Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information: Computational exploration of heteroatom substitution in the decaniobate framework.

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Table S1: Comparison of different exchange correlation functional (XC) and basis set combinations for the energies of $[TiNb_9O_{28}]^{7-}$ isomers. Implicit solvation using PCM was used in all cases, except in entry 1.

Entry	XC	Basis set	Isomer A[a] Energy (Ha)	Relative Energy[b] (kcal/mol)	Isomer B Energy (Ha)	Relative Energy[c] (kcal/mol)	Isomer C Energy (Ha)	Relative Energy[c] (kcal/mol)
1 (NO PCM)	PBE0	def2-svp	-3465.70035817	0	-3465.68169185	11.71	-3465.68419552	10.14
2	PBE0	def2-svp	-3468.00218250	0	-3467.98177618	12.81	-3467.98433889	11.20
3	M06	def2-svp	-3469.28445685	0	-3469.26597663	11.60	-3469.26700193	10.95
4	B3PW91	def2-svp	-3470.01027446	0	-3469.99038915	12.48	-3469.99297260	10.86
5	B3LYP	def2-svp	-3470.66327848	0	-3470.64339048	12.48	-3470.64616461	10.74
6	PBE	def2-svp	-3468.57744957	0	-3468.55679156	12.96	-3468.56005273	10.92
7	BP86	def2-svp	-3471.59264621	0	-3471.57186557	13.04	-3471.57521132	10.94
8	OPBE	def2-svp	-3470.55069465	0	-3470.53441947	10.21	-3470.53643185	8.95
9	PBE0	def2-tzvp	-3470.68267149	0	-3470.66716450	9.73	-3470.66791484	9.26
10 (GD3BJ)[c]	PBE0	def2-tzvp	-3470.81219271	0	-3470.79629989	9.97	-3470.79707648	9.49
11	M06	def2-tzvp	-3471.85677598	0	-3471.84218973	9.15	-3471.84159953	9.52
12	B3PW91	def2-tzvp	-3472.69148778	0	-3472.67640573	9.46	-3472.67725891	8.93
13	B3LYP	def2-tzvp	-3473.37815736	0	-3473.36431342	8.69	-3473.36487910	8.33
14	PBE	def2-tzvp	-3471.25327347	0	-3471.23950155	8.64	-3471.24030292	8.14
15	BP86	def2-tzvp	-3474.28420148	0	-3474.26987239	8.99	-3474.27098300	8.29
16	OPBE	def2-tzvp	-3473.20434809	0	-3473.19338676	6.88	-3473.19336217	6.89
17 [d]	PW6B95D3	def2-qzvp	-3476.42355717	0	-3476.40799558	9.76	-3476.40904242	9.11

[a] A, B and C indicate the location of the substitution. See main text for key. [b] Energy relative to the A isomer at that level of theory. [c]Grimme Dispersion version 3 with Becke-Johnson damping. [d] Using same structures as entry 9. Calculation done in Gaussian 16, rev. C.01.

Table S2: Energies of isomers of first-row d-block element substituted niobates, $[M^{OS}Nb_9O_{28}]^{(11-OS)-}$, where OS is the oxidation state. All computations carried out at the PBE0/def2-tzvp level of theory with implicit solvation via PCM.

Entry	M (OS)	Mult.[a]	Isomer A		Isomer B			Isomer C		
			S[b]	Energy (Ha)	S	Energy (Ha)	Relative Energy[c] (kcal/mol)	S	Energy (Ha)	Relative Energy[c] (kcal/mol)
1	Ti (IV)	1	-	-3470.68267149	-	-3470.66716450	9.73	-	-3470.66791484	9.26
2	V (III)	3	1.0026	-3565.23176130	1.0052	-3565.18731160	27.89	1.0080	-3565.18085144	31.95
3	V (IV)	2	0.5041	-3565.13137100	0.5053	-3565.14031241	-5.61	0.5055	-3565.14011884	-5.49
4	V (V)	1	-	-3565.01000104	-	-3565.01616903	-3.87	-	-3565.02128841	-7.08
5	Cr (III)	4	1.5048	-3665.69287929	1.5065	-3665.62105401	45.07	1.5062	-3665.62532404	42.39
6	Cr (IV)	3	1.0192	-3665.54752303	1.0193	-3665.52860037	11.87	1.0215	-3665.53506992	7.81
7	Mn (II)	6	2.5009	-3772.27832155	2.5022	-3772.20230918	47.70	2.5023	-3772.20301962	47.25
8	Mn (III)	5	2.0089	-3772.16982653	2.0184	-3772.12900431	25.62	2.0170	-3772.13323901	22.96
9	Fe (II)	5	2.0021	-3884.95479716	2.1965[e]	-3884.87023416	53.06		*	
10	Fe (III)	6	2.5014	-3884.87727492	2.5028	-3884.83226362	28.24	2.5029	-3884.83275469	27.94
11	Co (II)	4	1.0138	-4003.96245362		*			*	
12	Co (II)	4	1.5000[d]	-4003.95957544		-			-	
13	Co (III)	5	2.0023	-4003.87520532	2.0038	-4003.84844224	16.79	2.0039	-4003.84880148	16.57
14	Ni (II)	3	1.0013	-4129.53510976	1.0053	-4129.44742347	55.02		*	
15	Cu (II)	2	0.5010	-4261.65752638		*			*	
16	Zn (II)	1	-	-4400.58001165		*			*	

[a] The requested spin multiplicity, 2S+1. [b] As computed by G09.[c] Energy relative to the A isomer at that level of theory. [d] Using restricted open-shell DFT (RO-DFT). Unrestricted DFT yielded unsatisfactory spin multiplicity. [e] Attempts were made to optimise this molecule using RO-DFT to constrain the spin multiplicity, but failed due to issues with SCF convergence, and were eventually abandoned. * Isomer is not stable as a decametalate structure.

