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

SUPPORTING INFORMATION

On the structure of the thiolated Au_6Ag_7 cluster

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PART I

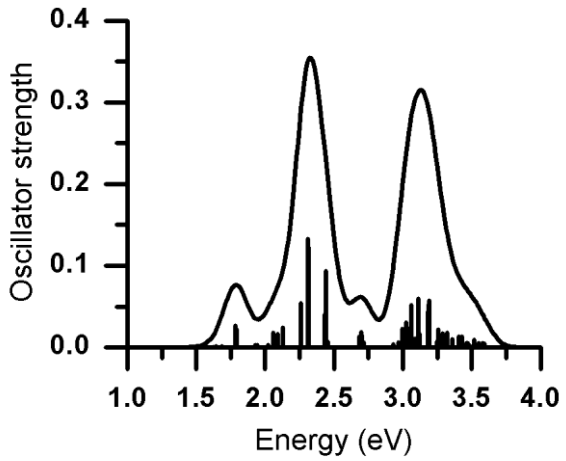


Figure S1. Calculated optical absorption spectrum for $[Ag_{13}Au_{12}(SH)_{18}]^-$ cluster in good agreement with the calculations reported in Fig. 1 of the reference: C. M Aitkens, *J. Phys. Chem. C* 2008, **112**, 19797-19800.

PART II

Table S1. Possible combinations for the $[Au_{13}(SR)_{10}]^+$ cluster.

No. core atoms	Ligands type	No. Atoms in ligands
4	1 level-9	9
5	2 level-4	8
5	1 level-2, 1 level-6	8
5	1 level-3, 1 level-5	8
6	2 level-2, 1 level-3	7

The ligands type follows the notation: Level-1 is a monomer motif; level-2 is a dimer motif and so on.

Table S2. Relative total energy (E_{rel}), core composition and HOMO-LUMO (HL) gap of **Iso1- Iso9** isomers.

Isomer	Core	E_{rel}, eV	HL gap, eV
Iso1	Ag_6	0.00	1.68
Iso2	Ag_4	0.33	1.59
Iso3	$AuAg_3$	0.41	1.62
Iso4	Au_2Ag_2	0.49	1.62
Iso5	Ag_4	0.51	1.57
Iso6	$AuAg_3$	0.58	1.68
Iso7	Au_2Ag_2	0.73	1.66
Iso8	Au_4	1.06	1.49
Iso9	Au_6	1.39	1.33

PART III

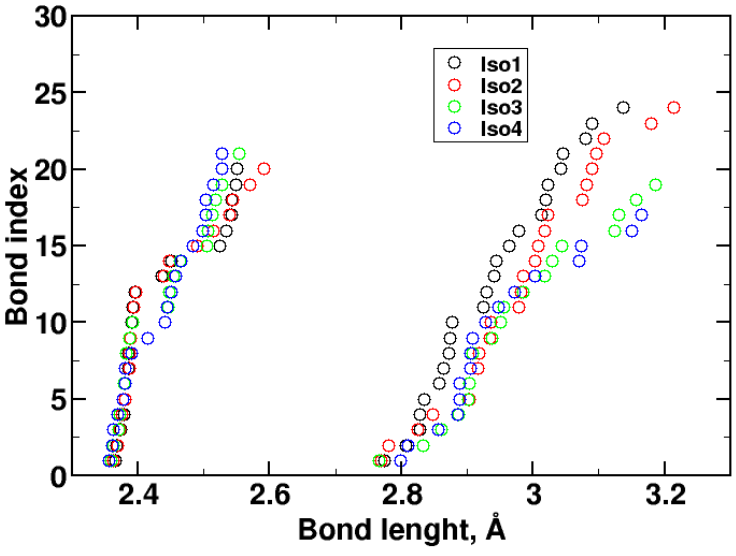
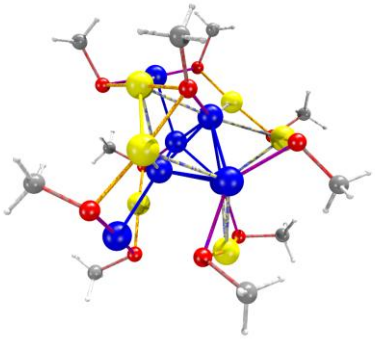


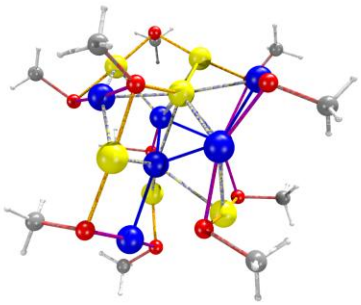
Figure S2. Bond length distribution of **Iso1-Iso4**.

