Supplementary Information

to accompany

"Noncovalent interactions determine the conformation of aurophilic complexes with 2-Mercapto-4-methyl-5-thiazoleacetic acid ligands"

by

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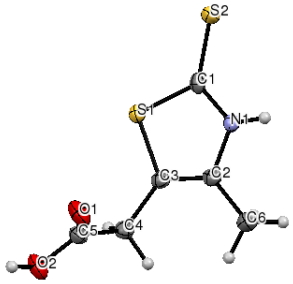
TABLE S1. Crystal data and data collection parameters for 2-Mercapto-4-methyl-5-thiazoleacetic acid H_2-(*mmta*).

Compound reference	4
Chemical formula	$C_6H_7NO_2S_2$
Formula Mass	189.25
Crystal system	Monoclinic
a/Å	7.3214(6)
b/Å	14.1820(13)
c/Å	15.5197(10)
α/°	90
β/°	95.774(7)
γ/°	90
Unit cell volume/Å^3	1603.3(2)
Space group	$I2/a$
No. of formula units per unit cell, Z	8
Radiation type	MoKα
Absorption coefficient, μ/mm^{-1}	0.61
No. of reflections measured	3825
No. of independent reflections	1816
R_{int}	0.0344
Final R_1 values ($I > 2\sigma(I)$)	0.0387
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.0944
Final R_1 values (all data)	0.05
Final $wR(F^2)$ values (all data)	0.1017
Goodness of fit on F^2	1.08

TABLE S2. The assymetric unit, selected bond lengths [Å] and angles for 2-Mercapto-4-methyl-5-thiazoleacetic acid.



S2-C1	1.674(2)
C1-S1	1.720(2)
C1-N1	1.341(3)
C2-C3	1.347(3)
S2-C1-S1	124.09(13)
N1-C1-S2	127.64(17)

I. ADDITIONAL INFORMATION ON MATERIALS

Hydrogen tetrachloroaurate(III) hydrate ($HAuCl_4\times$ xH_2O, 99.9% (metal basis), Au 49% min) was purchased from Alfa Aesar. 2-Mercapto-4-methyl-5-thiazoleacetic acid, 98% and thiourea, $\geq$ 99.0% were purchased from Sigma Aldrich. Methanol (ultrapure, HPLC grade, 99.8+%) and acetonitrile (ACS, 99.5+%) were both purchased from Alfa Aesar.

TABLE S3. Hydrogen bond network in (**1**)

D-H$\cdots A$	D-H (Å)	H$\cdots A$ (Å)	D$\cdots A$ (Å)	D-H$\cdots A$ (°)
N1-H1-O4[1]	0.85(5)	1.95(5)	2.774(6)	164(6)
N2-H2A-Cl1[2]	0.85(5)	2.31(5)	3.163(5)	176(6)
O2-H2-O3[3]	0.85(2)	1.73(3)	2.540(6)	159(8)
O12-H12-O5[4]	0.84(2)	1.84(3)	2.661(7)	164(8)
O3-H3A-O11	0.85(2)	2.09(8)	2.762(7)	135(9)
O3-H3B-O4	0.85(2)	2.17(3)	2.974(9)	158(8)
O4-H4C-O5[5]	0.85(2)	1.92(2)	2.763(6)	176(8)
O4-H4D-Cl1[6]	0.85(2)	2.31(4)	3.106(5)	157(9)
O5-H5A-Cl1	0.85(2)	2.21(2)	3.059(5)	177(6)
O5-H5B-Cl1[7]	0.85(2)	2.28(3)	3.107(5)	163(7)

Symmetry codes: [1] *1-x,1-y,1-z;* [2] *-1+x,+y,+z,* [3] *1+x,+y,+z;* [4] *2-x,-y,2-z;* [5] *+x,-1+y,+z;* [6] *1-x,1-y,2-z;* [7] *2-x,1-y,2-z*

TABLE S4. Characteristic of $\pi - \pi$ stacking interactions in (**2**) and (**3**). All distances given in Å, all angles given in degrees.