Table S3: Energies of isomers of second-row d-block element substituted niobates, $[M^{OS}Nb_9O_{28}]^{(11-OS)-}$, where OS is the oxidation state. All computations carried out at the PBE0/def2-tzvp level of theory with implicit solvation via PCM.

Entry	M (OS)	Mult.[a]	Isomer A		Isomer B			Isomer C		
			S[b]	Energy (Ha)	S	Energy (Ha)	Relative Energy[c] (kcal/mol)	S	Energy (Ha)	Relative Energy[c] (kcal/mol)
1	Zr (IV)	1	-	-2668.50709372	-	-2668.48426220	14.33	-	-2668.48215796	15.65
2	Nb (III)	3	1.0036	-2678.39901265	1.0036	-2678.39903787	-0.02	1.0036	-2678.39903847	-0.02
3	Nb (IV)	2	0.5027	-2678.35118728	0.5027	-2678.35118552	0.00	0.5027	-2678.35119486	0.00
4	Nb (V)	1	-	-2678.29152327	-	-	-	-	-	-
5	Mo (IV)	3	1.0029	-2689.51344468	1.0030	-2689.49198510	13.47	1.0060	-2689.48689455	16.66
6	Mo (V)	2	0.5020	-2689.41255361	0.5026	-2689.43581544	-14.60	0.5027	-2689.43335264	-13.05
7	Mo (VI)	1	-	-2689.29501230	-	-2689.31205538	-10.69	-	-2689.31459670	-12.29
8	Tc (VII)	1	-	-2701.60550067	-	-2701.63530252	-18.70	-	-2701.63831084	-20.59
9	Ru (II)	1	-	-2716.28327591	-	-2716.20583818	48.59		*	
10	Ru (III)	2	0.5018	-2716.21548613	0.5044	-2716.15709552	36.64	0.5098	-2716.15861635	35.69
11	Rh (III)	1	-	-2731.86364540	-	-2731.78194365	51.27	-	-2731.78564317	48.95
12	Pd (II)	1	-	-2749.25348763		*			*	
13	Pd (IV)	1	-	-2749.00950943	-	-2748.95148878	36.41	-	-2748.95717323	32.84
14	Ag (I)	1	-	-2768.42019083	-	*			*	
15	Cd (II)	1	-	-2789.15456331	-	-2789.08546778	43.36	-	-2789.08596361	43.05

[a] The requested spin multiplicity, 2S+1. [b] As computed by G09.[c] Energy relative to the A isomer at that level of theory. * Isomer is not stable as a decametalate structure.

Table S4: Energies of isomers of third-row d-block element substituted niobates, $[M^{OS}Nb_9O_{28}]^{(11-OS)-}$, where OS is the oxidation state. All computations carried out at the PBE0/def2-tzvp level of theory with implicit solvation via PCM.

Entry	M (OS)	Mult.[a]	Isomer A		Isomer B			Isomer C		
			S[b]	Energy (Ha)	S	Energy (Ha)	Relative Energy[c] (kcal/mol)	S	Energy (Ha)	Relative Energy[c] (kcal/mol)
1	Hf (IV)	1	-	-2669.47996725	-	-2669.45129288	17.99	-	-2669.44876623	19.58
2	Ta (V)	1	-	-2678.36012884	-	-2678.35576746	2.74	-	-2678.35458246	3.48
3	W (IV)	3	1.0029	-2688.39584920	1.0029	-2688.40536220	-5.97	1.0033	-2688.40570877	-6.19
4	W (V)	2	0.5020	-2688.33416140	0.5025	-2688.34918089	-9.42	0.5023	-2688.34548740	-7.11
5	W(VI)	1	-	-2688.23993299	-	-2688.25458708	-9.20	-	-2688.25493747	-9.42
6	Re (VII)	1	-	-2699.17460391	-	-2699.20363517	-18.22	-	-2699.20397061	-18.43
7	Os (VIII)	1	-	-2711.21597940	-	-2711.25317121	-23.34	-	-2711.25158938	-22.35
8	Ir (III)	1	-	-2725.65347739	-	-2725.57863525	46.96	-	-2725.57926047	46.57
9	Pt (IV)	1	-	-2740.49379106	-	-2740.42885494	40.75	-	-2740.43370410	37.70
10	Au (III)	3	1.0035	-2756.88929593		*			*	
11	Hg (II)	1	-	-2774.65830832		*			*	

[a] The requested spin multiplicity, 2S+1. [b] As computed by G09.[c] Energy relative to the A isomer at that level of theory.

