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

Sequential adsorption of up to six CO molecules on Au_{10}^- and Au_9Zn^- triangular clusters. The crucial role of a single atomic impurity

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Contents:

1) **$Au_{10}(CO)_n^-$ and $Au_9Zn^-(CO)_n^-$ isomers.**

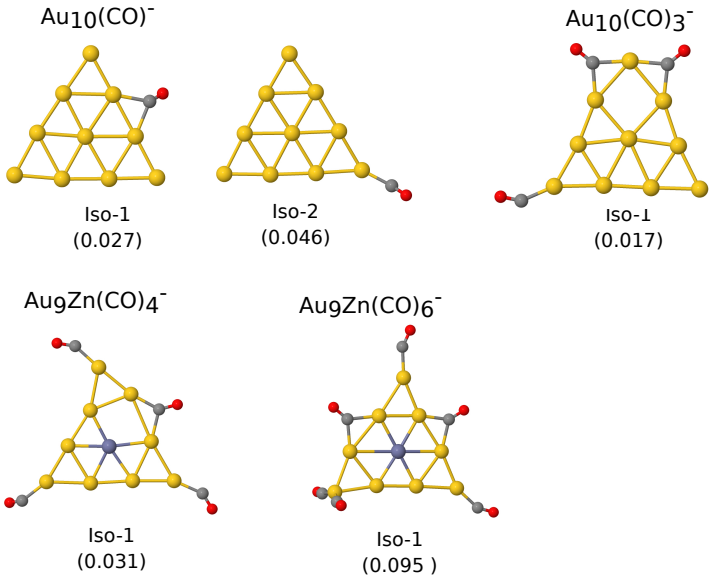

Figure S1: Some isomers of $Au_{10}(CO)_n^-$ and $Au_9Zn^-(CO)_n^-$ compounds with excess energy (below in parenthesis) less than 0.15 eV over the ground state given of Figure 1 of the main text. Note that the isomer $Au_{10}(CO)^-$ with CO adsorbed on top site has 0.046 eV excess energy. For $Au_9Zn(CO)^-$ all the isomers with CO in bridge sites have excess energy larger than 0.10 eV and are not included in this Figure-S1. All the compounds in this Figure have spin multiplicity 1 (2) corresponding to an even (odd) number of electrons.

2) **non-local van der Waals dispersion effects**.

Only after the work of Langreth, Lundqvist, and coworkers [1] the non-local dispersion correlations have been incorporated selfconsistently in DFT. These authors demonstrate that the vdW interaction can be expressed by a nonlocal functional depending only on the electron density. After that work, numerous efforts have been developed to include vdW forces within DFT [2,3,4]. Dion et al. [1] proposed to divide the exchange-correlation (xc) energy in three parts:

$$E_{xc}[n] = E_x^{GGA}[n] + E_c^{LDA}[n] + E_c^{nl}[n],$$

where $E_x^{GGA}[n]$ is the exchange energy corresponding to the chosen generalized gradient approximation (GGA) functional, $E_c^{LDA}[n]$ is the local density approximation (LDA) to the correlation energy, and $E_c^{nl}[n]$ is a nonlocal contribution to the correlation energy which contains the dispersion interaction.

Two different flavours of the Dion vdW-DF xc-functional have been choosen for the present test, the DRSLL and the KBM ones. In the original work of Dion et al.[1] (DRSLL functional), the exchange part is described through the GGA exchange functional of Zhang and Yang [5]. Insted, the KBM functional proposed by Klimes, Bowler, and Michaelides [6] uses the so-called optB88 exchange functional, which is a modification of the B88 exchange functional of Becke [7]. We have used these vdW-functionals in previous works concernig gold and mercury clusters [8].

Compound	isomer	RPBE	DRSLL	KBM
$Au_{10}(CO)^-$	iso-1	0.026	0.066	0.003
	iso-2	0.046	0.081	0.127
$Au_{10}(CO)_3^-$	iso-1	0.017	0.023	0.061
$Au_9Zn(CO)_4^-$	iso-1	0.031	0.032	0.045
$Au_9Zn(CO)_6^-$	iso-1	0.095	0.114	0.067

TABLE S1: Comparison of the difference in total energy (in eV) between the compounds of Figure S1 above and the corresponding minimum energy configurations shown in Figure 1 of the main text, for the RPBE functional and two PBE plus non-local van der Walls correlation functionals, namely, DRSLL [1] and KBM [6].

