Electronic Supplementary Information

The role of electronegativity on the extent of nitridation of group 5 metals as revealed by reactions of tantalum cluster cations with ammonia molecules

Masashi Arakawa,*[a] Kota Ando,[a] Shuhei Fujimoto,[a] Saurabh Mishra,[b] G. Naresh Patwari [b] and Akira Terasaki *[a]

[a] *Department of Chemistry, Faculty of Science, Kyushu University, 744 Motooka, Nishi−ku, Fukuoka 819−0395, Japan.*

[b] *Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai 400076, India.*

Table S1. Cartesian coordinates and natural charge distribution of the optimized structures shown in Fig. 4 calculated with TPSSh/def2-TZVP using Stuttgart/Dresden relativistic effective potential (ECP) for tantalum atoms.

Species	Symmetry	Total energy /Hartree	Atom	*x* /Å	*y* /Å	*z* /Å	Natural charge /*e*
$^{3}TaNH^{+}$	$C_{\infty v}$	−112.025719	Ta	0.000000	0.000000	0.182448	+1.445
			N	0.000000	0.000000	−1.537573	−0.867
			H	0.000000	0.000000	−2.555705	+0.421
$^{1}TaN_2H_2^{+}$	C_{2v}	−167.447170	Ta	0.000000	0.205515	0.000000	+1.974
			N	1.428205	−0.825573	0.000000	−0.891
			N	−1.428205	–0.825573	0.000000	−0.891
			H	1.909502	−1.722304	0.000000	+0.404
			H	−1.909495	−1.722307	0.000000	+0.404
$^{1}TaN_2^{+}$	C_{2v}	−166.135246	Ta	0.000000	0.000000	0.264284	+1.708
			N	0.000000	0.722422	−1.378052	−0.354
			N	0.000000	−0.722422	−1.378052	−0.354
$^{4}Ta_2^{+}$	$D_{\infty h}$	−113.549129	Ta	0.000000	0.000000	1.110866	+0.500
			Ta	0.000000	0.000000	−1.110866	+0.500
$^{2}Ta_2NH^{+}$	C_{2v}	−169.034315	Ta	0.000000	1.128951	−0.089413	+0.840
			Ta	0.000000	−1.128951	−0.089413	+0.840
			N	0.000000	0.000000	1.504652	−1.083
			H	0.000000	0.000000	2.521668	+0.402
$^{2}Ta_2N_2H_2^{+}$	C_{2v}	−224.499393	Ta	1.219799	0.000000	−0.061237	+1.147
			Ta	−1.219799	0.000000	−0.061237	+1.147
			N	0.000000	1.411766	0.514267	−1.047
			N	0.000000	−1.411766	0.514267	−1.047
			H	0.000000	−2.366216	0.870420	+0.400
			H	0.000000	2.366216	0.870420	+0.400
$^{4}Ta_2N_2^{+}$	D_{2h}	−223.306433	Ta	0.000000	0.000000	1.368087	+1.396
			Ta	0.000000	0.000000	−1.368087	+1.396
			N	0.000000	1.272131	0.000000	−0.896

