

Supplementary material

A Comparative Study of semiempirical, *ab initio* and DFT methods in evaluating metal-ligand bond strength, proton affinity, and interactions between first and second shell ligands in Zn-biomimetic complexes

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Table 6a. Protonation energy (in kJ/mol) of zinc-bound hydroxide of **4** obtained at various levels of calculation.

Method ^a	PM3	HF		BP86	B3LYP		mPW1PW91		MPW1K	MP2	
Basis set ^a		BS1	BS2	BS1	BS1	BS2	BS1	BS2	BS1	BS1	BS2
B3LYP/BS1 ^b	703	709	715	705	705	715	705	714	705	705	715
B3LYP/BS2 ^b	651	662	659	671	669	659	670	659	668	667	659
B3LYP/BS3 ^b	649	657	655	667	664	654	665	654	664	662	654
MP2/BS1 ^b	701	710	715	711	709	716	709	715	708	709	716
MP2/BS2 ^b	653	668	665	680	677	664	677	664	676	674	664
MP2/BS3 ^b	642	653	651	663	660	650	661	650	660	658	650
CCSD(T)/BS1 ^b	707	717	721	718	716	723	716	722	716	716	722
CCSD(T)/BS2 ^b	663	678	674	689	686	673	686	673	685	683	673
CCSD(T)/BS3 ^b	653	664	661	673	670	660	671	660	670	668	659

^a method and basis set used for geometry optimisation. ^b method and basis set used for the single-point energy calculation.

Table 6b. Protonation energy (in kJ/mol) of the zinc-bound hydroxide of **6** obtained at various levels of calculation.

Method ^a	PM3	HF		BP86	B3LYP		mPW1PW91		MPW1K	MP2	
Basis set ^a		BS1	BS2	BS1	BS1	BS2	BS1	BS2	BS1	BS1	BS2
B3LYP/BS1 ^b	715	723	728	719	717	725	718	723	718	718	725
B3LYP/BS2 ^b	676	686	684	696	692	683	692	683	691	689	683
B3LYP/BS3 ^b	675	682	680	691	687	680	688	680	686	684	680
MP2/BS1 ^b	713	721	726	723	720	724	720	722	719	719	724
MP2/BS2 ^b	676	689	687	701	696	686	696	686	694	692	686
MP2/BS3 ^b	664	672	671	681	677	670	678	670	676	674	670
CCSD(T)/BS1 ^b	721	728	732	731	728	731	728	730	727	727	731
CCSD(T)/BS2 ^b	686	698	696	710	705	695	706	696	704	702	695
CCSD(T)/BS3 ^b	676	683	681	692	687	680	688	681	687	685	680

^a method and basis set used for geometry optimisation. ^b method and basis set used for the single-point energy calculation.

Table 6c. Protonation energy (in kJ/mol) of the zinc-bound hydroxide of **8** obtained at various levels of calculation.

Method ^a	PM3	HF	B3LYP	mPW1PW91	
Basis set ^a		BS1	BS1	BS1	BS2
B3LYP/BS1 ^b	816	833	832	832	835
B3LYP/BS2 ^b	784	798	799	800	796
B3LYP/BS3 ^b	782	794	795	796	792
MP2/BS2 ^b	784	800	801	802	799
MP2/BS3 ^b	774	788	789	789	787

^a method and basis set used for geometry optimisation. ^b method and basis set used for the single-point energy calculation.

Table 8a. Metal-water bond dissociation energy E_{bond} of **3** (in kJ/mol) obtained at various levels of calculation.

