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# Supplementary Information (SI) File

# Formation of pyramidal structures through mixing gold and platinum atoms: The $Au_xPt_y^{2+}$ clusters with x + y = 10

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**Contents:**


i) Structures, relative energies (eV), and spin states (in bracket) of the low-lying isomers of $Au_xPt_y^{2+}$ with x + y =10) using B3PW91, TPSSh, BP86 and revTPSS/ aug-cc-pVTZ-PP + ZPE computations. (Figure S1 and S2)

ii) Adaptive natural density partitioning (AdNDP) analysis of the $Au_xPt_y^{2+}$ clusters with x + y = 10 at B3PW91/ cc-pVTZ-PP theory level (Figures S3-S14).

iii) Calculated density of states (DOS) of the $Au_xPt_y^{2+}$ (x + y = 10) at B3PW91/aug-cc-pVTZ-PP theory level (Figure S15).

iv) Optimized geometrical shapes and Cartesian coordinates of the lowest-lying $Au_xPt_y^{2+}$ (x + y = 10) isomers calculated at B3PW91/ aug-cc-pVTZ-PP method (Table S1).

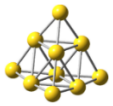
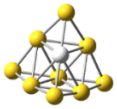
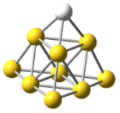
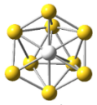
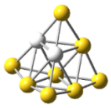
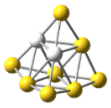
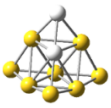
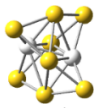
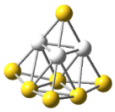
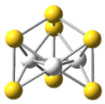
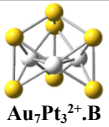
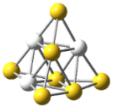
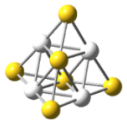
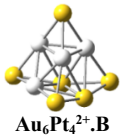
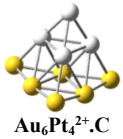
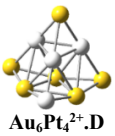
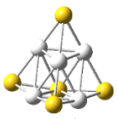
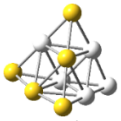
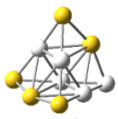
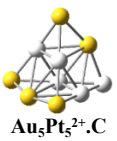
| Method | Structures | | | |
|---|---|---|---|---|
| |  $Au_{10}^{2+}$ (singlet) | | | |
| |  $Au_9Pt^{2+}$.A |  $Au_9Pt^{2+}$.B | $Au_9Pt^{2+}$.C |  $Au_9Pt^{2+}$.D |
| B3PW91 | 0.00 (doublet) | 0.42 (doublet) | 0.42 (doublet) | 0.47 (doublet) |
| TPSSh | 0.00 (doublet) | 0.42 (doublet) | 0.37 (doublet) | 0.30 (doublet) |
| BP86 | 0.00 (doublet) | 0.31 (doublet) | 0.48 (doublet) | 0.49 (doublet) |
| revTPSS | 0.00 (doublet) | 0.37 (doublet) | 0.35 (doublet) | 0.26 (doublet) |
| |  $Au_8Pt_2^{2+}$.A |  $Au_8Pt_2^{2+}$.A |  $Au_8Pt_2^{2+}$.B |  $Au_8Pt_2^{2+}$.D |
| B3PW91 | 0.00 (triplet) | 0.07 (singlet) | 0.17 (triplet) | 0.18 (singlet) |
| TPSSh | 0.00 (triplet) | 0.11 (singlet) | 0.16 (triplet) | 0.20 (triplet) |
| BP86 | 0.00 (triplet) | 0.10 (singlet) | 0.15 (triplet) | 0.13 (triplet) |
| revTPSS | 0.00 (triplet) | 0.12 (singlet) | 0.15 (triplet) | 0.24 (triplet) |
| |  $Au_7Pt_3^{2+}$.A |  $Au_7Pt_3^{2+}$.B |  $Au_7Pt_3^{2+}$.B |  $Au_7Pt_3^{2+}$.C |
| B3PW91 | 0.00 (quartet) | | 0.52 (quartet) | 0.52 (quartet) |
| TPSSh | 0.00 (quartet) | 0.22 (doublet) | 0.49 (quartet) | 0.44 (quartet) |
| BP86 | 0.00 (quartet) | 0.16 (doublet) | 0.37 (quartet) | 0.39 (quartet) |
| revTPSS | 0.00 (quartet) | | 0.42 (quartet) | 0.38 (quartet) |
| |  $Au_6Pt_4^{2+}$.A |  $Au_6Pt_4^{2+}$.B |  $Au_6Pt_4^{2+}$.C |  $Au_6Pt_4^{2+}$.D |
| B3PW91 | 0.00 (quintet) | 0.17 (quintet) | 0.34 (quintet) | 0.46 (quintet) |
| TPSSh | 0.00 (quintet) | 0.17 (quintet) | 0.26 (quintet) | 0.44 (quintet) |
| BP86 | 0.00 (quintet) | 0.17 (quintet) | 0.04 (quintet) | 0.25 (quintet) |
| revTPSS | 0.00 (quintet) | 0.16 (quintet) | 0.09 (quintet) | 0.33 (quintet) |
| |  $Au_5Pt_5^{2+}$.A |  $Au_5Pt_5^{2+}$.B |  $Au_5Pt_5^{2+}$.C |  $Au_5Pt_5^{2+}$.C |
| B3PW91 | 0.00 (sextet) | 0.11 (sextet) | 0.15 (quartet) | 0.17 (sextet) |
| TPSSh | 0.00 (sextet) | 0.14 (sextet) | 0.13 (quartet) | 0.15 (sextet) |
| BP86 | 0.03 (sextet) | 0.05 (sextet) | 0.00 (quartet) | 0.05 (sextet) |
| revTPSS | 0.00 (sextet) | 0.02 (sextet) | 0.03 (quartet) | 0.08 (sextet) |
| CCSD(T) (*) | 0.00 (sextet) | 0.13 (sextet) | | |

**Figure S1.** Structures, relative energies (eV), and spin states (in bracket) of the most stable isomers of $Au_xPt_y^{2+}$ with x + y =10 and y = 0 – 5) using B3PW91, TPSSh, BP86 and revTPSS/ aug-cc-pVTZ-PP + ZPE computations. (*) is calculated at CCSD(T)/ cc-pVDZ-PP method. Yellow ball = Au and white ball = Pt.

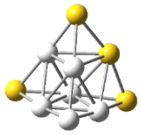
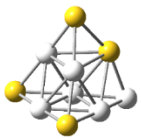
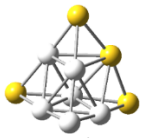
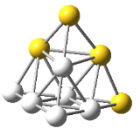
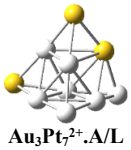
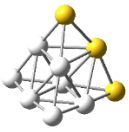
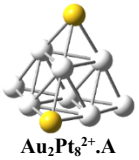
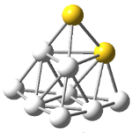
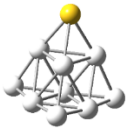
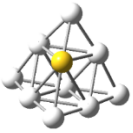
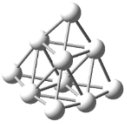
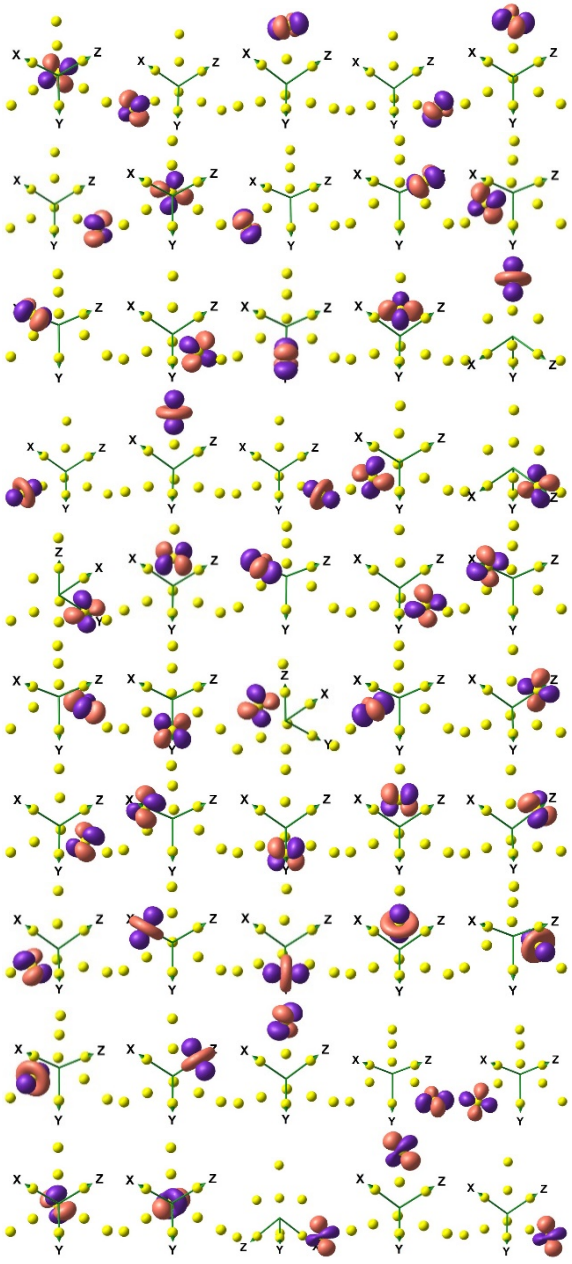
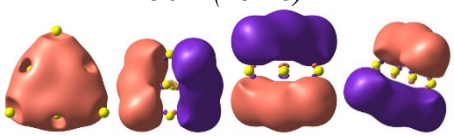
| Method | Structures | | | |
|---|---|---|---|---|
| |  $Au_4Pt_6^{2+}$.A/L |  $Au_4Pt_6^{2+}$.B |  $Au_4Pt_6^{2+}$.A |  $Au_4Pt_6^{2+}$.D |
| B3PW91 | 0.00 (septet) | 0.27 (septet) | 0.48 (quintet) | 0.61 (quintet) |
| TPSSh | 0.00 (septet) | 0.28 (septet) | 0.20 (quintet) | 0.55 (quintet) |
| BP86 | 0.00 (septet) | 0.22 (septet) | 0.12 (quintet) | 0.25 (quintet) |
| revTPSS | 0.00 (septet) | 0.26 (septet) | 0.17 (quintet) | 0.55 (quintet) |
| |  $Au_3Pt_7^{2+}$.A/L |  $Au_3Pt_7^{2+}$.B |  $Au_2Pt_8^{2+}$.A |  $Au_2Pt_8^{2+}$.B |
| B3PW91 | 0.00 (octet)<br>0.10 (sextet)<br>0.28 (quartet) | 0.11 (octet) | 0.00 (nonet)<br>0.36 (septet) | 0.56 (nonet)<br>0.64 (septet) |
| TPSSh | 0.01 (octet) | 0.00 (sextet)<br>0.05 (octet) | 0.00 (nonet)<br>0.35 (septet) | 0.59 (nonet)<br>0.56 (septet) |
| BP86 | 0.09 (sextet)<br>0.10 (octet) | 0.00 (sextet)<br>0.04 (octet) | 0.00 (nonet) | 0.08 (quintet)<br>0.16 (septet) |
| revTPSS | 0.10 (octet)<br>0.13 (sextet)<br>0.28 (quartet) | 0.00 (sextet)<br>0.06 (octet) | 0.00 (nonet)<br>0.28 (septet) | 0.26 (quintet)<br>0.42 (nonet) |
| |  $AuPt_9^{2+}$.A |  $AuPt_9^{2+}$.B |  $Pt_{10}^{2+}$ | |
| B3PW91 | 0.00 (10-et)<br>0.14 (octet)<br>0.17 (sextet) | 0.80 (quartet) | 0.00 (11-et)<br>0.10 (nonet)<br>0.30 (septet) | |
| TPSSh | 0.00 (10-et)<br>0.07 (octet)<br>0.12 (sextet) | 0.62 (quartet) | 0.00 (11-et)<br>0.07 (nonet)<br>0.04 (septet) | |
| BP86 | 0.00 (octet)<br>0.05 (sextet)<br>0.11 (10-et) | 0.13 (quartet) | 0.00 (septet)<br>0.00 (quintet)<br>0.30 (nonet)<br>0.30 (11-et) | |
| revTPSS | 0.07 (10-et)<br>0.00 (octet)<br>0.07 (sextet) | 0.29 (quartet) | 0.40 (11-et)<br>0.26 (nonet)<br>0.00 (septet) | |

