
Selenium as a Structural Surrogate of Sulfur: Template-Assisted Assembly of Five Types of Tungsten-Iron-Sulfur/Selenium Clusters and the Structural Fate of Chalcogenide Reactants

Bo Zheng, Xu-Dong Chen, Shao-Liang Zheng and R. H. Holm*

Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts 02138, United States

SUPPORTING INFORMATION

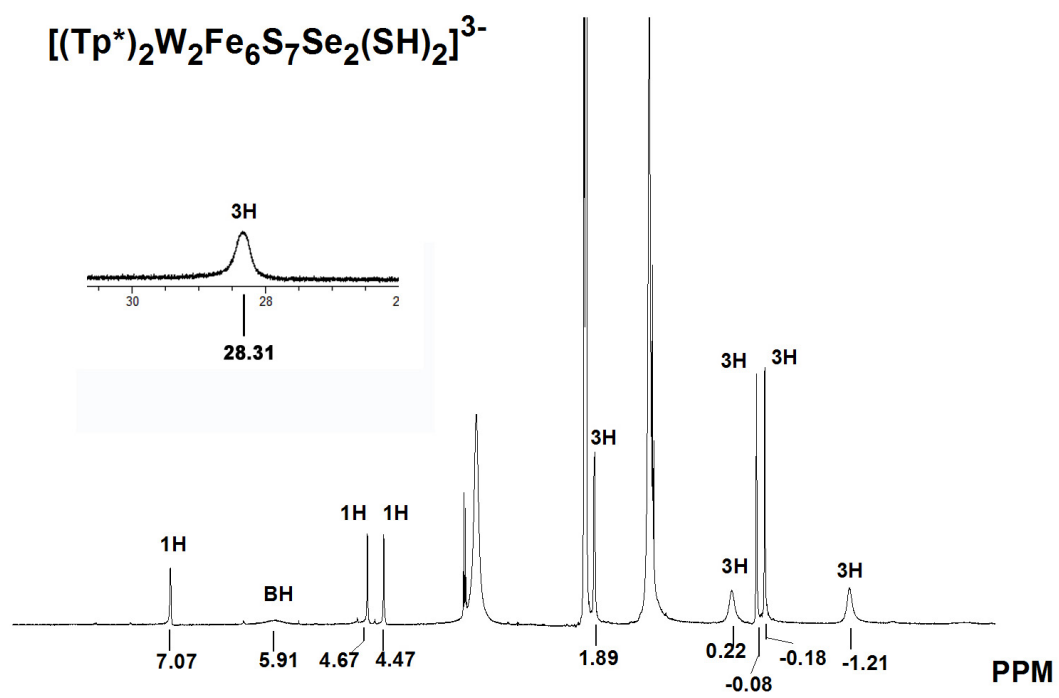


Figure S1. 1H NMR spectra of **9** in CD_3CN solution at ambient temperature. Signal assignments are indicated.

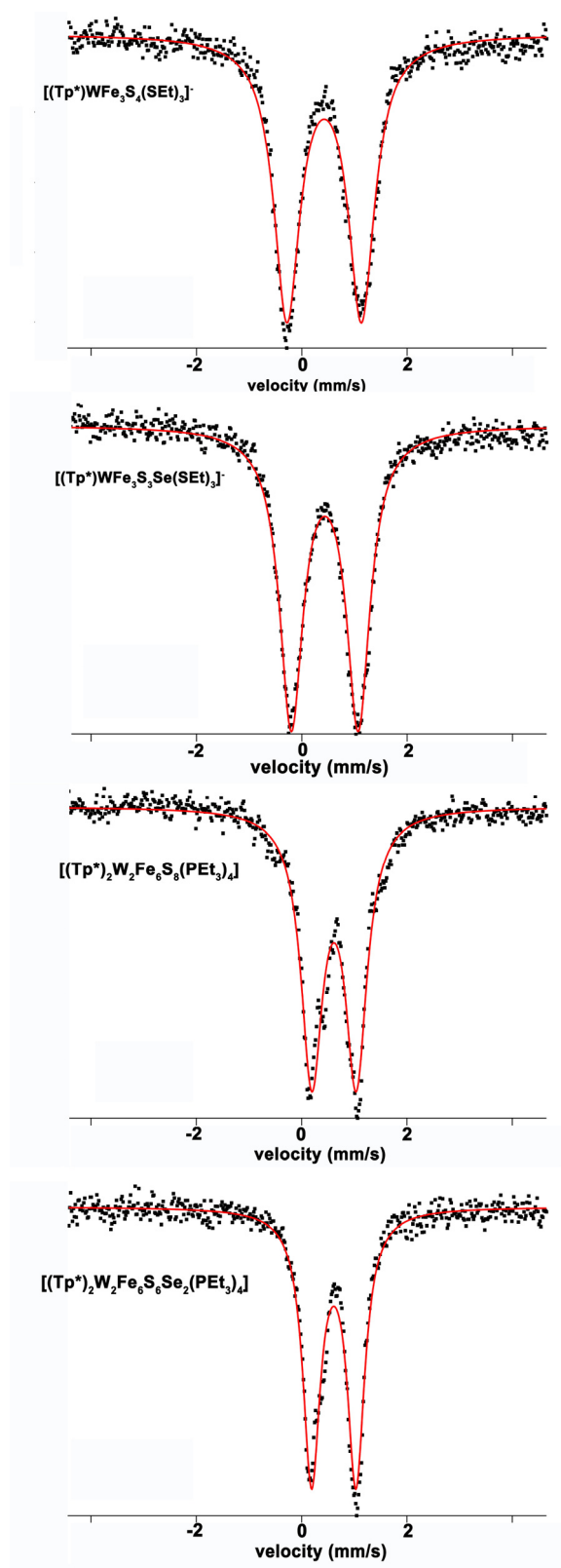
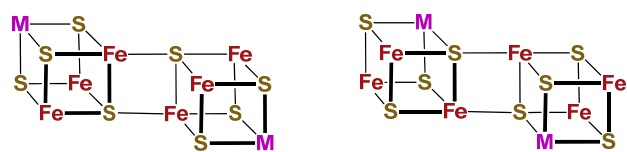


