Supporting Information for

The CUAGAU Set of Coupled-Cluster Reference Data for Small Copper, Silver and Gold Compounds, and Assessment of DFT Methods

Bun Chan

Graduate School of Engineering, Nagasaki University, Bunkyo 1-14, Nagasaki 852-8521, Japan

Additional Information

Table S1. Reference Bond Lengths (Å) and Deviations from These Values

species	ref	DSD-PBEP86 (full) WCVQZ	DSD-PBEP86 (full) WCVTZ	DSD-PBEP86 (FC) VQZ	DSD-PBEP86 (FC) VTZ	MN15 WCVQZ	MN15 WCVTZ	MN15 VQZ	MN15 VTZ	MN15 -L WCVQZ	MN15 -L WCVTZ	MN15 -L VQZ	MN15 -L VTZ
Cu_2	2.215	0.006	0.010	0.013	0.017	0.058	0.059	0.055	0.048	0.000	0.000	0.000	0.004
Ag_2	2.524	–0.001	0.007	0.011	0.021	0.012	0.016	0.012	0.019	0.034	0.039	0.036	0.045
Au_2	2.479	–0.001	0.006	0.002	0.011	0.005	0.010	0.009	0.014	0.019	0.024	0.023	0.027
CuH	1.455	–0.008	–0.010	–0.006	–0.005	0.038	0.039	0.037	0.041	0.001	0.001	0.001	0.003
AgH	1.610	–0.007	–0.008	–0.001	0.002	–0.004	–0.003	–0.004	–0.001	0.003	0.004	0.003	0.007
AuH	1.523	–0.003	–0.003	–0.004	–0.003	0.002	0.003	0.001	0.002	0.006	0.006	0.005	0.007
CuF	1.743	–0.013	–0.018	–0.010	–0.012	0.030	0.027	0.031	0.029	–0.024	–0.028	–0.023	–0.025
AgF	1.977	–0.003	–0.008	0.004	0.001	–0.015	–0.017	–0.013	–0.014	–0.002	–0.007	–0.001	–0.004
AuF	1.925	–0.004	–0.007	–0.002	–0.002	–0.023	–0.022	–0.021	–0.019	–0.013	–0.015	–0.011	–0.011
Cu_3(linear)	2.291	–0.014	–0.007	–0.005	0.004	–0.009	–0.006	–0.015	0.048	–0.005	–0.003	–0.005	0.001
Ag_3(linear)	2.593	–0.008	0.002	0.005	0.017	0.009	0.014	0.008	0.015	0.034	0.038	0.035	0.046
Au_3(linear)	2.547	–0.138	–0.132	–0.135	–0.128	–0.098	–0.093	–0.095	–0.090	0.016	0.021	0.019	0.024
$Cu_3(D_{3h})$	2.333	–0.005	0.000	0.002	0.010	0.066	0.072	0.062	0.057	–0.012	–0.005	–0.012	0.001
$Ag_3(D_{3h})$	2.657	–0.009	–0.002	0.004	0.015	0.009	0.014	0.007	0.016	0.029	0.036	0.029	0.046
$Au_3(D_{3h})$	2.624	–0.007	–0.001	–0.004	0.002	0.005	0.009	0.007	0.011	0.020	0.023	0.021	0.024
Cu_3^+(linear)	2.337	–0.013	–0.004	–0.005	0.006	0.031	0.036	0.027	0.018	–0.024	–0.018	–0.022	–0.014
Ag_3^+(linear)	2.629	–0.013	–0.002	0.000	0.014	–0.009	–0.002	–0.011	–0.001	0.029	0.035	0.030	0.044
Au_3^+(linear)	2.577	–0.129	–0.119	–0.126	–0.114	–0.190	–0.185	–0.187	–0.181	0.013	0.019	0.016	0.021
$Cu_3^+(D_{3h})$	2.337	–0.007	–0.001	0.001	0.011	0.058	0.064	0.055	0.051	–0.024	–0.017	–0.023	–0.010
$Ag_3^+(D_{3h})$	2.650	–0.009	–0.001	0.004	0.016	0.003	0.009	0.002	0.011	0.018	0.024	0.019	0.035