PART IV

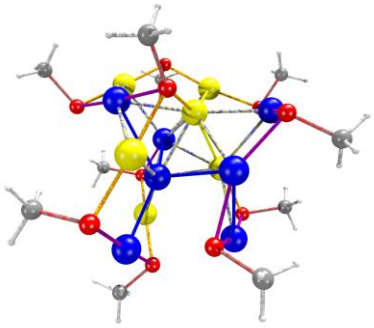
Iso5



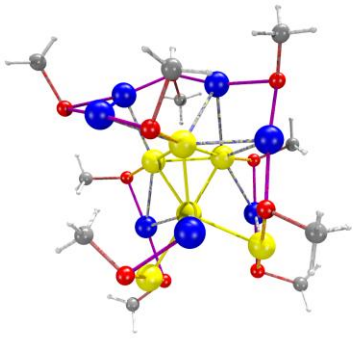
Iso6



Iso7



Iso8



Iso9

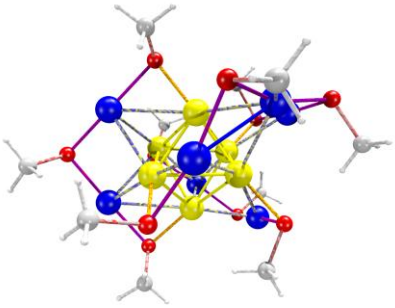


Figure S3. Structures of **Iso5-Iso9** isomers of the $[Au_6Ag_7(SCH_3)_{10}]^+$ cluster with higher energies. Their relative energies with respect to **Iso1** are shown in Table S2.

PART V

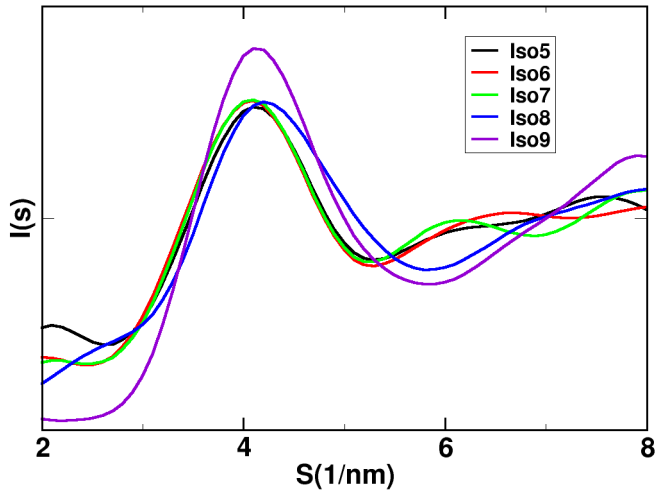


Figure S4. Simulated XRD patterns of **Iso5-Iso9.** The calculated XRD`s curves were obtained with a modified program of the provided by Dr. Yong Pei. **Iso9** curve resembles monometallic $[Au_{13}(SCH_3)_{10}]^+$ cluster curve. More information about the Debye formula used is in the reference: Y. Pei, R. Pal, C. Liu, Y. Gao, Z. Zhang and X-C. Zeng, *J. Am. Chem. Soc.* 2012, **134**, 3015-3024.

