Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Aqueous Tantalum Polyoxometalate Reactivity with Peroxide

Table SI-1. Theoretical and experimental Raman frequencies for peroxohexaniobate.

Mode	Observed Frequency [cm^{-1}]	Calculated Frequency [cm^{-1}]	Scaled Calculated Frequency [cm^{-1}]
M=O stretching	849, 817	874, 829	880, 834
O_2 vibration	865	920	865
M-O_2 stretching	617	604	568
M-O bending	456, 371	478, 430	450, 433

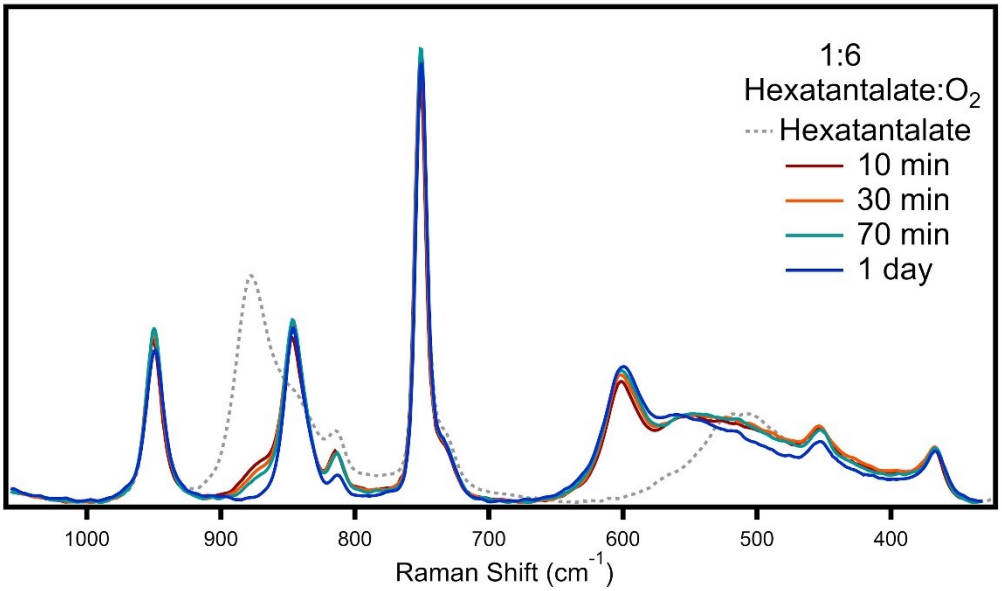

Fig. SI-1 Raman spectra monitoring the peroxylation of hexatantalate over time.

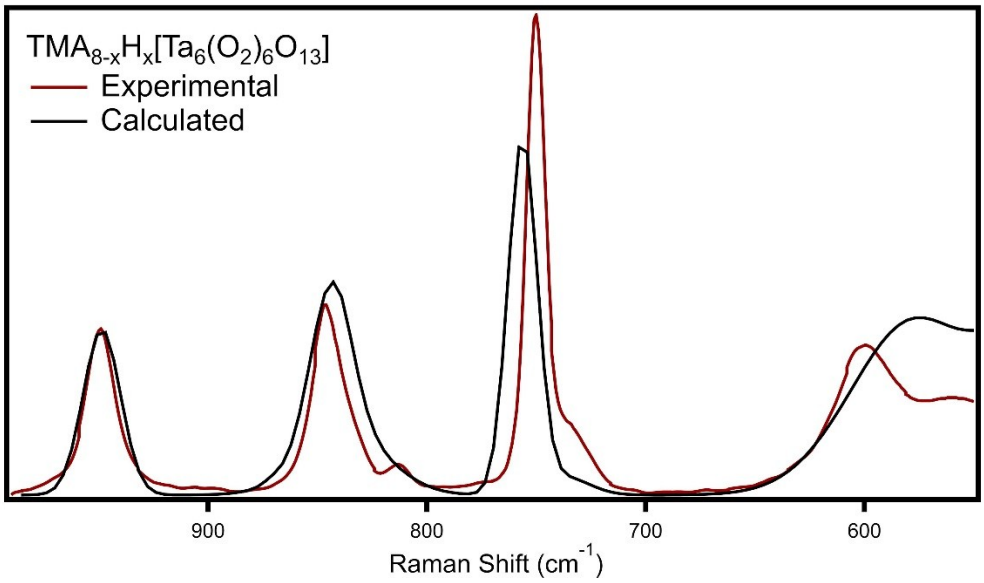

Fig. SI-2 Experimental and Calculated Raman spectra for peroxohexatantalate.

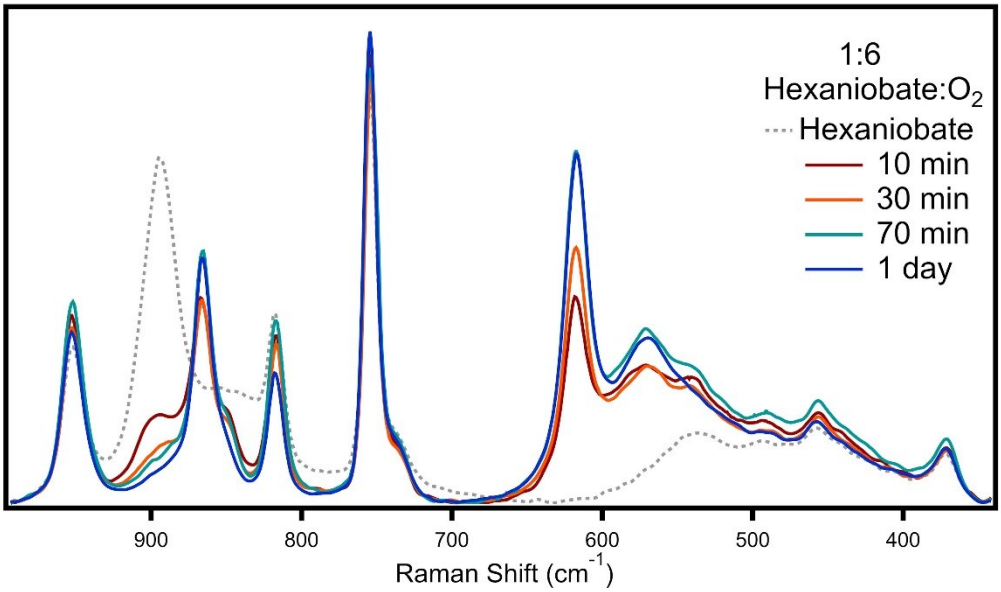

Fig. SI-3 Raman spectra monitoring the peroxylation of hexaniobate over time.

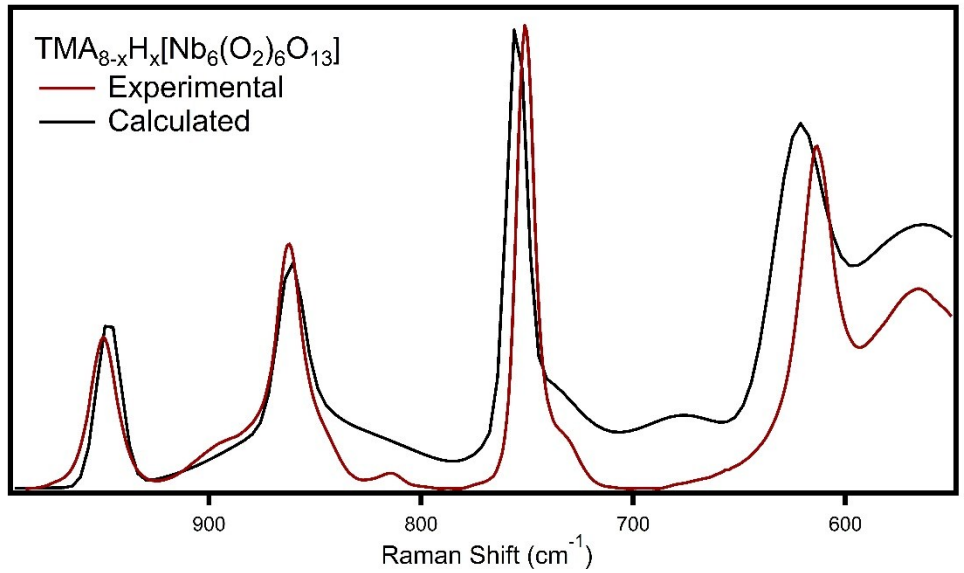

Fig. SI-4 Experimental and Calculated Raman spectra for peroxohexaniobate.

