Supplementary Information

Assessment of Quantum Mechanical Methods for Copper Complexes by Photoelectron Spectroscopy

Shuqiang Niu,[1] Dao-Ling Huang,[2] Phuong D. Dau,[2] Hong-Tao Liu,[2] Lai-Sheng Wang,[2] and Toshiko Ichiye[1,3*]

[1] Department of Chemistry, Georgetown University, Washington, DC 20057

[2] Department of Chemistry, Brown University, Providence, RI 02912

*Corresponding author. Tel: 202-687-3724; Fax: 202-687-6209; Email: ti9@georgetown.edu

Table S1. The Optimized and Experimental Bond lengths (r in Å) of $[Cu(NCS)_2]^{1-}$ and $[Cu(NCS)_2]^{0}$.

	B3LYP					
	[1–]			[0]		
	$r_{Cu—N}$	$r_{N—C}$	$r_{C—S}$	$r_{Cu—N}$	$r_{N—C}$	$r_{C—S}$
DZVP2	1.827	1.187	1.634	1.800	1.191	1.612
Def2-SVP	1.828	1.183	1.628	1.803	1.187	1.608
6-31G**	1.765	1.184	1.632	1.748	1.193	1.600
6-31(++)$_L$G**	1.779	1.185	1.632	1.759	1.195	1.599
Def2-SVPD	1.828	1.180	1.635	1.801	1.185	1.612
Def2-TZVPPD	1.830	1.174	1.623	1.800	1.179	1.599
aug-cc-pVTZ	1.832	1.174	1.628	1.801	1.179	1.604
				M06		
DZVP2	1.816	1.185	1.626	1.792	1.190	1.603
Def2-SVP	1.817	1.183	1.621	1.790	1.188	1.601
6-31G**	1.759	1.183	1.626	1.744	1.193	1.593
6-31(++)$_L$G**	1.768	1.183	1.626	1.751	1.193	1.592
ma-SVP	1.816	1.180	1.629	1.789	1.186	1.604
Def2-SVPD	1.818	1.180	1.628	1.790	1.186	1.605
Def2-TZVPPD	1.816	1.171	1.619	1.786	1.177	1.594
aug-cc-pVTZ	1.818	1.171	1.623	1.788	1.177	1.599
exp.[a]	1.808	1.137	1.639			

[a] Ref. 59

Table S2. The Optimized and Experimental Bond Lengths (r in Å), Angles (θ in ˚), and Dihedral Angles (ϕ in ˚) of $[Cu(SCH_3)_2]^{1-}$ and $[Cu(SCH_3)_2]^{0}$.

	B3LYP									
	[1–]					[0]				
	$r_{Cu—S}$	$r_{S—C}$	$\theta_{S–Cu–S}$	$\theta_{Cu–S–C}$	$\phi_{C–S–S–C}$	$r_{Cu—S}$	$r_{S—C}$	$\theta_{S–Cu–S}$	$\theta_{Cu–S–C}$	$\phi_{C–S–S–C}$
DZVP2	2.196	1.852	180.0	103.7	90.7	2.136	1.841	180.0	105.1	180.0
Def2-SVP	2.201	1.841	179.9	102.7	90.9	2.145	1.834	179.6	104.6	178.5
6-31G**	2.119	1.848	179.6	106.5	90.3	2.087	1.844	179.7	106.3	180.0
6-31(++)$_L$G**	2.121	1.854	155.9	99.2	–	2.085	1.844	179.5	106.2	180.0
Def2-SVPD	2.206	1.847	180.0	103.3	95.6	2.152	1.835	179.5	104.8	178.4
Def2-TZVPPD	2.195	1.841	178.9	106.2	89.7	2.136	1.829	179.9	106.5	180.0
aug-cc-pVTZ	2.195	1.845	178.8	105.2	89.8	2.136	1.834	180.0	106.5	179.6
	M06									
DZVP2	2.174	1.840	178.9	101.2	92.9	2.116	1.829	180.0	102.4	180.0
Def2-SVP	2.180	1.829	177.9	101.1	96.2	2.126	1.824	179.9	103.7	180.0
6-31G**	2.097	1.838	178.7	102.5	88.6	2.068	1.834	172.5	99.7	179.7
6-31(++)$_L$G**	2.112	1.845	152.7	85.5	–	2.067	1.834	169.3	99.5	180.0
Def2-SVPD	2.187	1.834	178.8	100.9	99.5	2.132	1.823	180.0	103.4	180.0
Def2-TZVPPD	2.178	1.829	178.7	102.1	81.3	2.119	1.817	179.9	104.2	180.0
aug-cc-pVTZ	2.176	1.835	179.7	102.8	84.6	2.118	1.824	180.0	104.2	180.0
exp.[a]	2.140	1.847	176.7	106.1	78.7					
	2.143	1.841	179.6	107.8	120.7					