Table S2. CM1 Energies (kJ mol^{-1}) and Their Components for the CUAGAU Set

reaction	CM1	HF	ΔCC	Δ(T)	ΔCV
1 (Cu)	193.7	46.3	123.7	23.8	–0.1
2 (Cu)	273.1	140.7	121.5	10.5	0.3
3 (Cu)	412.9	235.9	164.2	15.8	–3.0
4 (Cu)	272.2	37.7	194.8	39.6	0.1
5 (Cu)	–25.1	5.8	–23.5	–8.4	1.0
6 (Cu)	675.2	546.6	111.7	13.2	3.7
7 (Cu)	–149.6	–124.6	–26.1	2.3	–1.2
8 (Cu)	545.4	110.0	355.7	80.8	–1.1
9 (Cu)	1731.9	1407.0	267.8	53.5	3.7
10 (Cu)	70.9	–7.9	71.5	7.1	0.3
11 (Cu)	–64.8	–27.4	–29.7	–8.0	0.4
12 (Cu)	–64.1	–55.8	–8.2	–0.9	0.9
13 (Cu)	275.8	183.9	73.5	17.4	1.0
14 (Cu)	148.1	99.3	38.2	10.1	0.5
1 (Ag)	164.6	39.4	102.3	18.5	4.3
2 (Ag)	234.8	117.8	104.9	7.4	4.8
3 (Ag)	340.7	186.8	140.6	15.1	–1.8
4 (Ag)	233.8	30.0	166.8	29.3	7.7
5 (Ag)	–9.3	5.1	–10.1	–3.1	–1.2
6 (Ag)	661.8	533.8	110.6	5.8	11.5
7 (Ag)	–132.1	–120.6	–13.6	7.2	–5.0
8 (Ag)	455.0	110.5	277.5	53.1	13.9
9 (Ag)	1658.6	1339.0	261.9	40.5	17.2
10 (Ag)	48.8	–13.2	51.1	5.0	5.9
11 (Ag)	–42.1	–25.9	–19.8	1.9	1.8
12 (Ag)	–44.5	–47.3	–6.7	5.1	4.5
13 (Ag)	215.2	143.4	54.9	9.8	7.2
14 (Ag)	114.9	81.0	24.4	3.8	5.6
1 (Au)	220.6	75.9	115.8	21.1	7.8
2 (Au)	311.2	167.9	125.1	9.7	8.4
3 (Au)	290.5	121.8	146.3	19.7	2.8
4 (Au)	318.4	75.2	195.2	35.6	12.3
5 (Au)	–14.7	8.7	–15.7	–5.2	–2.5
6 (Au)	828.9	671.3	137.5	6.1	13.9
7 (Au)	–182.8	–165.9	–18.4	8.2	–6.7
8 (Au)	602.8	187.7	327.0	66.1	21.9
9 (Au)	1927.6	1575.0	291.7	42.3	18.6
10 (Au)	136.9	29.3	92.1	5.4	10.1
11 (Au)	1.6	15.8	–11.6	–5.2	2.6
12 (Au)	45.0	47.1	–2.3	–4.5	4.8

13 (Au)	297.9	201.4	74.9	12.1	9.6
14 (Au)	192.7	135.8	43.7	5.1	8.2

Table S3. Mean Absolute Deviations (kJ mol^{-1}), Mean Deviations and Standard Deviations of the Deviations for the Various DFT-Type Methods Used in Conjunction with the def2-TZVP Basis Set

method	MAD	MD	SD
GAM	23.1	−10.2	31.5
B97-D3BJ	14.4	−6.8	19.6
mBEEF	13.4	1.8	16.8
B97M-rV	14.4	−0.3	18.9
B97-1	16.7	−7.5	21.9
B97-3-D2	30.7	−21.6	36.9
MN15	12.7	0.5	15.9
PW6-B95-D2	17.0	−12.8	20.9
ωB97X	16.7	−11.1	25.3
ωB97X-V	25.3	−23.2	29.9
M11	42.6	−37.0	52.1
ωB97M-V	21.8	−19.6	27.6
DSD-PBEP86	13.3	−7.4	20.7

Table S4. Mean Absolute Deviations (MADs) (kJ mol^{-1}) from Benchmark Relative Energies for the CUAGAU Set for a Variety of DFT-Type Methods, and the Corresponding Mean Deviations (MDs) and Standard Deviations (SDs) for the Individual Deviations

method	ref	MAD	MD	SD
PBE	1	13.8	7.8	16.5
M06-L	2	20.2	–5.0	28.8
M06	3	14.7	–5.0	18.6
M06-2X	3	47.0	–35.6	54.0
B2-PLYP	4	9.4	–3.6	12.9
B2GP-PLYP	5	9.8	–6.3	12.3
PBE0-D3BJ	6,7	14.1	–12.0	16.5
B3LYP-D3BJ	8,7	14.9	–3.9	20.3
PBE-D3BJ	1,7	15.3	9.8	17.1
B2PLYP-D3BJ	4,7	6.1	–1.1	7.9
B2GP-PLYP-D3BJ	5,7	8.3	–1.8	12.2

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