Table S5: Energies of select spin configurations for isomer A of d-block element substituted niobates, $[M^{OS}Nb_9O_{28}]^{(11-OS)-}$, where OS is the oxidation state. All computations carried out at the OPBE/def2-tzvp level of theory with implicit solvation via PCM.

Entry	M (OS)	Mult.[a]	S[b]	Energy (OPBE) (Ha)	ΔE (OPBE)[c] (kcal/mol)	ΔE (PBE0)[c] (kcal/mol)
1	Mn (III)	3	1.0233	-3774.80315800	–	–
2	Mn (III)	5	2.0109	-3774.84742747	-27.78	-16.26
3	Fe (II)	1	0.0000	-3887.59183097	–	–
4	Fe (II)	5	2.0128	-3887.64652810	-34.32	-40.34
5	Fe (III)	2	0.5634	-3887.54291712	–	–
6	Fe (III)	6	2.5012	-3887.59133672	-30.38	-32.75
7	Co (II)	2	0.5072	-4006.72954702	–	–
8	Co (II)	4	1.5038	-4006.74541035	-9.95	3.69
9	Co (III)	1	0.0000	-4006.65759272	–	–
10	Co (III)	5	2.0022	-4006.65744519	0.09	-5.07
11	Ni (II)	1	0.0000	-4132.33870413	–	–
12	Ni (II)	3	1.0019	-4132.35230100	-8.53	26.73
13	Ru (II)	1	0.0000	-2718.74857048	–	–
14	Ru (II)	5	2.0053	-2718.68731508	38.44	22.59
15	Ru (III)	2	0.5027	-2718.67952798	–	–
16	Ru (III)	6	2.5015	-2718.62172493	36.27	31.18
17	Rh (III)	1	0.0000	-2734.35556244	–	–
18	Rh (III)	5	2.0021	-2734.27394750	51.21	48.36
19	Pd (II)	1	0.0000	-2751.75983250	–	–
20	Pd (II)	3	1.0014	-2751.73568566	15.15	6.44
21	Pd (IV)	1	0.0000	-2751.55461287	–	–
22	Pd (IV)	5	2.0038	-2751.46156604	58.39	65.11
23	Ir (III)	1	0.0000	-2728.15326040	–	–
24	Ir (III)	5	2.0021	-2728.04829287	65.87	63.02
25	Pt (IV)	1	0.0000	-2743.03530166	–	–
26	Pt (IV)	5	2.0028	-2742.90645891	80.85	81.52

[a] The requested spin multiplicity, 2S+1. [b] As computed by G09.[c] Energy relative to the lowest spin configuration at that level of theory.

Table S6: Implicit bond energy. As a crude measures of the bond energy and the destabilizing influence of the heterometal, the single-point energy of of the $[Nb_9O_{28}]^{11-}$ framework obtained by removing M^{OS} from $[MNb_9O_{28}]^{(11-OS)-}$ was calculated. The 'Bond' energy is the sum of the free metal and the niobate framework relative to the energy of the product, and the 'Geometry' energy is the energy of the niobate framework of the product relative to the corresponding structure obtained from the decaniobate molecule. A large absolute value thus indicates that the structure is distorted relative to the decaniobate molecule.

Entry	M (OS)	Mult.[a]	Energy (Ha) $[MNb_9O_{28}]^{(11-OS)-}$	$[Nb_9O_{28}]^{11-}$	M^{OS}	Energy Bond[b] (kcal/mol)	Geometry[c] (kcal/mol)
1	A, Nb(V)	1	-2678.29152331	-2621.12462448	-55.6184352963	-971.7	-
2	B, Nb(V)	1		-2621.03802529		-1026	-
3	C, Nb(V)	1		-2621.04318726		-1022	-
4	A, V(V)	1	-3565.01000104	-2621.07020267	-941.421077237	-1581	+34.15
5	B, V(V)	1	-3565.01616903	-2620.98780051		-1636	+31.52
6	C, V(V)	1	-3565.02128841	-2620.99729040		-1633	+28.80
7	A, V(III)	3	-3565.23176130	-2621.29098606	-943.166508186	-485.9	-104.4
8	B, V(III)	3	-3565.18731160	-2620.09992393		-1205	+588.7
9	C, V(III)	3	-3565.18085144	-2621.06579101		-595.2	-14.18

Computations at PBE0/def2-tzvp with PCM using G09. [a] The requested spin multiplicity, 2S+1. [b] $E([MNb_9O_{28}]^{(11-OS)-})-(E([Nb_9O_{28}]^{11-})+E(M^{OS}))$. [c] $E([MNb_9O_{28}]^{(11-OS)-})-E([Nb_9O_{28}]^{11-})$.