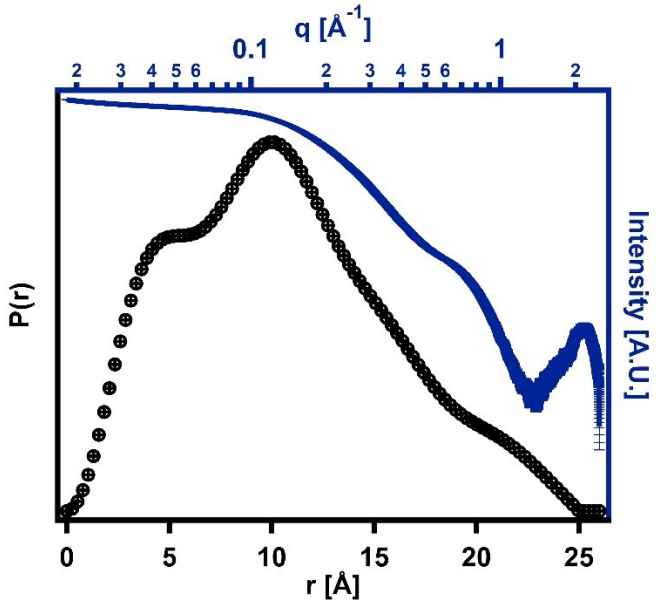

Fig. SI-5 Pair distance distribution function analysis (black) of peroxohexatantalate, with scattering curve (blue) overlaid.

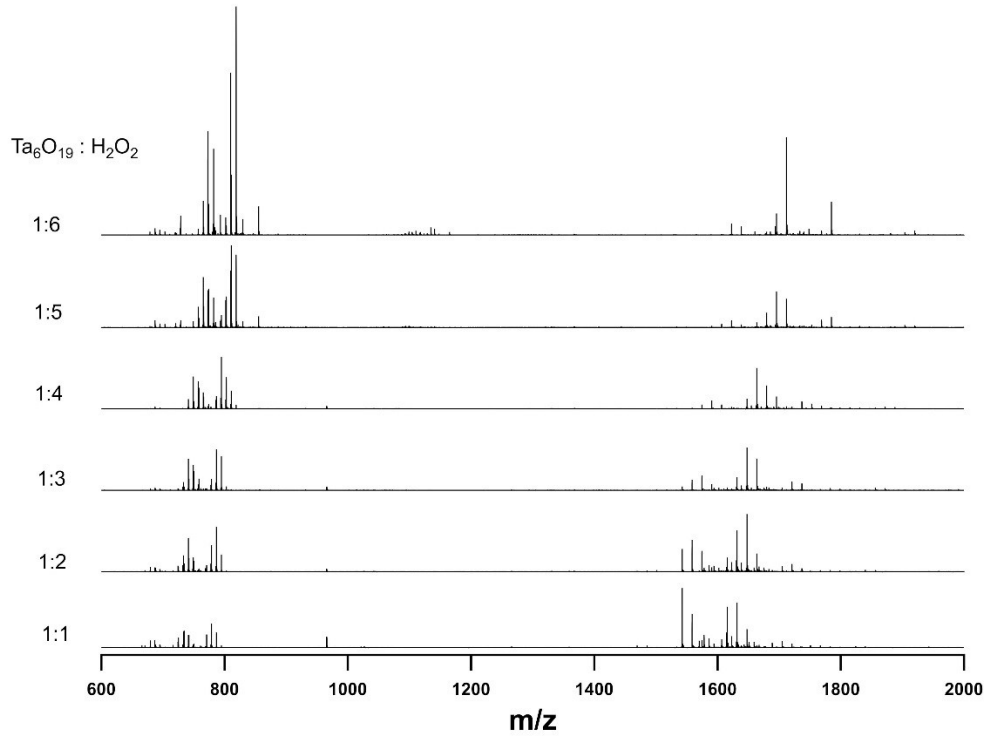

Fig. SI-6 ESI-MS of reaction solutions of peroxylated hexatantalate

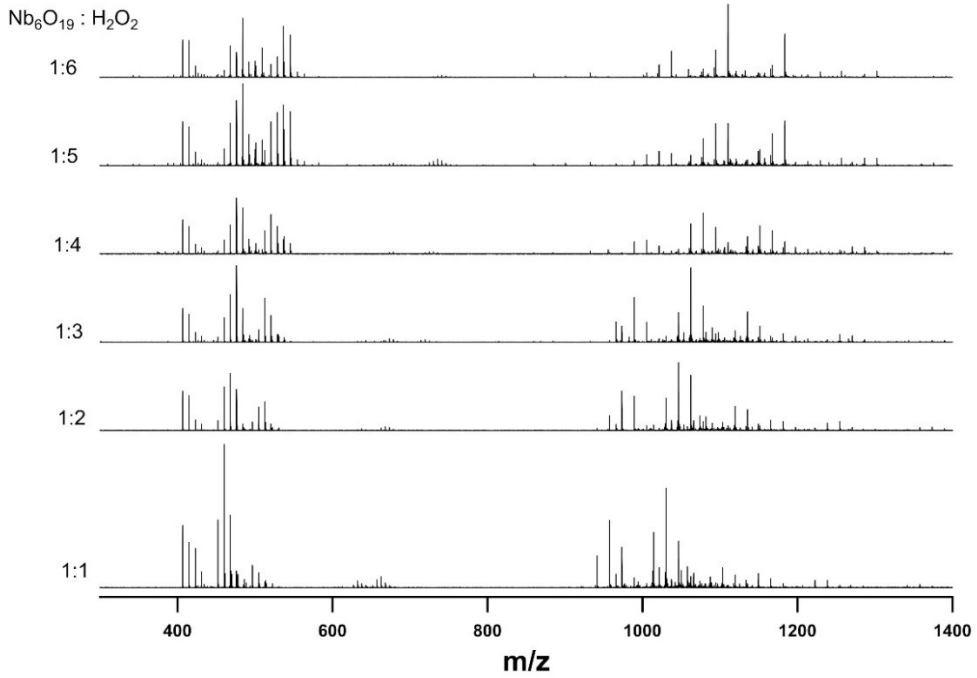

Fig. SI-7 ESI-MS of reaction solutions of peroxylated hexaniobate.

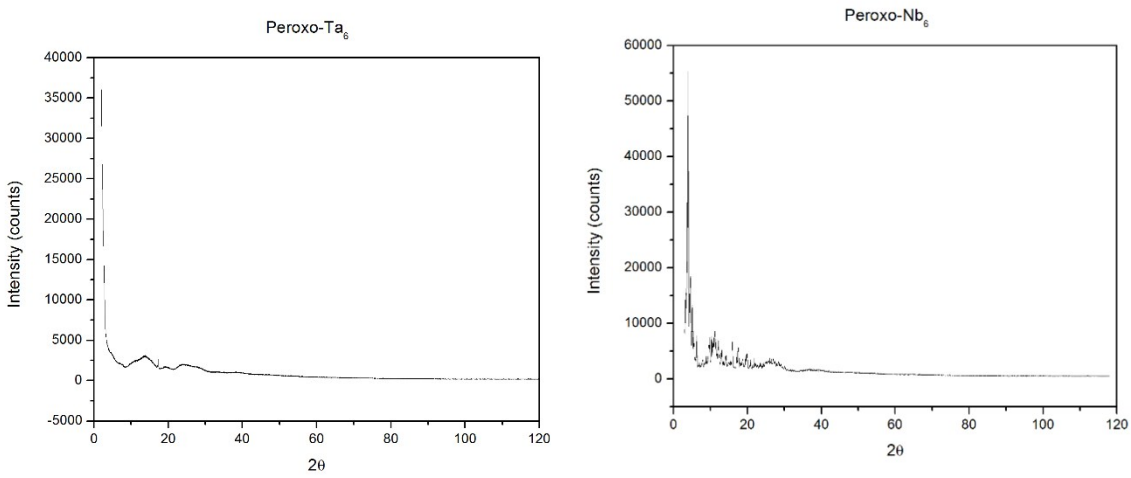

Fig. SI-8 Raw scattering data for solid TMA-$Ta_6(O_2)_6$ (left) and solid TMA-$Nb_6(O_2)_6$ (right). Bragg peaks in $Nb_6(O_2)_6$ indicate long range order, while $Ta_6(O_2)_6$ has only short-range order, observed in the PDF.