In Table S1 are presented the self-consistently calculated differences between the total energies (in eV) of those isomers in Figure S1 above and the corresponding minimum energy configurations given in Figure 1 of the main text. No change of the initial CO adsorption configurations occurs after the forces minimization process, but only slight changes in the bond lengths. The ground state adsorption configuration predicted by the RPBE xc-functional remains for the calculations with the more sophisticated (and expensive) vdW dispersion functionals. This result gives us confidence in the block RPBE calculations presented in the main text.

3) **Angles Au-C-O for all CO molecules adsorbed in the complexes of Figure 1 of the main text.**

Compound	Angle Au-C-O (α_1)					
$Au_{10}(CO)^-$	119.64/141.30					
$Au_{10}(CO)_2^-$	137.84/133.94	137.81/133.95				
$Au_{10}(CO)_3^-$	136.25/135.27	136.55/135.28	130.48/131.42			
$Au_{10}(CO)_4^-$	136.60/134.86	134.79/137.06	131.62/139.01	165.42		
$Au_{10}(CO)_5^-$	134.04/137.97	134.12/137.86	134.73/134.87	154.83	154.58	
$Au_{10}(CO)_6^-$	136.40/135.46		134.01/136.85	159.47	157.61	168.80
$Au_9Zn(CO)^-$	141.23					
$Au_9Zn(CO)_2^-$	141.55	141.54				
$Au_9Zn(CO)_3^-$	141.14	140.99	140.82			
$Au_9Zn(CO)_4^-$	140.98	139.32	143.18	135.43		
$Au_9Zn(CO)_5^-$	156.10	175.50	149.44	139.95/136.71	141.61/134.36	
$Au_9Zn(CO)_6^-$	155.34	179.24	146.54	130.82/120.74	140.63/134.28	140.33

TABLE S2: Angles Au-C-O (α_1) formed by the CO molecules with Au atoms of the compounds of Figure 1 of the main text. For those CO molecules bridging two Au atoms are given the corresponding two α_1 angles.

4) **Angle α_2 formed by the three corners Au atoms and the plane containing the Au-C-O molecule for each of the compounds shown of Figure 1 of the main text.**

The angle α_2 between the Au-C-O plane and that of gold substrate						
$Au_{10}(CO)^-$	0.99/1.00					
$Au_{10}(CO)_2^-$	0.13/0.13	0.24/0.21				
$Au_{10}(CO)_3^-$	0.25/0.24	0.13/0.10	0.22/0.21			
$Au_{10}(CO)_4^-$	0.48/0.55	0.60/0.66	0.45/0.43	1.63		
$Au_{10}(CO)_5^-$	0.08/0.07	0.20/0.15	0.53/0.53	0.21	1.38	
$Au_{10}(CO)_6^-$	2.27/2.39	1.31/1.31	1.16/1.03	2.75	1.48	85.40
$Au_9Zn(CO)^-$	85.41					
$Au_9Zn(CO)_2^-$	84.40	81.45				
$Au_9Zn(CO)_3^-$	86.43	82.26	88.90			
$Au_9Zn(CO)_4^-$	81.56	74.21	80.16	70.94		
$Au_9Zn(CO)_5^-$	3.19	8.36	0.65	0.90/0.88	2.2/2.08	
$Au_9Zn(CO)_6^-$	5.46	39.74	3.34	3.01/1.96	1.92/17.36	71.05

TABLE S3: Angle α_2 formed by the plane of the Au-C-O trimer with the plane formed by the three Au corner atoms of the compounds of Figure 1 of the main text. For those CO bridging two Au atoms are given the corresponding two α_2 angles.