**Figure S2.** Structures, relative energies (eV), and spin states (in bracket) of the most stable isomers of $Au_xPt_y^{2+}$ with x + y =10 and y = 6 - 10) using B3PW91, TPSSh, BP86 and revTPSS/ aug-cc-pVTZ-PP + ZPE computations. Yellow ball = Au and white ball = Pt.



50 x *(2c-1e)*



4 x *(10c-2e)*

**Figure S3**: AdNDP analysis showing muti-center bonds in the $\mathbf{Au_{10}^{2+}}$ cluster at singlet state, calculated at B3PW91/ cc-pVTZ-PP theory level.

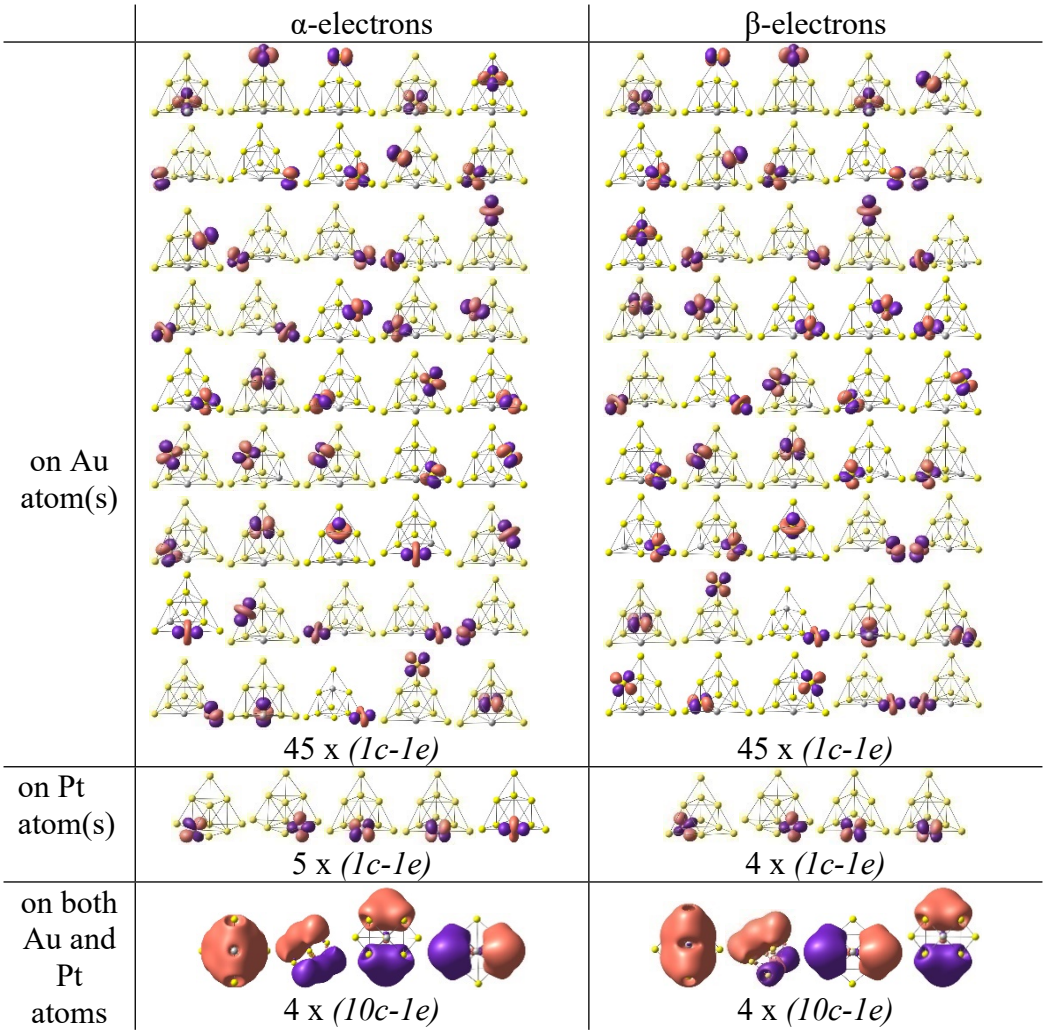



**Figure S4**: AdNDP analysis showing muti-center bonds in the $\mathbf{Au_9Pt^{2+}}$**.A** cluster at doublet state, calculated at B3PW91/ cc-pVTZ-PP theory level.