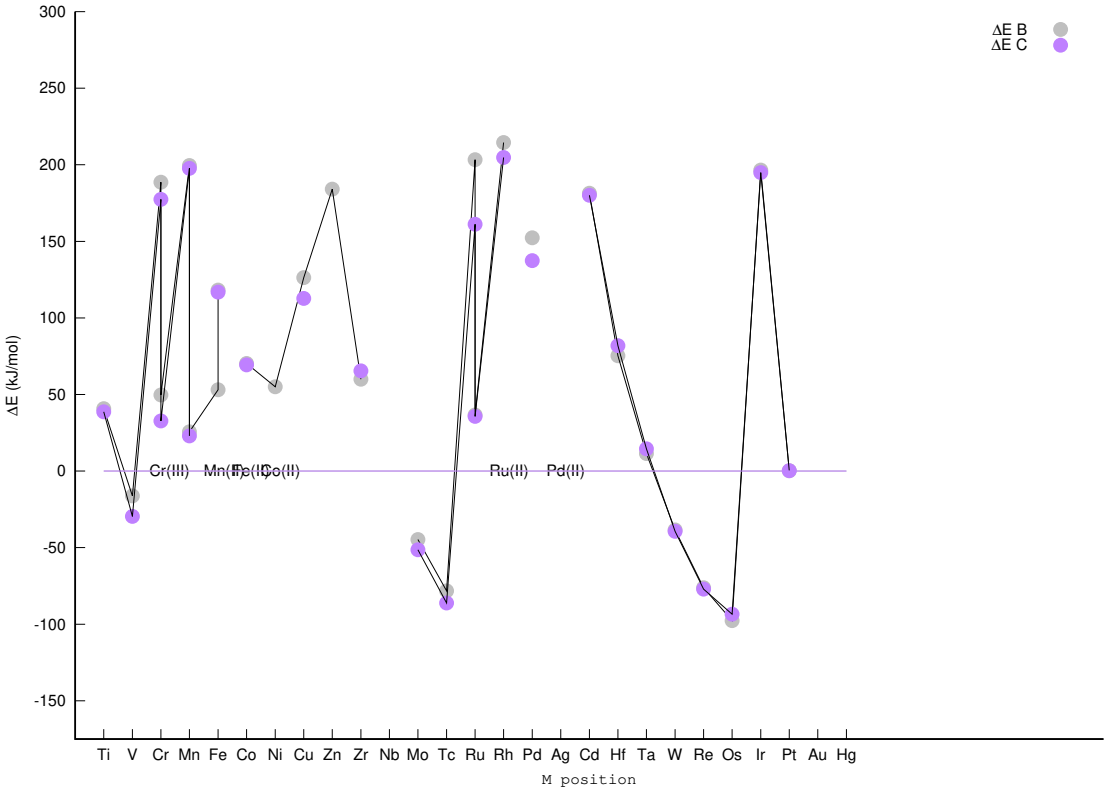

Figure S1: Energies of the B and C isomeres relative to the A isomer for $[M^zNb_9O_{28}]^{(11-z)-}$.

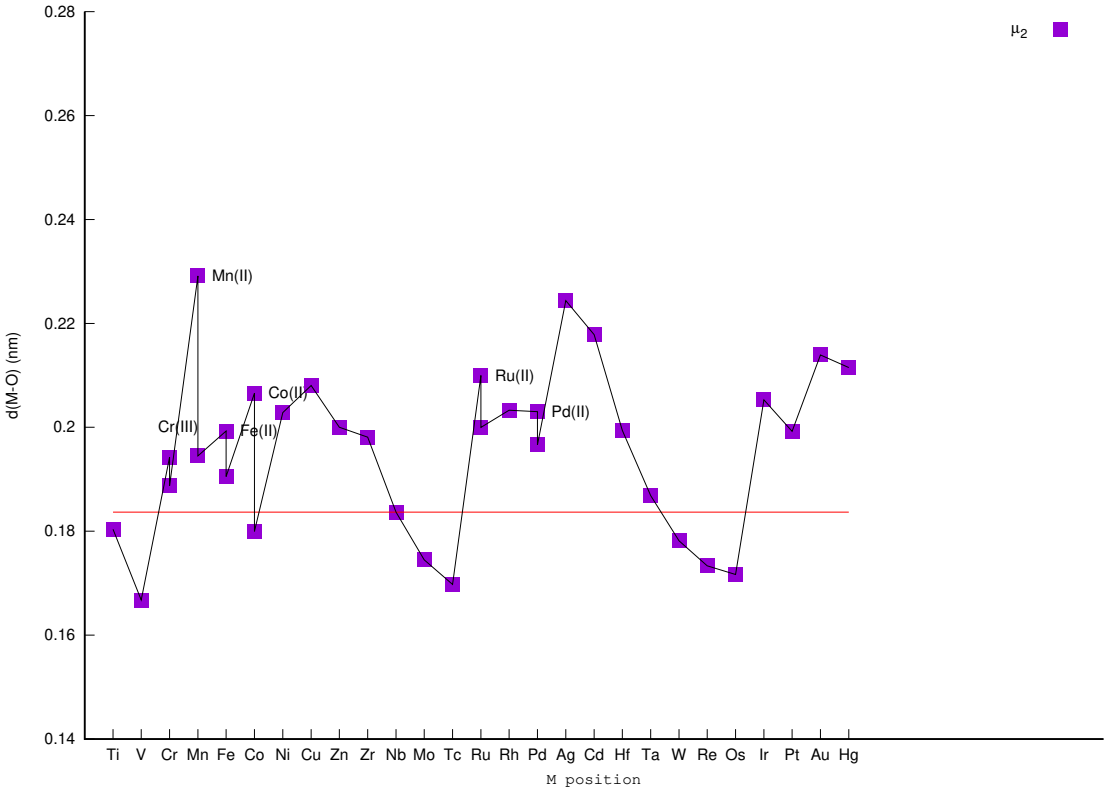

Figure S2: M-μ_2O bond distances in the A isomer for $[M^zNb_9O_{28}]^{(11-z)-}$.