PART VI

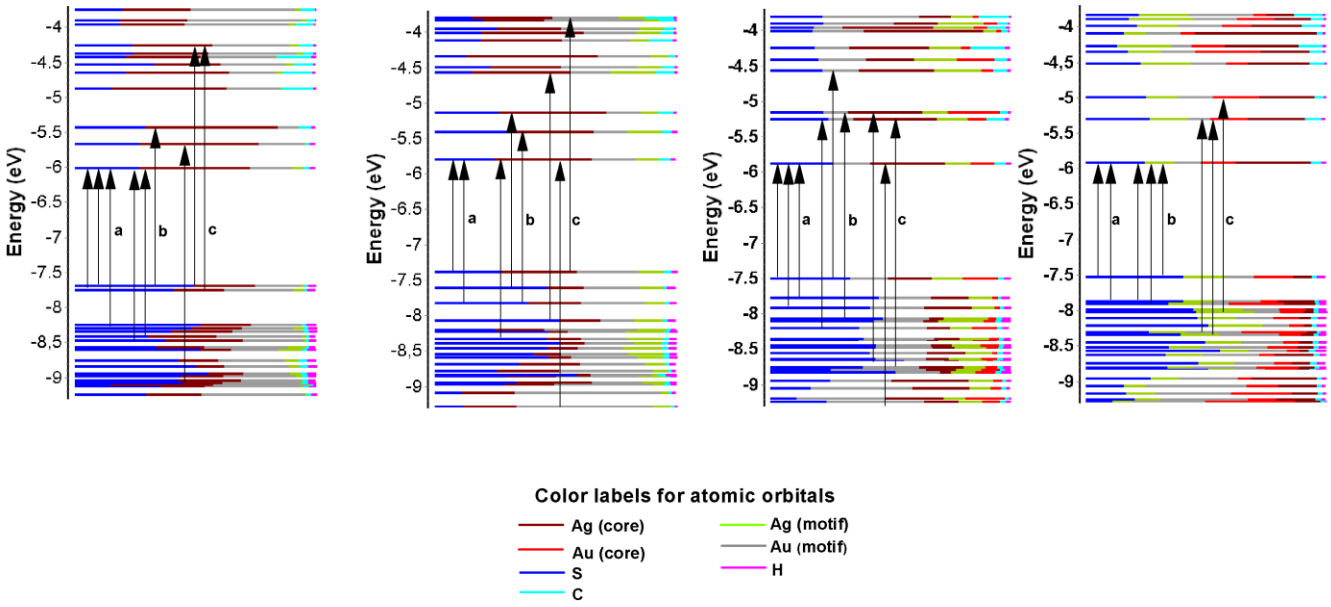


Figure S5. Kohn-Sham molecular orbital (MO) energies and the atomic orbital components in each MO for **Iso1-Iso4**. The electronic transitions of the three major peaks displayed in Figure 3 are depicted.

PART VII

Table S3. Excitation energy, oscillator strength, electronic transitions, and relative contributions (in percentage) of the atomic orbitals to each molecular orbital for the major peaks shown in Fig. 3 of **Iso1-Iso4**.

