

σ -Aromatic MAl_6S_6 (M = Ni, Pd, Pt) Stars Containing Planar Hexacoordinate Transition Metals

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Table S1. Cartesian coordinates for global-minimum (GM) clusters **1–3** of the MAl_6S_6 (M = Ni, Pd, Pt) series at the PBE0/def2-TZVP level, along with four lowest-lying ***nB–nE*** isomeric structures.

Table S2. Orbital composition analysis for the canonical molecular orbitals (CMOs) of GM NiAl_6S_6 (**1**, D_{6h} , $^1A_{1g}$) cluster. Main components greater than 15% are shown in bold.

Table S3. Orbital composition analysis for the lowest unoccupied molecular orbitals (LUMOs) of the MAl_6S_6 (M = Ni, Pd, Pt) series.

Figure S1. The AdNDP bonding pattern of PdAl_6S_6 . Occupation numbers (ONs) are shown.

Figure S2. The AdNDP bonding pattern of PtAl_6S_6 . Occupation numbers (ONs) are shown.

Figure S3. Nucleus independent chemical shifts (NICSs) for clusters **1–3**. Here the NICS(0) data (blue color) are calculated at the center of the Al-M-Al (M = Ni, Pd, Pt) triangle, whereas the NICS(1) values (red color) are at 1 Å above the center of the Al-S-Al triangle.

Figure S4. Calculated IR spectrums of PdAl_6S_6 and PtAl_6S_6 at the PBE0/def2-TZVP level.

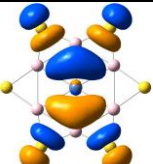
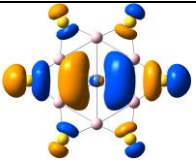
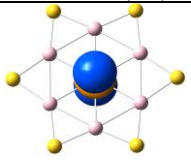

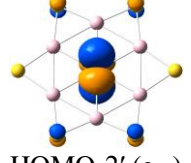
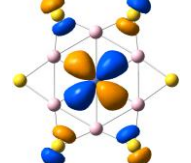
Table S1. Cartesian coordinates for global-minimum (GM) clusters **1–3** of the MAl_6S_6 ($\text{M} = \text{Ni, Pd, Pt}$) series at the PBE0/def2-TZVP level, along with four lowest-lying $n\text{B}–n\text{E}$ isomeric structures.

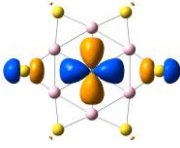
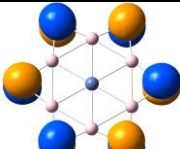
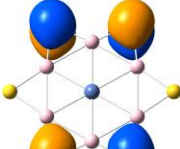
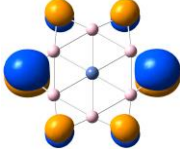
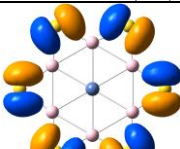

