

Supplementary Materials: Electronic Structure of Cubane-Like Vanadium–Nitrogen Cationic Clusters $[V_4N_4]^+$ and $[V_6N_6]^+$

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Table S1. Optimised coordinates and total energies for all states described in the text.

Optimised structure of the 4A_2 state of $[V_4N_4]^+$

TPSS -3994.34035583 au

V	-1.323010	0.000000	0.934375
V	1.323010	0.000000	0.934375
V	-0.000000	-1.323010	-0.934375
V	0.000000	1.323010	-0.934375
N	0.000000	1.305614	0.922249
N	-0.000000	-1.305614	0.922249
N	-1.305614	0.000000	-0.922249
N	1.305614	-0.000000	-0.922249

M06L -3994.91744085 au

V	0.000000	1.311335	0.927295
V	-0.000000	-1.311335	0.927295
V	-1.311335	0.000000	-0.927295
V	1.311335	-0.000000	-0.927295
N	1.312967	-0.000000	0.928184
N	-1.312967	-0.000000	0.928184
N	0.000000	1.312967	-0.928184
N	-0.000000	-1.312967	-0.928184

BP86 -3995.67644709 au

V	-1.326111	0.000000	0.937489
V	1.326111	0.000000	0.937489
V	-0.000000	-1.326111	-0.937489
V	0.000000	1.326111	-0.937489
N	0.000000	1.300550	0.919325
N	-0.000000	-1.300550	0.919325
N	-1.300550	0.000000	-0.919325
N	1.300550	-0.000000	-0.919325

BP86-D3 -3995.71325946 au

V	-1.325886	0.000000	0.937326
V	1.325886	0.000000	0.937326
V	-0.000000	-1.325886	-0.937326
V	0.000000	1.325886	-0.937326

N	0.000000	1.300063	0.918980
N	-0.000000	-1.300063	0.918980
N	-1.300063	0.000000	-0.918980
N	1.300063	-0.000000	-0.918980

BLYP -3995.23470675 au

V	-1.339212	0.000000	0.946522
V	1.339212	0.000000	0.946522
V	-0.000000	-1.339212	-0.946522
V	0.000000	1.339212	-0.946522
N	0.000000	1.309586	0.925720
N	-0.000000	-1.309586	0.925720
N	-1.309586	0.000000	-0.925720
N	1.309586	-0.000000	-0.925720

B3LYP -3995.04553835 au

V	0.000000	1.307253	0.930207
V	-0.000000	-1.307253	0.930207
V	-1.307253	0.000000	-0.930207
V	1.307253	-0.000000	-0.930207
N	1.300875	-0.000000	0.982598
N	-1.300875	-0.000000	0.982598
N	0.000000	1.300875	-0.982598
N	-0.000000	-1.300875	-0.982598

Optimised structure of the 6A_1 state of $[V_6N_6]^+$ **TPSS -3995.34738092 au**

V	0.000000	1.300507	0.915977
V	-0.000000	-1.300507	0.915977
V	-1.300507	0.000000	-0.915977
V	1.300507	-0.000000	-0.915977
N	1.317037	-0.000000	1.017561
N	-1.317037	-0.000000	1.017561
N	0.000000	1.317037	-1.017561
N	-0.000000	-1.317037	-1.017561

M06L -3994.93137303 au

V	0.000000	1.285900	0.902947
V	-0.000000	-1.285900	0.902947
V	-1.285900	0.000000	-0.902947
V	1.285900	-0.000000	-0.902947
N	1.325880	-0.000000	1.033271
N	-1.325880	-0.000000	1.033271
N	0.000000	1.325880	-1.033271
N	-0.000000	-1.325880	-1.033271

BP86 -3995.67331366 au

V	0.000000	1.302413	0.921931
V	-0.000000	-1.302413	0.921931
V	-1.302413	0.000000	-0.921931
V	1.302413	-0.000000	-0.921931
N	1.307545	-0.000000	1.020417
N	-1.307545	-0.000000	1.020417
N	0.000000	1.307545	-1.020417
N	-0.000000	-1.307545	-1.020417