5) **Excess/deffect of charge (per CO molecule) for CO, C, O, and Zn atoms.**

Bridge (b) and top (t) bonding, and excess/deffect of charge (per CO molecule) for CO, C, O, and Zn					
Compound	(b,t)	Δ(CO)	Δ(C)	Δ(O)	Δ(Zn)
$Au_{10}(CO)^-$	(1,0)	0.241	-0.573	0.814	
$Au_{10}(CO)_2^-$	(2,0)	0.252	-0.564	0.816	
$Au_{10}(CO)_3^-$	(3,0)	0.238	-0.570	0.808	
$Au_{10}(CO)_4^-$	(3*,1)	0.210	-0.598	0.807	
$Au_{10}(CO)_5^-$	(3,2)	0.204	-0.594	0.798	
$Au_{10}(CO)_6^-$	(3,3*)	0.189	-0.613	0.803	
$Au_9Zn(CO)^-$	(0,1)	0.147	-0.682	0.829	-0.849
$Au_9Zn(CO)_2^-$	(0,2)	0.144	-0.688	0.833	-0.842
$Au_9Zn(CO)_3^-$	(0,3)	0.150	0.672	0.822	-0.839
$Au_9Zn(CO)_4^-$	(0,4*)	0.153	-0.671	0.824	-0.822
$Au_9Zn(CO)_5^-$	(2*,3)	0.186	-0.636	0.823	-0.717
$Au_9Zn(CO)_6^-$	(3*,3*)	0.180	-0.647	0.827	-0.706

TABLE S4: In the second column is given the type of bonding, bridge (b) or on top (t), of the CO molecules. The asterisk (*) indicates that the last CO binds to highly coordinated gold (Au) atoms. In columns third to sixth, the excess or deficit of nominal charge per molecule is given for CO, C, O, and Zn atoms, respectively.

6) **The xyz coordinates of all the minimum energy structures given in Figure-1 and Figure-1S.**

REFERENCES

1. M.Dion, H. Rydberg, E. Schröder, D. C: Langreth and B. I. Lundqvis, Phys. Rev. Lett., 2004, 92, 2464001.
2. O. A. Vydrov and T. Von Voorhis, Phys. Rev. Lett., 2009, 103, 063004.
3. K. Lee, E. D. Murray, L. Kong, B. I. Lundqvist and D. C. Langreth, Phys. Rev. B: Condens. Matter Mater. Phys., 2010, 82, 081101.
4. O. A. Vydrov and T. Van Voorhis, J. Chem. Phys., 2010, 132, 164113.
5. Y. Zhang and W. Yang, Phys. Rev. Lett., 1998, 80, 890.
6. J. Klimes, D. R. Bowler and A. Michaelides, J. Phys.: Condens. Matter, 2010, 22, 022201.
7. A. D. Becke, Phys. Rev. A: At., Mol., Opt. Phys., 1988, 38, 3098.
8. E. M. Fernández and L. C. Balbás, Phys. Chem. Chem. Phys., 2011, **13**, 20863-20870

Au10(CO)$^-$ GS
12

O	-2.564717	5.292986	0.113609
C	-1.770339	4.403424	0.107772
Au	-0.086138	0.055222	-0.055300
Au	-2.878259	-0.005180	-0.306862
Au	-1.376822	-2.406539	-0.338637
Au	1.263202	-2.391491	-0.098701
Au	2.734580	0.030888	0.193102
Au	-4.088681	-2.382274	-0.585248
Au	3.977813	-2.337887	0.149807
Au	-1.656614	2.367640	-0.030107
Au	1.443272	2.361514	0.228477
Au	0.305274	4.843383	0.294987

Au10(CO)$^-$ isomer 1
12

O	4.363776	2.363477	-1.211385
C	3.566356	1.895705	-0.459363
Au	-0.117961	-0.097262	-0.273451
Au	-2.852619	0.105438	-0.018636
Au	-1.449515	-2.505464	-0.165921
Au	1.240462	-2.495234	-0.306716
Au	2.744370	-0.086112	-0.324869
Au	-4.143433	-2.274898	-0.003857
Au	3.975998	-2.442123	-0.363017
Au	-1.363791	2.349792	-0.036004
Au	1.469856	2.281861	-0.193850
Au	0.190744	4.602219	0.027774

Au10(CO)$^-$ isomer 2
12

O	6.729420	-3.599151	0.093739
C	5.921307	-3.070928	-0.574015
Au	0.042588	0.040550	-0.046110
Au	-2.734338	0.012956	-0.024255
Au	-1.243337	-2.400544	-0.422569
Au	1.447146	-2.311653	-0.409974
Au	2.799298	0.153502	-0.040556
Au	-3.962365	-2.360847	-0.387128
Au	4.156392	-2.144225	-0.636657
Au	-1.447540	2.352555	0.328629
Au	1.421394	2.434742	0.306382
Au	-0.098937	4.660228	0.672608

