Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Exploring the Electronic Properties and Cation Complexation of Polyoxoaurates $[Au^{III}_4X_4O_m]^{n-}$ (X = Si^{IV}, P^{V}, Ge^{IV}, As^{V}, Se^{IV}) from Quantum Chemical Calculations

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Table S1 Optimized geometric parameters of the averaged bond lengths (Å) in Au_4Se_4 with the coordinated cation

M	Li	Na	K	Rb
Au–O_{b1}	1.998	1.995	1.992	1.991
Au–O_{b2}	2.033	2.038	2.040	2.042
Au–Au	3.331	3.332	3.332	3.336
Se–O_t	1.687	1.689	1.690	1.691
Se–O_{b2}	1.781	1.780	1.780	1.780
M–O_{b1}	2.041	2.381	2.719	2.877

Table S2 Frontier molecular orbital energy (eV) of M-Au_4Se_4

M	Li	Na	K	Rb
HOMO	-5.889	-5.657	-5.426	-5.367
LUMO	-3.716	-3.610	-3.534	-3.513
ΔE(H-L)	2.173	2.047	1.892	1.854

Table S3 Interaction energy decomposition analysis terms and complexation energy (in kcal·mol^{-1}) for Au_4Se_4 with Li^+, Na^+, K^+ and Rb^+

M	Li	Na	K	Rb
electronic interactions				
ΔE_{Pauli}	27.30	24.95	26.73	24.70
ΔE_{elst}	-328.38	-307.01	-283.25	-272.29
ΔE_{oi}	-58.44	-37.19	-33.75	-33.11
ΔE	-359.52	-319.24	-290.27	-280.70
solvation energies				
MAu_4As_4	-349.56	-368.96	-381.97	-388.39
M	-93.65	-89.48	-80.49	-76.16
Au_4Se_4	-579.81	-577.44	-576.22	-575.40
$\Delta E_{Solvation}$	323.90	297.96	274.74	263.17
$\Delta E + \Delta E_{Solvation}$	-35.62	-21.28	-15.53	-17.53

Table S4 Interaction energy decomposition analysis terms and complexation energy (in kcal·mol^{-1}) for Au_4Se_4 with Li^+, Na^+, K^+ and Rb^+ calculated by the meta-hybrid M06 functional and CAM-B3LYP functional

M	Li*	Na*	K	Rb
	electronic interactions			
ΔE_{Pauli}	24.80 (22.13)	22.73 (19.77)	22.45	19.71
ΔE_{elst}	-336.31 (-334.66)	-312.85 (-311.85)	-287.93	-276.16
ΔE_{oi}	-52.40 (-55.25)	-32.53 (-34.45)	-29.90	-29.24
ΔE	-363.91 (-367.78)	-322.65 (-326.53)	-295.38	-285.69
	solvation energies			
MAu_4As_4	-370.49 (-366.40)	-389.45 (-385.64)	-403.03	-408.84
M	-93.65 (-93.66)	-89.48 (-89.48)	-80.48	-79.24
Au_4Se_4	-600.85 (-596.84)	-598.34 (-594.28)	-596.85	-596.00
$\Delta E_{Solvation}$	324.01 (324.1)	298.37 (298.12)	274.3	266.4
$\Delta E + \Delta E_{Solvation}$	-39.90 (-43.68)	-24.28 (-28.41)	-21.08	-19.29
$\Delta E_{Complexation}$	-41.89 (-45.05)	-20.22 (-24.12)	-12.68	-9.33

*The values in parentheses are the results of CAM-B3LYP functional calculation

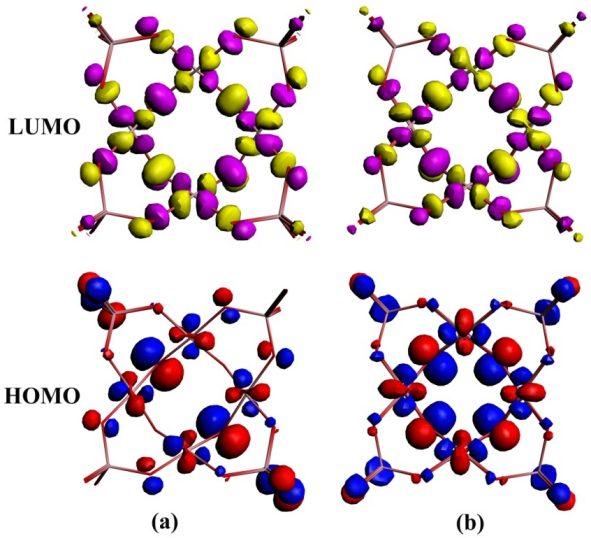

Figure S1. Frontier molecular orbitals for Au_4Si_4 (a) and Au_4Se_4 (b). (The frontier molecular orbitals of Au_4Ge_4 and Au_4P_4 are similar to that of Au_4Si_4 and Au_4As_4).