	Peak	E (eV), E (nm)	Oscillator Strength	From ---> To (%)	Contribution weight S, Ag(core), Ag(motif), Au(core), Au(motif) -> S, Ag(core), Ag(motif), Au(core), Au(motif)
Iso1		1.77, (699.3)	0.0000	HOMO->LUMO (65%)	52, 28, 0, 0, 14 -> 23, 50, 8, 0, 16
				H-1->LUMO (30%)	48, 20, 5, 0, 22 -> 23, 50, 8, 0, 16
	a	1.91, (650.4)	0.0457	H-1->LUMO (59%)	48, 20, 5, 0, 22 -> 23, 50, 8, 0, 16
				HOMO->LUMO (25%)	52, 28, 0, 0, 14 -> 23, 50, 8, 0, 16
				H-3->LUMO(3%)	57, 16, 0, 0, 16 -> 23, 50, 8, 0, 16
	b	2.54, (487.4)	0.0474	H-6->LUMO(37%)	48, 24, 0, 0, 22 -> 23, 50, 8, 0, 16
				H-5->LUMO(34%)	44, 15, 0, 0, 33 -> 23, 50, 8, 0, 16
				HOMO->L+2(8%)	52, 28, 0, 0, 14 -> -> 23, 61, 0, 0,11
	c	3.52, (352.6)	0.0254	H-15->L+1(41%)	30, 7, 0, 0, 53 -> 24, 47, 0, 0, 25
				HOMO->L+8(12%)	52, 28, 0, 0, 14 -> -> 23, 20, 0, 0, 42
				H-1->L+8(9%)	48, 20, 5, 0, 22 -> 23, 20, 10, 0, 42
		4.20, (295.0)	0.0276	H-8->L+6(37%)	61, 7, 8, 0, 16 -> 19, 32, 0, 0, 41
				H-5->L+8(14%)	44, 15, 0, 0, 33 -> 23, 20, 0, 10, 42
				H-8->L+7(8%)	61, 7, 8, 0, 16 -> 26, 20, 0, 0, 45
Iso2	**a**	1.78, (665.9)	0.0437	HOMO->LUMO (83%)	32, 30, 12, 0, 21 -> 19, 39, 13, 23, 0
				H-2 -> LUMO(3%)	48, 16, 0, 21, 0 -> 19, 39, 13, 23, 0
		2.22, (559.4)	0.0622	HOMO -> L+1 (77%)	32, 30, 12, 0, 21 -> 24, 31, 20, 0, 19
				HOMO -> L+2 (3%)	32, 30, 12, 0, 21 -> 15, 44, 11, 0, 21
				H-1 -> L+2 (3%)	55, 12, 0, 18, 0 -> 15, 44, 11, 0, 21
	b	2.58, (480.5)	0.0375	H-6 -> LUMO (63%)	60, 0, 14, 17, 0 -> 19, 39, 13, 23, 0
				H-1 -> L+2 (15%)	55, 12, 0, 18, 0 -> 15, 44, 11, 0, 21
				H-2 ->L+1 (5%)	48, 16, 0, 21, 0 -> 24, 31, 20, 0, 19
	c	3.57, (347.6)	0.0239	H-3 ->L+3 (59%)	65, 0, 11, 11, 0 -> 17, 20, 15, 0, 40
				H-18 -> LUMO (8%)	14, 11, 0, 61, 0 -> 19, 39, 13, 23, 0
				HOMO -> L+10 (4%)	32, 30, 12, 0, 21 -> 20, 0, 19, 0, 61
Iso3	**a**	1.83, (678.9)	0.0477	HOMO-> LUMO(80%)	41, 14, 14, 12, 13 -> 21, 32, 15, 8, 18
				H-2 -> LUMO(4%)	51, 13, 11,0,18 -> 21, 32, 15, 8, 18
				H-1 -> LUMO (3%)	54, 13, 9, 0, 17-> 21, 32, 15, 8, 18
		2.51, (494.5)	0.0331	HOMO -> L+2 (65%)	41, 14, 14, 12, 13 -> 18, 10, 22, 24,17
				H-8 -> LUMO (9%)	51, 5, 12, 5, 20 -> 21, 32, 15, 8, 18
				H-6 -> L+6 (6%)	48, 5, 12, 0, 25 -> 24, 21, 12, 0, 37
	b	3.04, (408.2)	0.0424	H-5 -> L+1 (40%)	48, 6, 10, 5,24 -> 20, 25, 22, 7, 17
				HOMO -> L+3 (21%)	41, 14, 14, 12, 13 -> 18, 0, 36, 14, 25
				H-3 -> L+2 (12%)	55, 0, 18, 0, 16 -> 18, 10, 22, 24,17
	c	3.57, (346.9)	0.0175	H-12 -> L+2 (24%)	60, 0, 11, 0, 14 -> 18, 10, 22, 24,17
				H-21 -> LUMO (19%)	8, 15, 5, 23, 47 -> 21, 32, 15, 8, 18
				H-13 -> L+1 (14%)	49, 8, 11, 0, 21 -> 20, 25, 22, 7, 17
		4.18, (296.5)	0.0210	H-36 -> LUMO (38%)	7, 25, 10, 12, 39-> 21, 32, 15, 8, 18
				H-5 -> L+6 (8%)	48, 6, 10, 5,24 -> 24, 21, 12, 0, 37
				H-6 -> L+5 (7%)	48, 5, 12, 0, 25 -> 17, 20, 26, 0, 30
Iso4	**a**	1.81, (685.0)	0.0478	HOMO->LUMO (83%)	45, 10, 17, 13, 9 -> 22, 27, 22, 10, 13
				H-1 -> LUMO (5%)	51, 9, 14, 0, 16 -> 22, 27, 22, 10, 13
	b	2.05, (604.4)	0.0311	H-1->LUMO (70%)	51, 9, 14, 0, 16 -> 22, 27, 22,10, 13
				H-2->LUMO (17%)	46, 7, 15, 15, 10 -> 22, 27, 22, 10, 13
				HOMO->LUMO (2%)	45, 10, 17, 13, 9 -> 22, 27, 22, 10, 13
		2.50, (494.0)	0.0095	H-8 -> LUMO (78%)	46, 0, 18, 9, 19 -> 22, 27, 22,10, 13
				H-7 -> LUMO (9%)	37, 0, 19, 13, 22 -> 22, 27, 22,10, 13
	c	3.13, (395.9)	0.0433	H-7->L+1 (35%)	37, 0, 19, 13, 22 -> 23, 17, 25, 0, 16
				H-8->L+1 (19%)	46, 0, 18, 9, 19 -> 23, 17, 25, 0, 16
				H-4->L+2 (16%)	53, 0, 24, 7, 8 -> 18, 0, 29, 26, 21
		3.56, (348.0)	0.0210	H-22->LUMO (62%)	10, 6, 6, 34, 40 -> 18, 0, 29, 26, 21
				H-4->L+3 (7%)	53, 0, 24, 7, 8 -> 18, 0, 41, 14, 20
				H-3->L+3 (6%)	55, 0, 19, 6, 13 -> 18, 0, 41, 14, 20