			N	0.000000	−1.272131	0.000000	−0.896
$^{2}Ta_2N_3H^+$	C_s	−278.749802	Ta	−0.839171	−1.209365	0.000000	+1.449
			Ta	0.859938	0.965219	0.000000	+1.809
			N	−0.034478	−0.195351	1.283151	−0.905
			N	−0.034478	−0.195351	−1.283151	−0.905
			N	−0.034478	2.485471	0.000000	−0.846
			H	−0.791974	3.159211	0.000000	+0.397
$^{2}Ta_2N_4H_2^+$	C_{2v}	−334.126483	Ta	0.000000	1.406805	−0.159101	+1.746
			Ta	0.000000	−1.406805	0.159101	+1.746
			N	−1.283187	0.000000	−0.271977	−0.853
			N	1.283187	0.000000	−0.271977	−0.853
			N	0.000000	−1.923307	1.563348	−0.784
			N	0.000000	1.923307	1.563348	−0.784
			H	0.000000	−1.839036	2.574756	+0.391
			H	0.000000	1.839036	2.574756	+0.391
$^{2}Ta_2N_4^+$	C_s	−332.818207	Ta	1.259094	−0.091452	0.017643	+1.632
			Ta	−1.259094	−0.091452	0.017642	+1.632
			N	0.000002	1.847356	0.081255	−0.280
			N	0.000001	−1.225743	−0.862552	−0.827
			N	0.000004	1.230056	−1.019129	−0.419
			N	−0.000005	0.055753	1.432460	−0.737
$^{3}Ta_3^+$	D_{3h}	−170.574764	Ta	0.000000	1.410137	0.000000	+0.334
			Ta	−1.221214	−0.705068	0.000000	+0.333
			Ta	1.221214	−0.705068	0.000000	+0.333
$^{3}Ta_3NH^+$	C_{2v}	−226.056553	Ta	0.000000	1.436078	−0.567469	+0.746
			Ta	0.000000	0.000000	1.354289	+0.205
			Ta	0.000000	−1.436078	−0.567469	+0.746
			N	0.000000	0.000000	−1.873941	−1.101
			H	0.000000	0.000000	−2.895085	+0.404
$^{1}Ta_3N_2H_2^+$	C_s	−281.507448	Ta	−0.936091	1.042542	0.000000	+1.046

			Ta	0.414644	−0.669395	1.268022	+0.657
			Ta	0.414644	−0.669395	−1.268022	+0.657
			N	0.414644	1.259834	−1.456456	−1.070
			N	0.414644	1.259834	1.456456	−1.070
			H	0.995833	1.994203	1.855881	+0.390
			H	0.995833	1.994203	−1.855881	+0.390
$^1Ta_3N_2^+$	C_1	−280.317386	Ta	−1.289395	−0.792519	−0.074956	+1.297
			Ta	1.495937	−0.495086	0.029010	+0.948
			Ta	−0.105682	1.406163	−0.073091	+0.558
			N	−1.337936	0.633936	1.167568	−0.876
			N	0.286115	−1.870330	0.073814	−0.927
$^1Ta_3N_3H^+$	C_1	−335.779856	Ta	−0.715069	1.275523	0.027251	+0.947
			Ta	−0.752330	−1.221048	0.095574	+1.530
			Ta	1.573311	0.088484	−0.069036	+1.172
			N	−1.956732	0.077156	−0.876960	−1.136
			N	0.866594	−1.431832	−0.873517	−0.867
			N	0.375601	−0.161009	1.408501	−1.039
			H	−2.729839	0.173777	−1.532769	+0.392
$^1Ta_3N_4H_2^+$	C_s	−391.254162	Ta	0.661134	1.240944	0.000000	+1.481
			Ta	−0.280070	−0.675747	1.359510	+1.559
			Ta	−0.280070	−0.675747	−1.359510	+1.559
			N	1.179214	−0.829285	0.000000	−1.085
			N	−1.481063	−1.195668	0.000000	−0.915
			N	−0.280070	1.304954	−1.765111	−1.183
			N	−0.280070	1.304954	1.765111	−1.183
			H	−0.669329	1.987716	2.412500	+0.384
			H	−0.669329	1.987716	−2.412500	+0.384
$^1Ta_3N_4^+$	C_s	−390.028676	Ta	0.341857	−0.766088	1.263129	+1.584
			Ta	−0.753210	1.529673	0.000000	+1.715
			Ta	0.341857	−0.766088	−1.263129	+1.584
			N	−1.203253	−0.458640	0.000000	−1.033
			N	0.341857	1.189469	−1.440361	−0.942

