Supporting Information

Models for The Trinuclear Copper(II) Cluster in the Particulate Methane Monooxygenase from Methanotrophic Bacteria: Synthesis, Spectroscopic and Theoretical Characterization of Trinuclear Cu(II) Complexes

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Table S1. Compositions of the atomic orbitals in the principal molecular orbitals for model compound **2** (**S** = 3/2).

Orb.	Energy (eV)	Occ.	Primary Contributors SFO (percent)
			（a）α – Spin
117	–18.9654	1.00	Br_4(P:z)(15.8), Cu_3(D:xy)(13.2), Br_5(P:z)(11.0), Cu_2(D:x^2-y^2)(10.7), Cu_1(D:x^2-y^2)(9.3),
118	–18.8671	1.00	Cu_3(D:z^2)(13.4), Br_4(P:y)(12.9), Cu_2(D:z^2)(8.1), Br_5(P:y)(6.9), Cu_1(D:x^2-y^2)(6.5),
119	–18.8657	1.00	Cu_1(D:z^2)(14.4), Br_4(P:x)(12.8), Br_5(P:x)(7.0), Cu_2(D:z^2)(6.6), Cu_3(D:xy)(6.6),Cu_1(D:yz)(5.0),
120	–18.7048	1.00	Cu_3(D:x^2-y^2)(14.7), Cu_1(D:xy)(11.3), Cu_2(D:xy)(11.1),
121	–18.1009	1.00	O_{16}(P:x)(10.6), O_{21}(P:z)(8.7), O_{21}(P:y)(8.3), O_{32}(P:y)(8.2), O_{16}(P:z)(8.2), O_{32}(P:z)(8.1),
122	–17.8776	1.00	O_{21}(P:z)(13.3), O_{21}(P:y)(12.1), O_{32}(P:z)(5.7),
123	–17.8741	1.00	O_{16}(P:x)(15.1), O_{16}(P:z)(12.2), O_{32}(P:y)(9.1), O_{32}(P:z)(8.5),
124	–17.4312	1.00	Cu_3(D:yz)(15.2), Br_4(P:y)(8.5), Br_5(P:y)(8.5), N_{11}(P:y)(5.8), N_{10}(P:y)(5.5),
125	–17.4306	1.00	Br_4(P:x)(8.5), Br_5(P:x)(8.5), Cu_2(D:xz)(8.4), Cu_1(D:xz)(7.1),
126	–17.2292	1.00	Br_5(P:z)(10.8), Br_4(P:z)(10.7), Cu_3(D:yz)(9.4), Cu_2(D:xz)(7.1), Cu_1(D:xz)(7.0),
127	–12.5511	0.00	Cu_3(S)(14.6), Cu_2(S)(14.6), Cu_1(S)(14.3), Cu_1(S)(6.5), Cu_3(S)(6.4), Cu_2(S)(6.4),
128	–12.0208	0.00	Cu_1(S)(24.7), Cu_3(S)(8.5), Cu_2(P:y)(7.0), Cu_3(P:x)(5.2),
129	–12.0169	0.00	Cu_2(S)(20.9), Cu_3(S)(16.5), Cu_1(P:y)(6.7),