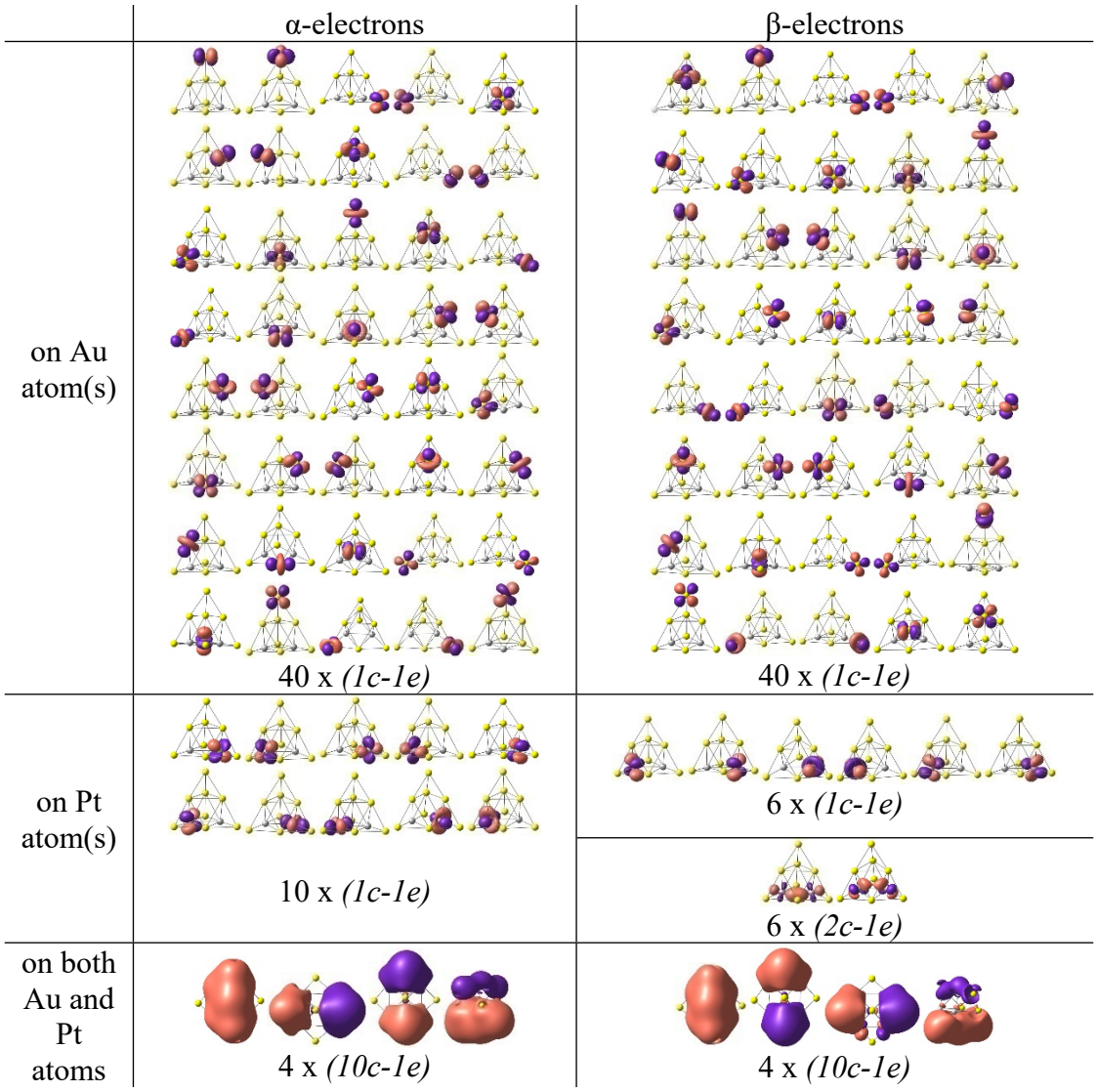



**Figure S5**: AdNDP analysis showing muti-center bonds in the **$Au_8Pt_2^{2+}$.A** cluster at triplet state, calculated at B3PW91/ cc-pVTZ-PP theory level.

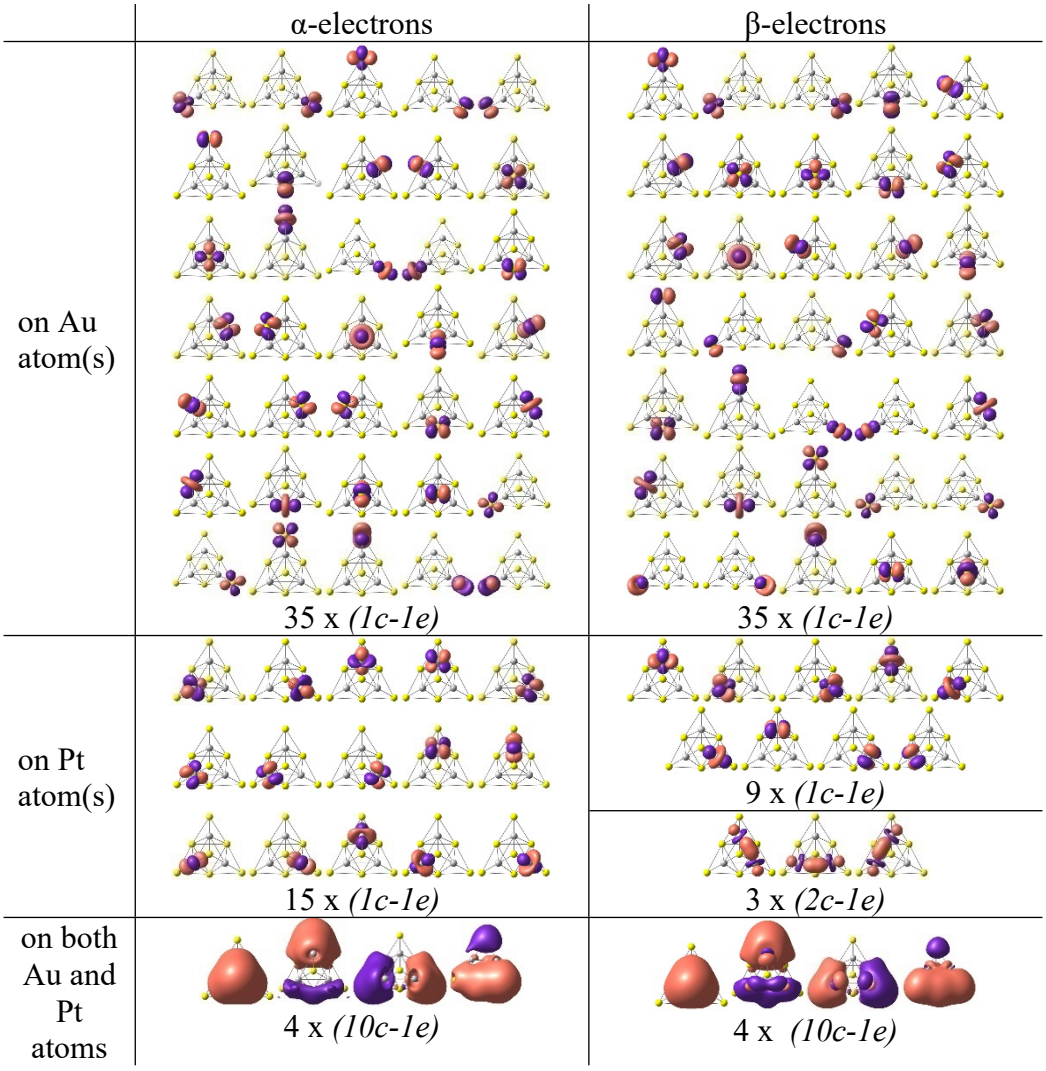



**Figure S6**: AdNDP analysis showing muti-center bonds in the **$Au_7Pt_3^{2+}$.A** cluster at quartet state, calculated at B3PW91/ cc-pVTZ-PP theory level.

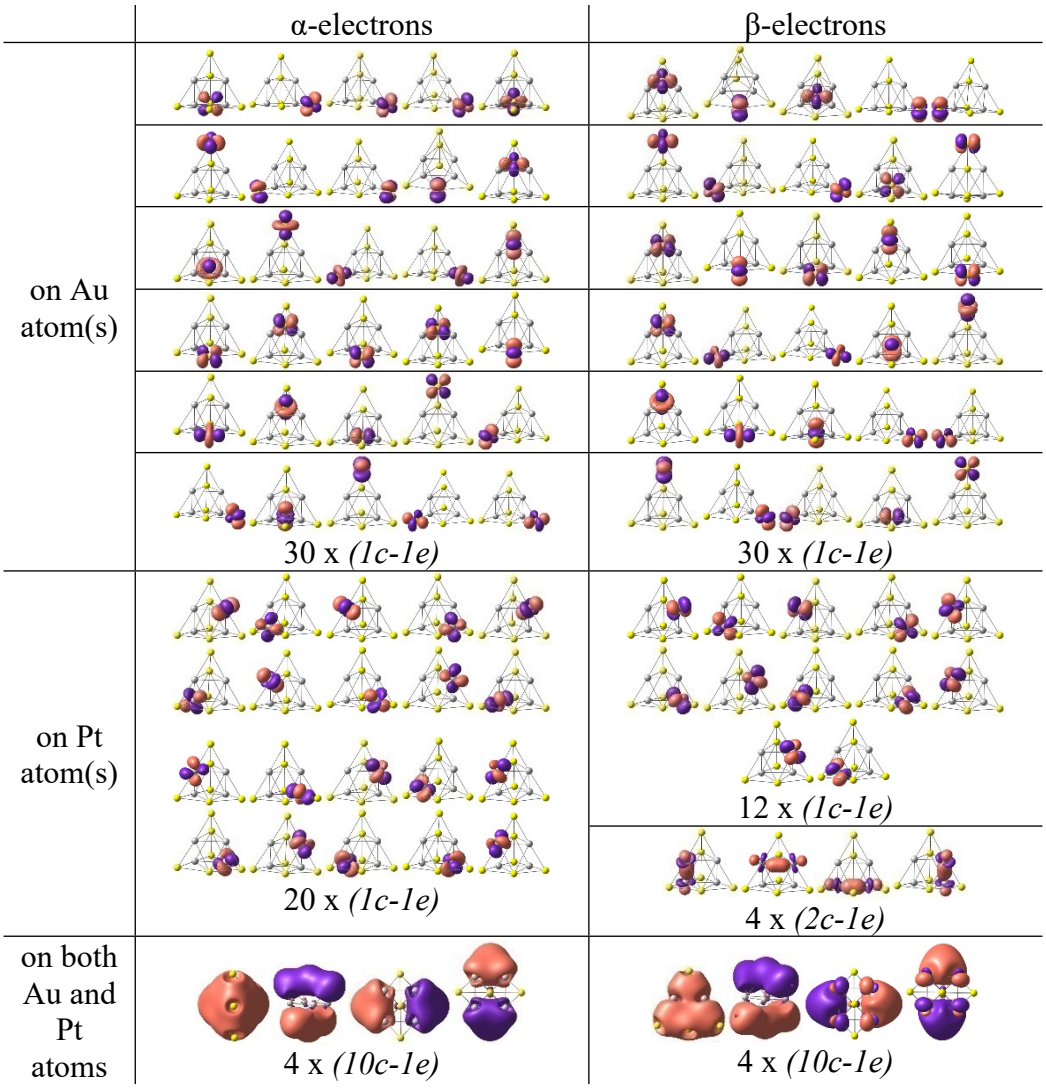



**Figure S7**: AdNDP analysis showing muti-center bonds in the **$Au_6Pt_4^{2+}$.A** cluster at quintet state, calculated at B3PW91/ cc-pVTZ-PP theory level.