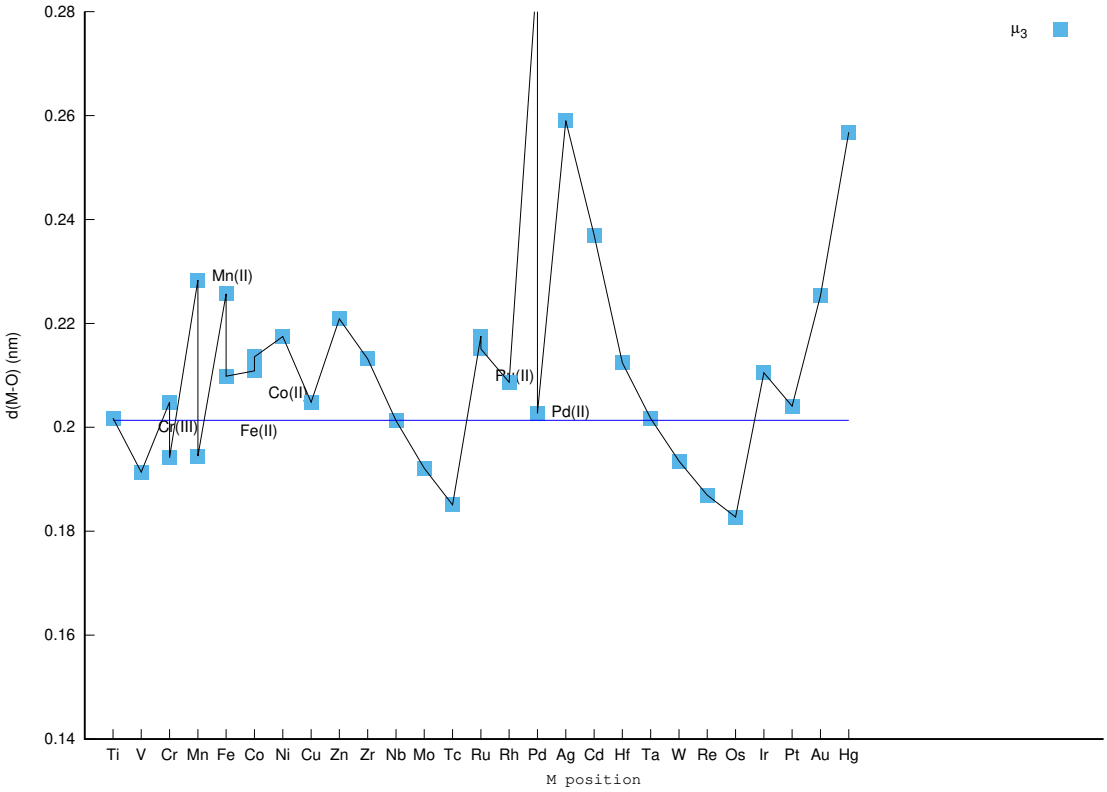

Figure S3: M-μ_3O bond distances in the A isomer for $[M^zNb_9O_{28}]^{(11-z)-}$.