			N	1.244281	−1.894192	0.000000	−0.965
			N	0.341857	1.189469	1.440361	−0.942
$^1Ta_3N_5H^+$	C_s	−445.480315	Ta	0.394859	−0.850338	1.419231	+1.739
			Ta	−0.671719	1.433701	0.000000	+1.904
			Ta	0.394859	−0.850338	−1.419231	+1.739
			N	−0.960097	−0.669528	0.000000	−1.023
			N	0.394859	0.953983	−1.638564	−0.927
			N	1.595359	−1.208945	0.000000	−0.919
			N	0.394859	0.953983	1.638564	−0.927
			N	−2.213393	2.348215	0.000000	−0.977
			H	−3.094958	2.845136	0.000000	+0.391
$^1Ta_3N_6H_2^+$	C_1	−500.831095	Ta	1.571098	0.214116	−0.063606	+1.850
			Ta	−1.184791	1.129503	0.206409	+1.754
			Ta	−0.639736	−1.651277	−0.013042	+1.738
			N	−0.048126	−0.205078	1.189524	−1.068
			N	−1.862148	−0.360354	−0.709414	−0.920
			N	0.877723	−1.447033	−0.977552	−0.894
			N	0.467169	1.763141	−0.695498	−0.611
			N	3.192170	0.216157	0.696176	−0.966
			N	−0.473081	2.782392	−0.770410	−0.650
			H	4.100168	0.195299	1.142729	+0.391
			H	−0.675871	3.019166	−1.745014	+0.376
$^1Ta_3N_6^+$	C_1	−499.543643	Ta	1.597116	0.226288	0.073496	+1.528
			Ta	−0.821295	−1.423571	−0.203984	+1.664
			Ta	−1.058186	1.410431	0.015315	+1.734
			N	−0.165204	0.156989	−1.173182	−1.025
			N	−1.687970	−0.252859	0.887715	−0.878
			N	0.472358	1.809281	0.835466	−0.870
			N	1.091919	−1.733297	0.730760	−0.359
			N	2.822132	0.475519	−1.102330	−0.606
			N	0.411434	−2.678464	1.022662	−0.188

Table S2. Change in relative energy of the reactants and possible products upon reaction of Ta_n^+ with NH_3 molecules. The change in relative energy exhibits the same trend in both calculations employing TPSSh and B3LYP functional.

Species	Formal oxidation number of Ta atoms	Change in relative energy / eV	
		TPSSh Stuttgart/Dresden ECP	B3LYP Stuttgart/Dresden ECP
$n = 1$			
$Ta^+ + 2NH_3$	+1	0.00	0.00
$TaNH^+ + H_2 + NH_3$	+3	−2.33	−2.24
$TaN_2H_2^+ + 2H_2$	+5	−1.19	−1.01
$TaN_2^+ + 3H_2$	+7	+3.89	+4.06
$n = 2$			
$Ta_2^+ + 4NH_3$	+0.5	0.00	0.00
$Ta_2NH^+ + H_2 + 3NH_3$	+1.5	−2.92	−2.62
$Ta_2N_2H_2^+ + 2H_2 + 2NH_3$	+2.5	−2.38	−2.15
$Ta_2N_2^+ + 3H_2 + 2NH_3$	+3.5	+0.65	+0.74
$Ta_2N_3H^+ + 4H_2 + NH_3$	+4.5	−1.78	−1.65
$Ta_2N_4H_3^+ + 4H_2 + H$	+5	+0.26	−1.35
$Ta_2N_4H_2^+ + 5H_2$	+5.5	−0.23	+0.21
$Ta_2N_4^+ + 6H_2$	+6.5	+3.79	+4.37
$n = 3$			
$Ta_3^+ + 6NH_3$	+0.3	0.00	0.00
$Ta_3NH^+ + H_2 + 5NH_3$	+1	−2.83	−2.64
$Ta_3N_2H_2^+ + 2H_2 + 4NH_3$	+1.7	−1.99	−1.70
$Ta_3N_2^+ + 3H_2 + 4NH_3$	+2.3	+0.58	+0.63
$Ta_3N_3H^+ + 4H_2 + 3NH_3$	+3	−2.30	−1.99
$Ta_3N_4H_2^+ + 5H_2 + 2NH_3$	+3.7	−2.63	−2.37
$Ta_3N_4^+ + 6H_2 + 2NH_3$	+4.3	+1.54	+1.49
$Ta_3N_5H^+ + 7H_2 + NH_3$	+5	−2.01	−2.00
$Ta_3N_6H_2^+ + 8H_2$	+5.7	+0.74	+0.87
$Ta_3N_6^+ + 9H_2$	+6.3	+1.83	+6.06

Table S3. Cartesian coordinates and natural charge distribution of the optimized structures shown in Fig. 5 calculated with TPSSh/def2-TZVP using Stuttgart/Dresden ECP for vanadium atoms.

