Supporting Information

New insight into electronic shell of $\operatorname{Au}_{38}(\operatorname{SR})_{24}$: a superatomic molecule

by

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Figure S1. (a) Geometry (Au: yellow; S: pink; H: white) and AdNDP localized natural bonding orbitals of $Au_{25}(SH)_{18}$: (b) lone pairs; (c) localized AuS and SH bonds (partly); (d) delocalized bonding. Labelled are occupancy numbers (ON). Au(5d) LPs (ON = 1.90 - 1.98 |e|) are not shown.



Computational details:

Geometries of Au₂₅(SH)₁₈⁻ and Au₃₈(SH)₂₄ are optimized by density functional theory (DFT) calculations performed on the Gaussian 09 package^{s1} using the generalized gradient approximation method developed by Perdew, Burke, and Ernzerhof (PBE)^{s2} with the LANL2DZ basis set for Au and 6-31G* for other elements (PBE/LANL2DZ/6-31G*). Natural bonding analysis by AdNDP is also at the PBE/LANL2DZ/6-31G* level. For similarity and clarity, a minimal LanL1MB basis set is used for the Kohn-Sham MO diagrams of Au₂₃⁽⁺⁹⁾ (and 3-21G for F₂). If using a larger LanL2DZ basis set, the overall framework of the Kohn-Sham MO diagrams for the Au(6*s*) orbitals does not change, but the σ_s , σ^*_s and $\pi_{px,py}$ MOs (Fig. 2a) will be lower than the MOs of Au(5*d*) orbitals. For clarity, the MOs of Au(5*d*) orbitals are excluded in the MO diagrams. Molecular orbital (MO) visualization is performed using MOLEKEL 5.4.^{s3}

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(s3) U. Varetto, Molekel 5.4.0.8, Swiss National Supercomputing Centre, Manno (Switzerland).

Coordinates (in angstrom):

<u>Au₂₅(SH)₁₈-</u>			
Au	0.000000	0.000000	0.000000
Au	1.535281	-0.779939	2.221473
Au	-0.092467	1.718166	2.222518
Au	-1.441175	-0.939735	2.222620
Au	2.393435	1.362745	0.572890
Au	-0.014139	-2.752427	0.573189
Au	-2.377371	1.389344	0.574874
Au	2.377371	-1.389344	-0.574874
Au	0.014139	2.752427	-0.573189
Au	-2.393435	-1.362745	-0.572890
Au	1.441175	0.939735	-2.222620
Au	0.092467	-1.718166	-2.222518
Au	-1.535281	0.779939	-2.221473

Au	2.744972	1.750761	3.723147
Au	0.145874	-3.253670	3.721129
Au	-2.890162	1.496851	3.718536
Au	4.634364	-0.612045	1.638670
Au	-1.787552	4.324748	1.643504
Au	-2.837452	-3.720339	1.639223
Au	2.837452	3.720339	-1.639223
Au	1.787552	-4.324748	-1.643504
Au	-4.634364	0.612045	-1.638670
Au	2.890162	-1.496851	-3.718536
Au	-0.145874	3.253670	-3.721129
Au	-2.744972	-1.750761	-3.723147
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S	-2.886715	-0.831161	4.240759
S	4.937534	0.846400	3.495140
S	-1.738519	-4.696527	3.512222
S	-3.196342	3.850115	3.503213
S	4.211234	3.010652	0.174931
S	0.475596	-5.154721	0.164719
S	-4.697527	2.177647	0.158633
S	4.697527	-2.177647	-0.158633
S	-0.475596	5.154721	-0.164719
S	-4.211234	-3.010652	-0.174931
S	3.196342	-3.850115	-3.503213
S	1.738519	4.696527	-3.512222
S	-4.937534	-0.846400	-3.495140
S	2.886715	0.831161	-4.240759
S	-0.724480	-2.904673	-4.247626
S	-2.162452	2.088912	-4.238558
Η	1.630255	-1.229884	5.134899
Η	0.247325	2.004115	5.134049
Η	-1.875443	-0.793986	5.134933
Η	5.434182	1.889749	2.793923
Η	-1.086367	-5.661027	2.825222
Η	-4.349813	3.764842	2.803766
Η	4.334943	-3.250125	0.578659
Η	0.639146	5.388361	0.561477
Η	-4.985739	-2.178253	0.554704
Н	4.985739	2.178253	-0.554704
Н	-0.639146	-5.388361	-0.561477
Н	-4.334943	3.250125	-0.578659
Н	4.349813	-3.764842	-2.803766
Н	1.086367	5.661027	-2.825222

Н	-5.434182	-1.889749	-2.793923
Н	1.875443	0.793986	-5.134933
Н	-0.247325	-2.004115	-5.134049
Н	-1.630255	1.229884	-5.134899
<u>Au₃₈(SI</u>	<u>H)</u> ₂₄		
Au	0.000000	0.000000	2.070462
Au	0.000000	0.000000	-2.070462
Au	0.000000	1.934853	0.000000
Au	1.675632	-0.967426	0.000000
Au	-1.675632	-0.967426	0.000000
Au	2.351470	1.415744	1.516562
Au	-2.401805	1.328561	1.516562
Au	0.050335	-2.744304	1.516562
Au	2.401805	1.328561	-1.516562
Au	-2.351470	1.415744	-1.516562
Au	-0.050335	-2.744304	-1.516562
Au	-0.104092	2.800769	2.698880
Au	2.477583	-1.310238	2.698880
Au	-2.373491	-1.490531	2.698880
Au	0.104092	2.800769	-2.698880
Au	2.373491	-1.490531	-2.698880
Au	-2.477583	-1.310238	-2.698880
Au	1.413484	1.053991	4.259511
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Au	0.206041	-1.751108	4.259511
Au	1.619525	0.697117	-4.259511
Au	-1.413484	1.053991	-4.259511
Au	-0.206041	-1.751108	-4.259511
Au	-4.262278	-2.460828	0.000000
Au	0.000000	4.921655	0.000000
Au	4.262278	-2.460828	0.000000
Au	2.756942	3.777156	3.553801
Au	-4.649584	0.499004	3.553801
Au	1.892642	-4.276160	3.553801
Au	4.649584	0.499004	-3.553801
Au	-2.756942	3.777156	-3.553801
Au	-1.892642	-4.276160	-3.553801
Au	-0.248811	3.314211	5.659737
Au	2.994596	-1.441629	5.659737
Au	-2.745785	-1.872582	5.659737
Au	0.248811	3.314211	-5.659737
Au	2.745785	-1.872582	-5.659737
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S	1.046297	5.101470	-2.180338
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S	2.148694	1.970032	-6.368381
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Н	5.347319	1.515634	-0.895177
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Н	0.056888	5.862397	-2.771694
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Η	-3.962616	1.309189	-5.799947
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Η	2.328153	4.552143	6.365339
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Н	2.778195	-4.292311	6.365339
Н	5.106348	-0.259832	-6.365339
Н	-2.328153	4.552143	-6.365339
Н	-2.778195	-4.292311	-6.365339