Table S5. Optimized Cartesian coordinates of the molecular models considered in this work

$[Au_4Si_4O_{20}]^{12-}$ (BP86/ZORA-scalar/TZ2P/COSMO)

Atom	X	Y	Z
Au	1.652488	-0.277147	1.652900
O	1.385401	0.780761	3.375619
O	-0.000280	-1.359468	2.009628
O	2.014666	-1.352760	0.000000
O	3.368733	0.791330	1.384878
Si	-0.000247	0.659907	4.347132
Au	-1.652257	-0.276534	1.651612
Au	1.652488	-0.277147	-1.652900
O	-0.004379	-0.680085	5.273928
O	0.000560	2.031906	5.241836
O	-1.381760	0.786827	3.370449
O	-2.014324	-1.355287	0.000000
O	-0.000280	-1.359468	-2.009628
O	1.385401	0.780761	-3.375619
Au	-1.652257	-0.276534	-1.651612
Si	-0.000247	0.659907	-4.347132
O	-3.369028	0.790837	-1.384368
O	-1.381760	0.786827	-3.370449
O	-0.004379	-0.680085	-5.273928
O	-5.291397	-0.646721	0.000000
O	5.289534	-0.647552	0.000000
Si	-4.343503	0.677915	0.000000
O	-5.218731	2.064207	0.000000
O	-3.369028	0.790837	1.384368
Si	4.342460	0.677805	0.000000
O	5.219109	2.063328	0.000000
O	3.368733	0.791330	-1.384878
O	0.000560	2.031906	-5.241836

$[Au_4Ge_4O_{20}]^{12-}$ (BP86/ZORA-scalar/TZ2P/COSMO)

Atom	X	Y	Z
Au	-1.693670	-1.685906	-0.275445
O	-3.471603	-1.495293	0.692736
O	-2.026189	0.000000	-1.314341
O	0.000000	-2.024261	-1.298234
O	-1.498735	-3.447181	0.721710
Ge	-4.503918	0.000000	0.424273
Au	-1.693670	1.685906	-0.275445

Au	1.693670	-1.685906	-0.275445
O	-5.381528	0.000000	-1.101551
O	-5.595678	0.000000	1.816082
O	-3.471603	1.495293	0.692736
O	0.000000	2.024261	-1.298234
O	2.026189	0.000000	-1.314341
O	3.471603	-1.495293	0.692736
Au	1.693670	1.685906	-0.275445
Ge	4.503918	0.000000	0.424273
O	1.498735	3.447181	0.721710
O	3.471603	1.495293	0.692736
O	5.381528	0.000000	-1.101551
O	0.000000	5.397774	-1.020411
O	0.000000	-5.397774	-1.020411
Ge	0.000000	4.480828	0.481232
O	0.000000	5.536578	1.900128
O	-1.498735	3.447181	0.721710
Ge	0.000000	-4.480828	0.481232
O	0.000000	-5.536578	1.900128
O	1.498735	-3.447181	0.721710
O	5.595678	0.000000	1.816082

$[Au_4P_4O_{20}]^{8-}$ (BP86/ZORA-scalar/TZ2P/COSMO)

Atom	X	Y	Z
Au	1.618363	1.609293	-0.303750
O	3.311441	1.303838	0.820151
O	1.995307	0.000539	-1.408555
O	0.001072	1.982860	-1.395018
O	1.304935	3.288426	0.838592
P	4.249459	-0.000098	0.700609
Au	1.618187	-1.609405	-0.305774
Au	-1.618187	1.609405	-0.305774
O	5.068119	0.003609	-0.592897
O	5.104546	-0.002266	1.977496
O	3.313984	-1.306321	0.814796
O	-0.001072	-1.982860	-1.395018
O	-1.995307	-0.000539	-1.408555
O	-3.313984	1.306321	0.814796
Au	-1.618363	-1.609293	-0.303750
P	-4.249459	0.000098	0.700609
O	-1.304935	-3.288426	0.838592
O	-3.311441	-1.303838	0.820151
O	-5.068119	-0.003609	-0.592897