1 NiAl₆S₆ (<i>D</i>_{6h}, ¹A_{1g})				1B NiAl₆S₆ (<i>C</i>_s, ¹A')			
Ni	0.00000000	0.00000000	0.00000000	Ni	0.67460200	0.19444800	0.00000000
Al	0.00000000	2.53498700	0.00000000	Al	−0.92387700	1.95041800	0.00000000
Al	−2.19536300	1.26749400	0.00000000	Al	0.19351400	−1.83175300	1.38505000
Al	2.19536300	1.26749300	0.00000000	Al	0.19351400	−1.83175300	−1.38505000
Al	2.19536300	−1.26749400	0.00000000	Al	2.17457400	1.74292300	0.00000000
Al	0.00000000	−2.53498700	0.00000000	Al	−0.08436800	0.74303800	−2.18111900
Al	−2.19536300	−1.26749300	0.00000000	Al	−0.08436800	0.74303800	2.18111900
S	−1.98667600	3.44102400	0.00000000	S	−0.08436800	−1.07057000	−3.43346600
S	1.98667600	3.44102400	0.00000000	S	−1.45421900	2.48469800	−2.06270100
S	3.97335200	0.00000000	0.00000000	S	−1.27640800	−2.71849400	0.00000000
S	1.98667600	−3.44102400	0.00000000	S	−0.08436800	−1.07057000	3.43346600
S	−1.98667600	−3.44102400	0.00000000	S	1.97947600	−1.68172500	0.00000000
S	−3.97335200	0.00000000	0.00000000	S	−1.45421900	2.48469800	2.06270100
1C NiAl₆S₆ (<i>C</i>_s, ¹A')				1D NiAl₆S₆ (<i>C</i>₁, ¹A)			
Ni	0.89493600	0.18857400	0.00000000	Ni	−0.00994900	−0.10477900	−1.05421000
Al	−1.69017400	−0.25659500	0.00000000	Al	0.14649000	0.49894800	1.53118700
Al	−0.52794500	0.71487400	2.11094400	Al	2.34013800	0.08478700	0.46138700
Al	0.36169200	−1.72833600	−1.40043700	Al	−1.96328800	−0.99705000	−0.02846100
Al	0.36169200	−1.72833600	1.40043700	Al	0.55646900	−2.00192000	0.28476100
Al	−0.52794500	0.71487400	−2.11094400	Al	−1.62404900	1.64300600	−0.62907800
Al	−0.21701600	2.30513000	0.00000000	Al	0.78533700	2.07657300	−0.68678300
S	−1.19350700	−2.64301300	0.00000000	S	−0.58216500	2.61788400	1.23284000
S	2.12988900	−1.73767000	0.00000000	S	−0.99288300	−1.49985400	1.98127500
S	0.18656100	−0.92324400	−3.43384400	S	−0.81414100	−2.29792500	−1.45734700
S	0.18656100	−0.92324400	3.43384400	S	−3.50877700	0.51089500	−0.29614800
S	−0.52794500	2.93980400	2.07949800	S	2.73827700	−2.10026200	0.28873600
S	−0.52794500	2.93980400	−2.07949800	S	2.98120600	1.89284700	−0.66256200
1E NiAl₆S₆ (<i>C</i>_s, ¹A')				2 PdAl₆S₆ (<i>D</i>_{6h}, ¹A_{1g})			
Ni	−0.92651300	−0.24786300	0.00000000	Pd	0.00000000	0.00000000	0.00000000
Al	0.08428900	−2.07002200	1.23503700	Al	0.00000000	2.58196200	0.00000000
Al	−0.09184000	0.46054300	2.10353400	Al	2.23604500	1.29098100	0.00000000
Al	0.45194600	2.16173400	0.00000000	Al	−2.23604500	1.29098100	0.00000000
Al	1.67946500	0.03531900	0.00000000	Al	−2.23604500	−1.29098100	0.00000000
Al	0.08428900	−2.07002200	−1.23503700	Al	0.00000000	−2.58196200	0.00000000