Species	Symmetry	Total energy /Hartree	Atom	*x* /Å	*y* /Å	*z* /Å	Natural charge /*e*
$^4V_2^+$	$D_{\infty h}$	−141.377560	V	0.000000	0.000000	0.836972	+0.500
			V	0.000000	0.000000	−0.836972	+0.500
$^2V_2NH^+$	C_{2v}	−196.786484	V	0.000000	0.872701	–0.254879	+0.725
			V	0.000000	–0.872701	–0.254879	+0.725
			N	0.000000	0.000000	1.338195	−0.842
			H	0.000000	0.000000	2.357049	+0.392
$^6V_2N_2H_2^+$	C_{2v}	−252.250293	V	1.355463	0.000000	–0.035231	+1.107
			V	–1.355463	0.000000	–0.035231	+1.107
			N	0.000000	1.262242	0.114163	−0.981
			N	0.000000	–1.262242	0.114163	−0.981
			H	0.000000	–2.279627	0.011164	+0.374
			H	0.000000	2.279627	0.011164	+0.374
$^4V_2N_2^+$	D_{2h}	−251.041795	V	0.000000	0.000000	1.256102	+1.052
			V	0.000000	0.000000	–1.256102	+1.052
			N	0.000000	1.183998	0.000000	−0.552
			N	0.000000	–1.183998	0.000000	−0.552
$^4V_2N_3H^+$	C_1	−306.406515	V	1.365261	0.247314	0.004780	+0.967
			V	–1.023126	–0.664089	0.014412	+1.091
			N	0.712812	–1.271982	–0.025374	−0.598
			N	–0.139176	1.138533	0.012242	−0.333
			N	–1.428876	1.217645	–0.104039	−0.528
			H	–1.882424	1.996459	0.378788	+0.400
$^2V_2N_4H_2^+$	C_1	−361.746380	V	1.308675	–0.565905	0.160696	+1.109
			V	–1.141375	–0.005115	–0.429864	+0.825
			N	0.357517	1.069919	–0.425192	−0.248
			N	–0.188796	–1.417158	–0.015279	−0.500
			N	–2.024359	0.349962	0.884392	−0.492
			N	1.417436	1.460047	0.132449	−0.491

			H	–2.341047	0.434472	1.851661	+0.386
			H	1.560549	2.459600	0.304606	+0.410
$^{1}V_3^{+}$	D_{3h}	−212.188944	V	0.000000	1.04716	0.000000	+0.333
			V	–0.906867	–0.52358	0.000000	+0.334
			V	0.906867	–0.52358	0.000000	+0.334
$^{3}V_3NH^{+}$	C_{2v}	−267.683752	V	0.000000	1.376211	–0.520755	+0.713
			V	0.000000	0.000000	1.687418	+0.273
			V	0.000000	−1.376211	–0.520755	+0.713
			N	0.000000	0.000000	–1.729169	−1.067
			H	0.000000	0.000000	–2.751686	+0.368
$^{1}V_3N_2H_2^{+}$	C_s	−323.041065	V	–0.84920	0.779703	0.000000	+0.701
			V	0.295308	–0.769235	1.062416	+0.531
			V	0.295308	–0.769235	–1.062416	+0.531
			N	0.295308	1.004865	–1.388389	−0.769
			N	0.295308	1.004865	1.388389	−0.769
			H	0.906675	1.691771	1.826561	+0.388
			H	0.906675	1.691771	–1.826561	+0.388
$^{5}V_3N_2^{+}$	C_1	−321.869345	V	0.423036	1.363954	–0.115475	+0.946
			V	–1.592672	–0.622484	0.087316	+0.801
			V	1.114097	−1.111850	–0.181644	+0.637
			N	1.463105	0.173177	0.789131	−0.671
			N	–1.280620	1.043787	–0.099780	−0.712
$^{3}V_3N_3H^{+}$	C_1	−377.326275	V	1.409528	–0.930120	–0.034656	+1.006
			V	–0.032351	1.275064	0.311951	+0.937
			V	–1.481764	–0.784819	–0.157985	+0.945
			N	1.591178	0.813387	–0.535055	−0.966
			N	–1.299288	0.958209	–0.693153	−0.524
			N	–0.272479	–0.516698	0.992325	−0.775
			H	2.269624	1.332833	–1.092931	+0.376
$^{1}V_3N_4H_2^{+}$	C_s	−432.752916	V	0.662345	1.027837	0.000000	+0.920