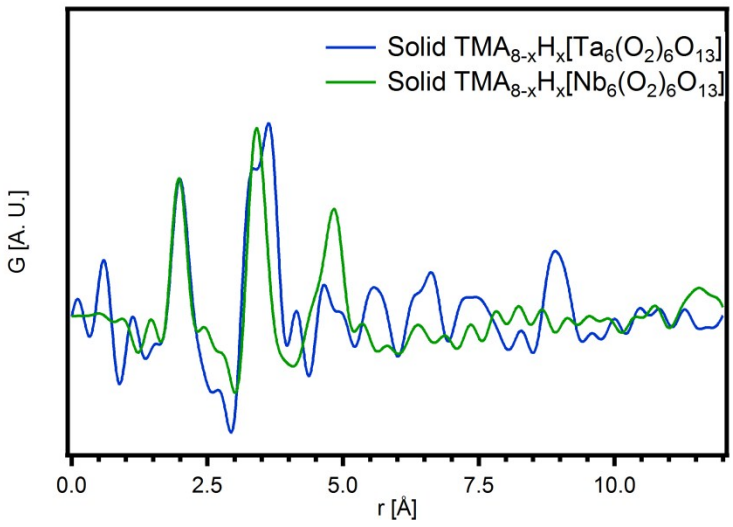

Fig. SI-9 PDF of solid-state peroxohexatantalate (blue) and peroxohexaniobate (green) overlaid.

Table SI-2. All species identified by ESI-MS for mono-peroxylated hexatantalate.

Mono-peroxylated hexatantalate reaction solution			
Species	**Experimental m/z**	**Calculated m/z**	**Relative Abundance (%)**
$Ta_6(O_2)_2O_{14}^{-2}$	686.795	686.789	12.97
$TMAHTa_6(O_2)O_{16}^{-2}$	724.329	724.351	10.02
$TMAH_3Ta_6O_{18}^{-2}$	725.336	725.358	16.69
$TMAHTa_6(O_2)O_{16}^{-2} \cdot H_2O$	733.333	733.356	26.77
$TMAH_5Ta_6O_{19}^{-2}$	734.341	734.364	28.11
$TMAH_3Ta_6(O_2)_2O_{16}^{-2}$	741.335	741.343	21.34
$TMAH_5Ta_6(O_2)O_{18}^{-2}$	742.339	742.351	20.79
$TMA_2H_4Ta_6O_{19}^{-2}$	770.884	770.908	22.10
$TMA_2H_4Ta_6(O_2)O_{18}^{-2}$	778.882	778.906	40.44
$TMA_2H_4Ta_6(O_2)_2O_{17}^{-2}$	786.879	786.893	25.34
$TMATa_3(O_2)_6(OH)_5^{-1} \cdot 4H_2O$	965.974	965.936	18.39
$TMA_2H_5Ta_6O_{19}^{-1}$	**1542.788**	**1542.825**	**100**
$TMA_2H_5Ta_6(O_2)O_{18}^{-1}$	1558.782	1558.819	56.89
$TMA_2H_5Ta_6(O_2)_2O_{17}^{-1}$	1574.773	1574.814	13.10
$TMA_3H_4Ta_6(O_2)O_{18}^{-1}$	1631.872	1631.909	75.71
$TMA_3H_4Ta_6(O_2)_2O_{17}^{-1}$	1647.864	1647.904	30.72
$TMA_4H_3Ta_6(O_2)O_{18}^{-1}$	1704.958	1704.998	11.32

Table SI-3. All species identified by ESI-MS for di-peroxylated hexatantalate.

Di-peroxylated hexatantalate reaction solution			
Species	**Experimental m/z**	**Calculated m/z**	**Relative Abundance (%)**
$TMAHTa_6(O_2)O_{16}^{-2}$	724.328	724.351	10.50
$TMAHTa_6(O_2)_2O_{15}^{-2}$	732.326	732.348	11.50
$TMAHTa_6(O_2)O_{16}^{-2} \cdot H_2O$	733.333	733.356	28.65
$TMAH_5Ta_6O_{19}^{-2}$	734.341	734.364	14.44
$TMAH_3Ta_6(O_2)_2O_{16}^{-2}$	741.332	741.343	57.66
$TMAH_5Ta_6(O_2)O_{18}^{-2}$	742.338	742.351	23.25
$TMAH_3Ta_6(O_2)_3O_{15}^{-2}$	749.331	749.351	25.30
$TMAH_5Ta_6(O_2)_2O_{17}^{-2}$	750.336	750.359	19.32
$TMA_2H_4Ta_6O_{19}^{-2}$	770.884	770.906	11.02
$TMA_2H_2Ta_6(O_2)_2O_{16}^{-2}$	777.874	777.898	13.93
$TMA_2H_4Ta_6(O_2)O_{18}^{-2}$	778.882	778.896	45.64
$TMA_2H_4Ta_6(O_2)_2O_{17}^{-2}$	786.880	786.903	78.31
$TMA_2H_4Ta_6(O_2)_3O_{16}^{-2}$	794.876	794.901	30.06
$TMA_2H_5Ta_6O_{19}^{-1}$	1542.786	1542.825	39.36
$TMA_2H_5Ta_6(O_2)O_{18}^{-1}$	1558.781	1558.819	54.91
$TMA_2H_5Ta_6(O_2)_2O_{17}^{-1}$	1574.778	1574.794	36.37
$TMA_3H_4Ta_6(O_2)O_{18}^{-1}$	1631.870	1631.888	71.83
$TMA_3H_4Ta_6(O_2)_2O_{17}^{-1}$	**1647.865**	**1647.904**	**100**
$TMA_3H_4Ta_6(O_2)_3O_{16}^{-1}$	1663.857	1663.898	31.80
$TMA_4H_3Ta_6(O_2)_2O_{17}^{-1}$	1720.954	1720.993	13.53

Table SI-4. All species identified by ESI-MS for tri-peroxylated hexatantalate.

