6)	22(6)	36(6)	-6(5)	-4(5)	1(5)
N4D	66(6)	59(5)	51(5)	9(4)	-8(4)	-9(4)
C28D	44(8)	30(7)	44(8)	-10(6)	4(6)	4(6)
C8D	22(5)	41(7)	39(7)	4(6)	7(5)	11(5)
C3B	15(4)	17(5)	23(5)	-1(4)	1(4)	3(4)
C36D	45(7)	37(7)	27(6)	-14(5)	-3(5)	-8(6)
C33D	30(6)	37(7)	24(5)	-3(5)	6(4)	-16(5)
C1D	77(12)	63(11)	26(7)	8(7)	5(7)	30(9)
C9D	41(7)	33(7)	39(7)	-14(6)	3(6)	-16(6)
C6D	46(8)	31(7)	42(7)	14(6)	16(6)	6(6)
C31D	33(6)	28(6)	26(6)	-6(5)	6(5)	2(5)
C5D	36(7)	14(5)	52(8)	4(5)	17(6)	-4(5)
C27D	34(6)	21(6)	39(7)	2(5)	0(5)	1(5)
C10D	46(8)	62(10)	37(7)	-11(7)	2(6)	12(8)
C29D	48(3)	45(3)	58(4)	-7(3)	-11(3)	-15(3)
C14D	43(8)	28(7)	58(9)	-17(6)	-6(6)	-3(6)
C25D	24(6)	35(7)	42(7)	-4(5)	-3(5)	5(5)
C23D	48(4)	50(5)	62(5)	-10(4)	13(4)	-13(4)
C34D	39(7)	45(8)	36(7)	5(6)	12(6)	-3(6)
C17D	48(3)	45(3)	58(4)	-7(3)	-11(3)	-15(3)
N1D	66(6)	59(5)	51(5)	9(4)	-8(4)	-9(4)
C19D	48(3)	45(3)	58(4)	-7(3)	-11(3)	-15(3)
C21D	48(4)	50(5)	62(5)	-10(4)	13(4)	-13(4)
C32D	34(7)	57(9)	35(7)	-8(6)	-1(5)	-9(6)
N2D	66(6)	59(5)	51(5)	9(4)	-8(4)	-9(4)
C15D	60(9)	42(8)	39(8)	-6(6)	-6(7)	-4(7)
C18D	48(3)	45(3)	58(4)	-7(3)	-11(3)	-15(3)
C2D	130(19)	67(13)	32(8)	-5(8)	6(10)	33(13)
C26D	39(8)	44(8)	60(9)	-13(7)	-6(7)	17(7)
C3D	63(10)	38(8)	47(8)	9(7)	-12(7)	-19(7)
C24D	48(4)	50(5)	62(5)	-10(4)	13(4)	-13(4)
C4D	48(10)	92(16)	100(16)	-39(13)	25(10)	-28(11)
C13D	48(3)	45(3)	58(4)	-7(3)	-11(3)	-15(3)
C22D	48(4)	50(5)	62(5)	-10(4)	13(4)	-13(4)
C20D	48(3)	45(3)	58(4)	-7(3)	-11(3)	-15(3)
C16D	48(3)	45(3)	58(4)	-7(3)	-11(3)	-15(3)

Table S15 Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for $(Et_4N)_4[Nb_4O_4(ca)_2(\mu^2\text{-}O)_2Cl_8]\cdot 2CH_3CN$ (6).

Atoms	x	y	z	U(eq)
H30A	1324.77	984.55	2451.74	42
H30B	1002.81	-249.73	2631.51	42
H30C	618.15	1029.27	2587.68	42
H7DA	3737.54	8677.97	3542.74	29
H7DB	3548.12	9009.55	3055.88	29
H11A	4730.45	8099.15	3302.75	25
H11B	4534.36	8502.84	2823.34	25
H12A	5409.02	9826.1	2811.85	53
H12B	5603.8	8395.17	2892.27	53
H12C	5610.26	9361.96	3284.66	53
H35A	692.21	23.16	1171.95	35
H35B	15.14	378.54	1319.29	35
H28A	1374.55	-30.51	3468.12	59
H28B	1748.17	1261.62	3512.59	59
H28C	1006.72	1266.95	3498.77	59
H8DA	3238.23	11071.34	3291.65	51
H8DB	3364.62	10617.79	3776.04	51
H8DC	2828.03	9973.07	3484.77	51
H36A	168.42	1223.9	647.63	54
H36B	770.72	1958.84	826.05	54
H36C	100.31	2347.07	982.64	54
H33A	1327.6	2453.42	1414.66	36
H33B	1530.91	2066.71	1893.64	36
H9DA	5059.4	10750.87	3619.93	45
H9DB	4386.88	11067.1	3786.58	45
H6DA	4010.18	11470.58	2351.2	59
H6DB	3669.04	10266.7	2537.17	59
H6DC	4355.51	10142.88	2366.17	59
H31A	559.72	2710.39	2103.5	35
H31B	333.72	3021.55	1621.21	35
H5DA	4760.79	11324.34	2935.9	40
H5DB	4082.49	11661.34	3087.73	40
H27A	1045.03	118.41	4161.71	38
H27B	1779.95	280.83	4180.27	38
H10A	4947.15	8681.36	3918.71	72
H10B	4336.53	9180.27	4138.27	72
H10C	4996.73	9779.61	4267.82	72
H29A	306.84	-222.42	2013.57	61
H29B	1008.81	-501.94	1900.61	61
H14A	4458.38	7712.86	5660.5	64
H14B	4445.15	7079.89	6125.09	64
H14C	4068.22	8347.03	6028.62	64
H25A	372.07	1761.88	4282.45	40
H25B	651.94	2596.74	3912.23	40
H23A	1382.46	2426.11	4962.57	64
H23B	1810.23	1253.31	4860.09	64