PART VIII

Relaxed Cartesian coordinates of **Iso1-Iso4**.

Coordinates **Iso1**.

Ag	-1.922099	0.655387	0.743552
Ag	1.007576	1.056831	1.102176
Ag	-0.231724	-1.601563	1.316326
Ag	-0.228908	1.442376	-1.351752
Ag	1.429460	-0.920023	-0.876748
Ag	-1.396857	-1.258842	-1.270803
Au	2.572000	-1.838119	1.896619
Au	0.717174	-3.778337	-0.554821
Au	-3.612399	-1.654496	0.846519
Au	-0.825425	3.451975	1.242970
Au	3.896017	0.716590	-1.439222
Ag	2.332597	3.489283	-0.245528
Au	-3.456095	0.734068	-1.882921
S	0.294141	4.848029	-0.306276
S	-5.030203	-0.747219	-0.850052
S	-2.215028	-2.678263	2.469617
S	-2.092877	2.158134	2.797862
S	2.493080	-4.057230	1.023994
S	2.664714	0.323187	2.885508
S	3.283300	-1.274958	-2.589698
S	-1.124121	-3.642723	-2.057258
S	4.640847	2.755504	-0.500167
S	-1.923064	2.055621	-3.144959
C	0.807283	6.328308	0.684538
C	-6.190837	0.359618	0.068833
C	-2.518821	-1.712333	4.015531
C	-3.758578	2.964497	2.780239
C	4.005625	-4.197778	-0.029517
C	1.751169	0.167675	4.484413
C	2.705829	-0.625240	-4.224340
C	-0.316117	-3.540853	-3.716644
C	5.350428	2.365468	1.158486
C	-2.446389	3.798223	-2.820809
H	1.491527	6.920148	0.059632
H	1.306118	6.039756	1.618306
H	-0.091925	6.919622	0.906401
H	-6.782068	0.911537	-0.675407
H	-5.654819	1.058914	0.722493
H	-6.856141	-0.281654	0.664182
H	-1.800361	-2.074972	4.765613
H	-3.539307	-1.921037	4.365594
H	-2.384081	-0.633136	3.856942
H	-4.463139	2.275851	3.270071
H	-4.096167	3.179490	1.757953
H	-3.705406	3.898317	3.357097
H	4.880383	-4.129685	0.632233
H	4.041341	-3.414912	-0.798289
H	3.977982	-5.189915	-0.502322
H	2.338526	-0.460819	5.167858
H	0.751388	-0.261504	4.340424
H	1.660045	1.180309	4.903530
H	2.333462	-1.482209	-4.804922
H	3.559896	-0.178920	-4.751659
H	1.907197	0.118835	-4.108604
H	-1.083277	-3.226336	-4.439002
H	0.050658	-4.541060	-3.986409
H	0.515851	-2.824532	-3.714512
H	6.269638	1.783384	1.004816
H	4.649630	1.805525	1.790545
H	5.602779	3.323896	1.634721