Tri-peroxylated hexatantalate reaction solution			
Species	**Experimental m/z**	**Calculated m/z**	**Relative Abundance (%)**
$TMAHTa_6(O_2)O_{16}^{-2} \cdot H_2O$	733.332	733.356	19.72
$TMAH_3Ta_6(O_2)_2O_{16}^{-2}$	741.331	741.343	75.05
$TMAH_5Ta_6(O_2)O_{18}^{-2}$	742.337	742.351	27.36
$TMAH_3Ta_6(O_2)_4O_{14}^{-2}$	757.328	757.348	14.22
$TMAH_5Ta_6(O_2)_3O_{16}^{-2}$	758.332	758.356	27.60
$TMA_2H_2Ta_6(O_2)_2O_{16}^{-2}$	777.873	777.898	12.86
$TMA_2H_2Ta_6(O_2)_3O_{15}^{-2}$	785.870	785.895	18.21
$TMA_2H_4Ta_6(O_2)_2O_{17}^{-2}$	786.880	786.903	97.30
$TMA_2H_4Ta_6(O_2)_3O_{16}^{-2}$	794.877	794.901	80.61
$TMA_2H_5Ta_6(O_2)O_{18}^{-1}$	1558.780	1558.819	24.86
$TMA_2H_5Ta_6(O_2)_2O_{17}^{-1}$	1574.775	1574.794	34.86
$TMA_2H_5Ta_6(O_2)_3O_{16}^{-1}$	1590.773	1590.809	14.95
$TMA_3H_4Ta_6(O_2)O_{18}^{-1}$	1631.869	1631.888	32.19
$TMA_3H_4Ta_6(O_2)_2O_{17}^{-1}$	**1647.865**	**1647.904**	**100**
$TMA_3H_4Ta_6(O_2)_3O_{16}^{-1}$	1663.859	1663.898	75.37
$TMA_4H_3Ta_6(O_2)_2O_{17}^{-1}$	1720.953	1720.993	20.33
$TMA_4H_3Ta_6(O_2)_3O_{16}^{-1}$	1736.950	1736.988	16.06

Table SI-5. All species identified by ESI-MS for tetra-peroxylated hexatantalate.

Tetra-peroxylated hexatantalate reaction solution			
Species	**Experimental m/z**	**Calculated m/z**	**Relative Abundance (%)**
$TMAH_3Ta_6(O_2)_2O_{16}^{-2}$	741.330	741.343	18.88
$TMAH_3Ta_6(O_2)_3O_{15}^{-2}$	749.328	749.351	62.78
$TMAH_5Ta_6(O_2)_2O_{17}^{-2}$	750.334	750.359	15.14
$TMAH_3Ta_6(O_2)_5\,O_{13}^{-2}$	765.324	765.346	32.03
$TMAH_5Ta_6(O_2)_4\,O_{15}^{-2}$	766.329	766.354	23.75
$TMA_2H_2Ta_6(O_2)_3O_{15}^{-2}$	785.872	785.895	17.50
$TMA_2H_4Ta_6(O_2)_2O_{17}^{-2}$	786.879	786.903	24.43
$TMA_2Ta_6(O_2)_4O_{13}^{-2} \cdot H_2O$	793.870	793.893	21.59
$TMA_2H_4Ta_6(O_2)_3O_{16}^{-2}$	**794.877**	**794.901**	**100**
$TMA_2H_2Ta_6(O_2)_5O_{13}^{-2}$	801.866	801.890	18.02
$TMA_2H_4Ta_6(O_2)_4O_{15}^{-2}$	802.874	802.898	61.31
$TMA_2H_4Ta_6(O_2)_5O_{14}^{-2}$	810.871	810.896	35.39
$TMA_2H_5Ta_6(O_2)_3O_{16}^{-1}$	1590.770	1590.809	16.41
$TMA_3H_4Ta_6(O_2)_2O_{17}^{-1}$	1647.862	1647.904	19.89
$TMA_3H_4Ta_6(O_2)_3O_{16}^{-1}$	1663.860	1663.898	79.39
$TMA_3H_4Ta_6(O_2)_4O_{15}^{-1}$	1679.854	1679.893	45.52
$TMA_3H_4Ta_6(O_2)_5O_{14}^{-1}$	1695.847	1695.888	24.07
$TMA_4H_3Ta_6(O_2)_3O_{16}^{-1}$	1736.943	1736.988	14.43
$TMA_4H_3Ta_6(O_2)_4O_{15}^{-1}$	1752.941	1752.982	10.18

Table SI-6. All species identified by ESI-MS for penta-peroxylated hexatantalate.

Penta-peroxylated hexatantalate reaction solution			
Species	**Experimental m/z**	**Calculated m/z**	**Relative Abundance (%)**
$TMAH_3Ta_6(O_2)_4O_{14}^{-2}$	757.325	757.348	25.42
$TMAH_3Ta_6(O_2)_5\ O_{13}^{-2}$	765.323	765.346	61.41
$TMAH_5Ta_6(O_2)_4\ O_{15}^{-2}$	766.330	766.354	26.23
$H_8Ta_6(O_2)_6O_{14}^{-2} \cdot 2H_2O$	772.816	772.820	33.13
$TMAH_3Ta_6(O_2)_6O_{12}^{-2}$	773.321	773.343	45.49
$TMAH_5Ta_6(O_2)_5\ O_{14}^{-2}$	774.327	774.351	47.26
$TMAHTa_6(O_2)_6O_{11}^{-2} \cdot 2H_2O$	782.325	782.349	36.48
$TMA_2H_2Ta_6(O_2)_5O_{13}^{-2}$	801.866	801.890	33.07
$TMA_2H_4Ta_6(O_2)_4O_{15}^{-2}$	802.873	802.898	37.80
$TMA_2H_2Ta_6(O_2)_6O_{12}^{-2}$	809.863	809.888	69.45
$TMA_2H_4Ta_6(O_2)_5O_{14}^{-2}$	**810.871**	**810.896**	**100**
$TMA_2H_4Ta_6(O_2)_6O_{13}^{-2}$	818.869	818.893	88.69
$TMA_3H_4Ta_6(O_2)_4O_{15}^{-1}$	1679.854	1679.893	18.04
$TMA_3H_4Ta_6(O_2)_5O_{14}^{-1}$	1695.850	1695.888	43.96
$TMA_3H_4Ta_6(O_2)_6O_{13}^{-1}$	1711.843	1711.883	34.98
$TMA_4H_3Ta_6(O_2)_6O_{13}^{-1}$	1784.931	1784.972	12.80

Table SI-7. All species identified by ESI-MS for hexa-peroxylated hexatantalate.

Hexa-peroxylated hexatantalate reaction solution			
Species	**Experimental m/z**	**Calculated m/z**	**Relative Abundance (%)**
$TMAH_3Ta_6(O_2)_5\ O_{13}^{-2}$	765.323	765.346	14.87
$H_8Ta_6(O_2)_6O_{14}^{-2} \cdot 2H_2O$	772.816	772.820	32.76
$TMAH_3Ta_6(O_2)_6O_{12}^{-2}$	773.321	773.343	45.51
$TMAH_5Ta_6(O_2)_5\ O_{14}^{-2}$	774.328	774.351	13.66
$TMAHTa_6(O_2)_6O_{11}^{-2} \cdot 2H_2O$	782.325	782.349	37.65
$TMA_2H_2Ta_6(O_2)_6O_{12}^{-2}$	809.865	809.888	70.95
$TMA_2H_4Ta_6(O_2)_5O_{14}^{-2}$	810.871	810.896	26.40
$TMA_2H_4Ta_6(O_2)_6O_{13}^{-2}$	**818.870**	**818.893**	**100**
$TMA_3H_3Ta_6(O_2)_6O_{13}^{-2}$	855.413	855.438	12.53
$TMA_3H_4Ta_6(O_2)_6O_{13}^{-1}$	1711.845	1711.883	42.87
$TMA_4H_3Ta_6(O_2)_6O_{13}^{-1}$	1784.931	1784.972	14.53

Table SI-8. All species identified by ESI-MS for mono-peroxylated hexaniobate.