Method ^a	PM3	HF		BP86	B3LYP		mPW1PW91		MPW1K	MP2	
Basis set ^a		BS1	BS2	BS1	BS1	BS2	BS1	BS2	BS1	BS1	BS2
B3LYP/BS1 ^b	127	147	146	147	147	146	147	146	147	147	146
B3LYP/BS2 ^b	121	138	138	137	137	138	137	137	137	137	137
B3LYP/BS3 ^b	117	131	131	130	130	131	130	131	130	131	131
MP2/BS1 ^b	134	155	155	155	155	155	155	155	155	155	155
MP2/BS2 ^b	132	148	148	148	148	148	148	148	148	148	148
MP2/BS3 ^b	129	142	141	141	142	142	142	142	142	142	142
CCSD(T)/BS1 ^b	134	155	155	155	155	155	155	155	155	155	156
CCSD(T)/BS2 ^b	134	150	150	150	150	150	150	150	150	151	151
CCSD(T)/BS3 ^b	131	144	144	144	144	144	144	144	144	144	144

^a method and basis set used for geometry optimisation. ^b method and basis set used for the single-point energy calculation.

Table 8b. Metal-water bond dissociation energy E_{bond} of **5B** (in kJ/mol) obtained at various levels of calculation.

Method ^a	PM3	HF		BP86	B3LYP		mPW1PW91		MPW1K	MP2	
Basis set ^a		BS1	BS2	BS1	BS1	BS2	BS1	BS2	BS1	BS1	BS2
B3LYP/BS1 ^b	97	110	109	110	110	108	110	110	109	110	109
B3LYP/BS2 ^b	73	78	79	78	78	79	77	79	77	78	79
B3LYP/BS3 ^b	68	73	74	72	72	74	72	74	72	73	74
MP2/BS1 ^b	101	113	112	114	114	112	114	113	113	114	113
MP2/BS2 ^b	85	90	91	90	90	91	90	91	91	91	91
MP2/BS3 ^b	78	85	85	85	85	86	85	86	86	85	86
CCSD(T)/BS1 ^b	100	113	112	113	113	112	113	113	112	113	113
CCSD(T)/BS2 ^b	86	92	93	93	93	93	92	93	93	93	93
CCSD(T)/BS3 ^b	80	87	87	88	88	88	87	88	88	88	88

^a method and basis set used for geometry optimisation. ^b method and basis set used for the single-point energy calculation.

Table 8c. Metal-water bond dissociation energy E_{bond} of **7** (in kJ/mol) obtained at various levels of calculation.

Method ^a	PM3	HF	B3LYP	mPW1PW91	
Basis set ^a		BS1	BS1	BS1	BS2
B3LYP/BS1 ^b	93	108	109	109	108
B3LYP/BS2 ^b	81	94	93	92	93
B3LYP/BS3 ^b	77	88	86	86	87
MP2/BS2 ^b	100	113	113	113	114
MP2/BS3 ^b	93	105	105	105	105

^a method and basis set used for geometry optimisation. ^b method and basis set used for the single-point energy calculation.

Table 10a. complex-second shell water bond dissociation energy E_{bond} of **6** (in kJ/mol) obtained at various levels of calculation.

Method ^a	PM3	HF		BP86	B3LYP		mPW1PW91		MPW1K	MP2	
Basis set ^a		BS1	BS2	BS1	BS1	BS2	BS1	BS2	BS1	BS1	BS2
B3LYP/BS1 ^b	102	112	111	114	115	117	115	119	115	115	117
B3LYP/BS2 ^b	73	82	81	82	84	83	84	83	84	85	83
B3LYP/BS3 ^b	67	76	74	76	79	76	78	75	78	79	76
MP2/BS1 ^b	99	112	111	112	114	116	113	117	113	114	116
MP2/BS2 ^b	77	88	86	88	91	88	90	88	91	92	88
MP2/BS3 ^b	72	86	84	87	89	86	89	86	89	90	86
CCSD(T)/BS1 ^b	95	109	109	106	109	112	109	113	109	110	113
CCSD(T)/BS2 ^b	77	88	86	86	90	87	89	87	90	91	87
CCSD(T)/BS3 ^b	71	86	83	86	89	85	88	85	88	89	85

^a method and basis set used for geometry optimisation. ^b method and basis set used for the single-point energy calculation.