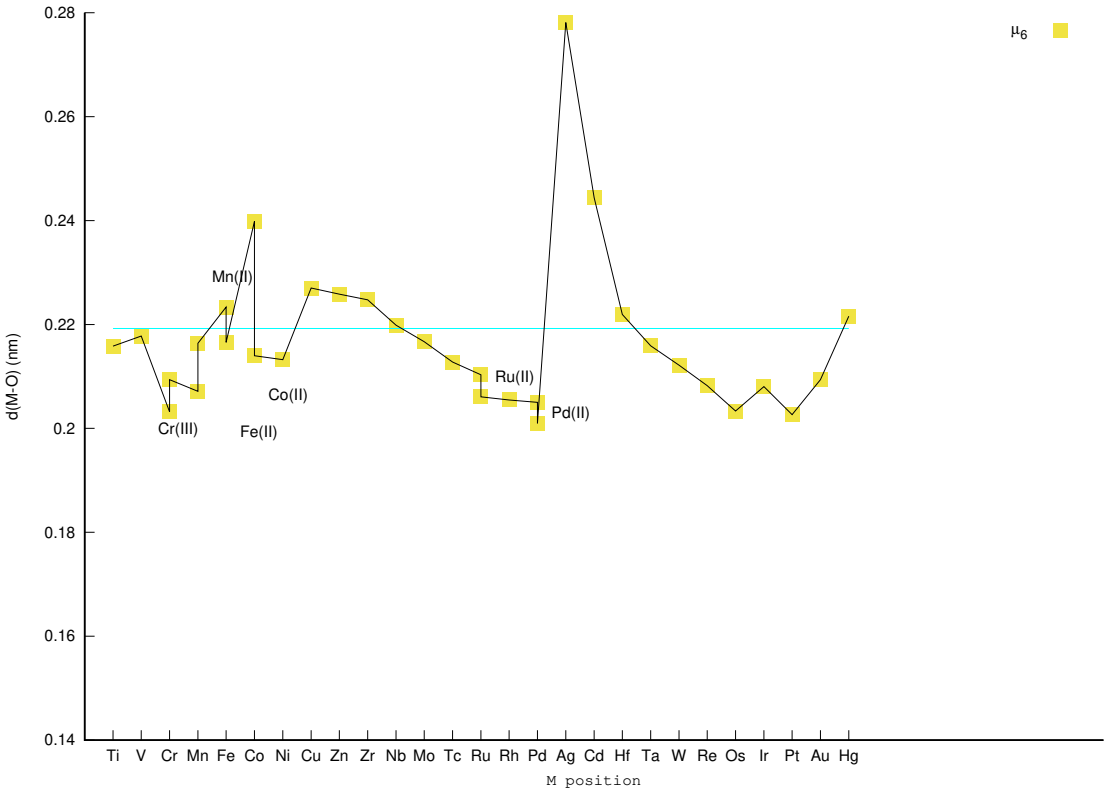

Figure S4: M-μ_6O bond distances in the A isomer for $[M^zNb_9O_{28}]^{(11-z)-}$.

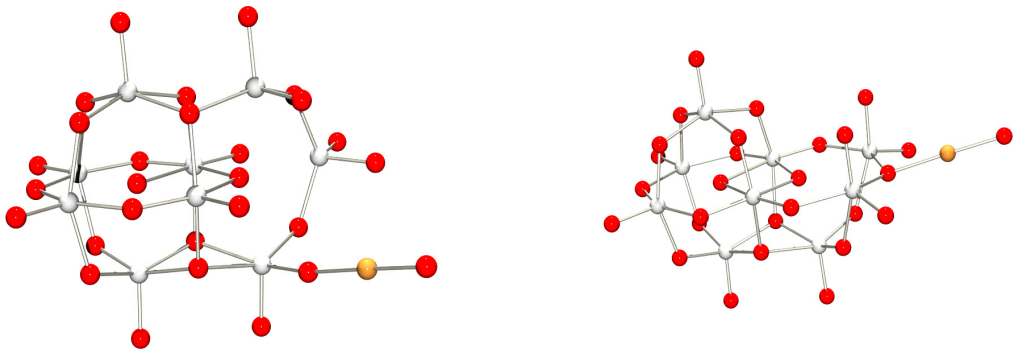

Figure S5: Isomer 'B' (left) and 'C' (right) of $[M^zNb_9O_{28}]^{(11-z)-}$, where M^z=Ag^+ (Mult.=1) (gold). Niobium and oxygen atoms are shown in grey and red, respectively. Bonds were added by "Ortep-3 for Windows" and do not reflect a statement on the presence of absence of bonding interactions between atom pairs.

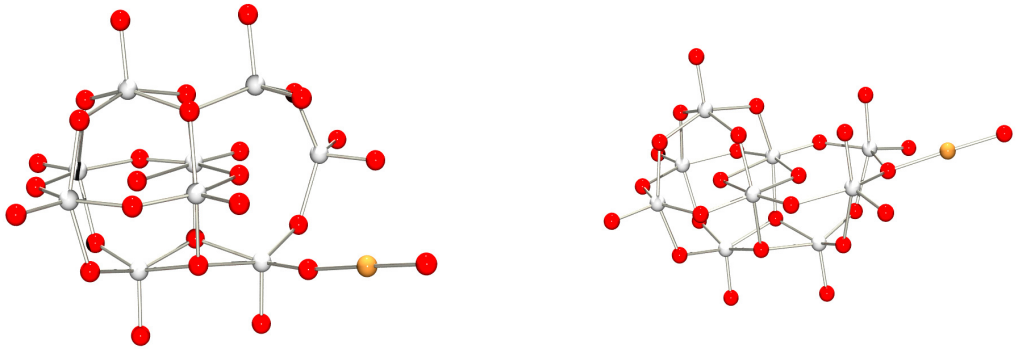

Figure S6: Isomer 'B' (left) and 'C' (right) of $[M^zNb_9O_{28}]^{(11-z)-}$, where M^z=Ag^+ (Mult.=1) (gold). Niobium and oxygen atoms are shown in grey and red, respectively. Bonds were added by "Ortep-3 for Windows" and do not reflect a statement on the presence of absence of bonding interactions between atom pairs.

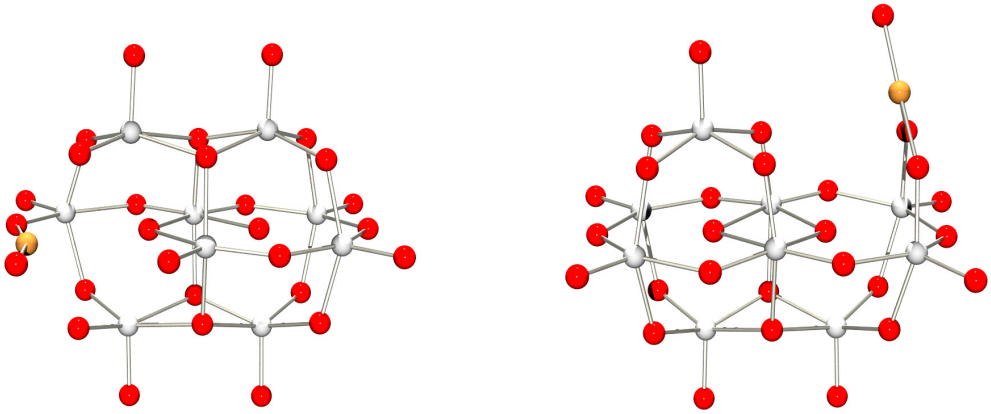

Figure S7: Isomer 'B' (left) and 'C' (right) of $[M^zNb_9O_{28}]^{(11-z)-}$, where M^z=Au^{3+} (Mult.=3) (gold). Niobium and oxygen atoms are shown in grey and red, respectively. Bonds were added by "Ortep-3 for Windows" and do not reflect a statement on the presence of absence of bonding interactions between atom pairs.