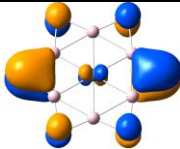
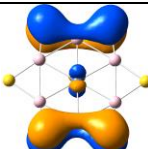
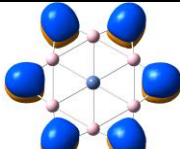
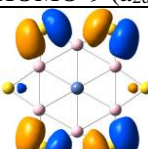
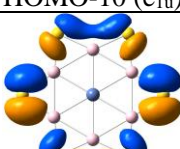
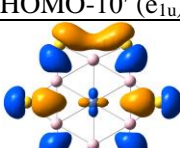
Al	-0.09184000	0.46054300	-2.10353400	Al	2.23604500	-1.29098100	0.00000000
S	-1.68829300	-1.09728900	-2.20871600	S	2.00134900	3.46643800	0.00000000
S	-0.22309800	2.64641500	2.06595000	S	-2.00134900	3.46643800	0.00000000
S	1.86233900	-0.91709700	2.11807400	S	-4.00269800	0.00000000	0.00000000
S	-1.68829300	-1.09728900	2.20871600	S	-2.00134900	-3.46643800	0.00000000
S	1.86233900	-0.91709700	-2.11807400	S	2.00134900	-3.46643800	0.00000000
S	-0.22309800	2.64641500	-2.06595000	S	4.00269800	0.00000000	0.00000000
2B PdAl₆S₆ (C_s, ¹A')				2C PdAl₆S₆ (C₁, ¹A)			
Pd	0.94425900	0.29292700	0.00000000	Pd	-0.03358200	0.10282800	-1.08965500
Al	-1.89134100	-0.33946000	0.00000000	Al	-0.31475700	-0.52137200	1.73044500
Al	-0.77327300	0.64643800	2.08625900	Al	-2.30136900	0.28775900	0.50066100
Al	0.40467500	-1.75743300	-1.37851000	Al	2.11229200	0.65629500	0.08203800
Al	0.40467500	-1.75743300	1.37851000	Al	-0.14796000	2.09015400	0.41540200
Al	-0.77327300	0.64643800	-2.08625900	Al	1.30484100	-1.96252700	-0.57971600
Al	-0.42487200	2.32881200	0.00000000	Al	-1.16240600	-2.00996500	-0.61155100
S	-1.19361200	-2.63791400	0.00000000	S	0.11770000	-2.69820700	1.30909800
S	2.17431600	-1.96983400	0.00000000	S	1.20693800	1.18917600	2.12551100
S	0.16599700	-0.91092200	-3.38009600	S	1.43598100	2.41372400	-1.12871100
S	0.16599700	-0.91092200	3.38009600	S	3.33212200	-1.11977900	-0.24766000
S	-0.77327300	2.88822400	2.08278300	S	-2.29376800	2.51774300	0.37429800
S	-0.77327300	2.88822400	-2.08278300	S	-3.28857100	-1.41231800	-0.54881800
2D PdAl₆S₆ (C₁, ¹A)				2E PdAl₆S₆ (C_s, ¹A')			
Pd	0.04861600	0.00524400	0.75912000	Pd	0.11113000	-0.97125700	0.00000000
Al	-1.74586700	1.23903600	-0.57162600	Al	2.03642500	0.09288700	1.25833800
Al	1.18526900	-2.07944400	-0.03216200	Al	-0.44578900	-0.00343500	2.20900500
Al	2.48059400	0.24719200	0.23668100	Al	-2.16302600	0.44501300	0.00000000
Al	-2.74840500	-0.89444100	1.58343000	Al	-0.15522200	1.85543300	0.00000000
Al	0.85384200	2.16953100	-0.20054400	Al	2.03642500	0.09288700	-1.25833800
Al	-1.32532000	-1.76466800	-0.45058900	Al	-0.44578900	-0.00343500	-2.20900500
S	3.05543600	2.26875700	-0.37449400	S	1.21763500	-1.41318300	-2.70093500
S	-0.76014500	3.02858800	-1.39283600	S	-2.63601300	-0.16722000	2.10009500
S	-0.08485900	-3.46254900	-1.14923600	S	0.90802500	1.96934900	2.02544900
S	-2.72091500	-0.44009400	-1.60299100	S	1.21763500	-1.41318300	2.70093500
S	3.35175000	-1.75923600	0.20237600	S	0.90802500	1.96934900	-2.02544900
S	-1.92488200	1.22923100	1.67549400	S	-2.63601300	-0.16722000	-2.10009500