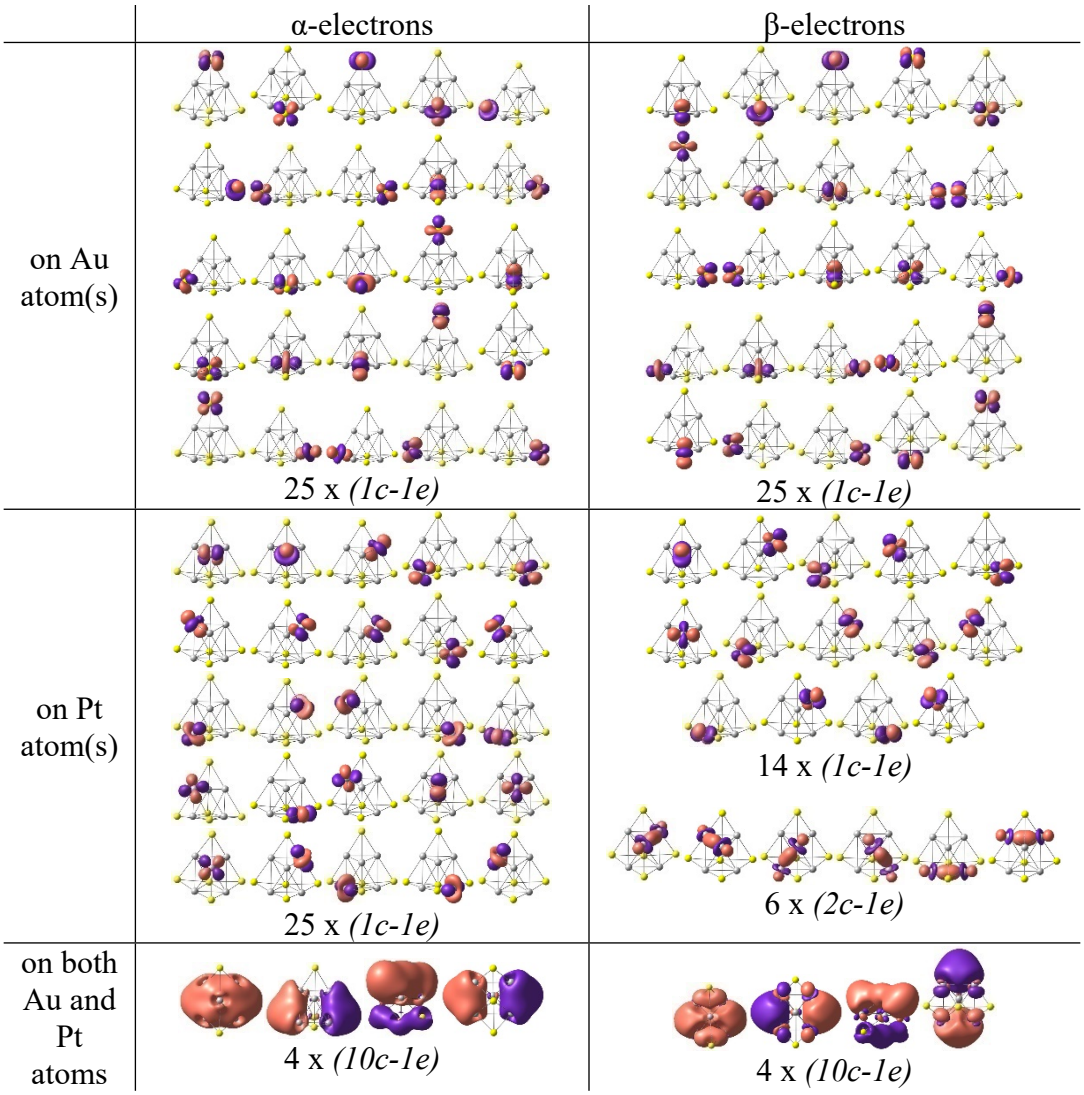



**Figure S8**: AdNDP analysis showing muti-center bonds in the **$Au_5Pt_5^{2+}$.A** cluster at sextet state, calculated at B3PW91/ cc-pVTZ-PP theory level.

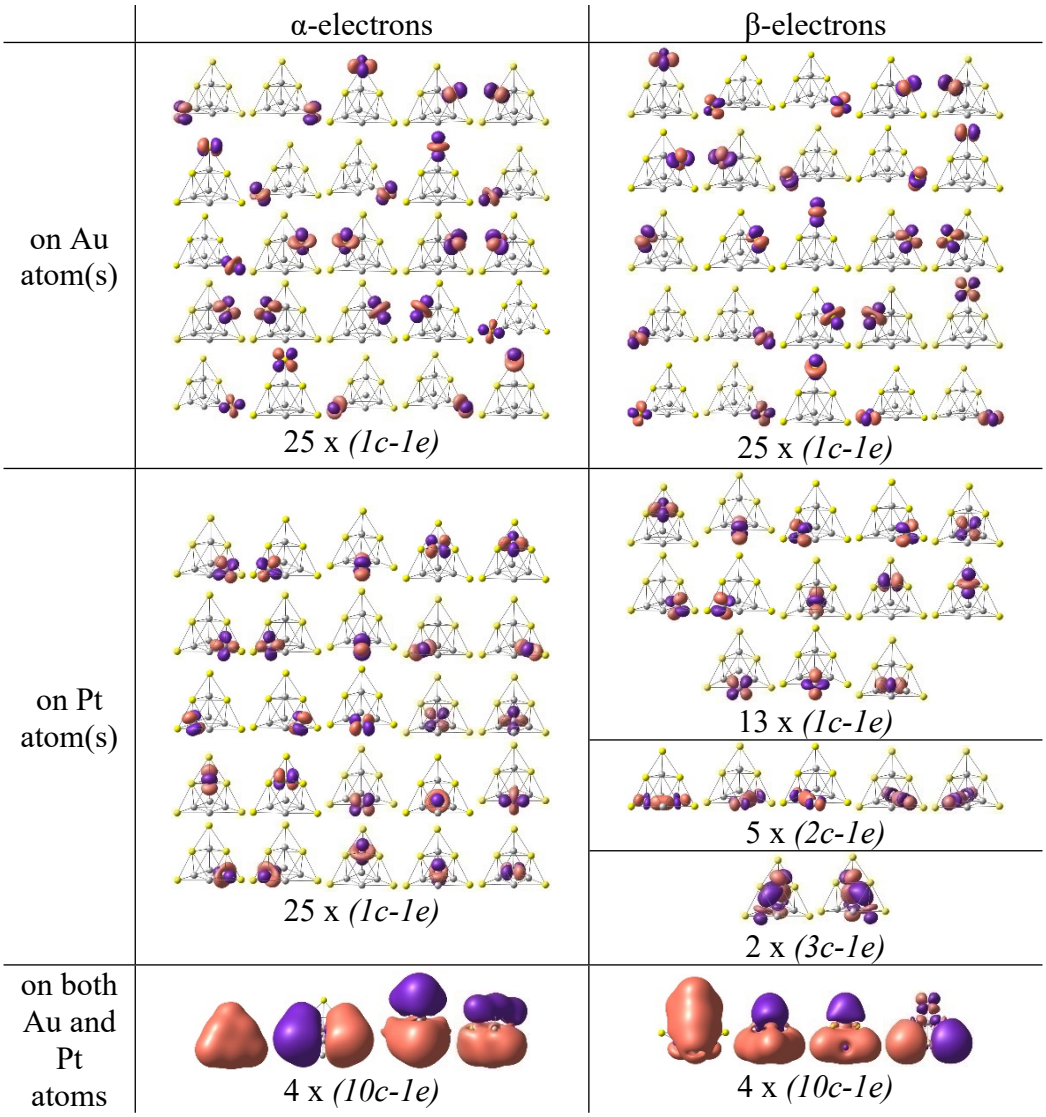



**Figure S9**: AdNDP analysis showing muti-center bonds in the **$Au_5Pt_5^{2+}$.B** cluster at sextet state, calculated at B3PW91/ cc-pVTZ-PP theory level.