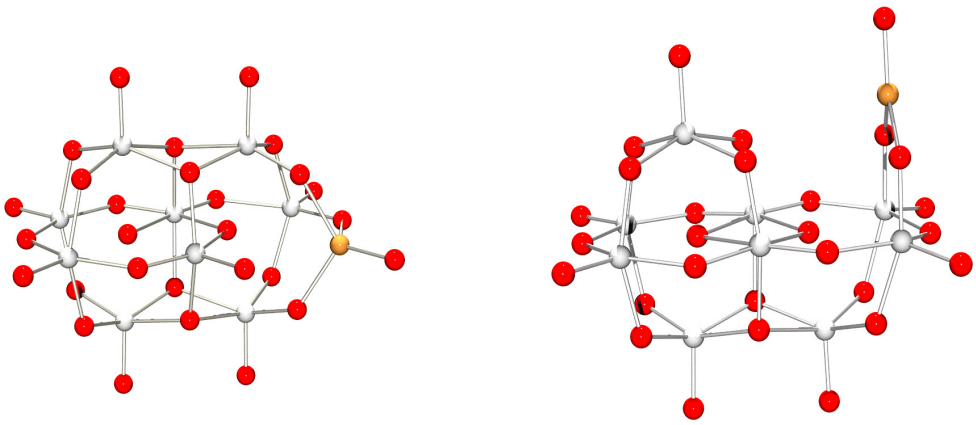

Figure S8: Isomer 'B' (left) and 'C' (right) of $[M^zNb_9O_{28}]^{(11-z)-}$, where M^z=Co^{2+} (Mult.=4) (gold). Niobium and oxygen atoms are shown in grey and red, respectively. Bonds were added by "Ortep-3 for Windows" and do not reflect a statement on the presence of absence of bonding interactions between atom pairs.

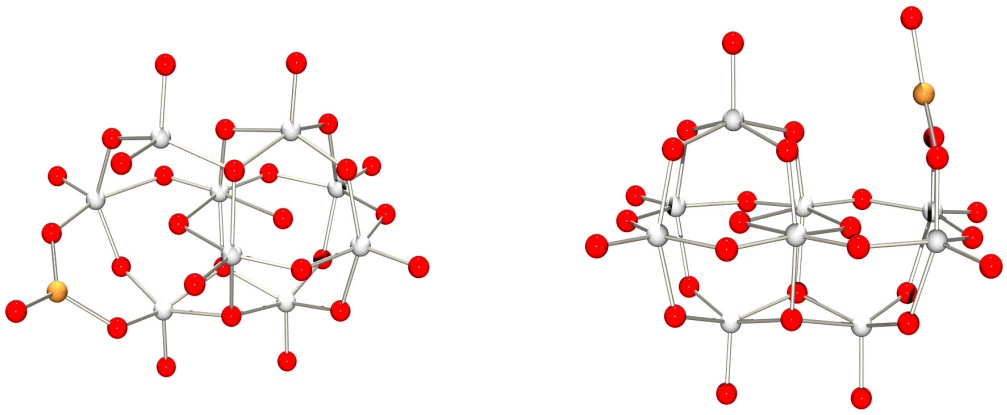

Figure S9: Isomer 'B' (left) and 'C' (right) of $[M^zNb_9O_{28}]^{(11-z)-}$, where M^z=Cu^{2+} (Mult.=2) (gold). Niobium and oxygen atoms are shown in grey and red, respectively. Bonds were added by "Ortep-3 for Windows" and do not reflect a statement on the presence of absence of bonding interactions between atom pairs.