H34A	1703.52	608.89	1146.22	59
H34B	1808.97	35.09	1617.29	59
H34C	2234.78	1164.62	1463.55	59
H17A	2866.13	4909.79	5715.45	61
H17B	2911.72	5566.15	5259.58	61
H19A	4505.6	5047.36	5984.89	61
H19B	4165.12	3855.51	5774.69	61
H21A	1689.39	3166.89	3905.78	64
H21B	1760.65	3630.36	4393.12	64
H32A	-526.55	1621.27	1708.11	63
H32B	-543.86	2815.15	2018.09	63
H32C	-316.07	1486.98	2203.36	63
H15A	4588.33	5929.74	5327.27	56
H15B	4261.79	4711.57	5121.89	56
H18A	3363.86	3750.39	5003.25	76
H18B	2672.88	3546.49	5157.44	76
H18C	3250.61	3100.54	5455.86	76
H2DA	1367.21	7755.9	-206.63	114
H2DB	885.27	7644.63	168.51	114
H2DC	1605.18	7371.06	267.31	114
H26A	85.06	3875.11	4363.56	72
H26B	798.78	4276.36	4405.69	72
H26C	503.18	3439.3	4771.19	72
H24A	898.84	-34.57	4825.53	80
H24B	510.39	1149.53	4979.66	80
H24C	1038.55	555.13	5290.87	80
H4DA	6412.63	9425.36	4825.15	119
H4DB	6405.55	9263.01	5334.83	119
H4DC	6011.05	10358.69	5104.52	119
H13A	3369.79	6723.37	6010.69	61
H13B	3414.15	7274.71	5538.18	61
H22A	2483.02	1709.92	4026.1	80
H22B	2541.58	2105.12	4520.79	80
H22C	2729.56	3077.2	4157.33	80
H20A	3375.3	3981.67	6279.76	76
H20B	3676.16	5234.47	6478.44	76
H20C	4033.22	3926.06	6533.02	76
H16A	4238.4	6453.66	4634.94	76
H16B	3812.3	7198.14	4957.45	76
H16C	3556.18	5956.12	4723.86	76

Table S16 Torsion angles (°) for $(Et_4N)_4[Nb_4O_4(ca)_2(\mu^2\text{-}O)_2Cl_8]\cdot 2CH_3CN$ (6).