3 PtAl₆S₆ (D_{6h}, ¹A_{1g})				3B PtAl₆S₆ (C_s, ¹A')			
Pt	0.00000000	0.00000000	0.00000000	Pt	0.62517100	0.25529800	0.00000000
Al	0.00000000	2.57597200	0.00000000	Al	-1.10890500	1.95446800	0.00000000
Al	2.23085700	1.28798600	0.00000000	Al	0.06991800	-1.91387500	1.39161300
Al	-2.23085700	1.28798600	0.00000000	Al	0.06991800	-1.91387500	-1.39161300
Al	-2.23085700	-1.28798600	0.00000000	Al	2.27563100	1.86022800	0.00000000
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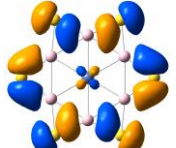
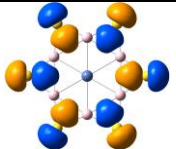
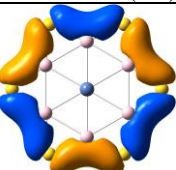
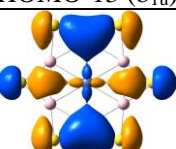
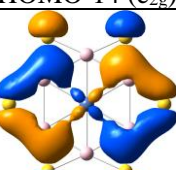
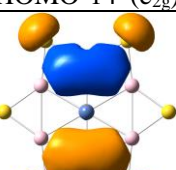
Al	2.23085700	-1.28798600	0.00000000	Al	-0.29879400	0.65583400	2.25114100
S	1.99791600	3.46049200	0.00000000	S	-0.29879400	-1.19024400	-3.44999300
S	-1.99791600	3.46049200	0.00000000	S	-1.71777900	2.35936800	-2.07068900
S	-3.99583200	0.00000000	0.00000000	S	-1.46252100	-2.68288200	0.00000000
S	-1.99791600	-3.46049200	0.00000000	S	-0.29879400	-1.19024400	3.44999300
S	1.99791600	-3.46049200	0.00000000	S	1.87191700	-1.95506900	0.00000000
S	3.99583200	0.00000000	0.00000000	S	-1.71777900	2.35936800	2.07068900
3C PtAl₆S₆ (C₁, ¹A)				3D PtAl₆S₆ (C₁, ¹A)			
Pt	0.05247200	-0.00061700	-0.63331700	Pt	0.03331900	-0.67736100	-0.48412800
Al	-1.76471900	-1.22313000	0.66700400	Al	-2.02280500	-1.71513400	-1.23071300
Al	1.19629800	2.06935000	0.13665600	Al	-0.16682700	1.69701500	-0.99546800
Al	2.48106600	-0.24797600	-0.15145300	Al	2.30480300	0.72133100	-0.15637200
Al	-2.72248300	0.90815200	-1.54794700	Al	-2.20650100	0.47041500	0.49944800
Al	0.82720600	-2.17848300	0.27878800	Al	1.89331300	-1.84924600	0.79039500
Al	-1.34481300	1.74899700	0.53651900	Al	0.26846200	0.05595200	1.81562300
S	3.02644300	-2.27471300	0.46485700	S	2.44594600	0.42982200	2.10737300
S	-0.79230400	-3.02329100	1.47858900	S	-3.76482500	-1.00896700	-0.17020500
S	-0.10124500	3.44692100	1.22411300	S	3.05003200	-1.17695300	-1.00205700
S	-2.78426400	0.45020000	1.66276300	S	-1.62164300	0.54996100	2.68164800
S	3.36448300	1.75269900	-0.07372700	S	1.81520300	2.58234800	-1.22418400
S	-1.89036500	-1.22379600	-1.60382400	S	-2.14437800	2.42940400	-0.61981600
3E PtAl₆S₆ (C_s, ¹A')							
Pt	0.81711800	0.02872600	0.00000000				
Al	-1.99342800	0.15528700	0.00000000				
Al	-0.65541600	0.83073000	2.08217400				
Al	-0.20348100	-1.82429200	-1.39334100				
Al	-0.20348100	-1.82429200	1.39334100				
Al	-0.65541600	0.83073000	-2.08217400				
Al	0.16631900	2.38979900	0.00000000				
S	-1.97181100	-2.24538200	0.00000000				
S	1.45245400	-2.48410500	0.00000000				
S	-0.20348100	-0.93246900	-3.38828000				
S	-0.20348100	-0.93246900	3.38828000				
S	-0.08844800	3.00052200	2.08384800				
S	-0.08844800	3.00052200	-2.08384800				