BP86-D3 -3995.71002009 au

V	0.000000	1.302413	0.921931
V	-0.000000	-1.302413	0.921931
V	-1.302413	0.000000	-0.921931
V	1.302413	-0.000000	-0.921931
N	1.307545	-0.000000	1.020417
N	-1.307545	-0.000000	1.020417
N	0.000000	1.307545	-1.020417
N	-0.000000	-1.307545	-1.020417

BLYP -3995.23280971 au

V	0.000000	1.316062	0.932493
V	-0.000000	-1.316062	0.932493
V	-1.316062	0.000000	-0.932493
V	1.316062	-0.000000	-0.932493
N	1.316460	-0.000000	1.020078
N	-1.316460	-0.000000	1.020078
N	0.000000	1.316460	-1.020078
N	-0.000000	-1.316460	-1.020078

B3LYP -3995.06962861 au

V	0.000000	1.307438	0.928485
V	-0.000000	-1.307438	0.928485
V	-1.307438	0.000000	-0.928485
V	1.307438	-0.000000	-0.928485
N	1.300492	-0.000000	0.996429
N	-1.300492	-0.000000	0.996429
N	0.000000	1.300492	-0.996429
N	-0.000000	-1.300492	-0.996429

Optimised structures of the $^4B_{3g}$ state of $[V_6N_6]^+$ **TPSS -5993.28600692 au**

V	-1.852096	1.300431	-0.000000
V	-1.851996	-1.300408	0.000000

V	-0.000000	0.000002	-1.116639
V	-0.000000	0.000002	1.116636
V	1.851999	1.300408	-0.000000
V	1.852097	-1.300431	-0.000000
N	-1.992202	0.000034	-1.287319
N	-1.992202	0.000034	1.287320
N	-0.000052	1.709444	-0.000003
N	0.000054	-1.709441	-0.000003
N	1.992204	-0.000038	-1.287319
N	1.992203	-0.000038	1.287320

M06L -5992.67938487 au

V	-1.842155	1.290514	0.000001
V	-1.841762	-1.290787	0.000001
V	-0.000013	0.000003	-1.114774
V	-0.000013	0.000003	1.114772
V	1.841783	1.290883	0.000001
V	1.842170	-1.290610	0.000001
N	-1.991282	-0.000104	-1.289480
N	-1.991282	-0.000104	1.289482
N	-0.000210	1.716075	-0.000003
N	0.000249	-1.716070	-0.000003
N	1.991246	0.000095	-1.289452
N	1.991246	0.000095	1.289454

BP86 -5993.78210611 au

V	-1.851960	1.308606	0.000001
V	-1.851819	-1.308700	0.000001
V	-0.000002	0.000000	-1.121903
V	-0.000002	0.000000	1.121902
V	1.851821	1.308700	0.000001
V	1.851961	-1.308605	0.000001
N	-1.985638	-0.000041	-1.277851
N	-1.985637	-0.000041	1.277853
N	-0.000072	1.712576	-0.000004
N	0.000076	-1.712576	-0.000004
N	1.985638	0.000039	-1.277851
N	1.985638	0.000039	1.277852

BLYP -5993.09766041 au

V	-1.872218	1.318882	0.000001
V	-1.872232	-1.318872	0.000000
V	-0.000002	-0.000002	-1.132613
V	-0.000002	-0.000002	1.132612
V	1.872233	1.318872	0.000000
V	1.872221	-1.318879	0.000001
N	-2.005628	0.000005	-1.286686
N	-2.005627	0.000005	1.286687

N	0.000008	1.722666	-0.000004
N	-0.000005	-1.722667	-0.000004
N	2.005627	-0.000002	-1.286686
N	2.005626	-0.000002	1.286688

B3LYP -5992.81178415 au

V	-1.866610	1.297415	0.000002
V	-1.866454	-1.297521	0.000002
V	-0.000001	-0.000001	-1.118572
V	-0.000001	-0.000001	1.118569
V	1.866454	1.297522	0.000002
V	1.866612	-1.297415	0.000002
N	-2.005344	-0.000041	-1.274673
N	-2.005342	-0.000041	1.274668
N	-0.000087	1.695771	-0.000003
N	0.000090	-1.695773	-0.000003
N	2.005345	0.000043	-1.274672
N	2.005343	0.000043	1.274668