Mono-peroxylated hexaniobate reaction solutions			
Species	**Experimental m/z**	**Calculated m/z**	**Relative Abundance (%)**
$Nb_3O_8^{-1}$	406.666	406.678	43.73
$TMA_6H_4Nb_2O_{11}^{-2} \cdot 2H_2O$	423.164	423.196	27.58
$TMA_2Nb(OH)_8^{-1} \cdot 3H_2O$	431.161	431.154	11.23
$TMAHNb_6O_{17}^{-2}$	452.214	452.228	47.42
$TMAHNb_6(O_2)O_{16}^{-2}$	**460.212**	**460.226**	**100**
$TMAHNb_6(O_2)_2O_{15}^{-2}$	468.210	468.223	50.80
$TMAHNb_6(O_2)_3O_{14}^{-2}$	476.207	476.221	11.72
$TMA_2Nb_6(O_2)O_{16}^{-2}$	496.756	496.770	15.81
$TMA_2Nb_6(O_2)_2O_{15}^{-2}$	504.752	504.768	10.54
$TMANb_6O_{16}^{-1} \cdot 3H_2O$	941.460	941.486	22.35
$TMANb_6(O_2)O_{15}^{-1} \cdot 3H_2O$	957.456	957.480	47.07
$TMAH_2Nb_6(O_2)_2O_{15}^{-1} \cdot 2H_2O$	973.450	973.475	28.50
$TMA_2HNb_6O_{17}^{-1} \cdot 2H_2O$	1014.548	1014.575	38.79
$TMA_2HNb_6(O_2)O_{16}^{-1} \cdot 2H_2O$	1030.535	1030.570	69.63
$TMA_2H_3Nb_6(O_2)_2O_{16}^{-1} \cdot H_2O$	1046.539	1046.565	32.69
$TMA_{15}H_8Nb_5(O_2)_6O_{19}^{-2} \cdot 2H_2O$	1058.083	1057.956	15.04
$TMA_3Nb_6(O_2)_5O_{12}^{-1} \cdot H_2O$	1149.635	1149.628	10.06

Table SI-9. All species identified by ESI-MS for di-peroxylated hexaniobate.

Di-peroxylated hexaniobate reaction solutions			
Species	**Experimental m/z**	**Calculated m/z**	**Relative Abundance (%)**
$Nb_3O_8^{-1}$	406.667	406.678	57.94
$TMA_6H_4Nb_2O_{11}^{-2} \cdot 2H_2O$	423.165	423.196	16.18
$TMA_2Nb(OH)_8^{-1} \cdot 3H_2O$	431.161	431.154	10.31
$TMAHNb_6O_{17}^{-2}$	452.214	452.228	14.82
$TMAHNb_6(O_2)O_{16}^{-2}$	460.212	460.226	64.34
$TMAHNb_6(O_2)_2O_{15}^{-2}$	468.210	468.223	84.04
$TMAHNb_6(O_2)_3O_{14}^{-2}$	476.207	476.221	60.36
$TMA_2Nb_6(O_2)O_{16}^{-2}$	496.755	496.770	13.01
$TMA_2Nb_6(O_2)_2O_{15}^{-2}$	504.753	504.768	35.36
$TMA_2Nb_6(O_2)_3O_{14}^{-2}$	512.750	512.765	37.77
$TMANb_6(O_2)O_{15}^{-1} \cdot 3H_2O$	957.456	957.480	22.10
$TMAH_2Nb_6(O_2)_2O_{15}^{-1} \cdot 2H_2O$	973.451	973.475	58.15
$TMAH_4Nb_6(O_2)_3O_{15}^{-1} \cdot H_2O$	989.446	989.470	51.19
$TMA_2HNb_6(O_2)O_{16}^{-1} \cdot 2H_2O$	1030.542	1030.570	47.92
$TMA_{14}Nb_4O_{18}^{-2} \cdot 21H_2O$	1037.532	1037.557	15.59
$TMA_2H_3Nb_6(O_2)_2O_{16}^{-1} \cdot H_2O$	**1046.537**	**1046.565**	**100**
$TMA_2HNb_6(O_2)_3O_{14}^{-1} \cdot 2H_2O$	1062.533	1062.559	81.32
$TMA_2HNb_6(O_2)_4O_{13}^{-1} \cdot 2H_2O$	1078.528	1078.554	13.67
$TMA_3H_2Nb_6(O_2)_2O_{16}^{-1} \cdot H_2O$	1119.625	1119.654	35.60
$TMA_3Nb_6(O_2)_3O_{14}^{-1} \cdot 2H_2O$	1135.621	1135.649	31.16
$TMA_3Nb_6(O_2)_5O_{12}^{-1} \cdot H_2O$	1149.628	1149.628	10.01
$TMA_3H_2Nb_6(O_2)_6O_{12}^{-1}$	1165.630	1165.623	15.77
$TMA_3Nb_6(O_2)_7O_{10}^{-1} \cdot H_2O$	1181.624	1181.618	13.11
$TMA_4HNb_6(O_2)_6O_{12}^{-1}$	1238.717	1238.712	11.70
$TMA_4HNb_6(O_2)_7O_{11}^{-1}$	1254.711	1254.707	13.79

Table SI-10. All species identified by ESI-MS for tri-peroxylated hexaniobate.

Tri-peroxylated hexaniobate reaction solutions			
Species	**Experimental m/z**	**Calculated m/z**	**Relative Abundance (%)**
$Nb_3O_8^{-1}$	406.667	406.678	44.52
$TMA_6H_4Nb_2O_{11}^{-2} \cdot 2H_2O$	423.164	423.196	13.36
$TMAHNb_6(O_2)O_{16}^{-2}$	460.212	460.226	32.64
$TMAHNb_6(O_2)_2O_{15}^{-2}$	468.210	468.223	62.50
$TMAHNb_6(O_2)_3O_{14}^{-2}$	**476.206**	**476.221**	**100**
$TMAHNb_6(O_2)_4O_{13}^{-2}$	484.204	484.218	44.12
$TMA_2Nb_6(O_2)_2O_{15}^{-2}$	504.752	504.768	16.75
$TMA_2Nb_6(O_2)_3O_{14}^{-2}$	512.751	512.765	57.90
$TMA_2Nb_6(O_2)_4O_{13}^{-2}$	520.747	520.763	35.27
$TMA_2Nb_6(O_2)_5O_{12}^{-2}$	528.742	528.760	10.36
$TMA_5Nb_4(O_2)O_{12}^{-1}$	965.975	966.039	26.74
$TMAH_2Nb_6(O_2)_2O_{15}^{-1} \cdot 2H_2O$	973.450	973.475	21.34
$TMAH_4Nb_6(O_2)_3O_{15}^{-1} \cdot H_2O$	989.445	989.470	58.66
$TMA_2H_3Nb_6(O_2)_2O_{16}^{-1} \cdot H_2O$	1046.538	1046.565	39.09
$TMA_{14}H_2Nb_4(O_2)_2O_{17}^{-2} \cdot 20H_2O$	1053.530	1053.552	13.07
$TMA_2HNb_6(O_2)_3O_{14}^{-1} \cdot 2H_2O$	1062.533	1062.559	97.21
$TMA_2HNb_6(O_2)_4O_{13}^{-1} \cdot 2H_2O$	1078.527	1078.554	47.90
$TMA_2HNb_6(O_2)_5O_{12}^{-1} \cdot 2H_2O$	1094.521	1094.549	11.33
$TMA_3H_2Nb_6(O_2)_2O_{16}^{-1} \cdot H_2O$	1119.624	1119.654	15.49
$TMA_3Nb_6(O_2)_3O_{14}^{-1} \cdot 2H_2O$	1135.621	1135.649	40.11
$TMA_3Nb_6(O_2)_4O_{13}^{-1} \cdot 2H_2O$	1151.614	1151.644	21.75
$TMA_3Nb_6(O_2)_7O_{10}^{-1} \cdot H_2O$	1181.623	1181.618	11.53
$TMA_4HNb_6(O_2)_7O_{11}^{-1}$	1254.715	1254.707	10.77

Table SI-11. All species identified by ESI-MS for tetra-peroxylated hexaniobate.