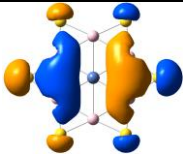
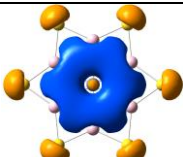
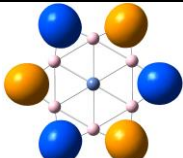
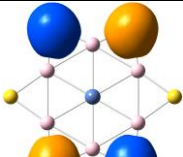
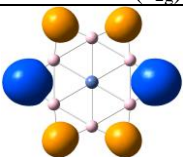

Table S2. Orbital composition analysis for the canonical molecular orbitals (CMOs) of GM NiAl₆S₆ (**1**, D_{6h} , $^1A_{1g}$) cluster. Main components greater than 15% are shown in bold.

CMO	Al ₆ (%)		S ₆ (%)		Ni (%)	
	s/p	total	s/p	total	s/p/d	total
 HOMO (e_{1u})	11.64/ 20.38	32.02	0.00/ 43.27	43.27	0.00/ 22.85 /0.00	22.85
 HOMO' (e_{1u})	11.64/ 20.39	32.03	0.00/ 43.29	43.29	0.00/ 22.85 /0.00	22.85
 HOMO-1 (a_{1g})	0.00/3.89	3.89	0.00/0.00	0.00	0.00/0.00/ 85.47	85.47
 HOMO-2 (e_{1g})	0.00/0.00	0.00	0.00/9.06	9.06	0.00/0.00/ 90.55	90.55
 HOMO-2' (e_{1g})	0.00/0.00	0.00	0.00/9.06	9.06	0.00/0.00/ 90.55	90.55
 HOMO-3 (e_{2g})	0.00/0.00	0.00	0.00/ 15.95	15.95	0.00/0.00/ 81.88	81.88

CMO	Al ₆ (%)		S ₆ (%)		Ni (%)	
	s/p	total	s/p	total	s/p/d	total
 HOMO-3' (e _{2g})	0.00/0.00	0.00	0.00/ 15.87	15.87	0.00/0.00/ 81.88	81.88
 HOMO-4 (b _{1g})	0.00/0.00	0.00	0.00/ 97.64	97.64	0.00/0.00/0.00	0.00
 HOMO-5 (e _{2u})	0.00/7.87	7.87	0.00/90.33	90.33	0.00/0.00/0.00	0.00
 HOMO-5' (e _{2u})	0.00/7.87	7.87	0.00/ 90.33	90.33	0.00/0.00/0.00	0.00
 HOMO-6 (a _{2g})	0.00/6.05	6.05	0.00/ 91.37	91.37	0.00/0.00/0.00	0.00
 HOMO-7 (a _{1g})	0.00/14.37	14.37	0.00/ 57.38	57.38	14.05/0.00/10.19	24.24

CMO	Al ₆ (%)		S ₆ (%)		Ni (%)	
	s/p	total	s/p	total	s/p/d	total
 HOMO-8 (e _{1g})	0.00/ 20.54	20.54	0.00/ 70.32	70.32	0.00/0.00/7.97	7.97
 HOMO-8' (e _{1g})	0.00/ 20.54	20.54	0.00/ 70.32	70.32	0.00/0.00/7.97	7.97
 HOMO-9 (a _{2u})	0.00/ 28.41	28.41	0.00/ 70.06	70.06	0.00/0.52/0.00	0.52
 HOMO-10 (e _{1u})	2.17/10.10	12.27	0.00/ 84.28	84.28	0.00/0.00/0.00	0.00
 HOMO-10' (e _{1u})	1.45/11.77	13.22	0.00/ 84.25	84.25	0.00/0.00/0.00	0.00
 HOMO-11 (e _{2g})	1.22/ 16.50	17.72	1.22/ 74.09	75.31	0.00/0.00/4.23	4.23