130	–11.6636	0.00	H_{52}(S)(6.0), H_{54}(S)(6.0), H_{38}(S)(5.9), H_{53}(S)(5.7), H_{51}(S)(5.7), H_{33}(S)(5.6), Cu_3(P:z)(5.4),Cu_2(P:z)(5.4), Cu_1(P:z)(5.3),
			（b）β – Spin
114	–18.9928	1.00	Cu_3(D:xz)(19.9), Cu_2(D:yz)(16.0), Cu_1(D:yz)(13.9), Cu_1(D:xz)(6.2),
115	–18.7729	1.00	Cu_3(D:xz)(18.9), Cu_3(D:x^2-y^2)(8.3), Br_5(P:x)(6.0), Cu_2(D:x^2-y^2)(5.3),
116	–18.7710	1.00	Cu_2(D:yz)(12.1), Cu_1(D:yz)(8.6), Cu_1(D:xy)(7.7), Cu_2(D:xy)(6.1), Br_5(P:y)(6.1),
117	–18.6937	1.00	Cu_3(D:xy)(14.7), Br_4(P:z)(14.1), Cu_2(D:x^2-y^2)(12.1), Cu_1(D:x^2-y^2)(10.2), Br_5(P:z)(9.6),
118	–18.6136	1.00	Cu_3(D:z^2)(16.1), Br_4(P:y)(12.1), Cu_2(D:z^2)(9.4), Cu_1(D:x^2-y^2)(7.8), Br_5(P:y)(7.0),Cu_2(D:x^2-y^2)(5.8),
119	–18.6121	1.00	Cu_1(D:z^2)(17.0), Br_4(P:x)(12.1), Cu_3(D:xy)(8.6), Cu_2(D:z^2)(8.1), Br_5(P:x)(7.0),Cu_1(D:yz)(5.4),
120	–18.4472	1.00	Cu_3(D: x^2-y^2)(15.6), Cu_1(D:xy)(12.0), Cu_2(D:xy)(11.7),
121	–18.0659	1.00	O_{16}(P:x)(10.7), O_{21}(P:z)(8.7), O_{32}(P:y)(8.4), O_{16}(P:z)(8.3), O_{32}(P:z)(8.3), O_{21}(P:y)(8.1),
122	–17.7757	1.00	O_{21}(P:z)(13.2), O_{21}(P:y)(11.4), O_{32}(P:z)(7.2), O_{32}(P:y)(5.7), Cu_3(D:x^2-y^2)(5.5),
123	–17.7723	1.00	O_{16}(P:x)(16.1), O_{16}(P:z)(13.5), O_{32}(P:y)(7.8), O_{32}(P:z)(7.3),
124	–16.8598	0.00	Cu_3(D:yz)(20.1), Br_4(P:y)(7.9), Cu_1(D:xz)(7.8), Br_5(P:y)(7.2), N_{11}(P:y)(5.4),N_{10}(P:y)(5.1),
125	–16.8589	0.00	Cu_2(D:xz)(12.8), Cu_1(D:xz)(8.1), Br_4(P:x)(7.9), Br_5(P:x)(7.2), Cu_2(D:yz)(5.6),N_9(P:x)(5.0),
126	–16.6157	0.00	Cu_3(D:yz)(11.8), Br_5(P:z)(9.3), Br_4(P:z)(9.2), Cu_1(D:xz)(8.9), Cu_2(D:xz)(8.8),
127	–12.4694	0.00	Cu_3(S)(13.6), Cu_2(S)(13.5), Cu_1(S)(13.3), Cu_1(S)(6.9), Cu_3(S)(6.9), Cu_2(S)(6.8),