(**2**)	
Plane 1	S2-C1-N1-C2-C3
Plane 2	S32-C31-N31-C32-C33
Plane 1 to plane angle	4.9(4)
Plane centroid to plane centroid distance	3.615(5)
Plane [1] to plane centroid distance	3.472(7)
Plane [2] to plane centroid distance	-3.529(7)
Plane 1	N21-C21-S22-C23-C22
Plane 2	N11-C11-S12-C13-C12
Plane 1 to plane angle	6.3(5)
Plane centroid to plane centroid distance	3.645(5)
Plane [1] to plane centroid distance	3.481(8)
Plane [2] to plane centroid distance	-3.502(7)
(**3**)	
Plane 1	S1-C1-N1-C2-C3
Plane 2	(S1-C1-N1-C2-C3)^i
Plane 1 to plane angle	3.4(3)
Plane centroid to plane centroid distance	3.635(6)
Plane [1] to plane centroid distance	-3.413(8)
Plane [1] to plane shift	1.250(15)

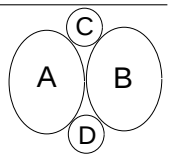
$i = 7/4 - x,\ 3/4 - y,\ +z$

TABLE S5. A schematic representation of the structure of (**1**) and (**3**). Interaction energy components between different components of the (**1**) and (**3**). All interaction energies are given in kcal/mol and were calculated with the CP correction.

$E_{\text{complex}} = E_{\text{ABCD}} - E_{\text{A}} - E_{\text{B}} - E_{\text{C}} - E_{\text{D}}$

$E_{\text{int}}^{\text{c-ions}} = E_{\text{ABCD}} - E_{\text{AB}} - E_{\text{CD}}$

$E_{\text{int}}^{\text{Au-dim}} = E_{\text{AB}} - E_{\text{A}} - E_{\text{B}}$



(**1**)	E_{complex}	$E_{\text{int}}^{\text{c-ions}}$	$E_{\text{int}}^{\text{Au-dim}}$	$E_{\text{disp}}^{\text{Au-dim}}$
PBE0-D3[1]	-209.1	-257.1	20.18	-6.48
PBE0-MBD	-205.3	-257.3	24.36	-2.30
MCSh-D3	-205.5	-252.8	19.68	-8.93
MCSh-MBD	-201.9	-254.7	25.18	-3.43
HF	-170.7	-232.9	34.72	
MP2	-208.4	-254.8	18.85	
SCS-MP2	-198.9	-249.0	22.62	
DLPNO-CCSD(T)	-200.0	-251.0	23.52	
(**3**)				
PBE0-D3	-216.7	-287.9	40.76	-6.46
PBE0-MBD	-212.6	-287.1	44.11	-2.56
MCSh-D3	-215.1	-286.4	40.94	-8.88
MCSh-MBD	-211.6	-287.8	45.90	-3.91
HF	-173.2	-263.1	59.14	
MP2	-207.1	-277.1	39.53	
SCS-MP2	-197.9	-272.7	44.36	
DLPNO-CCSD(T)	-199.8	-275.4	45.24	

[1] The discrepancy between different DFT approaches should be attributed to the D3 correction overestimating the dispersion energy between the charged aurophilic units due to the positive partial charge on gold atoms [Hansen *et al.* ChemistryOpen, **3**, 177 (2014)].

TABLE S6. The Mulliken (Mull.), NBO and AIM charges in the S-Au-S region of (**1**) – (**3**).

	(**1**)				(**2**)		
	S2	Au1	S4	Cl	S1	Au1	S11
Mull.	-0.26	0.09	-0.26	-0.73	-0.39	0.08	-0.40
NBO	-0.02	0.13	-0.03	-0.85	-0.17	0.05	-0.15
AIM	0.14	0.14	0.10	-0.83	-0.15	0.10	-0.14

	(**3**)			
	S2	Au1	$S2^{iii}$	$Na2^{i}$
Mull.	-0.39	0.12	-0.39	0.64
NBO	-0.15	0.10	-0.15	0.75
AIM	-0.14	0.13	-0.15	0.90

II. CHARGE ANALYSIS IN THE SELECTED (**1**) – (**3**) MOTIFS

Although similar in magnitude, the Na^+–mediated intermolecular attraction obtained in the case of (**3**) is larger than the Cl^-–mediated case of (**1**). To understand this effect we examine the electronic charge distribution for (**1**) and (**3**) in the vicinity of the stabilizing ions by performing Mulliken, NBO and QTAIM charge analyses (see Table S6).

As one can infer from the data in Table S6, the accumulation of a negative charge on the Au-ligating sulfur atoms in the $[Au(H\text{-}mmta)_2]^-$ anion in (**3**) should result in a pronounced electrostatic attraction with the sodium cation. On the other hand, in the case of the $[Au(H_2\text{-}mmta)_2]^+$ cation in (**1**) both NBO and Mulliken analyses imply the presence of the electrostatic repulsion in interaction of the S atoms with the Cl^- anion, whereas only QTAIM points to electrostatic attraction.