CMO	Al ₆ (%)		S ₆ (%)		Ni (%)	
	s/p	total	s/p	total	s/p/d	total
 HOMO-11' (e _{2g})	0.00/16.49	16.49	0.00/74.09	74.09	0.00/0.00/4.23	4.23
 HOMO-12 (b _{2u})	0.00/9.58	9.58	7.77/79.07	86.84	0.00/0.00/0.00	0.00
 HOMO-13 (b _{1u})	19.94/7.53	27.47	0.00/68.86	68.86	0.00/0.00/0.00	0.00
 HOMO-14 (e _{2g})	19.59/0.00	19.59	8.19/59.64	67.83	0.00/0.00/6.85	6.85
 HOMO-14' (e _{2g})	19.59/1.81	21.40	8.18/59.63	67.81	0.00/0.00/6.85	6.85
 HOMO-15 (e _{1u})	24.57/10.03	34.60	13.15/43.28	56.43	0.00/5.35/0.00	5.35

CMO	Al ₆ (%)		S ₆ (%)		Ni (%)	
	s/p	total	s/p	total	s/p/d	total
 HOMO-15' (e _{1u})	24.58 /10.67	35.25	13.15/ 43.15	56.30	0.00/5.35/0.00	5.35
 HOMO-16 (a _{1g})	24.50 / 24.36	48.86	12.13/ 20.96	33.09	11.24/0.00/3.52	14.76
 HOMO-17 (b _{2u})	0.00/ 17.45	17.45	80.56 /0.00	80.56	0.00/0.00/0.00	0.00
 HOMO-18 (e _{2g})	3.06/ 15.55	18.61	78.46 /0.00	78.46	0.00/0.00/0.00	0.00
 HOMO-18' (e _{2g})	2.04/14.97	17.01	77.28 /1.20	78.48	0.00/0.00/0.00	0.00
 HOMO-19 (e _{1u})	12.14/7.78	19.92	74.31 /1.87	76.18	0.00/0.00/0.00	0.00

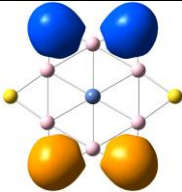
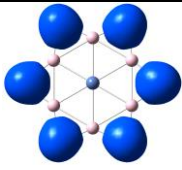
CMO	Al ₆ (%)		S ₆ (%)		Ni (%)	
	s/p	total	s/p	total	s/p/d	total
 HOMO-19' (e _{1u})	12.14/7.78	19.92	75.44 /0.00	75.44	0.00/0.00/0.00	0.00
 HOMO-20 (a _{1g})	19.01 /0.00	19.01	74.24 /1.13	75.37	0.78/0.00/0.00	0.78

Table S3. Orbital composition analysis for the lowest unoccupied molecular orbitals (LUMOs) of the MAl_6S_6 ($\text{M} = \text{Ni}, \text{Pd}, \text{Pt}$) series.

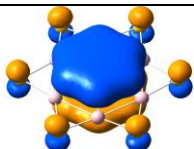
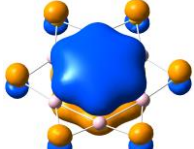
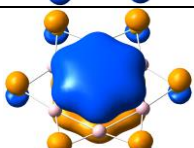
Species	LUMO	Symmetry	Al_6 (%)	S_6 (%)	M (%)
1 NiAl_6S_6		a_{2u}	52.72	25.18	22.09
2 PdAl_6S_6		a_{2u}	43.88	23.87	32.23
3 PtAl_6S_6		a_{2u}	42.12	23.98	33.87

Figure S1. The AdNDP bonding pattern of PdAl₆S₆. Occupation numbers (ONs) are shown.