α-electrons β-electrons

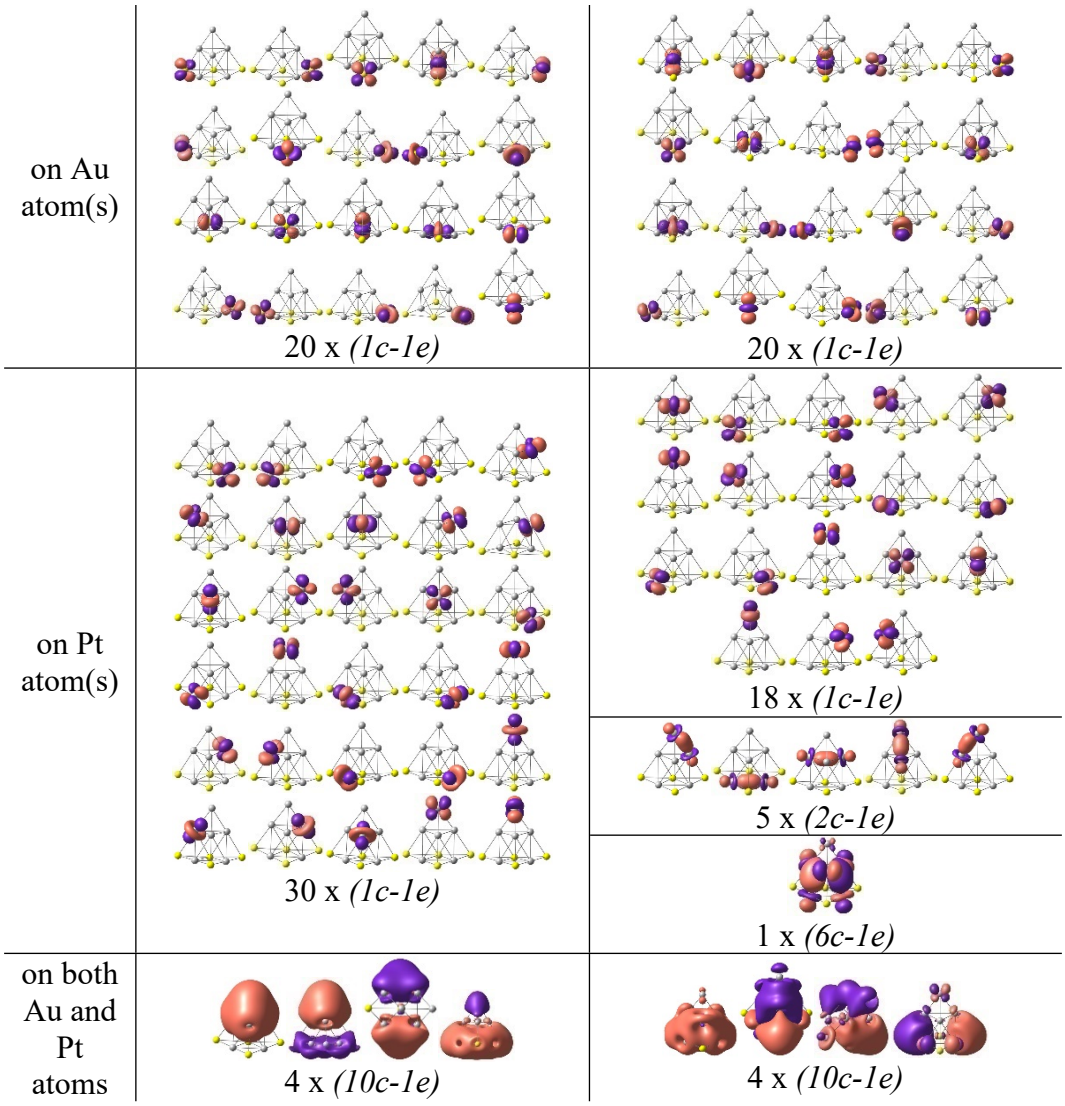



**Figure S10**: AdNDP analysis showing muti-center bonds in the **$Au_4Pt_6^{2+}$.A** cluster at septet state, calculated at B3PW91/ cc-pVTZ-PP theory level.

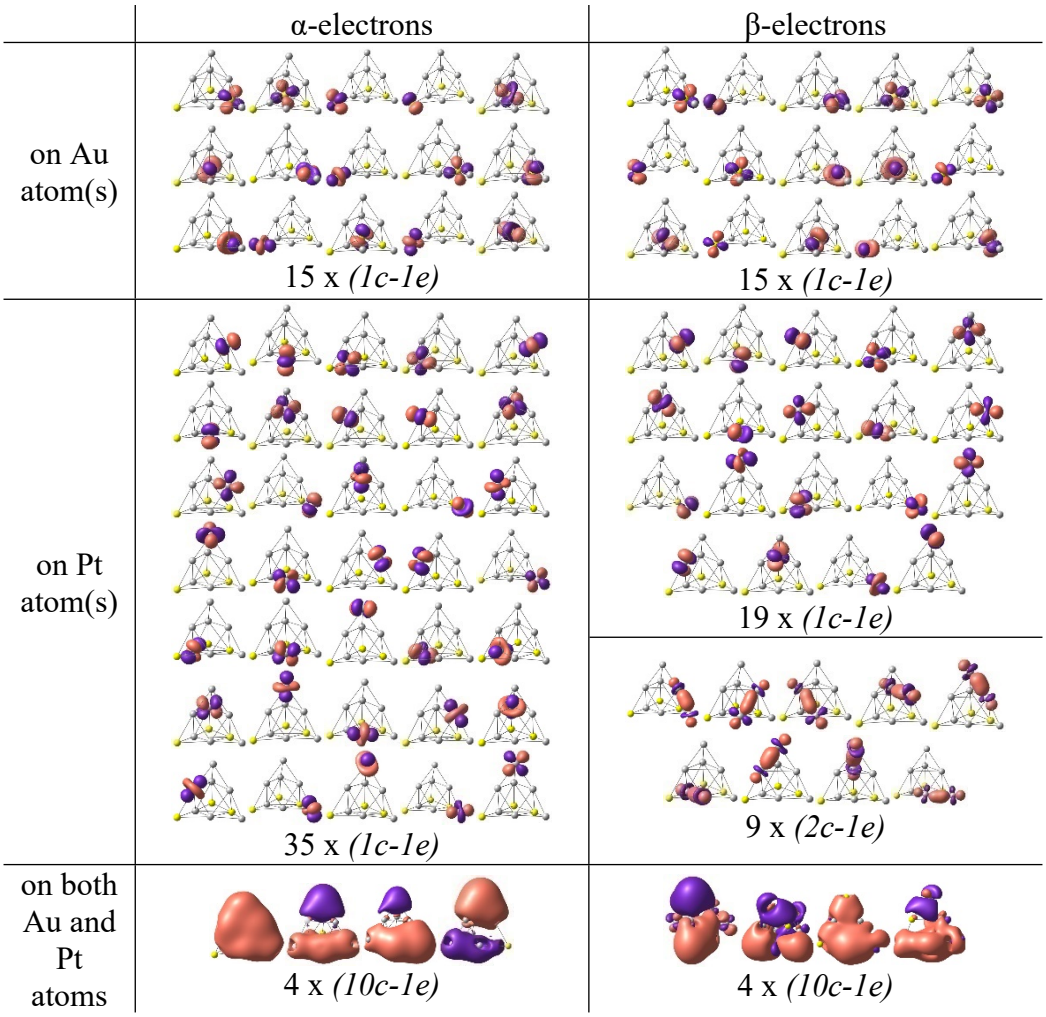



**Figure S11**: AdNDP analysis showing muti-center bonds in the **$Au_3Pt_7^{2+}$.A** cluster at octet state, calculated at B3PW91/ cc-pVTZ-PP theory level.

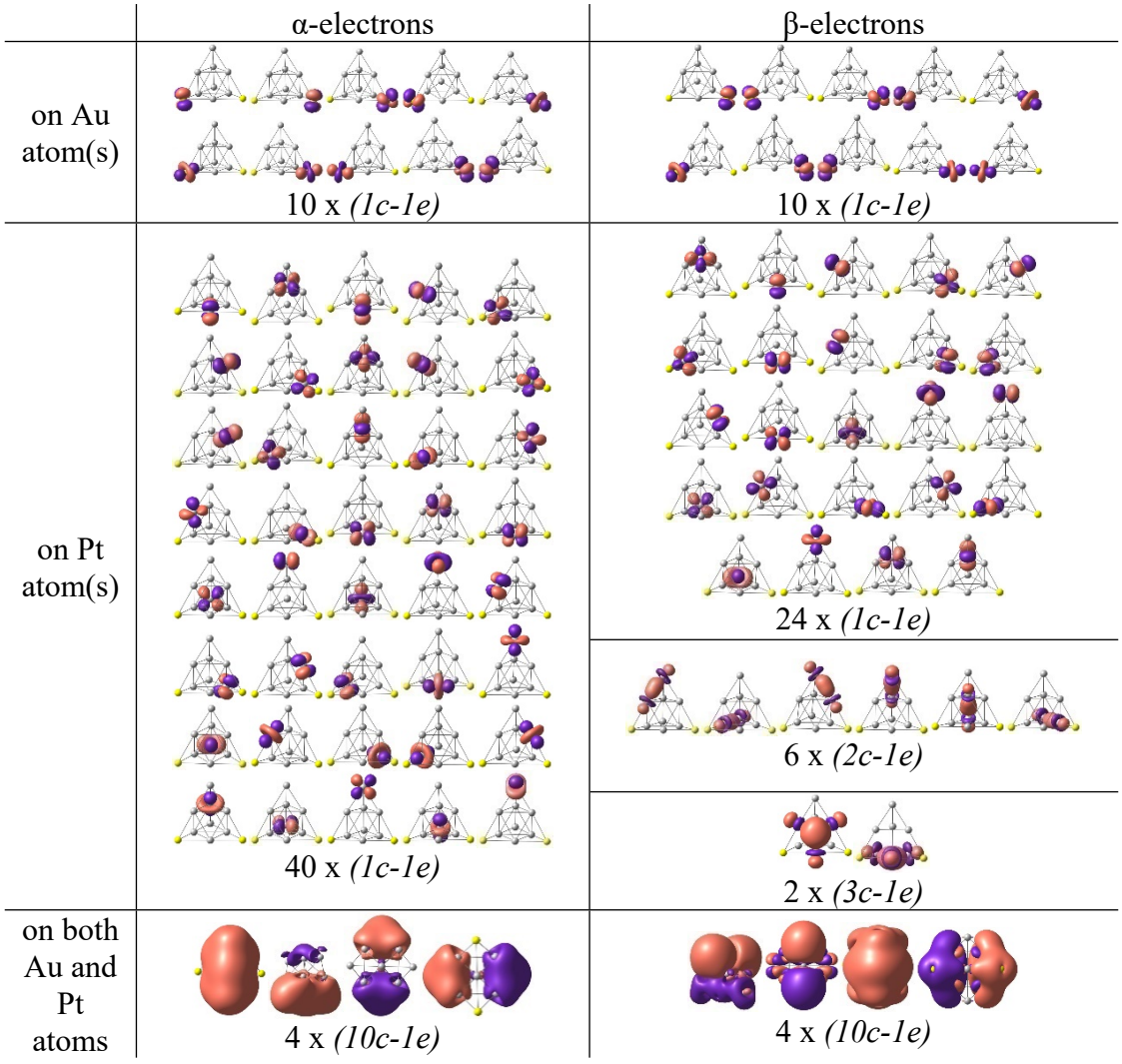



**Figure S12**: AdNDP analysis showing muti-center bonds in the **$Au_2Pt_8^{2+}$.A** cluster at nonet state, calculated at B3PW91/ cc-pVTZ-PP theory level.