Finally, both NBO and QTAIM analyses evidence that the deprotonation of the H_2-*mmta* ligands in (**2**) and (**3**) with respect to (**1**) results in the increased negative charge on the Au-ligating sulfur atoms and a slightly diminished charge on the Au(I) centre. Moving from (**1**) to (**3**) we observe that the charge drop on gold atoms accompanied by the increased dispersion energy in the MBD picture (see Table S5) corresponds to the shortened Au(I)-Au(I) distance (see Table 2) which points towards the stronger unsupported aurophilic interactions.

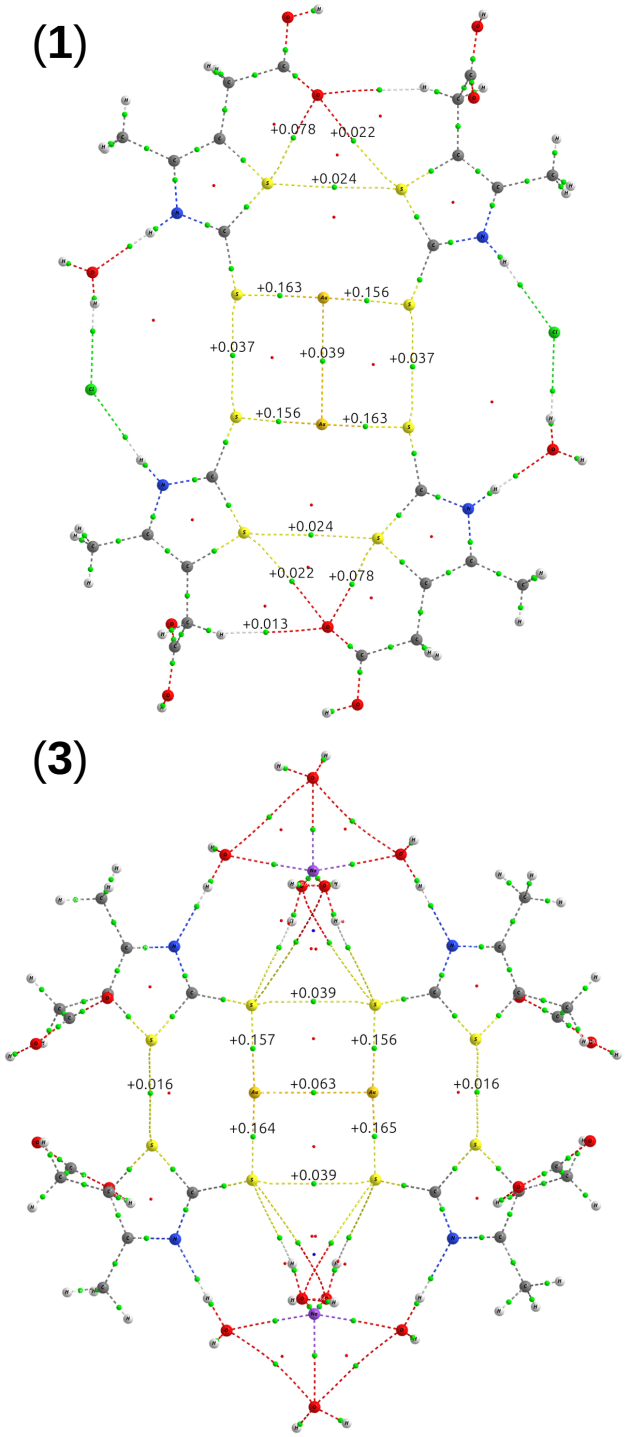
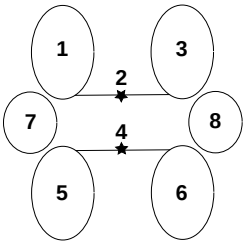


FIG. S1. Molecular graph of (**1**) and (**3**) with BCPs marked as green spheres and RCPs marked as red spheres. The values denote $\nabla^2\rho_c(r)$.