Tetra-peroxylated hexaniobate reaction solutions			
Species	**Experimental m/z**	**Calculated m/z**	**Relative Abundance (%)**
$Nb_3O_8^{-1}$	406.667	406.678	61.48
$TMA_6H_4Nb_2O_{11}^{-2} \cdot 2H_2O$	423.166	423.196	17.71
$TMA_2Nb(OH)_8^{-1} \cdot 3H_2O$	431.161	431.154	11.51
$TMAHNb_6(O_2)O_{16}^{-2}$	460.212	460.226	25.68
$TMAHNb_6(O_2)_2O_{15}^{-2}$	468.210	468.223	52.02
$TMAHNb_6(O_2)_3O_{14}^{-2}$	**476.206**	**476.221**	**100**
$TMAHNb_6(O_2)_4O_{13}^{-2}$	484.203	484.218	82.39
$TMANb_6(O_2)_5O_{12}^{-2}$	492.201	492.216	27.40
$TMAH_3Nb_6(O_2)_5O_{13}^{-2}$	501.205	501.221	18.93
$TMA_2Nb_6(O_2)_3O_{14}^{-2}$	512.749	512.765	41.74
$TMA_2Nb_6(O_2)_4O_{13}^{-2}$	520.747	520.763	71.09
$TMA_2Nb_6(O_2)_5O_{12}^{-2}$	528.745	528.760	50.06
$TMA_2Nb_6(O_2)_6O_{11}^{-2}$	536.741	536.758	26.33
$TMA_2H_2Nb_6(O_2)_5O_{13}^{-2}$	537.750	537.765	31.38
$TMA_2H_2Nb_6(O_2)_6O_{12}^{-2}$	545.746	545.763	19.30
$TMAH_4Nb_6(O_2)_3O_{15}^{-1} \cdot H_2O$	989.444	989.470	22.69
$TMAH_6Nb_6(O_2)_4O_{15}^{-1}$	1005.438	1005.465	25.08
$TMANb_6(O_2)_5O_{11}^{-1} \cdot 3H_2O$	1021.432	1021.460	14.52
$TMA_2HNb_6(O_2)_3O_{14}^{-1} \cdot 2H_2O$	1062.532	1062.559	54.49

$TMA_2HNb_6(O_2)_4O_{13}^{-1} \cdot 2H_2O$	1078.527	1078.554	73.68
$TMA_2HNb_6(O_2)_5O_{12}^{-1} \cdot 2H_2O$	1094.521	1094.549	48.15
$TMA_2HNb_6(O_2)_6O_{11}^{-1} \cdot 2H_2O$	1110.516	1110.544	21.23
$TMA_3Nb_6(O_2)_3O_{14}^{-1} \cdot 2H_2O$	1135.620	1135.649	31.76
$TMA_3Nb_6(O_2)_5O_{12}^{-1} \cdot H_2O$	1149.599	1149.628	13.94
$TMA_3Nb_6(O_2)_4O_{13}^{-1} \cdot 2H_2O$	1151.614	1151.644	50.52
$TMA_3H_2Nb_6(O_2)_5O_{13}^{-1} \cdot H_2O$	1167.608	1167.638	41.84
$TMA_3Nb_6(O_2)_7O_{10}^{-1} \cdot H_2O$	1181.617	1181.618	11.59
$TMA_3H_2Nb_6(O_2)_6O_{12}^{-1} \cdot H_2O$	1183.604	1183.633	22.85
$TMA_4HNb_6(O_2)_8O_{10}^{-1}$	1270.705	1270.702	13.46
$TMA_4HNb_6(O_2)_9O_9^{-1}$	1286.700	1286.697	12.56

Table SI-12. All species identified by ESI-MS for penta-peroxylated hexaniobate.

Penta-peroxylated hexaniobate reaction solutions			
Species	**Experimental m/z**	**Calculated m/z**	**Relative Abundance (%)**
$Nb_3O_8^{-1}$	406.665	406.678	54.20
$TMA_6H_4Nb_2O_{11}^{-2} \cdot 2H_2O$	423.163	423.196	23.00
$TMAHNb_6(O_2)O_{16}^{-2}$	460.212	460.226	20.78
$TMAHNb_6(O_2)_2O_{15}^{-2}$	468.209	468.223	52.36
$TMAHNb_6(O_2)_3O_{14}^{-2}$	476.206	476.221	80.09
$TMAHNb_6(O_2)_4O_{13}^{-2}$	**484.203**	**484.218**	**100**
$TMANb_6(O_2)_5O_{12}^{-2}$	492.200	492.216	38.33
$TMAHNb_6(O_2)_6O_{11}^{-2}$	500.197	500.213	20.28
$TMAH_3Nb_6(O_2)_5O_{13}^{-2}$	501.204	501.221	28.42
$TMAH_3Nb_6(O_2)_6O_{12}^{-2}$	509.203	509.218	31.71
$TMA_2Nb_6(O_2)_3O_{14}^{-2}$	512.750	512.765	19.02
$TMA_2Nb_6(O_2)_4O_{13}^{-2}$	520.747	520.765	54.05
$TMA_2Nb_6(O_2)_5O_{12}^{-2}$	528.744	528.763	65.25
$TMA_2Nb_6(O_2)_6O_{11}^{-2}$	536.741	536.758	74.53
$TMA_2H_2Nb_6(O_2)_5O_{13}^{-2}$	537.748	537.765	44.31
$TMA_2H_2Nb_6(O_2)_6O_{12}^{-2}$	545.746	545.763	66.51
$TMANb_6(O_2)_4O_{12}^{-1} \cdot 3H_2O$	1005.438	1005.465	13.63
$TMANb_6(O_2)_5O_{11}^{-1} \cdot 3H_2O$	1021.433	1021.460	17.91
$TMANb_6(O_2)_6O_{10}^{-1} \cdot 3H_2O$	1037.426	1037.455	15.34
$TMA_2HNb_6(O_2)_3O_{14}^{-1} \cdot 2H_2O$	1062.532	1062.559	13.23
$TMA_2HNb_6(O_2)_4O_{13}^{-1} \cdot 2H_2O$	1078.526	1078.554	33.66
$TMA_2HNb_6(O_2)_5O_{12}^{-1} \cdot 2H_2O$	1094.521	1094.549	51.53
$TMA_2HNb_6(O_2)_6O_{11}^{-1} \cdot 2H_2O$	1110.516	1110.544	51.90
$TMA_3Nb_6(O_2)_5O_{12}^{-1} \cdot H_2O$	1149.598	1149.628	17.62
$TMA_3Nb_6(O_2)_4O_{13}^{-1} \cdot 2H_2O$	1151.613	1151.644	20.22
$TMA_3H_2Nb_6(O_2)_6O_{12}^{-1}$	1165.595	1165.623	13.24
$TMA_3H_2Nb_6(O_2)_5O_{13}^{-1} \cdot H_2O$	1167.609	1167.638	39.67
$TMA_3H_2Nb_6(O_2)_6O_{12}^{-1} \cdot H_2O$	1183.604	1183.633	54.70

Table SI-13. All species identified by ESI-MS for hexa-peroxylated hexaniobate.

Hexa-peroxylated hexaniobate reaction solutions			
Species	**Experimental m/z**	**Calculated m/z**	**Relative Abundance (%)**
$Nb_3O_8^{-1}$	406.667	406.678	51.57
$TMA_6H_4Nb_2O_{11}^{-2} \cdot 2H_2O$	423.165	423.196	16.16
$TMAHNb_6(O_2)O_{16}^{-2}$	460.214	460.226	10.10