Figure S2. ^{57}Fe Mössbauer spectra of polycrystalline salts of the clusters $[(\text{Tp}^*)\text{WFe}_3\text{S}_4(\text{SEt})_3]$, $[(\text{Tp}^*)\text{WFe}_3\text{S}_3\text{Se}(\text{SEt})_3]$, $[(\text{Tp}^*)_2\text{W}_2\text{Fe}_6\text{S}_8(\text{PEt}_3)_4]$ and $[(\text{Tp}^*)_2\text{W}_2\text{Fe}_6\text{S}_6\text{Se}_2(\text{PEt}_3)_4]$ at 95 K in zero field. Solid lines are fits to the data using the parameters of Table 2.

Symmetric



Asymmetric

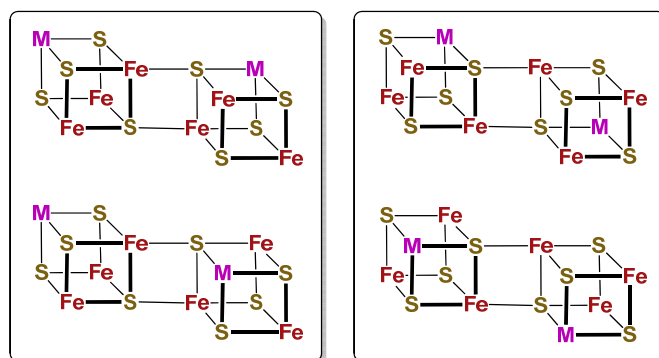


Figure S3. Possible isomers of edge-bridged double cubane.

Table S1. Crystallographic Data for complexes (**2-15**) at 100 K^a.