[a] Ref. 58

Table S3. The Calculated and Experimental ADE and VDE (eV)[a] of $[Cu(SMe)_2]^{1-}$ and $[Cu(NCS)_2]^{1-}$.

	$[Cu(NCS)_2]^{1-}$		$[Cu(SMe)_2]^{1-}$	
	ADE	VDE	ADE	VDE
B3LYP/DZVP2	4.331	4.357	2.627	2.986
B3LYP/Def2-SVP	3.893	3.915	2.198	2.556
B3LYP/6-31G**	3.721	3.768	1.899	2.292
B3LYP/6-31(++)$_L$G**	3.910	3.963	2.071	2.434
B3LYP/Def2-SVPD	4.328	4.357	2.756	3.070
B3LYP/Def2-TZVPPD	4.300	4.333	2.730	3.094
B3LYP/aug-cc-pVTZ	4.310	4.341	2.729	3.089
M06/DZVP2	4.434	4.461	2.790	3.152
M06/Def2-SVP	4.106	4.132	2.346	2.677
M06/6-31G**	3.822	3.873	2.070	2.503
M06/6-31(++)$_L$G**	3.963	4.018	2.345	2.826
M06/Def2-SVPD	4.530	4.524	2.832	3.121
M06/Def2-TZVPPD	4.406	4.439	2.867	3.286
M06/aug-cc-pVTZ	4.447	4.479	2.888	3.291
CCSD/Def2-SVPD//M06/Def2-SVP	4.939	4.931	3.128	3.437
CCSDDef2-SVPD//M06/DZVP2	4.942	4.939	3.121	3.438
CCSD/Def2-TZVPPD//M06/Def2-SVP	5.063	5.081	3.188	3.370
CCSD/Def2-TZVPPD//M06/DZVP2	5.064	5.088	3.139	
CCSD(T)/Def2-SVPD//M06/Def2-SVP	4.750	4.747	3.028	3.156
CCSD(T)/Def2-SVPD//M06/DZVP2	4.752	4.754	3.037	3.353
CCSD(T)/Def2-TZVPPD//M06/Def2-SVP	4.855	4.890	3.073	3.255
CCSD(T)/Def2-TZVPPD//M06/DZVP2	4.856	4.897	3.037	
exp.	4.86(5)	4.92(5)	~3.2	3.43(7)

[a] The calculated ADE and VDE do not take the zero point vibrational energy into account.
[b] at 20 K

TABLE S4. T1 AND T2

	$[Cu(SCH_3)_2]^{1-}$	$[Cu(NCS)_2]^{1-}$	$FeCl_4^-$	$[Fe(SCH_3)_4]^{1-}$
T1 (reduced)	0.021	0.023	0.028	0.032
T1 (vertical oxidized)	0.039	0.040	0.052	0.044
T1 (adiabatic oxidized)	0.028	0.037	0.053	0.048
T2 (reduced)	0.044	0.067	0.108	0.146
T2 (vertical oxidized)	0.286	0.251	0.160	0.206
T2 (adiabatic oxidized)	0.164	0.228	0.185	0.210

Figure S1. Calculated VDE from the difference in energy between the reduced form and a Franck-Condon transition (black) and from the HOMO energy (blue) for $[Cu(NCS)_2]^{1-}$ (triangle), $[Cu(SCH_3)_2]^{1-}$ (square), $FeCl_4^-$ (circle), and $[Fe(SCH_3)_4]^{1-}$ (diamond), using the DZVP2 basis set for RS functionals in order of increasing (short-range) HF exchange. From left to right, the RS functionals (solid symbols) are BNL, CAM-B3LYP, and LRC-ωPBEh and the highly optimized RS functionals (lighter colored symbols) are ωB97, ωB97X, and M11. The symbols are connected by dotted lines to guide the eye and the results for the Fe complexes are shifted upwards by 3 eV to avoid overlaps. The experimental PES values (gray line with error indicated approximately by width of line) are also shown.