H	-3.424300	3.965862	-3.292952
H	-2.492200	4.017840	-1.746361
H	-1.695987	4.449768	-3.291445

Coordinates of **Iso2.**

Ag	1.534573	2.019275	1.401651
Ag	-1.448247	-0.981180	-1.119071
Ag	1.145412	-0.562313	-0.081160
Ag	-0.193877	1.645847	-1.282561
Ag	-0.627047	-2.070247	1.960519
Au	-1.588033	3.508702	0.624686
Ag	3.875564	-1.579313	-0.247765
Au	2.082662	-0.969765	2.723466
Ag	-1.246139	0.665397	1.098269
Au	1.281170	-1.779226	-2.797116
Au	-3.837051	0.872237	-0.557329
Au	-3.201114	-2.739323	0.387855
Au	2.779997	1.855958	-1.342978
H	-0.009764	-1.468703	5.473711
C	-0.268521	-0.426061	5.249522
S	-0.016421	-0.066763	3.448674
H	0.361780	0.260563	5.831311
H	-1.328374	-0.241322	5.475470
S	-1.013948	-2.192610	-3.278805
C	-1.240660	-3.995828	-2.938929
H	-2.315981	-4.211503	-3.025026
H	-0.694971	-4.566426	-3.703438
H	-0.893471	-4.277415	-1.936510
S	3.624149	-1.379715	-2.665257
C	4.326203	-2.971538	-3.305866
H	4.090065	-3.042095	-4.376896
H	5.417076	-2.928607	-3.174409
H	3.918009	-3.841637	-2.775742
S	3.972925	1.501959	0.693886
C	4.957433	3.051403	0.937617
H	5.321228	3.044729	1.975424
H	5.812461	3.040647	0.247415
H	4.347587	3.947033	0.762292
H	-2.866266	-5.906112	2.077103
C	-2.156425	-5.160088	2.460527
S	-1.458057	-4.222268	1.024390
H	-2.660728	-4.497731	3.175169
H	-1.317999	-5.672479	2.954498
H	-4.950440	3.840229	0.626782
C	-4.725650	4.089924	-0.417448
S	-3.260760	3.143683	-1.038556
H	-4.492213	5.160127	-0.511465
H	-5.579358	3.839190	-1.063147
H	-4.514819	-1.766251	-2.598860
C	-5.391093	-1.734126	-1.938340
S	-4.924583	-1.227193	-0.221992
H	-5.858057	-2.727197	-1.873004
H	-6.124161	-1.006129	-2.313571
H	1.178088	4.549065	-2.494761
C	1.311822	4.022601	-3.448608
S	1.344303	2.185977	-3.229070
H	2.251747	4.338911	-3.922480
H	0.471026	4.255388	-4.118393
H	2.978522	-4.085969	1.843528
C	3.873359	-3.747087	2.381600
S	4.163711	-1.932754	2.157039
H	4.760682	-4.270318	1.996722
H	3.768589	-3.954091	3.455599
H	1.241685	5.376172	0.736459
C	0.879159	5.437249	1.770789
S	0.044274	3.873841	2.301700
H	0.172715	6.272682	1.873434
H	1.728009	5.595094	2.452771

Coordinates of **Iso3.**

Ag	2.014167	1.900045	1.305210
Ag	-1.569318	-1.055424	-0.990568
Ag	1.121529	-0.761755	-0.065419
Ag	0.033452	1.290125	-1.809426
Ag	-2.296441	-1.548384	2.390361
Au	-0.718022	3.893731	0.321463
Ag	3.542954	-2.294296	0.396309
Au	1.385574	-0.871626	2.905465
Au	-0.933877	1.021399	0.721493
Au	1.219681	-2.789366	-2.119485
Ag	-2.856212	1.651575	-1.426035
Au	-4.267453	-1.668213	-0.110623
Au	3.034088	1.071673	-1.565257
H	-0.800505	0.268128	5.572470
C	-0.951956	1.011617	4.778528
S	-0.729263	0.202356	3.132367
H	-0.222863	1.829202	4.856944
H	-1.974109	1.412876	4.815299
S	-1.115273	-3.072293	-2.428034
C	-1.557226	-4.517011	-1.363020
H	-2.654649	-4.564318	-1.309100
H	-1.172210	-5.431669	-1.834983
H	-1.147891	-4.415443	-0.349502
S	3.590017	-2.579690	-2.032465
C	4.147217	-4.330158	-2.281255
H	3.963837	-4.601175	-3.330296
H	5.227243	-4.364269	-2.077783
H	3.619071	-5.027832	-1.618709
S	4.149251	0.795614	0.526344
C	5.445387	2.120118	0.539287
H	5.829820	2.187553	1.567234
H	6.255623	1.822253	-0.140549
H	5.032888	3.088564	0.228952
H	-6.087524	-3.776021	2.190111
C	-5.263427	-3.241839	2.682945
S	-3.793386	-3.295566	1.557159
H	-5.569950	-2.212945	2.908737
H	-4.989883	-3.765366	3.610238
H	-3.993270	4.606273	-0.164777
C	-3.556045	5.010643	-1.086427
S	-2.069129	4.044819	-1.621235
H	-3.252641	6.055353	-0.930170
H	-4.290896	4.960004	-1.903019
H	-3.575922	-1.326482	-3.457491
C	-4.539817	-0.808025	-3.365569
S	-4.730833	0.003055	-1.715433
H	-5.364699	-1.522771	-3.492732
H	-4.618564	-0.020377	-4.128705
H	1.846446	3.786309	-3.118561
C	2.006138	3.144121	-3.994274
S	1.791950	1.350088	-3.591118
H	3.017973	3.296578	-4.395048
H	1.266487	3.391153	-4.769716
H	2.127643	-4.154102	2.873162
C	2.959827	-3.727965	3.448114
S	3.430461	-2.045652	2.835440
H	3.848030	-4.368769	3.348663
H	2.685316	-3.651597	4.509184
H	2.230985	5.308992	1.113313
C	1.767398	5.251341	2.106445
S	0.656421	3.778342	2.259145
H	1.174279	6.157395	2.293864
H	2.546047	5.159377	2.877961