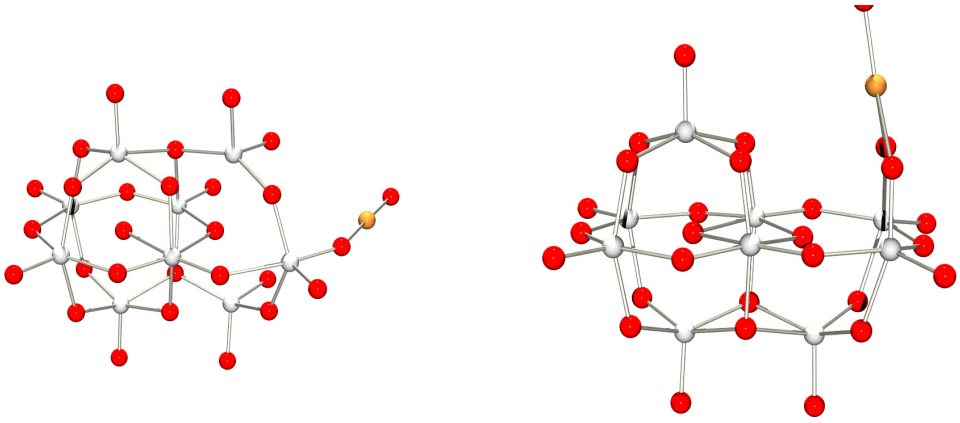

Figure S10: Isomer 'B' (left) and 'C' (right) of $[M^zNb_9O_{28}]^{(11-z)-}$, where M^z=Hg^{2+} (Mult.=1) (gold). Niobium and oxygen atoms are shown in grey and red, respectively. Bonds were added by "Ortep-3 for Windows" and do not reflect a statement on the presence of absence of bonding interactions between atom pairs.

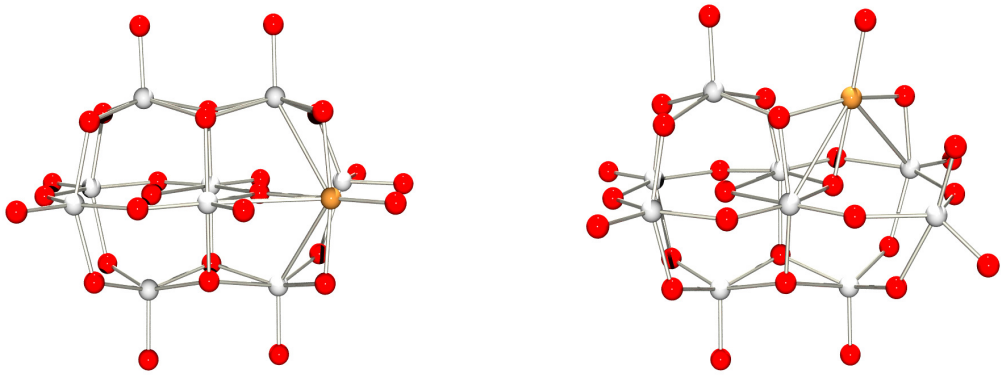

Figure S11: Isomer 'B' (left) and 'C' (right) of $[M^zNb_9O_{28}]^{(11-z)-}$, where M^z=Pd^{2+} (Mult.=1) (gold). Niobium and oxygen atoms are shown in grey and red, respectively. Bonds were added by "Ortep-3 for Windows" and do not reflect a statement on the presence of absence of bonding interactions between atom pairs.

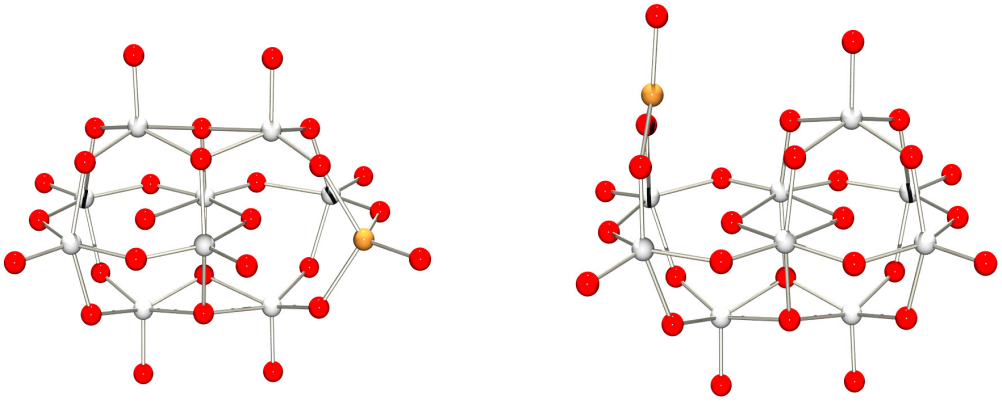

Figure S12: Isomer 'B' (left) and 'C' (right) of $[M^zNb_9O_{28}]^{(11-z)-}$, where M^z=Zn^{2+} (Mult.=1) (gold). Niobium and oxygen atoms are shown in grey and red, respectively. Bonds were added by "Ortep-3 for Windows" and do not reflect a statement on the presence of absence of bonding interactions between atom pairs.

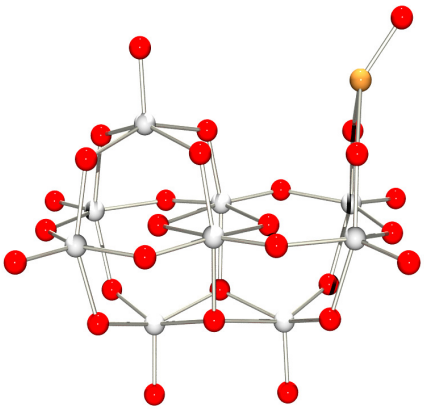

Figure S13: Isomer 'C' of $[M^zNb_9O_{28}]^{(11-z)-}$, where M^z=Ru^{2+} (Mult.=1) (gold). Niobium and oxygen atoms are shown in grey and red, respectively. Bonds were added by "Ortep-3 for Windows" and do not reflect a statement on the presence of absence of bonding interactions between atom pairs.