TABLE S7. The fragment PBE0-D3 dispersion energy analysis of (**1**) and (**3**). Labels 2 and 4 denote the Au(I) centers, 1,3,5,6 the *mmta* rings and 7,8 refer to the respective counterions and water molecules. All energies given in kcal/mol.



	intermonomer				
	(**1**)	(**3**)		(**1**)	(**3**)
2-4	-1.48	-0.92	1-5	-0.62	-0.59
1-4	-0.78	-1.01	3-6	-0.62	-0.59
3-4	-0.96	-1.00	1-6	-0.14	-0.17
2-5	-0.96	-1.01	3-5	-0.16	-0.17
2-6	-0.78	-1.00	$\sum$	-1.54	-1.52
$\sum$	-4.96	-4.94			

	c-ions			intramonomer	
3-8	-1.38	-3.36	1-2	-1.77	-1.67
5-7	-1.38	-3.33	2-3	-1.79	-1.66
6-8	-1.53	-3.36	1-3	-2.65	-1.72
1-7	-1.53	-3.33	$\sum$	-6.21	-5.05
$\sum$	-5.28	-13.41			

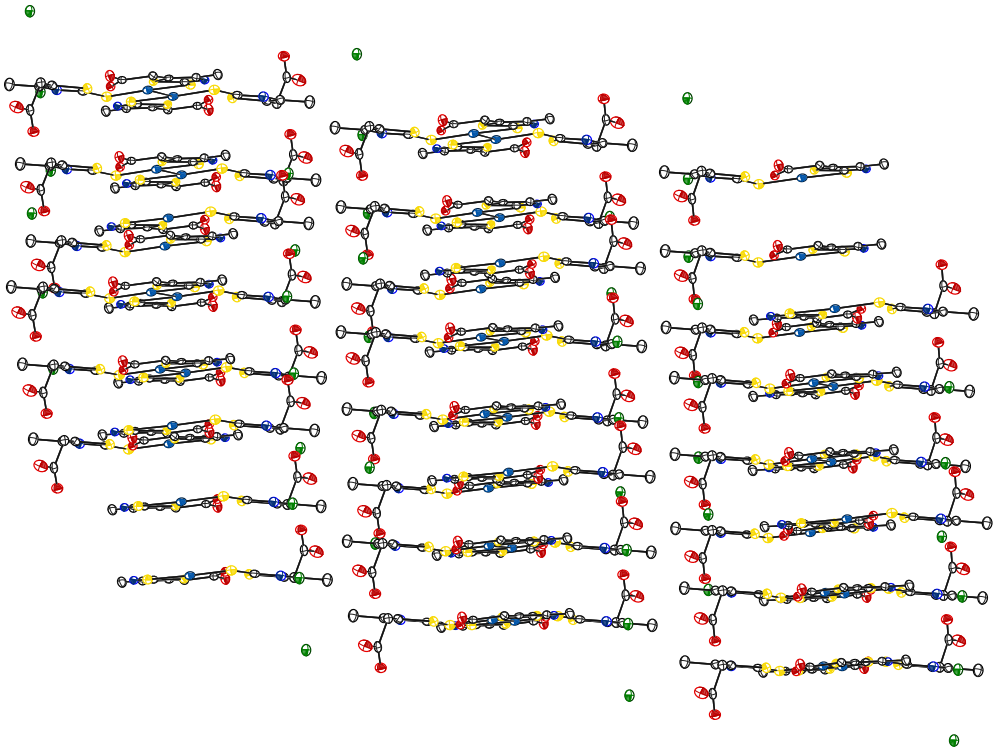


FIG. S2. A drawing of a portion of the structure of [Au(H_2-*mmta*)$_2$]Cl·3H_2O that shows the parallel stacking of the [Au_2(H_2-*mmta*)$_4$]$^{2+}$ dimers. Color code: Au - navy blue, S - yellow, O - red, N -blue, Cl^- - green.