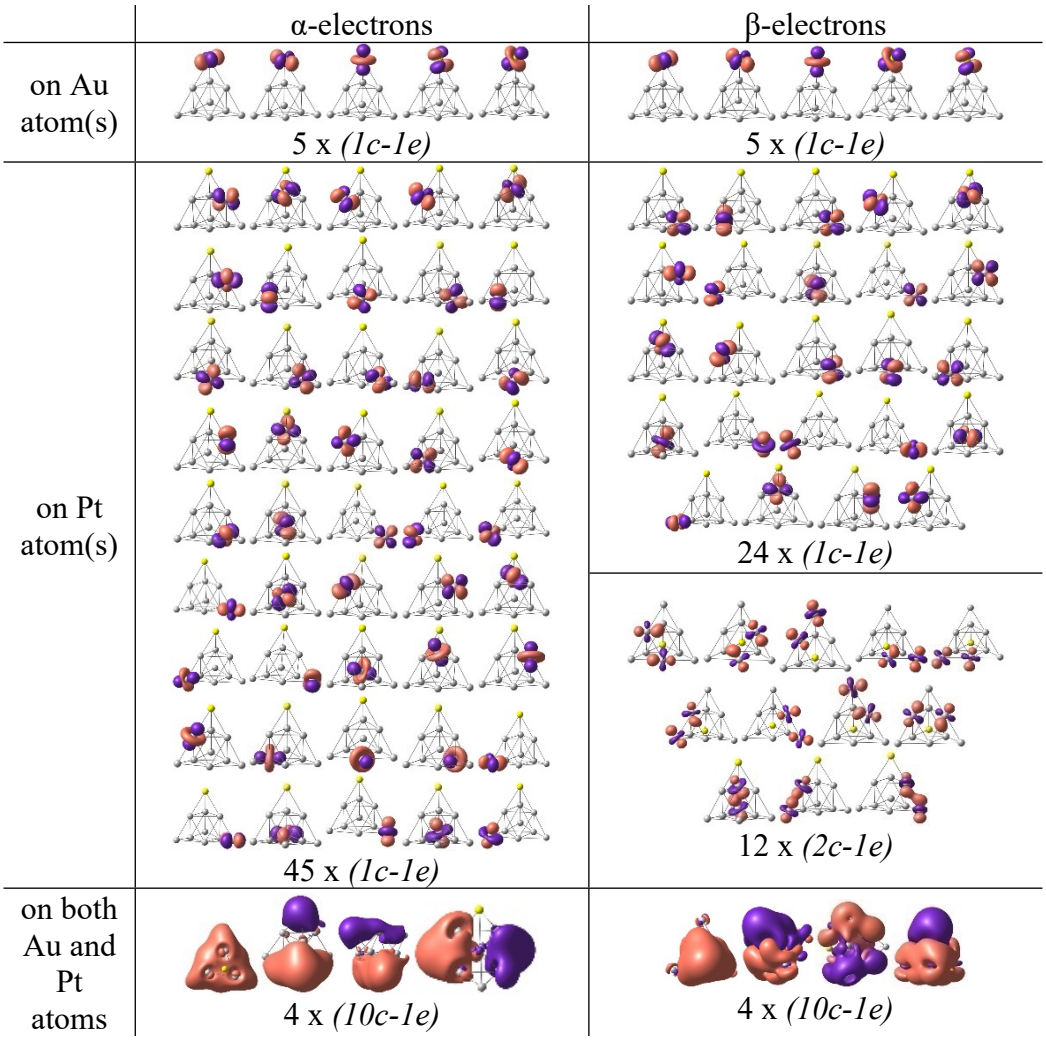



**Figure S13**: AdNDP analysis showing muti-center bonds in the **$AuPt_9^{2+}$.A** cluster at 10-et state, calculated at B3PW91/ cc-pVTZ-PP theory level.

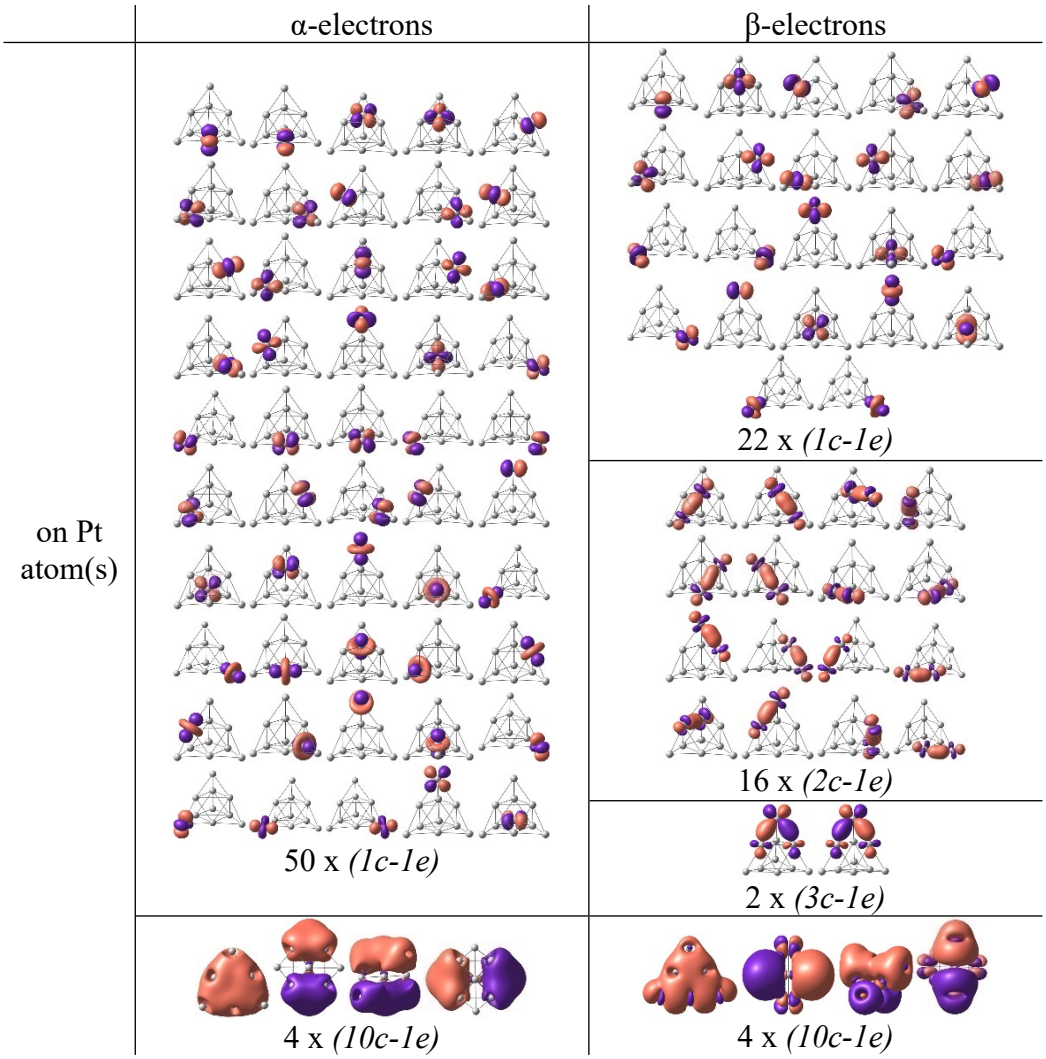
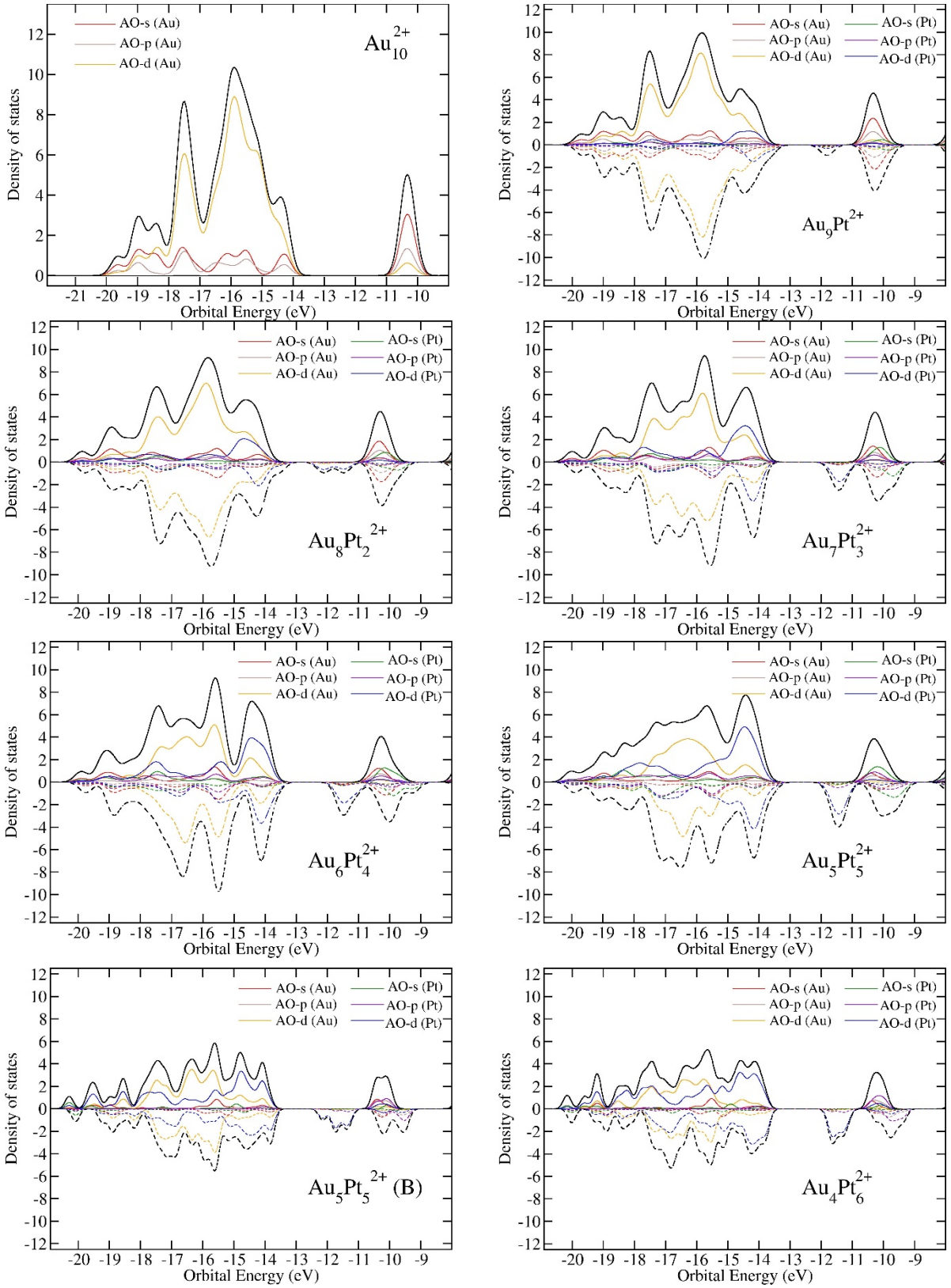