Coordinates of **Iso4.**

Ag	2.193394	1.998390	0.893689
Ag	-1.446175	-1.223428	-0.891959
Ag	1.286762	-0.765760	-0.088790
Au	-0.041364	1.134928	-1.845082
Ag	-2.179040	-1.594753	2.524244
Au	-0.811583	3.836786	0.466891
Ag	3.869582	-1.950241	0.429293
Au	1.656110	-0.529733	2.882452
Au	-0.776678	0.959328	0.727367
Au	1.437924	-2.955229	-1.915446
Ag	-2.898119	1.455571	-1.293223
Au	-4.110704	-1.911582	0.037014
Ag	2.877479	1.299367	-2.222057
H	-0.657675	0.746297	5.479081
C	-0.886352	1.305953	4.562160
S	-0.604566	0.212296	3.105147
H	-0.235672	2.184846	4.458641
H	-1.941486	1.611810	4.549831
S	-0.886584	-3.379484	-2.085883
C	-1.205900	-4.725765	-0.861442
H	-2.296076	-4.817403	-0.749575
H	-0.796316	-5.665390	-1.257403
H	-0.756989	-4.502096	0.114973
S	3.788319	-2.578214	-1.938884
C	4.466591	-4.302674	-1.967375
H	4.266001	-4.732457	-2.958566
H	5.552687	-4.231977	-1.811643
H	4.016426	-4.932867	-1.189683
S	4.224825	1.031446	-0.204734
C	5.453388	2.421174	-0.168282
H	5.853287	2.495663	0.852712
H	6.266156	2.173580	-0.865551
H	4.993008	3.373943	-0.459744
H	-5.912075	-3.932250	2.435563
C	-5.111036	-3.344218	2.904581
S	-3.623283	-3.430054	1.804745
H	-5.449246	-2.311909	3.057506
H	-4.838533	-3.798381	3.867999
H	-4.193627	4.062726	0.560949
C	-3.965696	4.620029	-0.356556
S	-2.470810	3.945916	-1.212508
H	-3.786286	5.677541	-0.116922
H	-4.808765	4.542016	-1.058557
H	-3.318797	-1.626088	-3.314375
C	-4.319401	-1.176324	-3.265997
S	-4.624533	-0.338693	-1.646391
H	-5.086722	-1.951055	-3.401396
H	-4.426341	-0.413729	-4.050743
H	1.044475	3.906142	-3.352606
C	0.947622	3.311942	-4.270237
S	1.098584	1.496301	-3.943416
H	1.737741	3.589803	-4.982816
H	-0.035550	3.496331	-4.725278
H	2.978833	-3.598660	3.300300
C	3.754315	-2.945429	3.720441
S	3.868325	-1.338013	2.809631
H	4.736782	-3.433006	3.639222
H	3.539748	-2.736613	4.777528
H	2.138062	5.434718	0.837757
C	1.854207	5.294376	1.888577
S	0.883978	3.737362	2.131003
H	1.241491	6.142677	2.224513
H	2.755669	5.224457	2.514954