$Au10(CO)_2^-$ GS
14

C	1.89748578	4.82265423	-0.10099869
O	2.79718535	5.60902325	-0.09580500
O	-3.24648535	5.30615076	-0.09352760
C	-2.27249685	4.61401082	-0.09790071
Au	0.02447868	0.48237315	-0.12219478
Au	-2.74618847	0.05449805	-0.11577335
Au	-1.16078576	-2.22319005	-0.13322123
Au	1.46642679	-2.09094516	-0.14205408
Au	2.82472069	0.33080024	-0.13119654
Au	-3.86692886	-2.38300696	-0.12461453
Au	4.17476430	-1.98761403	-0.15129359
Au	-1.96452781	2.56438398	-0.10685624
Au	1.79645174	2.75107616	-0.11347236
Au	-0.19464982	4.86049993	-0.09979526

$Au10(CO)_3^-$ GS
16

C	0.21240644	-3.73879850	0.05895336
O	0.54647264	-4.89273307	0.09383222
C	1.90607066	4.87681112	-0.09508997
O	2.71918661	5.75262007	-0.09575142
O	-3.21288811	5.28813141	-0.19426777
C	-2.27698694	4.54617269	-0.16552885
Au	0.11122613	0.67826669	-0.04517736
Au	-2.48644802	-0.13563778	-0.07749575
Au	-1.63107630	-2.86923786	0.00147549
Au	1.34277071	-2.02245251	0.03965283
Au	2.84554414	0.29972231	0.01557258
Au	-4.21877633	-2.18948821	-0.06637030
Au	4.10571760	-2.05202000	0.09186566
Au	-2.02991758	2.49045368	-0.12198823
Au	1.97250556	2.80525782	-0.05352570
Au	-0.18781938	4.74174058	-0.13253366

$Au_{10}(CO)_3^-$ isomer 1

16

O	7.455888	-1.665443	-0.372239
C	6.338854	-2.021185	-0.319945
C	1.515253	5.178613	-0.107263
O	2.351760	6.031487	-0.096672
O	-3.641530	5.268383	-0.089066
C	-2.629025	4.632378	-0.095673
Au	-0.008229	0.741020	-0.153951
Au	-2.715946	0.044249	-0.122318
Au	-0.946136	-2.106691	-0.165524
Au	1.658280	-1.681887	-0.208569
Au	2.823840	0.754692	-0.195253
Au	-3.629757	-2.477220	-0.123378
Au	4.417872	-1.427797	-0.254375
Au	-2.169130	2.618190	-0.112886
Au	1.597298	3.100536	-0.141528
Au	-0.573715	5.043394	-0.099216

$Au_{10}(CO)_4^-$ GS

18

O	-7.11647528	-2.73830959	0.18229613
C	-5.94418306	-2.77950690	0.15465496
C	0.35083452	-3.70238072	0.08219110
O	0.67437601	-4.85356220	0.09571532
C	1.91907490	4.96217788	-0.08496325
O	2.71250956	5.85735812	-0.09911732
O	-3.23635619	5.31114101	-0.09019259
C	-2.27939643	4.59768913	-0.07364808
Au	0.15768579	0.74920985	0.00052250
Au	-2.47280728	-0.09293121	0.03871278
Au	-1.35850939	-2.57907958	0.08066991
Au	1.47372433	-1.95222927	0.04363559
Au	2.89900592	0.41186407	-0.00768658
Au	-4.02324588	-2.35102746	0.11061792
Au	4.21955555	-1.91506242	0.02822895
Au	-1.98431797	2.53787329	-0.02767579
Au	1.96909883	2.90015927	-0.04913090
Au	-0.18813028	4.84276043	-0.08120021

$Au10(CO)_5^-$ GS

20

O	6.83564871	-2.89113815	0.19339760
C	5.66822389	-3.01914694	0.19597300
O	-7.64800030	-2.35137182	-0.00052916
C	-6.49872680	-2.59152740	0.01928795
C	-0.40637555	-3.86952817	0.14948058
O	-0.41500427	-5.06526776	0.18413963
C	1.92726568	4.60886895	-0.00205274
O	2.79937044	5.42599329	-0.00265629
O	-3.15225901	5.55352150	-0.09260343
C	-2.31729745	4.69903433	-0.06476684
Au	-0.28366989	0.64491240	0.04280456
Au	-2.97155559	0.06381872	0.01580305
Au	-1.85399735	-2.40877384	0.08870149
Au	1.06734024	-2.43048212	0.13220962
Au	2.37567361	-0.05516881	0.09472208
Au	-4.56749929	-2.13254841	0.03829521
Au	3.79395609	-2.36850595	0.16522234
Au	-2.23451648	2.63381218	-0.02418810
Au	1.75654065	2.54715343	0.03322108
Au	-0.19316694	4.71023630	-0.03524323