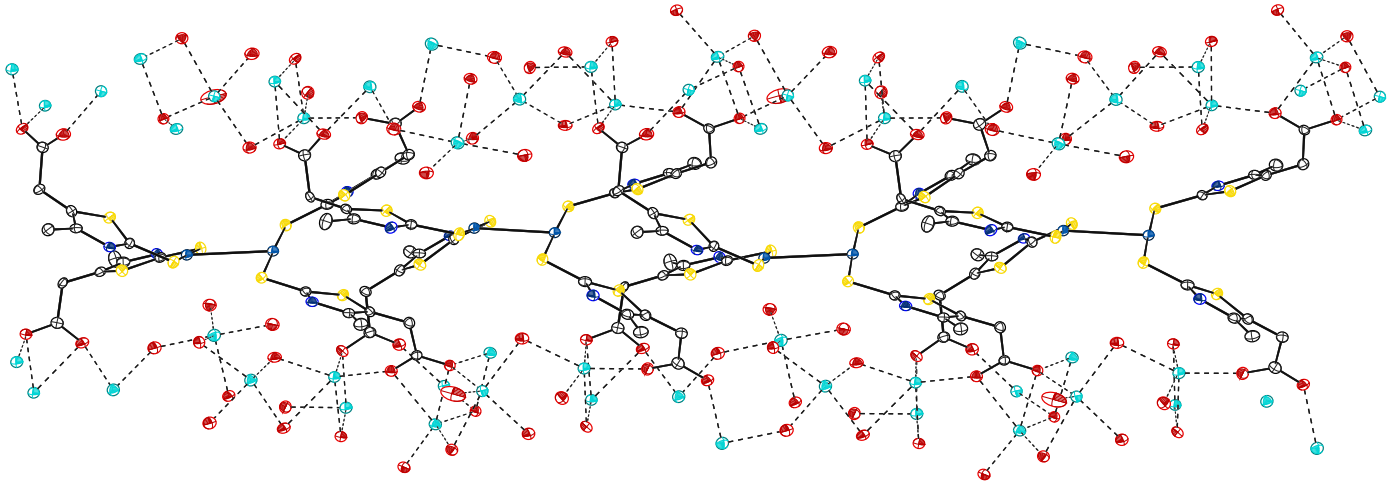


FIG. S3. A drawing of a portion of the structure of $Na_3[Au(mmta)_2]\cdot 6H_2O$ that shows the $\pi - \pi$ stacking of the dimers along the b axis. Color code: Au - navy blue, S - yellow, O - red, N -blue, Na - cyan.

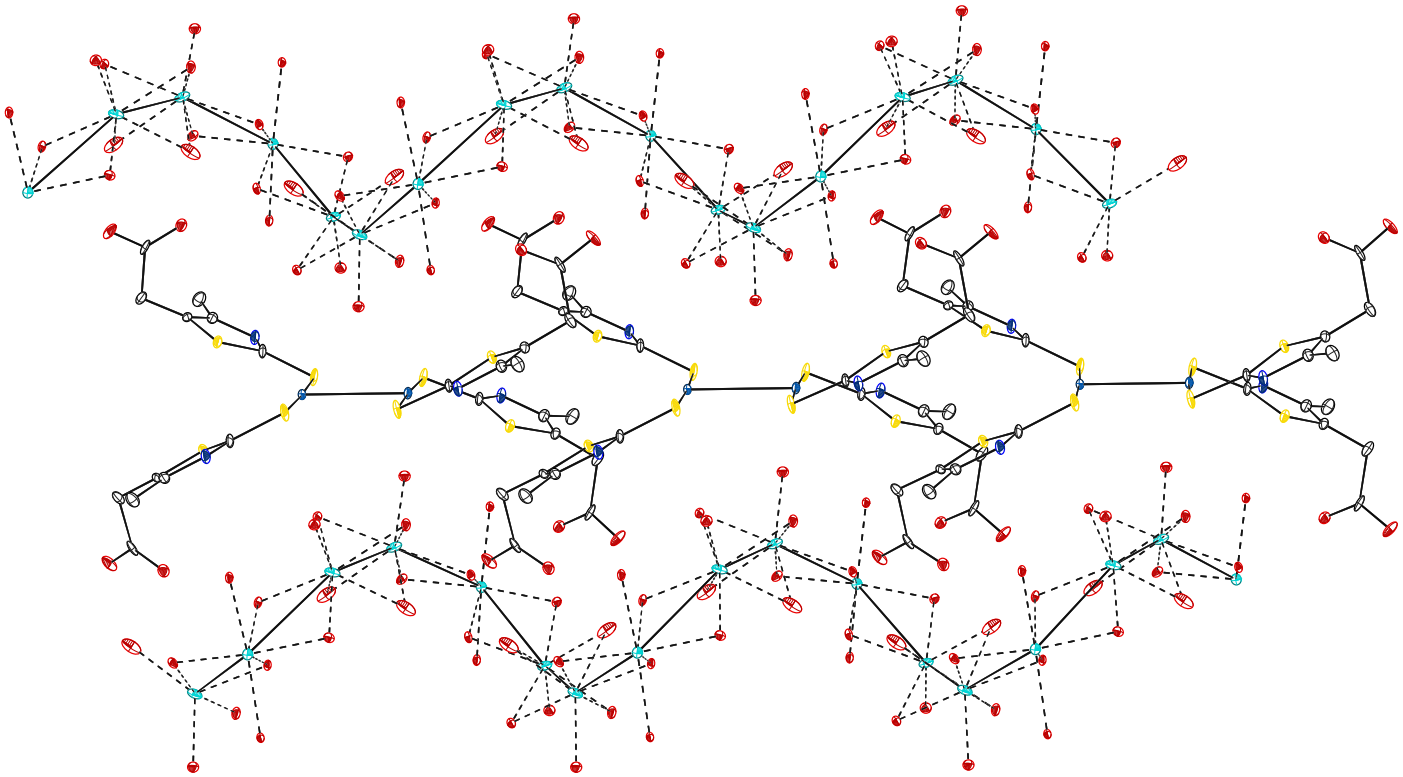


FIG. S4. A drawing of a portion of the structure of $Na_3[Au(mmta)_2]\cdot 10.5H_2O$ that shows the $\pi - \pi$ stacking of the dimers along the a axis. The helical structure formed by sodium cations along the a axis is also presented. Color code: Au - navy blue, S - yellow, O - red, N -blue, Na - cyan.