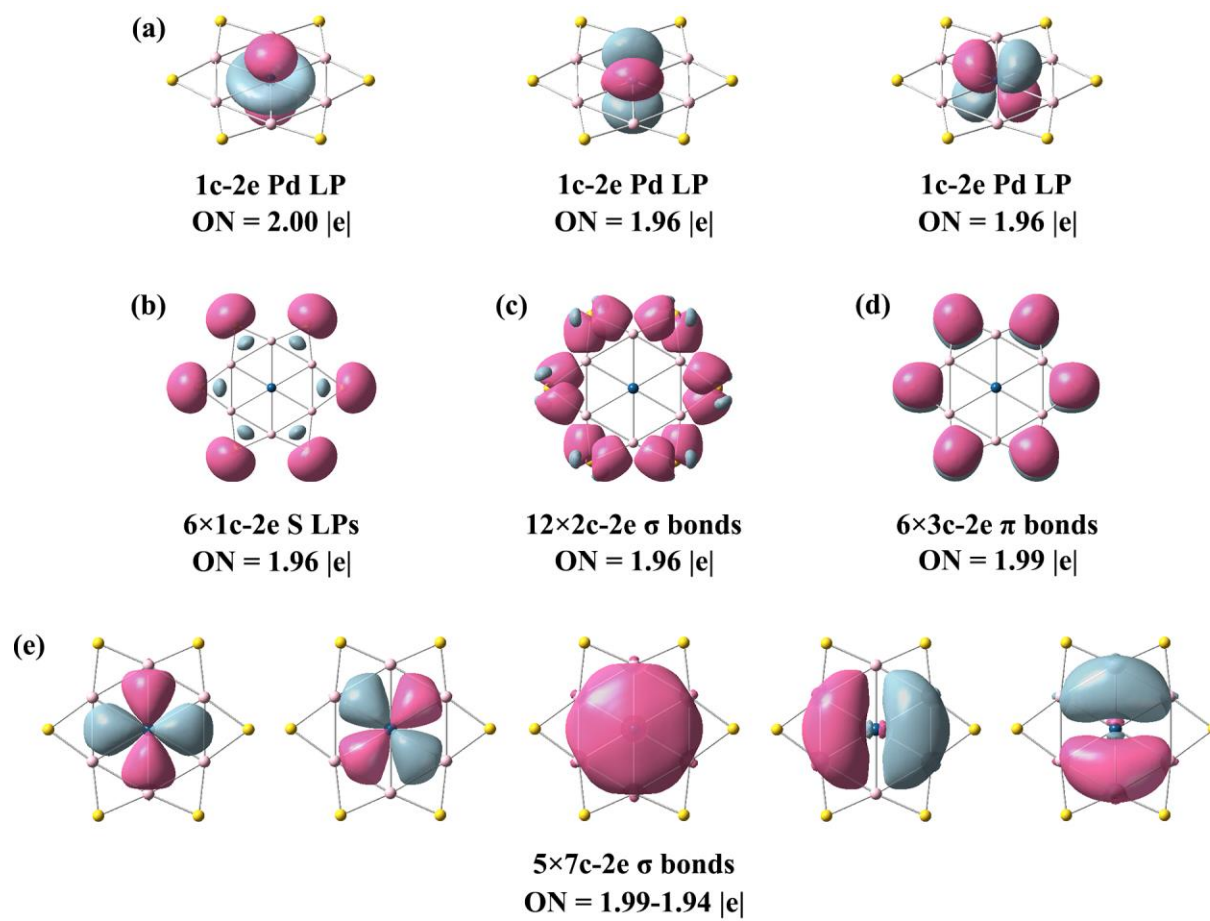


Figure S2. The AdNDP bonding pattern of PtAl_6S_6 . Occupation numbers (ONs) are shown.