Torsion angles	Angle (°)	Torsion angles	Angle (°)
Nb2B-O3B-C6B-C5B	-174.4(7)	C4B-C5B-C6B-O3B	-178.8(9)
Nb2B-O3B-C6B-C1B	4.9(11)	C4B-C5B-C6B-C1B	1.9(14)
Nb2B-O2B-C1B-C6B	-2.9(10)	C6B-C5B-C4B-O5B	178.6(9)
Nb2B-O2B-C1B-C2B	176.9(8)	C6B-C5B-C4B-C3B	-2.9(14)
Nb2A-O5A-C4A-C5A	-178.4(7)	C6B-C1B-C2B-Cl3B	179.0(7)
Nb2A-O5A-C4A-C3A	2.1(11)	C6B-C1B-C2B-C3B	1.7(15)
Nb2A-O4A-C3A-C2A	173.3(7)	C2B-C1B-C6B-O3B	179.4(9)
Nb2A-O4A-C3A-C4A	-3.9(10)	C2B-C1B-C6B-C5B	-1.2(13)
Nb1A-O2A-C1A-C2A	-173.1(7)	C7D-N3D-C11D-C12D	-179.6(10)
Nb1A-O2A-C1A-C6A	5.4(11)	C7D-N3D-C9D-C10D	61.9(14)
Nb1A-O3A-C6A-C1A	-2.7(10)	C7D-N3D-C5D-C6D	-60.7(13)
Nb1A-O3A-C6A-C5A	174.9(7)	C11D-N3D-C7D-C8D	-177.2(10)
Nb3B-O5B-C4B-C5B	175.5(7)	C11D-N3D-C9D-C10D	-56.8(14)
Nb3B-O5B-C4B-C3B	-2.9(10)	C11D-N3D-C5D-C6D	57.8(13)
Nb3B-O4B-C3B-C4B	4.8(11)	C35D-N6D-C33D-C34D	-58.0(13)
Nb3B-O4B-C3B-C2B	-178.0(8)	C35D-N6D-C31D-C32D	63.6(13)
Cl4A-C5A-C4A-O5A	-1.9(14)	C35D-N6D-C29D-C30D	-174.8(11)
Cl4A-C5A-C4A-C3A	177.6(6)	C33D-N6D-C35D-C36D	-60.4(13)
Cl4A-C5A-C6A-O3A	2.9(13)	C33D-N6D-C31D-C32D	-177.3(10)
Cl4A-C5A-C6A-C1A	-179.7(6)	C33D-N6D-C29D-C30D	66.0(15)
Cl4B-C5B-C4B-O5B	-5.8(13)	C9D-N3D-C7D-C8D	61.4(13)
Cl4B-C5B-C4B-C3B	172.6(7)	C9D-N3D-C11D-C12D	-57.9(13)
Cl4B-C5B-C6B-O3B	5.7(14)	C9D-N3D-C5D-C6D	178.7(10)
Cl4B-C5B-C6B-C1B	-173.6(7)	C31D-N6D-C35D-C36D	56.1(13)
Cl3A-C2A-C3A-O4A	-4.4(14)	C31D-N6D-C33D-C34D	-178.5(10)
Cl3A-C2A-C3A-C4A	172.7(7)	C31D-N6D-C29D-C30D	-51.7(15)
Cl3B-C2B-C3B-O4B	2.9(15)	C5D-N3D-C7D-C8D	-55.2(13)
Cl3B-C2B-C3B-C4B	-180.0(7)	C5D-N3D-C11D-C12D	59.4(13)
O5A-C4A-C3A-O4A	1.6(12)	C5D-N3D-C9D-C10D	-178.3(11)
O5A-C4A-C3A-C2A	-175.8(8)	C27D-N5D-C25D-C26D	176.4(12)
O2A-C1A-C2A-Cl3A	3.7(14)	C27D-N5D-C23D-C24D	-62.1(16)
O2A-C1A-C2A-C3A	-178.7(9)	C27D-N5D-C21D-C22D	-53.1(16)
O2A-C1A-C6A-O3A	-1.3(12)	C29D-N6D-C35D-C36D	179.7(12)
O2A-C1A-C6A-C5A	-179.0(8)	C29D-N6D-C33D-C34D	59.4(14)
O5B-C4B-C3B-O4B	-0.7(12)	C29D-N6D-C31D-C32D	-56.5(13)
O5B-C4B-C3B-C2B	-178.2(9)	C25D-N5D-C27D-C28D	65.0(13)
O2B-C1B-C6B-O3B	-0.8(12)	C25D-N5D-C23D-C24D	55.5(17)
O2B-C1B-C6B-C5B	178.5(9)	C25D-N5D-C21D-C22D	-170.6(12)
O2B-C1B-C2B-Cl3B	-0.7(14)	C23D-N5D-C27D-C28D	-175.1(11)
O2B-C1B-C2B-C3B	-178.0(10)	C23D-N5D-C25D-C26D	57.8(15)
C1A-C2A-C3A-O4A	177.9(9)	C23D-N5D-C21D-C22D	68.5(16)
C1A-C2A-C3A-C4A	-5.0(13)	C17D-N4D-C19D-C20D	-61.3(18)
C5A-C4A-C3A-O4A	-178.0(9)	C17D-N4D-C15D-C16D	59.5(17)
C5A-C4A-C3A-C2A	4.6(13)	C17D-N4D-C13D-C14D	-177.8(14)
C2A-C1A-C6A-O3A	177.3(9)	C19D-N4D-C17D-C18D	-59(2)
C2A-C1A-C6A-C5A	-0.4(13)	C19D-N4D-C15D-C16D	178.5(12)
C5B-C4B-C3B-O4B	-179.2(9)	C19D-N4D-C13D-C14D	58(2)
C5B-C4B-C3B-C2B	3.3(13)	C21D-N5D-C27D-C28D	-52.4(15)
C4A-C5A-C6A-O3A	-177.3(9)	C21D-N5D-C25D-C26D	-63.1(15)
C4A-C5A-C6A-C1A	0.1(13)	C21D-N5D-C23D-C24D	174.4(14)
C1B-C2B-C3B-O4B	-179.8(10)	C15D-N4D-C17D-C18D	54(2)