$TMAHNb_6(O_2)_2O_{15}^{-2}$	468.208	468.223	43.82
$TMAHNb_6(O_2)_3O_{14}^{-2}$	476.207	476.221	34.71
$TMAHNb_6(O_2)_4O_{13}^{-2}$	484.204	484.218	81.34
$TMANb_6(O_2)_5O_{12}^{-2}$	492.200	492.216	21.38
$TMAHNb_6(O_2)_6O_{11}^{-2}$	500.197	500.213	22.63
$TMAH_3Nb_6(O_2)_5O_{13}^{-2}$	501.205	501.221	15.75
$TMAH_3Nb_6(O_2)_6O_{12}^{-2}$	509.203	509.218	40.72
$TMA_2Nb_6(O_2)_4O_{13}^{-2}$	520.745	520.765	18.06
$TMA_2Nb_6(O_2)_5O_{12}^{-2}$	528.744	528.763	28.51
$TMA_2Nb_6(O_2)_6O_{11}^{-2}$	536.742	536.758	70.68
$TMA_2H_2Nb_6(O_2)_5O_{13}^{-2}$	537.748	537.765	21.41
$TMA_2H_2Nb_6(O_2)_6O_{12}^{-2}$	545.747	545.763	58.20
$TMANb_6(O_2)_5O_{11}^{-1} \cdot 3H_2O$	1021.431	1021.460	17.76
$TMANb_6(O_2)_6O_{10}^{-1} \cdot 3H_2O$	1037.427	1037.455	36.33
$TMA_2HNb_6(O_2)_4O_{13}^{-1} \cdot 2H_2O$	1078.527	1078.554	12.10
$TMA_2HNb_6(O_2)_5O_{12}^{-1} \cdot 2H_2O$	1094.520	1094.549	38.02
$TMA_2HNb_6(O_2)_6O_{11}^{-1} \cdot 2H_2O$	**1110.517**	**1110.544**	**100**
$TMA_3H_2Nb_6(O_2)_6O_{12}^{-1}$	1165.593	1165.623	11.98
$TMA_3H_2Nb_6(O_2)_5O_{13}^{-1} \cdot H_2O$	1167.608	1167.638	16.92
$TMA_3H_2Nb_6(O_2)_6O_{12}^{-1} \cdot H_2O$	1183.604	1183.633	59.89

Table SI-14. Energetics of peroxylation of hexatantalate. Stepwise addition of peroxide as well as full peroxylation in a single step are included, with and without the protons included in the structure.

Reaction	ΔH, kcal/mol (x = 0)	ΔH, kcal/mol (x = 2)
$H_2O_2 + H_xTa_6O_{19}^{(8-x)-} \rightarrow H_2O + H_xTa_6(O_2)O_{18}^{(8-x)-}$	-12.8	-12.9
$H_2O_2 + H_xTa_6(O_2)O_{18}^{(8-x)-} \rightarrow H_2O + H_xTa_6(O_2)_2O_{17}^{(8-x)-}$	-13.4	-14.2
$H_2O_2 + H_xTa_6(O_2)_2O_{17}^{(8-x)-} \rightarrow H_2O + H_xTa_6(O_2)_3O_{16}^{(8-x)-}$	-11.5	-13.6
$H_2O_2 + H_xTa_6(O_2)_3O_{16}^{(8-x)-} \rightarrow H_2O + H_xTa_6(O_2)_4O_{15}^{(8-x)-}$	-15.1	-11.7
$H_2O_2 + H_xTa_6(O_2)_4O_{15}^{(8-x)-} \rightarrow H_2O + H_xTa_6(O_2)_5O_{14}^{(8-x)-}$	-13.3	-10.8
$H_2O_2 + H_xTa_6(O_2)_5O_{14}^{(8-x)-} \rightarrow H_2O + H_xTa_6(O_2)_6O_{13}^{(8-x)-}$	-14.4	-12.7
$H_2O_2 + H_xTa_6O_{19}^{(8-x)-} \rightarrow H_2O + H_xTa_6(O_2)O_{18}^{(8-x)-}$	-12.8	-12.9
$2H_2O_2 + H_xTa_6O_{19}^{(8-x)-} \rightarrow 2H_2O + H_xTa_6(O_2)_2O_{17}^{(8-x)-}$	-26.2	-27.1
$3H_2O_2 + H_xTa_6O_{19}^{(8-x)-} \rightarrow 3H_2O + H_xTa_6(O_2)_3O_{16}^{(8-x)-}$	-47.6	-40.8
$4H_2O_2 + H_xTa_6O_{19}^{(8-x)-} \rightarrow 4H_2O + H_xTa_6(O_2)_4O_{15}^{(8-x)-}$	-52.7	-52.5
$5H_2O_2 + H_xTa_6O_{19}^{(8-x)-} \rightarrow 5H_2O + H_xTa_6(O_2)_5O_{14}^{(8-x)-}$	-66.0	-63.3
$6H_2O_2 + H_xTa_6O_{19}^{(8-x)-} \rightarrow 6H_2O + H_xTa_6(O_2)_6O_{13}^{(8-x)-}$	-80.4	-76.0

Table SI-15. Energetics of peroxylation of hexaniobate. Stepwise addition of peroxide as well as full peroxylation in a single step are included, as well as with and without the protons included in the structure.

Reaction	ΔH, kcal/mol (x = 0)	ΔH, kcal/mol (x = 2)
$H_2O_2 + H_xNb_6O_{19}^{(8-x)-} \rightarrow H_2O + H_xNb_6(O_2)O_{18}^{(8-x)-}$	-14.4	-15.2
$H_2O_2 + H_xNb_6(O_2)O_{18}^{(8-x)-} \rightarrow H_2O + H_xNb_6(O_2)_2O_{17}^{(8-x)-}$	-15.1	-13.6

$H_2O_2 + H_xNb_6(O_2)_2O_{17}^{(8-x)-} \rightarrow H_2O + H_xNb_6(O_2)_3O_{16}^{(8-x)-}$	-12.1	-13.9
$H_2O_2 + H_xNb_6(O_2)_3O_{16}^{(8-x)-} \rightarrow H_2O + H_xNb_6(O_2)_4O_{15}^{(8-x)-}$	-17.0	-13.2
$H_2O_2 + H_xNb_6(O_2)_4O_{15}^{(8-x)-} \rightarrow H_2O + H_xNb_6(O_2)_5O_{14}^{(8-x)-}$	-14.2	-10.9
$H_2O_2 + H_xNb_6(O_2)_5O_{14}^{(8-x)-} \rightarrow H_2O + H_xNb_6(O_2)_6O_{13}^{(8-x)-}$	-15.3	-12.2
$H_2O_2 + H_xNb_6O_{19}^{(8-x)-} \rightarrow H_2O + H_xNb_6(O_2)O_{18}^{(8-x)-}$	-14.4	-15.2
$2H_2O_2 + H_xNb_6O_{19}^{(8-x)-} \rightarrow 2H_2O + H_xNb_6(O_2)_2O_{17}^{(8-x)-}$	-29.5	-28.8
$3H_2O_2 + H_xNb_6O_{19}^{(8-x)-} \rightarrow 3H_2O + H_xNb_6(O_2)_3O_{16}^{(8-x)-}$	-41.6	-42.7
$4H_2O_2 + H_xNb_6O_{19}^{(8-x)-} \rightarrow 4H_2O + H_xNb_6(O_2)_4O_{15}^{(8-x)-}$	-58.6	-55.9
$5H_2O_2 + H_xNb_6O_{19}^{(8-x)-} \rightarrow 5H_2O + H_xNb_6(O_2)_5O_{14}^{(8-x)-}$	-72.8	-66.7
$6H_2O_2 + H_xNb_6O_{19}^{(8-x)-} \rightarrow 6H_2O + H_xNb_6(O_2)_6O_{13}^{(8-x)-}$	-88.1	-78.9