**Figure S14**: AdNDP analysis showing muti-center bonds in the **$Pt_{10}^{2+}$.A** cluster at 11-et state, calculated at B3PW91/ cc-pVTZ-PP theory level.


AO-s (Au)
AO-p (Au)
AO-d (Au)
AO-s (Pt)
AO-p (Pt)
AO-d (Pt)
Density of states
Orbital Energy (eV)
Au10 2+
Au9Pt2+
Au8Pt2 2+
Au7Pt3 2+
Au6Pt4 2+
Au5Pt5 2+
Au5Pt5 2+ (B)
Au4Pt6 2+

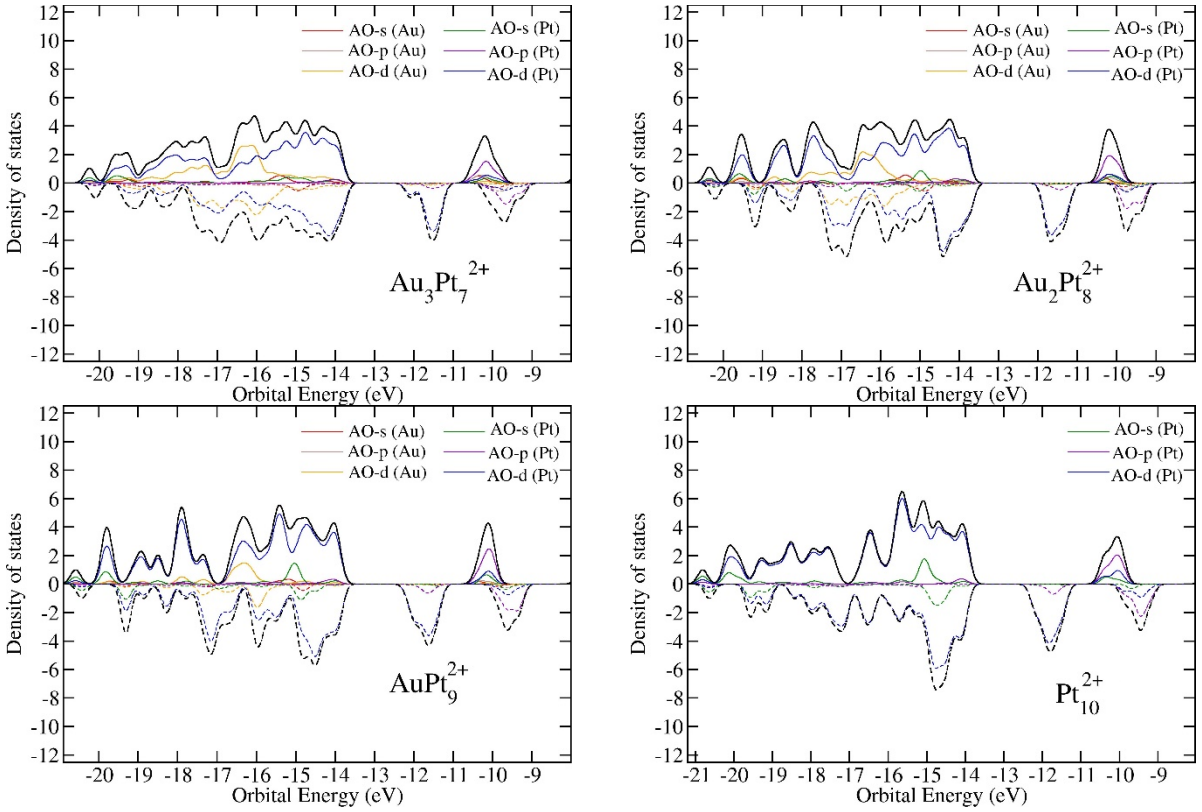
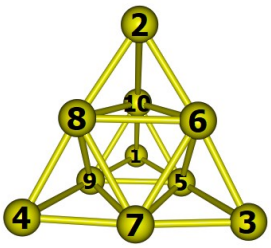
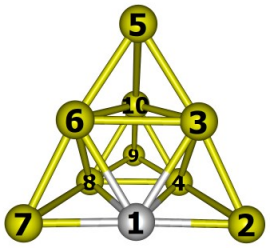
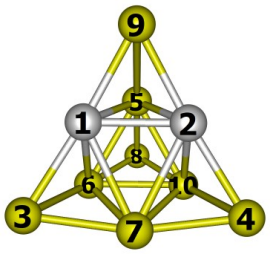
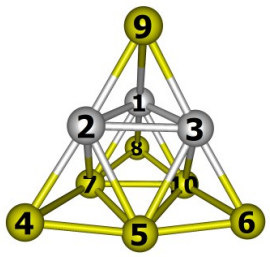
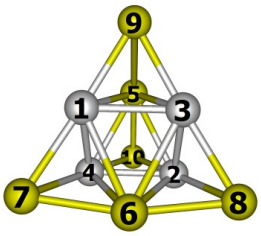



**Figure S15:** Calculated density of states (DOS) of $\mathbf{Au_xPt_y^{2+}}$ (x+y = 10) at B3PW91/aug-cc-pVTZ-PP level. Positive and negative DOS represent spin-up and spin-down electrons, respectively.

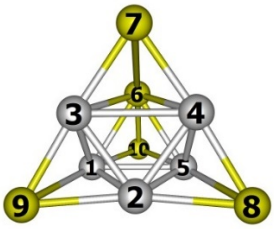
**Table S1:** Optimized geometrical shapes and Cartesian coordinates of the lowest-lying $Au_xPt_y^{2+}$ (x + y = 10) isomers calculated at B3PW91/aug-cc-pVTZ-PP method.

| Isomer | Coordinates | | | |
|---|---|---|---|---|
|  **$Au_{10}^{2+}$** ($T_d$) singlet | Au | -1.90919614 | 1.90919614 | 1.90919614 |
| | Au | 1.90919614 | -1.90919614 | 1.90919614 |
| | Au | 1.90919614 | 1.90919614 | -1.90919614 |
| | Au | -1.90919614 | -1.90919614 | -1.90919614 |
| | Au | -0.00000000 | 2.02642215 | 0.00000000 |
| | Au | 2.02642215 | -0.00000000 | 0.00000000 |
| | Au | -0.00000000 | 0.00000000 | -2.02642215 |
| | Au | 0.00000000 | -2.02642215 | -0.00000000 |
| | Au | -2.02642215 | 0.00000000 | 0.00000000 |
| | Au | 0.00000000 | -0.00000000 | 2.02642215 |
|  **$Au_9Pt^{2+}.A$** ($C_{2v}$) doublet | Pt | 0.00000000 | -0.00000000 | -1.90497415 |
| | Au | 0.00000000 | 2.63733420 | -1.95262215 |
| | Au | 1.45503911 | 1.44306111 | -0.00612800 |
| | Au | -1.45503911 | 1.44306111 | -0.00612800 |
| | Au | 2.70442921 | -0.00000000 | 1.90662515 |
| | Au | 1.45503911 | -1.44306111 | -0.00612800 |
| | Au | 0.00000000 | -2.63733420 | -1.95262215 |
| | Au | -1.45503911 | -1.44306111 | -0.00612800 |
| | Au | -2.70442921 | 0.00000000 | 1.90662515 |
| | Au | -0.00000000 | 0.00000000 | 1.99736915 |
|  **$Au_8Pt_2^{2+}.A$** ($C_s$) triplet | Pt | 1.14144281 | 0.81770330 | 1.25838410 |
| | Pt | 1.14144281 | 0.81770330 | -1.25838410 |
| | Au | 1.14144281 | -1.44589787 | 2.68187220 |
| | Au | 1.14144281 | -1.44589787 | -2.68187220 |
| | Au | -1.15710836 | 1.63808536 | 0.00000000 |
| | Au | -1.18545936 | -0.86639583 | 1.42614911 |
| | Au | 1.16466782 | -1.76958090 | 0.00000000 |
| | Au | -3.31907953 | -0.02144677 | 0.00000000 |
| | Au | 1.14556481 | 3.16282448 | 0.00000000 |
| | Au | -1.18545936 | -0.86639583 | -1.42614911 |
|  **$Au_7Pt_3^{2+}.A$** ($C_{3v}$) quartet | Pt | 1.29498210 | -0.74765806 | 1.14725809 |
| | Pt | -0.00000009 | 1.49531657 | 1.14725809 |
| | Pt | -1.29498201 | -0.74765822 | 1.14725809 |
| | Au | 0.00000000 | 3.10231624 | -0.99291807 |
| | Au | -1.44459311 | 0.83403606 | -1.25428709 |
| | Au | -2.68668459 | -1.55115797 | -0.99291807 |
| | Au | 1.44459289 | 0.83403645 | -1.25428709 |
| | Au | 2.68668459 | -1.55115797 | -0.99291807 |
| | Au | 0.00000000 | 0.00000010 | 3.34340826 |
| | Au | 0.00000022 | -1.66807222 | -1.25428709 |