			V	–0.207486	–0.661542	1.237011	+0.901
			V	–0.207486	–0.661542	–1.237011	+0.901
			N	1.134819	–0.834447	0.000000	−0.576
			N	–1.346702	–1.033262	0.000000	−0.387
			N	–0.207486	1.155083	–1.587613	−0.771
			N	–0.207486	1.155083	1.587613	−0.771
			H	–0.650803	1.846731	2.191310	+0.391
			H	–0.650803	1.846731	–2.191310	+0.391
$^{3}V_3N_4^+$	C_s	−431.537315	V	0.275182	–0.702210	1.292875	+0.900
			V	–0.832198	1.244006	0.000000	+0.901
			V	0.275182	–0.702210	–1.292875	+0.900
			N	–1.030245	–0.586272	0.000000	−0.535
			N	0.275182	1.033556	–1.320523	−0.389
			N	1.405909	–0.953765	0.000000	−0.388
			N	0.275182	1.033556	1.320523	−0.389
$^{1}V_3N_5H^+$	C_1	−486.894737	V	1.497568	–0.727400	–0.154846	+0.948
			V	0.286334	1.487554	0.231391	+0.922
			V	–1.055333	–0.921900	0.369353	+0.860
			N	0.479740	–0.108024	1.181549	−0.600
			N	–1.469468	1.055258	–0.349482	−0.269
			N	–0.055139	–1.655677	–0.681105	−0.427
			N	1.485222	0.908517	–0.846089	−0.493
			N	–2.377605	0.249230	–0.607545	−0.337
			H	–3.196351	0.575017	–1.136962	+0.396
$^{3}V_3N_6H_2^+$	C_1	−542.254336	V	−1.042144	–0.798859	–0.057799	+0.650
			V	1.499514	–0.009823	0.464353	+0.859
			V	−0.415493	1.692163	–0.075774	+0.865
			N	−0.287406	0.436509	1.144506	−0.503
			N	1.277382	1.357785	–0.513274	−0.389
			N	–1.244708	0.661923	–1.103381	−0.294
			N	0.756447	–1.517561	–0.539501	−0.214
			N	–2.458497	–1.440694	0.411251	−0.436
			N	1.969994	–1.782838	–0.455446	−0.327

			H	–3.392606	–1.710963	0.719828	+0.390
			H	2.336947	–2.614979	–0.936845	+0.397
$^1V_3N_6^+$	C_1	−541.044845	V	0.645203	1.209871	–0.135811	+0.653
			V	–1.366851	–0.547473	0.479265	+0.807
			V	1.079806	–1.367486	–0.040147	+0.893
			N	0.372798	–0.26585	1.113443	−0.499
			N	–0.742289	–1.559218	–0.609120	−0.349
			N	1.678979	–0.238950	–0.995307	−0.304
			N	–1.395128	1.300749	–0.580875	−0.124
			N	1.351285	2.242766	0.727544	−0.100
			N	–2.442447	0.837217	–0.652264	−0.023

