Electronic Supplementary Information for:

Asymmetric terminal ligation on substituted sites in a disorder-free Keggin anion, [β-SiFe$_2$W$_{10}$O$_{36}$(OH)$_2$(H$_2$O)Cl]$^{5-}$

Bogdan Botar,[a] **Yurii V. Geletii,**[a] **Paul Kögerler,**[b] **Djamaladdin G. Musaev,**[c] **Keiji Morokuma,**[a,c] **Ira A. Weinstock,**[d] **and Craig L. Hill**[a]*

[a] *Department of Chemistry, Emory University, Atlanta, GA 30322, USA; E-mail: chill@emory.edu*
[b] *Ames Laboratory, Iowa State University, Ames, IA 50011, USA*
[c] *Emerson Center for Scientific Computation, Emory University, Atlanta, GA 30322, USA*
[d] *Department of Chemistry, City College of The City University New York, New York, NY 10031,USA*

DFT calculations.
The geometries, relative energies and charge distributions of both **1** (Fe-Cl unit in the non-rotated triad and the Fe-OH$_2$ unit in the rotated triad) and the other isomer (Fe-Cl unit in the rotated triad and the Fe-OH$_2$ unit in the non-rotated triad) were calculated by DFT methods (See Table S1 below).¶ Unfortunately, DFT methods can't rigorously describe states in which some of the spins are antiferromagnetically coupled to each other, so we have resorted, as others have done with more antiferromagnetically coupled spins than is seen in **1** (cf. M-H. Baik, M. Newcomb, R. A. Friesner, and S. J. Lippard, *Chem. Rev. 2003*, **103**, 2385-2419), to calculating the ferromagnetic states (the 2S+1 = 11 high-spin states in our case).

Table S1. The calculated geometrical (distances in Å) parameters, relative energy (in kcal/mol) and natural atomic charges (in e) of **Isomer_1** and **Isomer_2** (pictured in Fig S1) of **1**. **Isomer_1** is **1**.

Properties	Isomer_1	Isomer_2	Experimental
Fe1 or 2-Cl1	2.314	2.353	2.282(6)
Fe1-O11	1.931	1.956	1.932(14)
Fe1-O3	1.923	1.870	1.952(14)
Fe1-O13(H, Isomer_1)	2.063	2.002	2.008(14)
Fe1-O25(H, Isomer_1)	2.060	2.005	2.002(14)
Fe1-O16(Si1)	2.373	2.084	2.254(13)

Fe2-O4(H, Isomer_2)	2.008	2.043	1.980(13)
Fe2-O14(H, Isomer_2)	1.954	2.042	1.964(13)
Fe2-O15	2.002	1.973	1.972(13)
Fe2-O20	1.945	1.962	1.967(13)
Fe2-O7(Si1)	2.158	2.232	2.139(13)
W10-O11	1.855	1.864	1.807(13)
W7-O3	1.857	1.880	1.781(13)
W2-O13(H, Isomer_1)	2.126	1.834	2.139(14)
W1-O25 H, Isomer_1)	2.124	1.834	2.037(13)
W2-O4(H, Isomer_2)	1.896	2.070	1.810(12)
W1-O14(H, Isomer_2)	1.884	2.075	1.786(12)
W8-O15	1.870	1.856	1.811(12)
W4-O20	1.883	1.857	1.843(12)
E (kcal/mol)	0.0	0.21	---

NBO (Charges)

Fe1	1.81	1.76
Fe2	1.77	1.75
Cl1	-0.75	-0.70
O29	-1.02(0.03)[b]	-1.02(0.03)[b]
O11	-0.91	-0.96
O3	-0.91	-0.90
O13 (H, Isomer_1)	-1.07(-0.54)[c]	-0.93
O25 (H, Isomer_1)	-1.07(-0.54)[c]	-0.87
O4 (H, Isomer_2)	-0.91	-1.05(-0.52)[c]
O14 (H, Isomer_2)	-0.87	-1.05(-0.52)[c]
O15	-0.96	-0.88
O20	-0.89	-0.88
O16	-1.30	-1.28
O7	-1.28	-1.31

a) In these calculations the Fe-O29(H_2) distance is fixed to be 2.15 Å. See Fig. S1 for notation of the atoms.

b) In parenthesis is the total charge of the water molecule.

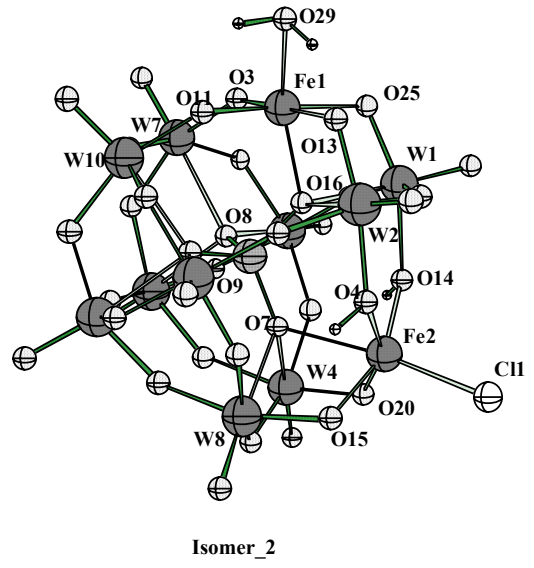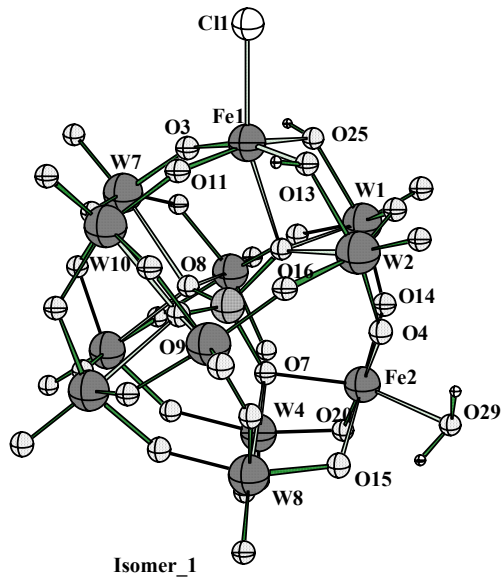c) In parenthesis are the total charges of the hydroxy group.

Fig. S1 The two calculated isomers.