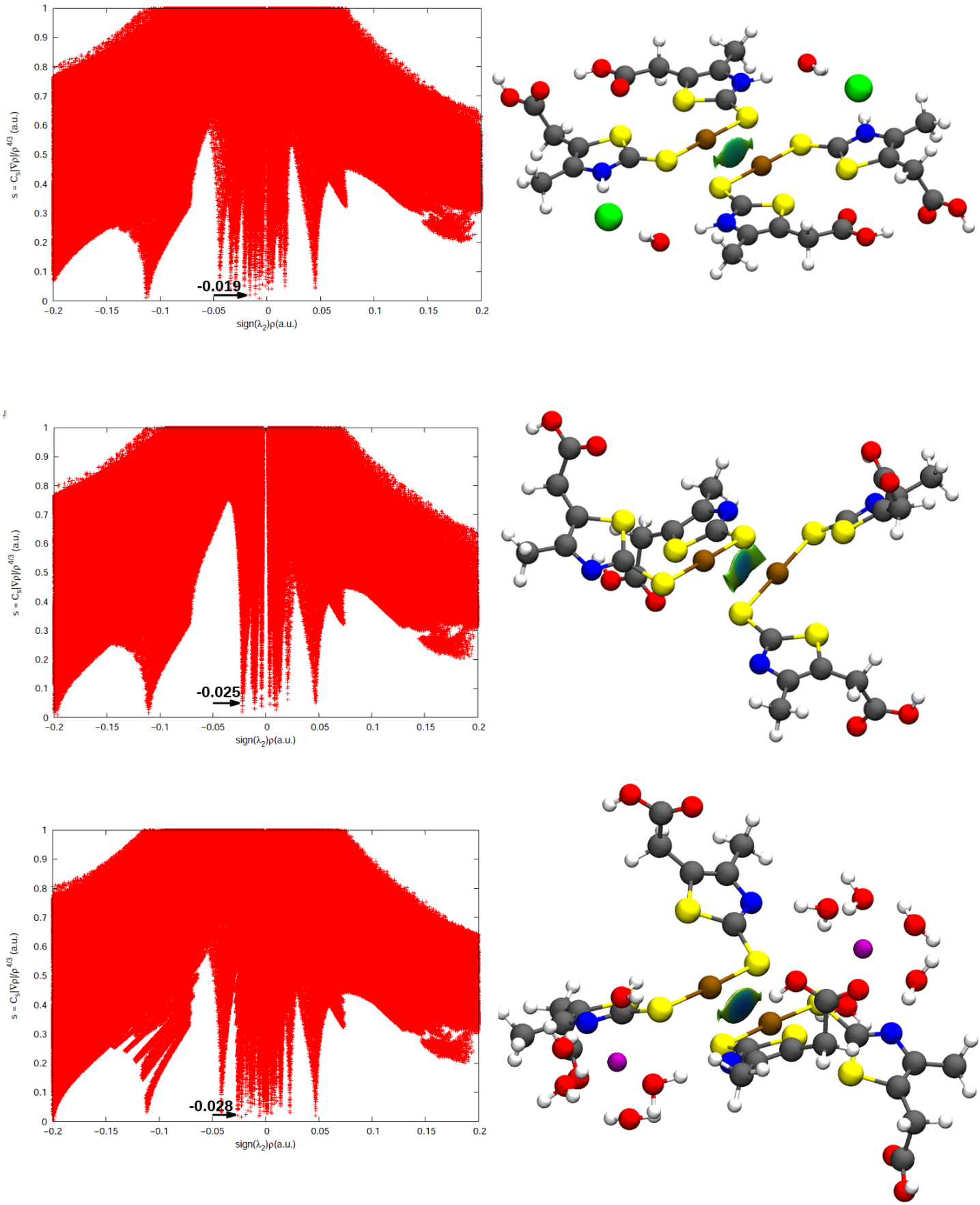


FIG. S5. Left: The reduced density gradient versus the electron density multiplied by the sign of the second Hessian eigenvalue. Marked are the peaks corresponding to the Au-Au interaction. Right: Gradient isosurfaces plotted in 1 Å radius around the midpoint of the Au-Au line with s=0.5 a.u.