Table S4. Change in relative energy of the reactants and possible products upon reaction of V_n^+ with NH_3 molecules. The change in relative energy obtained by either of the methods exhibits the same trend for n = 2 and 3; the result depends neither on functional nor on the use of ECP. For n = 1, the result is dependent on the method; the use of ECP resulted in far off from a previous experiment, where the total energy of $VNH^+ + H_2$ is reported to be about 0.1 eV lower than that of $V^+ + NH_3$.[a]

Species	Formal oxidation number of V atoms	Change in relative energy / eV			
		TPSSh Stuttgart/Dresden ECP	TPSSh All electrons	B3LYP Stuttgart/Dresden ECP	B3LYP All electrons
n = 1					
$V^+ + 4NH_3$	+1	0.00	0.00	0.00	0.00
$VNH^+ + H_2 + 3NH_3$	+3	+0.76	+0.01	+0.96	+0.25
$VN_2H_2^+ + 2H_2 + 2NH_3$	+5	+0.04	+0.30	+0.34	−0.01
$VN_2^+ + 3H_2 + 2NH_3$	+7	+1.61	+1.42	+1.47	+1.91
n = 2					
$V_2^+ + 4NH_3$	+0.5	0.00	0.00	0.00	0.00
$V_2NH^+ + H_2 + 3NH_3$	+1.5	−0.85	−1.15	−1.33	−0.75
$V_2N_2H_2^+ + 2H_2 + 2NH_3$	+2.5	−2.34	−2.32	−2.47	−2.59
$V_2N_2^+ + 3H_2 + 2NH_3$	+3.5	+1.08	+0.89	+1.37	+1.25
$V_2N_3H^+ + 4H_2 + NH_3$	+4.5	+0.71	+0.64	+0.76	+0.70
$V_2N_4H_2^+ + 5H_2$	+5.5	+0.68	+0.29	+0.81	+0.47
n = 3					
$V_3^+ + 6NH_3$	+0.3	0.00	0.00	0.00	0.00
$V_3NH^+ + H_2 + 5NH_3$	+1	−3.18	−2.57	−3.80	−2.72
$V_3N_2H_2^+ + 2H_2 + 4NH_3$	+1.7	+0.56	−1.21	−0.12	−1.54
$V_3N_2^+ + 3H_2 + 4NH_3$	+2.3	+0.08	+1.15	+0.83	+0.77
$V_3N_3H^+ + 4H_2 + 3NH_3$	+3	−2.15	−2.31	−1.73	−2.06
$V_3N_4H_2^+ + 5H_2 + 2NH_3$	+3.7	−1.33	−2.17	−0.82	−1.59
$V_3N_4^+ + 6H_2 + 2NH_3$	+4.3	+1.27	+1.60	+1.94	+1.83
$V_3N_5H^+ + 7H_2 + NH_3$	+5	+0.55	+0.23	+0.31	+0.21
$V_3N_6H_2^+ + 8H_2$	+5.7	+0.50	+0.26	+0.70	+0.43
$VN_6^+ + 9H_2$	+6.3	+1.10	+1.50	+0.27	−1.39

[a] D. E. Clemmer, L. S. Sunderlin and P. B. Armentrout, *J. Phys. Chem.*, 1990, **94**, 208–217.

Table S5. Bond dissociation energies obtained by DFT calculations along with experimental reports.

Species	Bond dissociation energy / eV				
	TPSSh Stuttgart/Dresden ECP	TPSSh All electrons	B3LYP Stuttgart/Dresden ECP	B3LYP All electrons	Experiment
Ta^+−Ta	4.50		4.19		6.87[a]
Ta_2^+−Ta	5.55		4.74		6.60[a]
Ta_3^+−Ta	6.56		5.64		7.60[a]
V^+−V	2.26	2.88	2.12	1.95	3.14[b]
V_2^+−V	1.67	2.35	0.53	0.37	2.27[b]

[a] P. B. Armentrout, D. A. Hales and D. Lian, in *Advances in Metal and Semiconductor Clusters*, ed. M. A. Duncan, JAI Press, Greenwich, 1994, vol. 2, pp. 1–39.

[b] C.-X. Su, D. A. Hales and P. B. Armentrout, *J. Chem. Phys.*, 1993, **99**, 6613–6623.