C1B-C2B-C3B-C4B	-2.7(15)	C15D-N4D-C19D-C20D	179.8(12)
C6A-C1A-C2A-Cl3A	-174.8(7)	C15D-N4D-C13D-C14D	-56.1(19)
C6A-C1A-C2A-C3A	2.9(13)	C13D-N4D-C17D-C18D	175.4(15)
C6A-C5A-C4A-O5A	178.3(9)	C13D-N4D-C19D-C20D	61.2(18)
C6A-C5A-C4A-C3A	-2.1(13)	C13D-N4D-C15D-C16D	-60.4(17)

Table S17 General hydrogen-bond distances and angles for $(Et_4N)_4[Nb_4O_4(ca)_2(\mu^2\text{-}O)_2Cl_8]\cdot 2CH_3CN$ (6).

Interactions	D-H…A	D-H (Å)	H…A (Å)	D…A (Å)	D-H…A (°)
I	C13-H13B…Cl10[a]	0.98	2.81	3.721(12)	156
II	C14-H14B…O3[b]	0.99	2.60	3.535(14)	158
III	C18-H8A…O9	0.99	2.54	3.288(16)	132
IV	C19-H19B…Cl9	0.99	2.67	3.655(13)	173
V	C22-H22A…O10[c]	0.99	2.42	3.388(14)	167
VI	C34-H34A…Cl9	0.99	2.72	3.568(13)	144
VII	C35-H35B…O11[c]	0.99	2.35	3.060(16)	128
VIII	C41-H41C…Cl7[d]	0.98	2.75	3.715(19)	169
IX	C43-H43A…Cl8[c]	0.99	2.81	3.605(17)	137
X	C46-H46B…Cl8	0.98	2.71	3.650 (2)	161
XI	C46-H46C…Cl11[e]	0.98	2.60	3.574(16)	176
XII	C47-H47B…Cl7[f]	0.98	2.76	3.640(2)	150
XIII	C47-H47B…Cl8[f]	0.98	2.79	3.540(2)	134

Symmetry code: (a) -x + 1, y - ½, - z + ½ (b) x, y -1, z (c), 1- x, y + ½, ½ - z (d), 1 - x, y + ½ + 1, ½- z (e), x, -y + ½, z - ½ (f), x, -y + ½, z + ½

Table S18 Temperature and [DMAP] dependence of the *pseudo* first-order reaction between *cis*-[NbO(ca)$_2$(H$_2$O)OPPh$_3$]$^-$ and 4-(dimetylamino)pyridine. [Nb] = 1.0 x 10^{-3} M, λ = 430 nm, MeCN.

10^{-3} k_{obs}(s^{-1})				
[DMAP] M	**15.5 ^{o}C**	**24.5 ^{o}C**	**31.2 ^{o}C**	**45.9 ^{o}C**
0.05	0.990(6)	1.203(8)	1.904(7)	5.433(4)
0.15	1.522(9)	2.497(7)	3.902(6)	11.895(1)
0.25	2.216(3)	3.726(5)	5.945(2)	17.503(9)
0.35	2.989(5)	4.906(1)	7.679(3)	23.585(6)
0.50	3.931(9)	7.031(8)	11.155(4)	31.132(7)

Table S19 Substituent dependence of the *pseudo* first-order reaction between *cis*-[NbO(ca)$_2$(H$_2$O)OPPh$_3$]$^-$ and pyridine derivative ligands (Py). [Nb] = 1.0 x 10^{-3} M, λ = 430 nm, 31.2 ^{o}C, MeCN.

10^{-3} k_{obs}(s^{-1})					
[Py] M	**py**	**DMAP**	**4Mepy**	**3Clpy**	**3Brpy**
0.05	1.271(1)	1.904(7)	1.027(6)	0.892(4)	0.777(8)
0.15	1.416(4)	3.902(6)	1.202(5)	1.033(2)	0.887(7)
0.25	1.568(2)	5.945(2)	1.413(6)	1.232(2)	1.043(6)
0.35	1.663(9)	7.679(3)	1.599(4)	1.438(2)	1.194(8)
0.50	1.869(3)	11.155(8)	1.828(9)	1.790(4)	1.431(9)