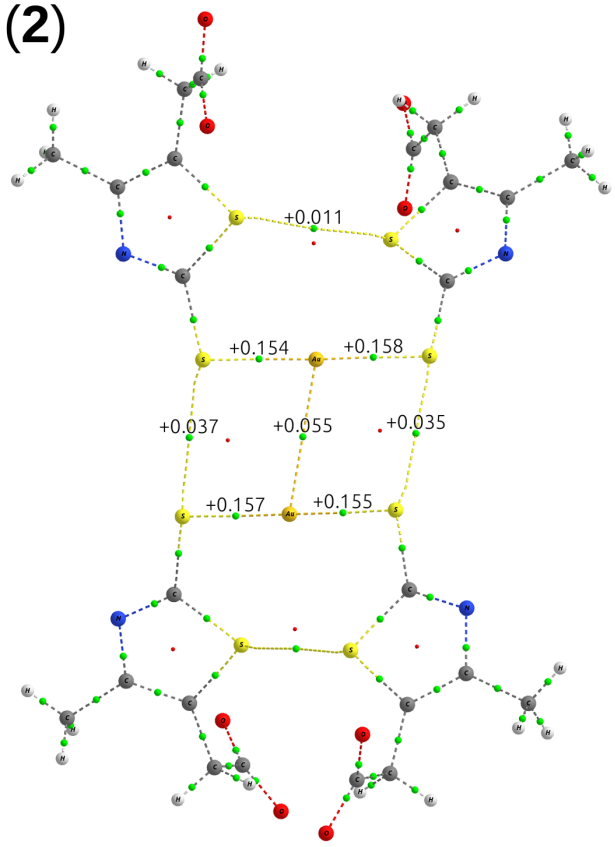


FIG. S6. Molecular graph of cluster (**2**) with BCPs marked as green spheres and RCPs marked as red spheres. The values denote $\nabla^2\rho_c(r)$.

3_clust.xyz

Au	5.72405	10.03721	14.41676
S	5.79966	10.06211	16.70969
S	5.79084	10.01176	12.12357
C	7.36749	10.78427	17.03585
C	7.35171	9.27731	11.79151
S	8.43028	11.32570	15.79718
N	7.83030	10.95027	18.25666
S	8.41486	8.72754	13.02619
N	7.80860	9.10770	10.56898
C	9.56996	11.82992	17.01168
C	9.07700	11.55805	18.22151
C	9.54597	8.21439	11.80742
C	9.05061	8.49015	10.59944
C	10.83583	12.49481	16.62245
C	9.73652	11.87407	19.52168
C	10.80803	7.53958	12.19189
C	9.70274	8.16898	9.29681
H	11.26777	12.10965	15.70181
H	11.58725	12.42357	17.41254
C	10.58173	14.04505	16.38197
H	9.98240	12.93481	19.61887
H	10.67107	11.31960	19.64183
H	9.07775	11.59946	20.34445
H	11.25416	7.98894	13.08608
H	11.54830	7.60961	11.38832
C	10.54267	5.99138	12.43335
H	10.78507	8.31134	9.33854
H	9.30774	8.81474	8.51313
H	9.50142	7.13268	9.00929
O	9.58159	14.58522	16.90923
O	11.45675	14.65415	15.70621
O	9.53634	5.45909	11.90986
O	11.41542	5.37542	13.10582
H	9.01845	13.89528	17.30889
H	12.09827	5.97129	13.43403
Au	2.63053	10.04936	14.42258
S	2.56352	10.01961	16.71572
S	2.55513	10.07968	12.12971
C	0.99691	9.29675	17.04623
C	0.99301	10.81483	11.80508
S	-0.07052	8.75795	15.81041
N	0.53870	9.12817	18.26842
S	-0.06549	11.36197	13.04490
N	0.53155	10.98702	10.58463
C	-1.20563	8.25115	17.02812
C	-0.70812	8.52046	18.23666
C	-1.20116	11.87770	11.83147
C	-0.71034	11.60450	10.62107
C	-2.47296	7.58709	16.64223

