Supporting Information

Experimental Observation of TiN_{12}^+ Cluster and Theoretical Investigation of Its Stable and Metastable Isomers

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Table S1 NBO data for TiN_2 (LP: lone pair; BD: bonding; BD*: antibonding; E_2: stabilization energy)

NPA (Natural Population Analysis)				
Atom	Natural Electron Configuration		Natural Charge	
Ti	$3d^{2.50}4s^{0.93}4p^{0.08}$		0.499	
N1	$2s^{1.54}2p^{3.87}3s^{0.02}3p^{0.02}$		-0.452	
N2	$2s^{1.62}2p^{3.39}3s^{0.01}3p^{0.01}3d^{0.01}$		-0.048	
Main BO (Bond Orbital) analysis				
Bond Orbital	Occupancy(e)	Hybridization		Spin
BD(1)N1-N2	0.99975	N1: p 99.90%; N2: p 99.53%		Up
BD(2)N1-N2	0.99975	N1: p 99.90%; N2: p 99.53%		
BD(3)N1-N2	0.99983	N1: s 40.63%, p 59.31%; N2: s 34.65%, p 64.98%		
LP(1)Ti	0.99997	d 100%		
LP(2)Ti	0.99916	s 89.12%, p 5.96%, d 4.92%		
LP(3)Ti	0.67637	d 99.51%		
LP(4)Ti	0.67637	d 99.51%		
LP*(5)Ti	0.07212	s 9.81%, p 13.64%, d 76.34%		
LP(1)N1	0.93292	s 60.25%, p 39.75%		
LP(1)N2	0.99108	s 66.16%, p 33.78%		
BD*(1)N1-N2	0.31628	N1: p 99.90%; N2: p 99.53%		
BD*(2)N1-N2	0.31628	N1: p 99.90%; N2: p 99.53%		
BD(1)N1-N2	0.99896	N1: s 40.92%, p 59.03%; N2: s 35.86%, p 63.72%		Down
BD(2)N1-N2	0.99575	N1: p 99.91%; N2: p 99.33%		
BD(3)N1-N2	0.99575	N1: p 99.91%; N2: p 99.33%		
LP*(1)Ti	0.07632	s 44.00%, p 5.94%, d 49.88%		
LP(1)N1	0.92921	s 60.02%, p 39.98%		
LP(1)N2	0.98899	s 64.88%, p 35.09%		
Main second order Perturbation analysis				
Donor	Acceptor	Transferred charge	E_2(kcal/mol)	Spin
LP(3)Ti	BD*(1)N1-N2	0.32	41.94	Up
LP(4)Ti	BD*(2)N1-N2	0.32	41.94	
LP(1)N1	LP*(5)Ti	0.072	28.55	
LP(1)N1	LP*(1)Ti	0.072	31.01	Down

Table S2 NBO data for TiN_2^+ (LP: lone pair; BD: bonding; BD*: antibonding; E_2: stabilization energy)

NPA(Natural Population Analysis)				
Atom	Natural Electron Configuration		Natural Charge	
Ti	$3d^{2.25}4s^{0.72}4p^{0.01}$		1.026	
N1	$2s^{1.55}2p^{3.65}3s^{0.03}3p^{0.01}$		-0.242	
N2	$2s^{1.62}2p^{3.13}3s^{0.01}3d^{0.02}$		0.216	
Main BO(Bond Orbital) analysis				
Bond Orbital	Occupancy(e)	Hybridization		Spin
BD(1)N1-N2	0.99998	N1: p 99.88%; N2: p 99.30%		up
BD(2)N1-N2	0.99998	N1: p 99.88%; N2: p 99.30%		
BD(3)N1-N2	0.99961	N1: s 42.51%, p 57.43%; N2: s 35.96%, p 63.61%		
LP(1)Ti	0.99961	s 68.06%, p 31.77%		
LP(2)Ti	0.94512	d 100%		
LP(3)Ti	0.94512	d 100%		
LP*(4)Ti	0.04510	s 30.75%, p 6.93%, d 62.14%		
LP(1)N1	0.95614	s 58.69%, p 41.31%		
LP(1)N2	0.99254	s 64.92%, p 35.02%		
BD*(1)N1-N2	0.05350	N1: p 99.88%; N2: p 99.30%		
BD*(2)N1-N2	0.05350	N1: p 99.88%; N2: p 99.30%		
BD(1)N1-N2	0.99971	N1: s 42.34%, p 57.61%; N2: s 36.28%, p 63.27%		down
BD(2)N1-N2	0.99914	N1: p 99.89%; N2: p 99.25%		
BD(3)N1-N2	0.99914	N1: p 99.89%; N2: p 99.25%		
LP*(1)Ti	0.04020	s 54.78%, p 5.40%, d 39.62%		
LP(1)N1	0.96085	s 58.96%, p 41.04%		
LP(1)N2	0.99247	s 64.59%, p 35.36%		
Main second order Perturbation analysis				
Donor	Acceptor	Transferred charge	E_2(kcal/mol)	Spin
LP(1)N1	LP*(4)Ti	0.045	15.92	up
LP(1)N1	LP*(1)Ti	0.040	14.94	down