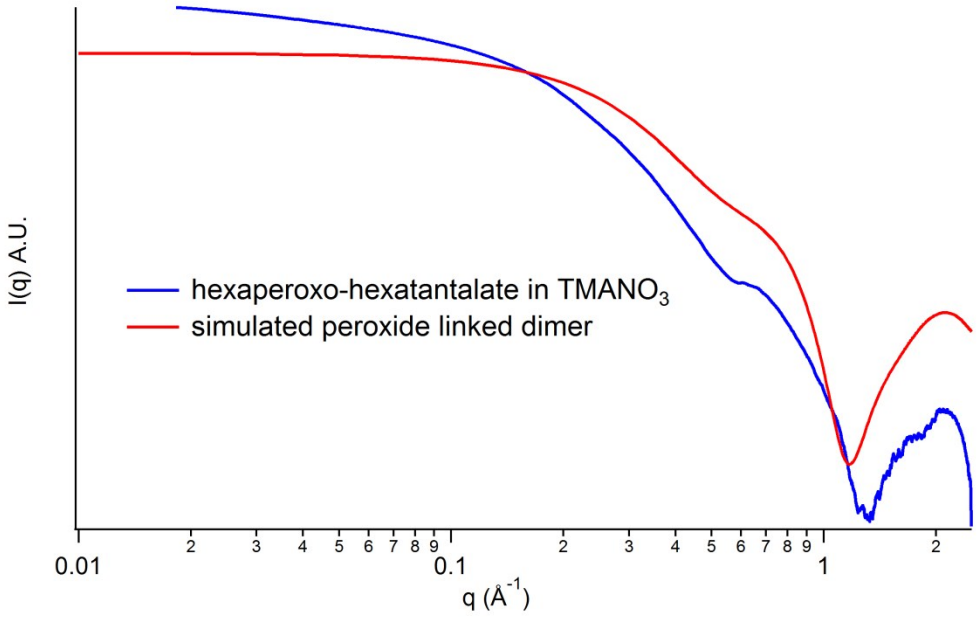

Fig. SI-10 Simulated SWAXS data for a peroxide linked dimer of peroxohexametalate, and experimental SWAXS data for hexaperoxo-hexatantalate, dissolved in 1M $TMANO_3$.

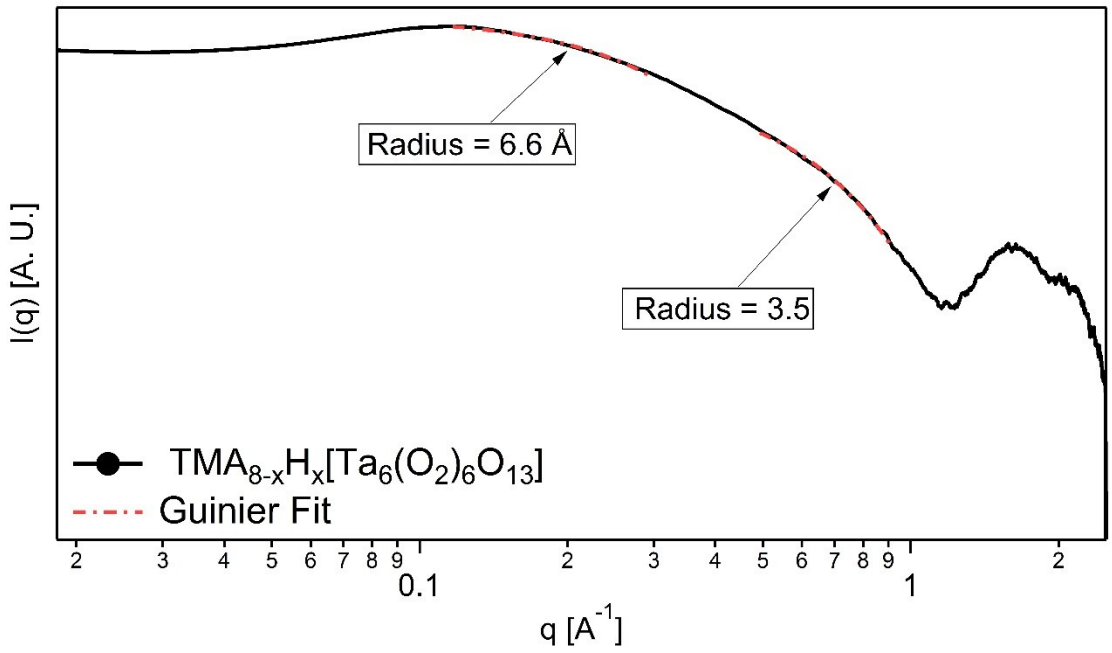

Fig. SI-11 Guinier fit of hexaperoxo-hexatantalate reaction solution, corresponding to the approximate size of hexatantalate and dimers of hexatantalate.

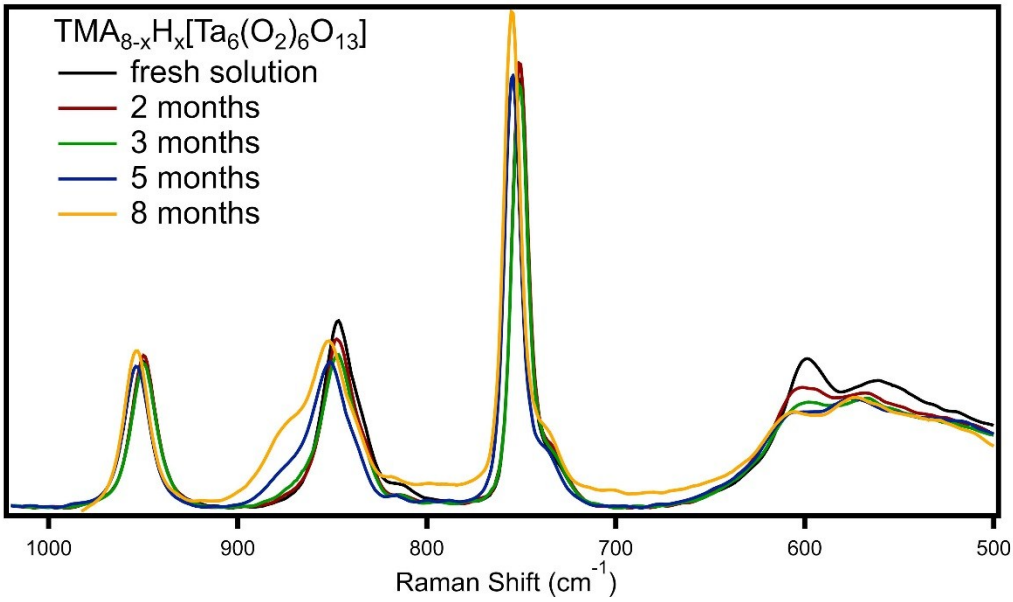

Fig. SI-12 Raman spectra of peroxohexatantalate dissolved in water.

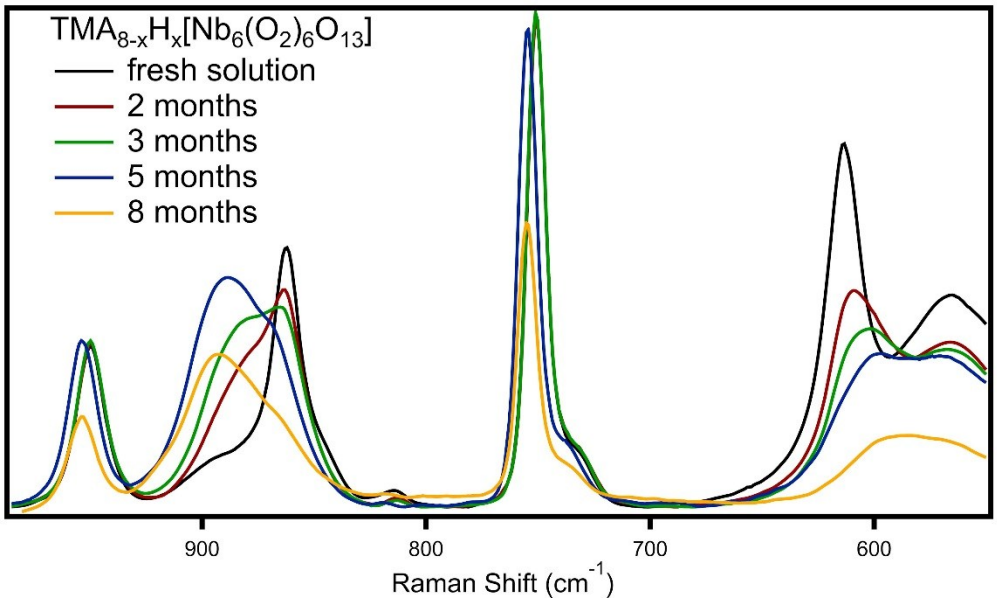

Fig. SI-13 Raman spectra of peroxohexaniobate dissolved in water.