Table S2. Compositions of the atomic orbitals in the principal molecular orbitals for model compound **3** (**S** = 3/2).

Orb.	Energy (eV)	Occ.	Primary Contributors SFO (percent)
			（a） α – Spin
107	−19.0551	1.00	Cu_3(D:xz)(24.0), Cu_1(D:yz)(8.2), Cu_2(D:xz)(7.8), Cu_3(D:yz)(7.7),
108	−18.8186	1.00	Cu_1(D:xy)(13.1), Cu_3(D:xy)(13.0), Cu_2(D:xy)(11.8), Cu_3(D:z^2)(11.1), O_{11}(P:y)(5.2),
109	−18.8045	1.00	Cu_3(D:x^2-y^2)(15.2), Cu_2(D:x^2-y^2)(15.0), Cu_1(D:x^2-y^2)(10.0), Cu_1(D:z^2)(9.0),Cu_2(D:z^2)(6.7), O_{11}(P:x)(6.2),
110	−18.5111	1.00	Cu_1(D:x^2-y^2)(15.9), Cu_3(D:xy)(12.1), Cu_2(D:xy)(11.9),
111	−18.2162	1.00	O_{14}(P:y)(11.7), O_{13}(P:x)(10.2), O_{12}(P:x)(8.7), O_{13}(P:z)(7.4), O_{14}(P:z)(6.2), O_{12}(P:z)(6.2),
112	−17.9038	1.00	O_{13}(P:x)(13.2), O_{13}(P:z)(10.2), O_{14}(P:y)(5.9), Cu_1(D:x^2-y^2)(5.4),
113	−17.8624	1.00	O_{14}(P:y)(14.2), O_{12}(P:x)(12.6), O_{12}(P:z)(8.5), O_{14}(P:z)(8.1), Cu_3(D:xy)(6.1),
114	−17.5282	1.00	Cu_1(D:xz)(10.2), Cu_2(D:yz)(8.0), Cu_3(D:yz)(7.7),
115	−17.2296	1.00	Cu_1(D:xz)(15.6), Cu_2(D:yz)(13.1), O_{11}(P:x)(6.8),
116	−17.1703	1.00	Cu_3(D:yz)(15.9), O_{11}(P:y)(6.8), N_8(P:y)(5.9), Cu_1(D:xz)(5.3), Cu_3(D:xz)(5.2),
117	−13.1709	0.00	Cu_2(S)(10.8), Cu_1(S)(10.7), H_{48}(S)(10.7), H_{47}(S)(10.2), Cu_3(S)(9.3), Cu_2(S)(6.4),Cu_1(S)(6.3), Cu_3(S)(5.7),
118	−12.4739	0.00	H_{47}(S)(11.7), H_{48}(S)(11.0),
119	−11.8372	0.00	Cu_3(S)(20.8), Cu_3(S)(11.2), Cu_2(S)(6.1),
120	−11.8168	0.00	Cu_1(S)(17.0), Cu_2(S)(15.2), Cu_1(S)(8.3), Cu_2(S)(7.7),
			（b）β – Spin
104	−18.8869	1.00	Cu_1(D:yz)(22.1), Cu_3(D:xz)(19.5), Cu_2(D:xz)(18.9), Cu_3(D:yz)(8.2), Cu_2(D:yz)(5.8),
105	−18.8092	1.00	Cu_1(D:xy)(15.2), Cu_1(D:yz)(14.2), Cu_2(D:x^2-y^2)(11.2), Cu_3(D:x^2-y^2)(10.2),Cu_2(D:xz)(9.9), Cu_3(D:xy)(5.0),
106	−18.7942	1.00	Cu_1(D:yz)(16.2), Cu_2(D:yz)(11.6), Cu_3(D:x^2-y^2)(10.4), Cu_2(D:xz)(9.3), Cu_1(D:xy)(5.8),Cu_2(D:x^2-y^2)(5.0),
107	−18.7302	1.00	Cu_3(D:xz)(27.6), Cu_1(D:yz)(10.4), Cu_3(D:yz)(9.1), Cu_2(D:xz)(8.7),
108	−18.5042	1.00	Cu_1(D:xy)(15.8), Cu_3(D:z^2)(12.4), Cu_2(D:xy)(9.7), Cu_3(D:xy)(7.7), Cu_2(D:x^2-y^2)(6.2),O_{11}(P:y)(5.7),
109	−18.4674	1.00	Cu_3(D:x^2-y^2)(17.0), Cu_2(D:x^2-y^2)(13.6), Cu_1(D:z^2)(8.0), Cu_2(D:z^2)(7.7), Cu_1(D:xy)(7.0),O_{11}(P:x)(6.5), Cu_3(D:xy)(5.0),
110	−18.2052	1.00	Cu_1(D:x^2-y^2)(16.2), Cu_3(D:xy)(12.7), Cu_2(D:xy)(9.9),
111	−18.1817	1.00	O_{14}(P:y)(10.0), O_{13}(P:x)(9.6), O_{12}(P:x)(6.6), O_{12}(P:z)(5.8), O_{13}(P:z)(5.7), O_{14}(P:z)(5.3),
112	−17.7782	1.00	O_{13}(P:x)(11.4), Cu_1(D:x^2-y^2)(9.1), O_{13}(P:z)(9.0), Cu_2(D:xy)(7.2),
113	−17.7327	1.00	O_{14}(P:y)(12.1), O_{12}(P:x)(10.7), Cu_3(D:xy)(10.3), O_{12}(P:z)(7.1), O_{14}(P:z)(7.0),
114	−16.7682	0.00	Cu_1(D:xz)(14.1), Cu_2(D:yz)(11.0), Cu_3(D:yz)(10.3),
115	−16.4709	0.00	Cu_1(D:xz)(20.2), Cu_2(D:yz)(16.4), O_{11}(P:x)(6.4),
116	−16.4011	0.00	Cu_3(D:yz)(20.6), Cu_3(D:xz)(6.8), Cu_1(D:xz)(6.5), O_{11}(P:y)(6.5),
117	−13.0911	0.00	H_{48}(S)(10.4), Cu_2(S)(10.2), Cu_1(S)(10.1), H_{47}(S)(9.9), Cu_3(S)(8.7), Cu_2(S)(6.8),