O	-0.000751	-5.052692	-0.562396
O	0.000751	5.052692	-0.562396
P	0.000006	-4.225928	0.725829
O	0.000615	-5.073315	2.007885
O	1.305276	-3.288703	0.836551
P	-0.000006	4.225928	0.725829
O	-0.000615	5.073315	2.007885
O	-1.305276	3.288703	0.836551
O	-5.104546	0.002266	1.977496

$[Au_4As_4O_{20}]^{8-}$ (BP86/ZORA-scalar/TZ2P/COSMO)

Atom	X	Y	Z
Au	0.006882	2.347577	-0.295569
O	1.405628	3.442792	0.714963
O	1.430601	1.430818	-1.336946
O	-1.421695	1.422759	-1.323040
O	-1.386093	3.424235	0.743181
As	3.138551	3.136781	0.466093
Au	2.348951	0.007066	-0.296833
Au	-2.349005	-0.007033	-0.300253
O	3.716238	3.711564	-1.013700
O	3.873582	3.877367	1.799595
O	3.446881	1.403891	0.713705
O	1.419994	-1.420149	-1.323333
O	-1.430734	-1.431964	-1.338972
O	-3.446261	-1.404824	0.710070
Au	-0.007180	-2.347423	-0.295274
As	-3.137996	-3.137825	0.468644
O	1.386265	-3.423458	0.742069
O	-1.404618	-3.442569	0.718438
O	-3.705481	-3.721159	-1.011607
O	3.703348	-3.703624	-0.976192
O	-3.702130	3.713014	-0.970558
As	3.120355	-3.120168	0.497837
O	3.850456	-3.852746	1.838561
O	3.428294	-1.386427	0.737767
As	-3.120407	3.120315	0.499837
O	-3.852696	3.844234	1.845344
O	-3.429086	1.386106	0.734080
O	-3.877508	-3.870725	1.804940

$[Au_4Se_4O_{20}]^{4-}$ (BP86/ZORA-scalar/TZ2P/COSMO)

Atom	X	Y	Z
Au	-0.163960	2.518271	0.091830
O	-1.507188	3.474922	-1.107424
O	-1.687164	1.685326	1.074360
O	1.194359	1.698235	1.300261
O	1.345586	3.484315	-0.883133
Se	-3.224555	3.222568	-0.632237
Au	-2.517993	0.163223	0.087860
Au	2.176686	0.179621	0.460487
O	-3.957764	3.965447	-1.936683
O	-3.466635	1.507035	-1.118351
O	-1.697455	-1.190808	1.301625
O	1.185466	-1.184581	1.526321
O	3.289731	-1.325150	-0.351943
Au	-0.179945	-2.176859	0.462693
Se	2.948035	-2.948031	0.347840
O	-1.532439	-3.302262	-0.569105
O	1.324453	-3.289506	-0.349623
Se	-3.246925	-2.965431	-0.137718
O	-3.990478	-3.900193	-1.306185
O	-3.477875	-1.347534	-0.890706
Se	2.966927	3.246614	-0.139324
O	3.896840	3.990711	-1.311742
O	3.297530	1.532239	-0.576331
O	3.870921	-3.872495	-0.694228

$[NaAu_4As_4O_{20}]^{7-}$ (BP86/ZORA-scalar/TZ2P/COSMO)

Atom	X	Y	Z
Au	-0.000230	2.355764	-0.216660
O	1.393281	3.431717	0.808777
O	1.414302	1.414602	-1.261952
O	-1.413813	1.414746	-1.263324
O	-1.392900	3.430021	0.813127
As	3.130097	3.130161	0.561855
Au	2.355526	0.000011	-0.216212
Au	-2.356038	-0.000032	-0.219451
O	3.696899	3.692037	-0.925372
O	3.863548	3.869976	1.893526
O	3.431123	1.393401	0.810740
O	1.414249	-1.414464	-1.262057
O	-1.413909	-1.414872	-1.262930
O	-3.431910	-1.393196	0.806566
Au	-0.000162	-2.355780	-0.216656

As	-3.129821	-3.130299	0.563688
O	1.393589	-3.431923	0.808240
O	-1.392772	-3.429921	0.813240
O	-3.690418	-3.702970	-0.921096
O	3.696690	-3.691854	-0.926602
O	-3.689586	3.702722	-0.922245
As	3.130313	-3.130320	0.560937
O	3.864183	-3.870388	1.892224
O	3.431296	-1.393605	0.810254
As	-3.129927	3.130419	0.563060
O	-3.867728	3.861318	1.897991
O	-3.432205	1.393339	0.806258
O	-3.866921	-3.859705	1.899993
Na	0.000709	-0.000239	-2.554391