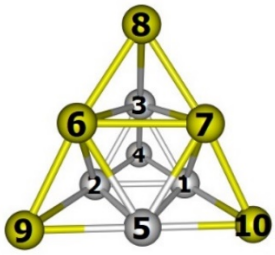

**$Au_6Pt_4^{2+}$.A**
($D_{2d}$)
quintet

| | | | |
|---|---|---|---|
| Pt | 1.29483810 | 1.29483810 | 0.00000000 |
| Pt | -1.29483810 | -1.29483810 | 0.00000000 |
| Pt | -1.29483810 | 1.29483810 | 0.00000000 |
| Pt | 1.29483810 | -1.29483810 | 0.00000000 |
| Au | 0.00000000 | 0.00000000 | 2.26016317 |
| Au | 0.00000000 | 0.00000000 | -2.26016317 |
| Au | 2.66886321 | 0.00000000 | -1.87859514 |
| Au | -2.66886321 | 0.00000000 | -1.87859514 |
| Au | 0.00000000 | 2.66886321 | 1.87859514 |
| Au | 0.00000000 | -2.66886321 | 1.87859514 |



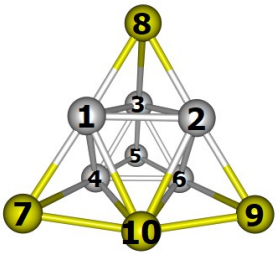

**$Au_5Pt_5^{2+}$.A**
($C_{2v}$)
sextet

| | | | |
|---|---|---|---|
| Pt | -1.52136112 | 1.29029010 | -0.01516100 |
| Pt | 0.00000000 | 0.00000000 | -1.65814813 |
| Pt | -1.52136112 | -1.29029010 | -0.01516100 |
| Pt | 1.52136112 | -1.29029010 | -0.01516100 |
| Pt | 1.52136112 | 1.29029010 | -0.01516100 |
| Au | 0.00000000 | 0.00000000 | 2.09950616 |
| Au | -0.00000000 | -2.66868620 | 1.69694013 |
| Au | 2.83403722 | -0.00000000 | -1.89817514 |
| Au | -2.83403722 | 0.00000000 | -1.89817514 |
| Au | 0.00000000 | 2.66868620 | 1.69694013 |



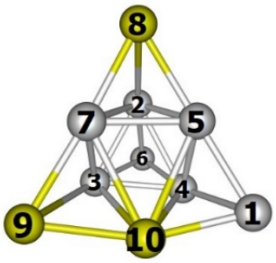

**$Au_5Pt_5^{2+}$.B**
($C_s$)
sextet

| | | | |
|---|---|---|---|
| Pt | 0.01264400 | 1.39250311 | 1.29322510 |
| Pt | 0.01264400 | 1.39250311 | -1.29322510 |
| Pt | -1.88017814 | 0.09212801 | 0.00000000 |
| Pt | -1.79734514 | 2.65057320 | -0.00000000 |
| Pt | 1.86005114 | 0.10289601 | -0.00000000 |
| Au | 0.01264400 | -1.52859812 | -1.44141611 |
| Au | 0.01264400 | -1.52859812 | 1.44141611 |
| Au | -2.00763016 | -2.60502820 | 0.00000000 |
| Au | 1.87591914 | 0.05144700 | -2.67775920 |
| Au | 1.87591914 | 0.05144700 | 2.67775920 |



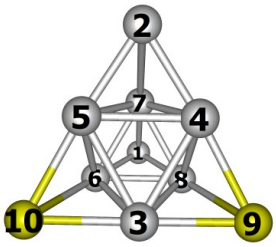

**$Au_4Pt_6^{2+}$.A**
($C_s$)
septet

| | | | |
|---|---|---|---|
| Pt | 1.08191108 | -0.79568106 | 1.29798410 |
| Pt | 1.08191108 | -0.79568106 | -1.29798410 |
| Pt | 1.14878909 | 1.62064913 | 0.00000000 |
| Pt | -1.06880508 | 0.85748406 | 1.31265310 |
| Pt | -0.93999007 | 3.02964323 | 0.00000000 |
| Pt | -1.06880508 | 0.85748406 | -1.31265310 |
| Au | -1.06880508 | -1.47201911 | 2.67873320 |
| Au | 3.26846125 | -0.05480600 | 0.00000000 |
| Au | -1.06880508 | -1.47201911 | -2.67873320 |
| Au | -1.36288810 | -1.71462513 | -0.00000000 |



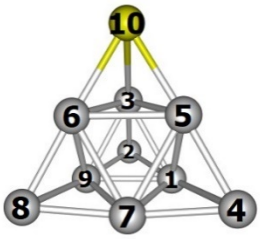

**$Au_3Pt_7^{2+}$.A**
($C_1$)
septet

| | | | |
|---|---|---|---|
| Pt | 1.64118924 | -1.49645925 | -2.20534308 |
| Pt | -1.81442278 | -0.56948653 | 0.68856613 |
| Pt | 0.45863957 | 0.30807548 | 1.83011522 |
| Pt | 0.82764889 | -1.71002417 | 0.17787910 |
| Pt | -0.60946049 | -0.42474314 | -1.65762304 |
| Pt | -0.49050561 | -2.01063842 | 2.31353526 |
| Pt | -0.65384360 | 1.72928908 | -0.20001093 |
| Au | -2.92398788 | 0.90690707 | -1.25724001 |
| Au | 1.52805878 | 2.63519622 | 1.00440916 |
| Au | 2.02857306 | 0.57904839 | -0.68229897 |



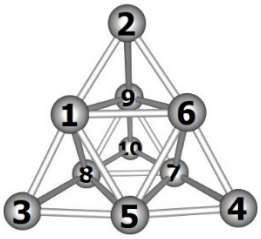

**$Au_2Pt_8^{2+}$.A**
($C_{2v}$)
nonet

| | | | |
|---|---|---|---|
| Pt | 0.00000000 | 2.55494218 | 1.82919213 |
| Pt | -0.00000000 | -2.55494218 | 1.82919213 |
| Pt | -0.00000000 | -0.00000000 | -1.89513314 |
| Pt | 1.34354210 | -1.39648710 | 0.03267100 |
| Pt | -1.34354210 | -1.39648710 | 0.03267100 |
| Pt | -1.34354210 | 1.39648710 | 0.03267100 |
| Pt | 0.00000000 | 0.00000000 | 1.91763214 |
| Pt | 1.34354210 | 1.39648710 | 0.03267100 |
| Au | 2.62910219 | -0.00000000 | -1.88166114 |
| Au | -2.62910219 | 0.00000000 | -1.88166114 |




**$AuPt_9^{2+}$.A**
($C_{3v}$)
dectet

| | | | |
|---|---|---|---|
| Pt | 1.30834417 | 0.75537292 | -1.18750708 |
| Pt | -0.00000010 | 2.96050021 | -1.01376208 |
| Pt | -0.00000005 | 1.56040611 | 1.09768408 |
| Pt | 2.56386844 | -1.48025002 | -1.01376208 |
| Pt | 1.35135136 | -0.78020301 | 1.09768408 |
| Pt | -1.35135130 | -0.78020310 | 1.09768408 |
| Pt | 0.00000005 | -1.51074575 | -1.18750708 |
| Pt | -2.56386834 | -1.48025020 | -1.01376208 |
| Pt | -1.30834422 | 0.75537283 | -1.18750708 |
| Au | 0.00000000 | 0.00000000 | 3.26884623 |




**$Pt_{10}^{2+}$**
($C_1$)
11-et

| | | | |
|---|---|---|---|
| Pt | 0.00000000 | 0.00000000 | -1.72233712 |
| Pt | 0.00000000 | 2.53834418 | -1.89170114 |
| Pt | -0.00000000 | -2.53834418 | -1.89170114 |
| Pt | -2.59671018 | 0.00000000 | 1.71971012 |
| Pt | -1.30402909 | -1.48296211 | 0.06612600 |
| Pt | -1.30402909 | 1.48296211 | 0.06612600 |
| Pt | 0.00000000 | 0.00000000 | 1.80181613 |
| Pt | 1.30402909 | -1.48296211 | 0.06612600 |
| Pt | 1.30402909 | 1.48296211 | 0.06612600 |
| Pt | 2.59671018 | -0.00000000 | 1.71971012 |