$Au10(CO)_6^-$ GS

22

C	4.45928442	0.67554627	0.37431378
O	5.52402424	1.11752181	0.18814121
O	6.25019615	-3.94678394	0.36961419
C	5.08943598	-3.77130752	0.34445353
O	-7.76525563	-1.79291626	-0.09634894
C	-6.65193940	-2.16043254	-0.08397573
C	-0.32229023	-3.87624902	0.09048320
O	-0.08285642	-5.04832289	0.09574004
C	1.80061910	4.69250672	0.09577638
O	2.65159245	5.53777905	0.09173070
O	-3.28728268	5.33224201	-0.09466850
C	-2.37989045	4.55624337	-0.04345815
Au	-0.11176492	0.60967184	0.12205280
Au	-2.77493321	-0.11723454	0.01888866
Au	-2.06890658	-2.76432757	0.03035609
Au	0.77078077	-2.09728158	0.14757166
Au	2.59312842	-0.07686996	0.30348009
Au	-4.67403734	-2.08255110	-0.04046580
Au	3.39963067	-2.75624992	0.28613730
Au	-2.20152283	2.47866285	0.00728956
Au	1.89633992	2.61498547	0.17419062
Au	-0.28493782	4.66970510	0.03102771

Au9Zn(CO)$^-$ GS
12

C	-5.311432	-2.991672	1.919743
O	-5.709513	-3.290820	2.983612
Zn	0.245693	0.240610	-0.036579
Au	1.416971	-2.172175	-0.411594
Au	-1.090151	-2.109792	0.365456
Au	-2.367762	0.279928	0.765836
Au	1.608471	2.537202	-0.442707
Au	2.826959	0.252709	-0.828516
Au	0.276299	4.839345	-0.021045
Au	-1.104340	2.547979	0.383566
Au	4.004662	-2.140763	-1.200891
Au	-3.749664	-2.070977	1.021136

Au9Zn(CO)$_2^-$ GS
14

C	-0.102328	6.691382	-0.299248
O	-0.193296	7.441635	-1.198489
C	5.645835	-3.251494	0.481534
O	6.260552	-3.666866	1.392216
Zn	-0.187505	0.005285	0.053136
Au	1.176764	-2.334613	0.127857
Au	-1.452607	-2.362464	0.063760
Au	-2.871382	0.109528	0.003706
Au	1.237590	2.342861	0.032980
Au	2.542981	0.056898	0.118310
Au	-0.150876	4.715568	0.124763
Au	-1.515778	2.362169	-0.014357
Au	3.897733	-2.338824	0.035342
Au	-4.153018	-2.269003	0.011479

Au9Zn(CO)$_3^-$ GS
16

C	-0.36291358	6.57958452	1.57570862
O	-0.46534051	7.15436369	2.59535922
C	-5.78765718	-3.18650733	-1.25364141
O	-6.40803253	-3.29717074	-2.24534978
C	5.72890080	-3.13258852	0.49197392
O	6.34379004	-3.56907487	1.39293760
Zn	-0.12912246	0.05831546	0.16347228
Au	1.26230422	-2.25023190	-0.07624713
Au	-1.35942086	-2.28310620	-0.40550593
Au	-2.81299525	0.05662447	-0.14952898
Au	1.16365194	2.36419491	0.72713833
Au	2.55292805	0.13009993	0.48459583
Au	-0.27606142	4.69634027	0.83766854
Au	-1.58391979	2.32529299	0.41681924
Au	3.99651242	-2.16677247	0.08666789
Au	-4.09383699	-2.33539061	-0.54491418

$Au_9Zn(CO)_4^-$ GS
18

O	3.551584	4.110024	1.684998
C	2.570143	3.626762	2.118904
C	-1.226617	6.595215	1.597849
O	-1.960903	7.256211	2.231258
C	-5.764908	-3.398292	-1.216978
O	-6.201467	-3.748928	-2.251074
C	5.696655	-2.921000	0.524693
O	6.364786	-3.360591	1.385229
Zn	-0.235096	0.037700	0.407857
Au	1.228909	-2.188391	0.028723
Au	-1.382516	-2.376426	-0.317544
Au	-2.878092	-0.087852	0.077193
Au	0.993498	2.477373	1.335460
Au	2.366814	0.219343	0.800180
Au	-0.753389	4.690495	1.147208
Au	-1.703754	2.205220	0.686744
Au	3.971465	-1.899539	0.237677
Au	-4.086505	-2.533007	-0.466704