C	-1.36277	8.20168	19.53863
C	-2.46177	12.55169	12.22211
C	-1.36736	11.92843	9.32157
H	-2.90105	7.97338	15.72022
H	-3.22967	7.66100	17.42509
C	-2.21977	6.03736	16.39752
H	-0.68109	7.63813	20.18010
H	-2.27081	7.61369	19.40796
H	-1.62604	9.11754	20.07481
H	-2.90004	12.09872	13.11845
H	-3.21010	12.47912	11.42725
C	-2.19550	14.09938	12.46585
H	-2.30893	12.45813	9.46009
H	-1.56042	11.01794	8.74793
H	-0.71232	12.56191	8.71938
O	-1.21765	5.49608	16.91987
O	-3.09732	5.42969	15.72376
O	-1.19114	14.63278	11.93972
O	-3.06571	14.71391	13.14290
H	-0.66121	6.18236	17.33487
H	-3.74754	14.11630	13.47013
Na	4.16636	10.04945	8.60405
O	6.46398	9.67642	8.16872
O	1.86713	10.42340	8.17814
O	4.16178	10.05204	6.15916
O	4.48576	12.39485	9.00542
O	3.84848	7.70321	9.00164
H	6.80038	10.55570	7.97523
H	6.93005	9.43395	9.01412
H	1.51784	9.61192	7.80325
H	1.36096	10.57642	9.01667
H	5.04491	9.83559	5.84988
H	3.82037	10.73285	5.57686
H	3.59375	12.75179	8.95748
H	4.74808	12.49447	9.92764
H	4.69071	7.24387	8.94218
H	3.55936	7.58734	9.91363
Na	4.18820	10.03712	20.23529
O	6.49030	10.39210	20.66197
O	1.88772	9.68124	20.66986
O	4.19279	10.03453	22.68019
O	4.48764	7.68930	19.83277
O	3.88725	12.38580	19.83888
H	6.81416	9.55446	21.00153
H	6.98211	10.54435	19.81418
H	1.55189	10.54813	20.91221
H	1.41191	9.47102	19.82329
H	4.66948	10.66216	23.22684
H	3.35048	9.87240	23.11026
H	3.64412	7.24072	19.93246
H	4.74030	7.56411	18.91126

```
H         4.77457       12.75357       19.88151
H         3.61447       12.48582       18.91951
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2_clust.xyz

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  Au     8.973778   11.430708   13.958012
  S      7.366874   11.343486   12.323447
  S      8.491956    8.495468   12.388463
  S     10.602770   11.551951   15.576564
  S      9.090949    8.998189   16.268859
  O      9.679318    6.498141    9.504478
  O     10.100309    4.592875   10.552536
  O      7.976587    7.797258   19.665707
  O      7.101087    5.874966   18.956920
  N      6.535817    9.203105   10.935266
  N     11.316712    9.649636   17.330670
  C      7.389407    9.666690   11.806372
  C      6.733068    7.848453   10.693615
  C      7.751347    7.289601   11.386325
  C      8.245727    5.881441   11.321475
  H      7.445945    5.234705   10.936541
  H      8.490939    5.502343   12.325077
  C      9.429441    5.662290   10.396279
  C      5.823024    7.140506    9.732771
  H      5.782370    6.066981    9.933210
  H      6.158277    7.287022    8.700912
  H      4.817052    7.553630    9.824247
  C     10.452954   10.053768   16.467366
  C     10.926314    8.438410   17.913158
  C      9.751628    7.937307   17.453367
  C      9.063936    6.663900   17.861147
  H      9.782225    5.974072   18.315389
  H      8.620202    6.144571   17.011704
  C      7.940322    6.814646   18.901071
  C     11.807496    7.788145   18.925308
  H     12.210215    8.536628   19.610917
  H     12.663337    7.308632   18.437348
  H     11.277635    7.029937   19.503671
  H      9.781098    4.103522   11.319837
  H      8.671957    8.410261   19.347487
  Au     8.426006   14.535900   13.512575
  S      6.370230   14.493474   12.486545
  S      6.316967   17.033910   14.172304
  S     10.478550   14.639374   14.530593
  S     10.213951   17.397749   13.197203
  O      4.754221   17.922277   16.738077
  O      4.519345   20.095543   17.066509
  O     11.882408   19.029881   10.855680
  O     11.735710   21.226339   11.020675
  N      4.637825   16.553871   12.322406
  N     11.931580   16.845629   14.990399
  C      5.703930   16.059032   12.892917
```

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  C      4.262318   17.752914   12.909896
  C      5.025600   18.178305   13.936956
  C      4.909287   19.379791   14.813830
  H      4.079705   20.012014   14.469514
  H      5.812658   20.007398   14.746546
  C      4.699369   19.093467   16.309508
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1_clust.xyz

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