	(Et ₄ N)[2].CH ₃ CN	(Et ₄ N)[3].0.5CH ₃ CN	(Et ₄ N)[4]	(Et ₄ N)[5b]	(Et ₄ N)[6b].0.5THF
formula	C ₂₅ H ₄₅ BCl ₂ FeN ₈ S ₃ W	C ₂₆ H _{48.5} BCl ₂ Fe ₂ N _{7.5} S ₄ W	C ₅₈ H ₁₁₄ B ₂ Fe ₄ N ₁₄ S ₁₂ W ₂	C ₂₃ H ₄₂ BCl ₃ Fe ₃ N ₇ S ₃ SeW	C ₃₁ H ₆₁ BFe ₃ N ₇ O _{0.5} S ₆ SeW
formula weight	875.28	971.72	2005.08	1060.34	1173.40
crystal system	monoclinic	triclinic	triclinic	monoclinic	triclinic
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> , Å	19.524(8)	10.416(2)	12.386(2)	9.803(2)	10.704(2)
<i>b</i> , Å	9.760(4)	10.456(2)	18.724(3)	33.054(6)	11.746(2)
<i>c</i> , Å	17.961(8)	18.830(3)	18.774(3)	11.733(2)	20.309(3)
<i>a</i> , deg	90	80.310(3)	71.878(2)	90	90.973(2)
<i>β</i> , deg	92.212(6)	80.003(3)	85.544(2)	111.846(3)	91.723(2)
<i>γ</i> , deg	90	82.389(3)	74.194(2)	90	110.001(2)
<i>V</i> , Å ³	3420(3)	1979.5(6)	3981(1)	3529(1)	2397.2(6)
<i>Z</i>	4	2	2	4	2
<i>μ</i> , mm ⁻¹	4.155	4.00	3.95	5.922	4.332
<i>R</i> ₁ ^b , <i>wR</i> ₂ ^c (<i>I</i> > 2σ(<i>I</i>))	0.0252, 0.0530	0.0469, 0.1163	0.0273, 0.0504	0.0328, 0.0610	0.0388, 0.1057
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0321, 0.0558	0.0540, 0.1195	0.0386, 0.0540	0.0380, 0.0623	0.0443, 0.1111
GOF (<i>F</i> ²)	1.035	1.127	1.046	1.163	1.077
	[7b](BPh ₄)	[8b]	(Et ₄ N) ₃ [9].CH ₃ CN .0.5Et ₂ O.3DMF	(Et ₄ N) ₃ [10].4DMF .0.5Et ₂ O	(Et ₄ N) ₃ [11].2DMF .0.5Et ₂ O
formula	C ₅₇ H ₈₇ B ₂ Fe ₃ N ₆ P ₃ S ₃ SeW	C ₅₄ H ₁₀₄ B ₂ Fe ₆ N ₁₂ P ₄ S ₆ Se ₂ W ₂	C ₆₇ H ₁₃₅ B ₂ Fe ₆ N ₁₉ O _{3.5} S ₅ Se ₂ W ₂	C ₆₈ H ₁₃₉ B ₂ Fe ₆ N ₁₉ O _{4.5} S ₆ Se ₃ W ₂	C ₆₅ H ₁₃₂ B ₂ Fe ₆ N ₁₇ O _{2.5} S ₉ Se ₂ W ₂
formula weight	1497.40	2120.07	2433.82	2606.56	2362.76
crystal system	monoclinic	monoclinic	monoclinic	triclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>
<i>Z</i>	4	4	4	2	4
<i>a</i> , Å	11.536(1)	30.352(9)	23.540(1)	16.210(2)	23.704(3)
<i>b</i> , Å	15.352(1)	11.039(3)	18.550(1)	16.571(3)	18.999(2)
<i>c</i> , Å	35.917(3)	22.117(7)	25.517(1)	21.420(4)	25.383(3)
<i>a</i> , deg	90	90	90	75.838(5)	90
<i>β</i> , deg	92.642(1)	92.148(6)	94.290(1)	87.466(5)	93.757(3)
<i>γ</i> , deg	90	90	90	66.487(3)	90
<i>V</i> , Å ³	6354.5(9)	7405(4)	11111(1)	5106(1)	11407(2)
<i>μ</i> , mm ⁻¹	3.264	5.516	3.690	5.024	3.591
<i>R</i> ₁ ^b , <i>wR</i> ₂ ^c (<i>I</i> > 2σ(<i>I</i>))	0.0354, 0.0725	0.0338, 0.0748	0.0404, 0.1082	0.0449, 0.1140	0.0481, 0.1380
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0473, 0.0768	0.0499, 0.0821	0.0660, 0.1212	0.0697, 0.1259	0.0663, 0.1489
GOF (<i>F</i> ²)	1.062	1.028	1.025	1.018	1.032
	(Et ₄ N)[12].2DMF	(Et ₄ N) ₂ [13].2.5DMF	[14]	(Et ₄ N) ₂ [15].3DMF	
formula	C ₄₄ H ₇₈ B ₂ Fe ₄ N ₁₅ O ₂ S ₉ W ₂	C _{53.5} H _{101.5} B ₂ Fe ₄ N _{16.5} O _{2.5} S ₉ W ₂	C ₃₀ H ₄₄ B ₂ Fe ₄ N ₁₂ S ₆ Se ₃ W ₂	C ₁₀₁ H ₁₈₉ B ₄ Fe ₈ N ₃₁ O ₃ S ₁₂ Se ₆ W ₄	
formula weight	1750.47	1917.27	1614.73	3969.75	
crystal system	monoclinic	monoclinic	monoclinic	triclinic	
space group	<i>C</i> 2/ <i>c</i>	<i>P</i> 2/ <i>n</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> $\bar{1}$	
<i>Z</i>	4	4	8	2	
<i>a</i> , Å	16.114(2)	20.431(6)	28.845(5)	20.22(1)	
<i>b</i> , Å	13.405(2)	10.277(3)	18.556(3)	20.24(1)	
<i>c</i> , Å	30.402(4)	37.27(1)	27.418(5)	21.45(1)	
<i>a</i> , deg	90	90	90	89.618(8)	
<i>β</i> , deg	101.553(2)	91.281(5)	111.003(2)	86.91(1)	
<i>γ</i> , deg	90	90	90	64.479(9)	
<i>V</i> , Å ³	6434(2)	7823(4)	13701(4)	7910(8)	
<i>μ</i> , mm ⁻¹	4.779	3.939	5.974	5.193	
<i>R</i> ₁ ^b , <i>wR</i> ₂ ^c (<i>I</i> > 2σ(<i>I</i>))	0.069, 0.237	0.070, 0.153	0.0524, 0.1407	0.0811, 0.1947	
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.079, 0.244	0.156, 0.194	0.0916, 0.1555	0.1981, 0.2462	
GOF (<i>F</i> ²)	1.081	1.008	1.037	1.027	

^a Collected using Mo Kα radiation (λ = 0.71073 Å). ^b *R*₁ = Σ||*F*_o| - |*F*_c||/Σ|*F*_o|. ^c *wR*₂ = {Σ[*w*(*F*_o² - *F*_c²)²]/Σ[*w*(*F*_o²)²]}^{1/2}.