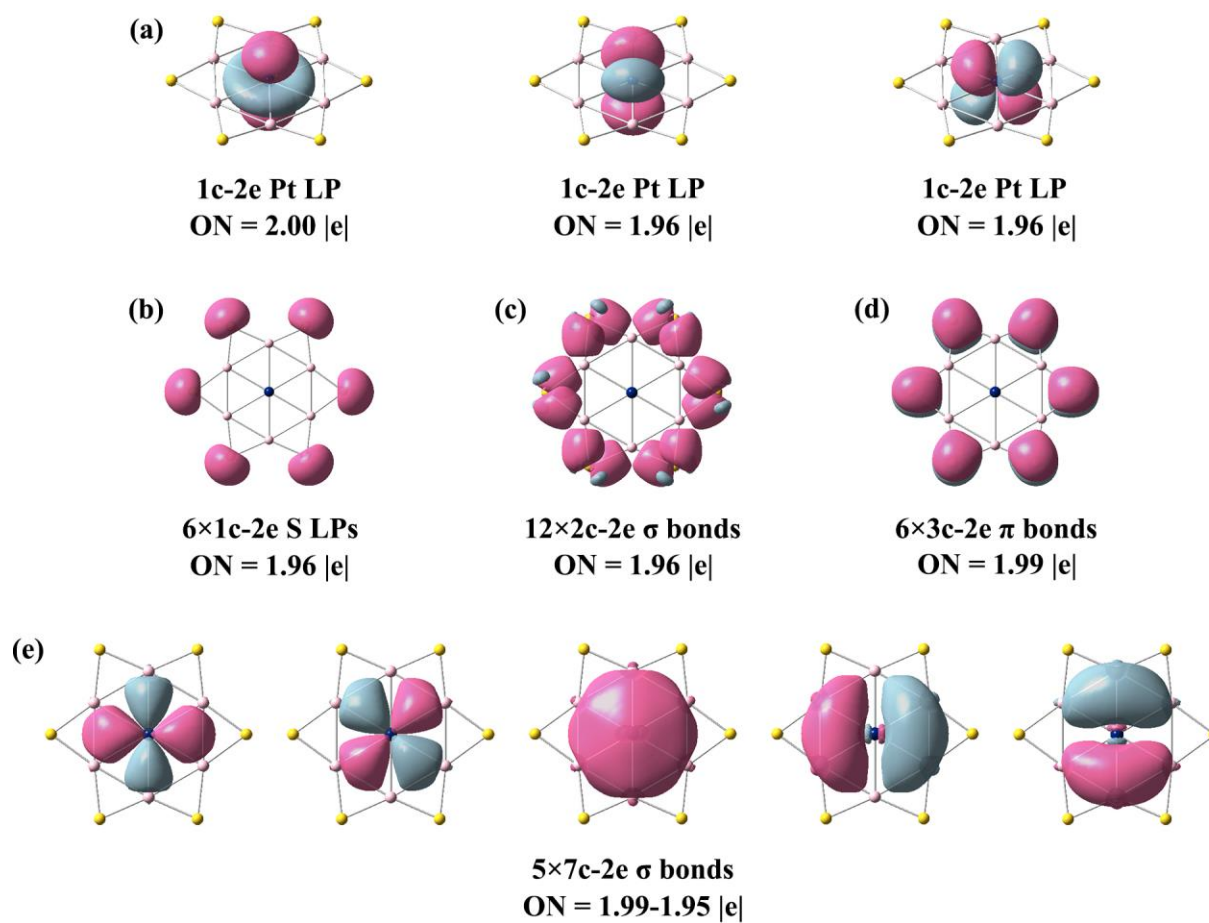


Figure S3. Nucleus independent chemical shifts (NICSs) for clusters **1–3**. Here the NICS(0) data (blue color) are calculated at the center of the Al-M-Al (M = Ni, Pd, Pt) triangle, whereas the NICS(1) values (red color) are at 1 Å above the center of the Al-S-Al triangle.

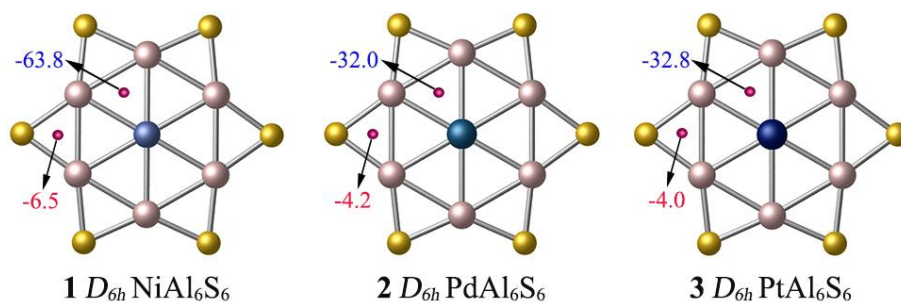


Figure S4. Calculated IR spectrums of PdAl₆S₆ and PtAl₆S₆ at the PBE0/def2-TZVP level.