Table S3 NBO data for TiN_{12} (LP: lone pair; BD: bonding; BD*: antibonding;E_2: stabilization energy)

NPA(Natural Population Analysis)			
Atom	Natural Electron Configuration	Natural Charge	
Ti	$3d^{2.72}4s^{0.30}4p^{0.58}4d^{0.01}5s^{0.01}5p^{0.01}$	0.383	
N1	$2s^{1.47}2p^{3.59}3s^{0.03}3p^{0.02}$	-0.120	
N2	$2s^{1.61}2p^{3.30}3s^{0.01}3p^{0.01}3d^{0.02}$	0.056	
Main BO(Bond Orbital) analysis			
Bond Orbital	Occupancy(e)	Hybridization	Spin
BD(1)N1-N2	0.99831	N1: p 99.88%; N2: p 99.40%	up
BD(2)N1-N2	0.99827	N1: p 99.76%; N2: p 99.31%	
BD(3)N1-N2	0.99734	N1: s 41.69%, p 58.25%; N2: s 36.48%, p 63.16%	
BD(1)N1-Ti	0.99485	N1(88.69%): s 60.08%, p 39.92%; Ti(11.31%): s 16.66%, p 49.92%, d 33.34%	
LP(1)N2	0.98996	s 64.14%, p 35.81%	
LP(1)Ti	0.60144	d 100%	
LP(2)Ti	0.60134	d 100%	
LP(3)Ti	0.53191	d 99.95%	
BD*(1)N1-N2	0.10160	N1: p 99.88%; N2: p 99.40%	
BD*(2)N1-N2	0.10457	N1: p 99.76%; N2: p 99.31%	
BD(1)N1-N2	0.99728	N1: s 28.95%, p 70.98%; N2: s 25.68%, p 73.87%	down
BD(2)N1-N2	0.99717	N1: s 12.44%, p 87.46%; N2: s 11.19%, p 88.26%	
BD(3)N1-N2	0.99553	N1: p 99.89%; N2: p 99.33%	
BD(1)N1-Ti	0.99524	N1(89.19%): s 60.53%, p 39.47%; Ti(10.81%): s 16.65%, p 49.91%, d 33.35%	
LP(1)N2	0.98985	s 63.82%, p 36.14%	
LP(1)Ti	0.45097	d 99.99%	
BD*(2)N1-N2	0.06306	N1: s 12.44%, p 87.46%; N2: s 11.19%, p 88.26%	
Main second order Perturbation analysis			
Donor	Acceptor	E_2(kcal/mol)	Spin
BD*(2)N1-N2	BD*(1)N1-N2	26.34	down

Table S4 NBO data for TiN_{12}^{+} (LP: lone pair; BD: bonding; BD*: antibonding; E_2：stabilization energy)

NPA(Natural Population Analysis)			
Atom	Natural Electron Configuration	Natural Charge	
Ti	$3d^{2.54}4s^{0.29}4p^{0.53}4d^{0.01}5s^{0.01}5p^{0.01}$	0.639	
N1	$2s^{1.49}2p^{3.57}3s^{0.03}3p^{0.02}$	-0.118	
N2	$2s^{1.61}2p^{3.17}3s^{0.01}3p^{0.01}3d^{0.02}$	0.178	
Main BO(Bond Orbital) analysis			
Bond Orbital	Occupancy(e)	Hybridization	Spin
BD(1)N1-N2	0.99881	N1: p 99.87%; N2: p 99.33%	up
BD(2)N1-N2	0.99881	N1: p 99.87%; N2: p 99.33%	
BD(3)N1-N2	0.99797	N1: s 42.25%, p 57.69%; N2: s 36.23%, p 63.38%	
BD(3)N1-Ti	0.99535	N1(90.28%): s 59.54%, p 40.46%; Ti(9.72%): s 16.67%, p 49.94%, d 33.33%	
LP(1)N2	0.99076	s 64.54%, p 35.41%	
LP(1)Ti	0.71524	d 100%	
LP(2)Ti	0.71516	d 100%	
LP(3)Ti	0.71506	d 100%	
BD*(1)N1-N2	0.06953	N1: p 99.87%; N2: p 99.33%	
BD*(2)N1-N2	0.06953	N1: p 99.87%; N2: p 99.33%	
BD(1)N1-N2	0.99796	N1: s 41.93%, p 58.01%; N2: s 36.61%, p 62.99%	down
BD(2)N1-N2	0.99703	N1: p 99.88%; N2: p 99.28%	
BD(3)N1-N2	0.99703	N1: p 99.88%; N2: p 99.28%	
LP(1)N1	0.90663	s 59.89%, p 40.11%	
LP(1)N2	0.99071	s 64.14%, p 35.81%	
LP(1)*Ti	0.14054	s 100%	
LP(2)*Ti	0.08912	d 100%	
LP(3)*Ti	0.08908	d 100%	
LP(4)*Ti	0.08533	p 99.88%	
LP(5)*Ti	0.08525	p 99.88%	
LP(5)*Ti	0.08523	d 100%	
Second Order Perturbation analysis:			
No obvious stabilization interactions associated with charge transfer			