$Au_9Zn(CO)_4^-$ isomer 1
18

C	3.501140	2.353564	1.243502
O	4.680999	2.542384	1.411112
C	-1.492190	6.806508	1.565751
O	-2.627695	7.095864	1.499987
C	-5.553444	-2.461766	-1.130980
O	-6.286246	-2.397039	-2.047238
C	5.859944	-3.180782	0.442098
O	6.396757	-4.218139	0.290304
Zn	0.177447	0.353852	0.442972
Au	1.498255	-1.939518	0.150420
Au	-1.168544	-1.829147	-0.179110
Au	-2.417301	0.659865	0.173675
Au	1.796877	3.480859	1.276967
Au	2.858131	0.401164	0.780717
Au	-0.114029	5.342767	1.428677
Au	-0.841372	2.715353	0.804809
Au	4.106873	-2.208611	0.425118
Au	-3.959383	-1.476308	-0.343624

$Au_9Zn(CO)_5^-$ GS

20

C	3.185203	2.508145	1.420417
O	4.172493	3.075258	1.773639
C	-3.615424	2.752738	0.183833
O	-4.517453	3.541077	0.191764
C	-0.128362	7.134279	1.901607
O	0.391662	8.131183	2.242797
C	-5.427736	-3.110029	-1.481066
O	-6.085794	-4.030024	-1.789686
C	5.349463	-3.167248	0.422914
O	6.449463	-3.549764	0.561936
Zn	-0.169284	0.629028	0.334614
Au	1.106033	-1.589553	0.033035
Au	-1.546020	-1.442143	-0.413569
Au	-3.377060	0.739352	-0.236992
Au	1.130883	2.820149	1.100063
Au	2.748658	0.524817	0.843563
Au	0.001608	5.199816	1.457299
Au	-1.541049	2.884446	0.609707
Au	3.869164	-1.846036	0.463010
Au	-4.215880	-1.676299	-0.946780

$Au_9Zn(CO)_6^-$ GS

22

O	1.035003	-4.830804	-0.197556
C	1.307636	-3.787260	-0.661941
C	3.225785	2.478141	1.106475
O	4.270037	3.052022	1.122857
C	-3.629706	2.725974	0.259965
O	-4.441773	3.596959	0.369293
C	-0.300180	7.062615	2.042126
O	0.186106	8.056007	2.442673
C	-5.479775	-3.133221	-1.477511
O	-6.187863	-4.015802	-1.780841
C	5.436272	-3.089688	0.614924
O	6.532759	-3.439111	0.843791
Zn	-0.047610	0.591295	0.145616
Au	1.100005	-1.748274	-0.265276
Au	-1.611375	-1.348178	-0.515503
Au	-3.486268	0.740619	-0.239541
Au	1.169631	2.858880	0.959308
Au	2.629134	0.482062	0.639438
Au	-0.005439	5.162202	1.506072
Au	-1.503765	2.780005	0.536962
Au	3.952164	-1.786107	0.494723
Au	-4.317823	-1.653561	-0.955818

$Au_9Zn(CO)_6^-$ isomer 1

22

O	-3.474530	-0.668225	-4.929066
C	-3.811309	-1.059429	-3.873730
C	3.040416	2.342627	1.775315
O	4.010519	2.846469	2.251017
C	-3.591246	2.772311	-0.049125
O	-4.524060	3.521502	-0.020560
C	-0.345141	6.866066	2.567936
O	0.097089	7.822764	3.085856
C	-4.956819	-2.494864	-0.532348
O	-5.333177	-2.990289	0.464365
C	5.352523	-3.168929	0.294124
O	6.453161	-3.533025	0.470673
Zn	-0.171427	0.630442	0.123998
Au	1.157693	-1.533264	-0.342358
Au	-1.434705	-1.310359	-1.056517
Au	-3.279894	0.845573	-0.748417
Au	1.031786	2.700261	1.320260
Au	2.675100	0.445473	0.917046
Au	-0.133776	5.011845	1.892165
Au	-1.574142	2.841045	0.592325
Au	3.851952	-1.867079	0.358807
Au	-4.071985	-1.484332	-1.967940