Hydrocarbon Oxidation Catalyzed by Self-folded Metal-coordinated Cavitands

Katherine E. Djernes, Melissa Padilla, Magi Mettry, Michael C. Young and Richard J. Hooley

Department of Chemistry, University of California, Riverside, CA 92521
richard.hooley@ucr.edu

Electronic Supplementary Information

1. General Information

^{1}H and ^{13}C NMR spectra were recorded on a Varian Inova 300 or Inova 400 spectrometer. Proton (^{1}H) chemical shifts are reported in parts per million (δ) with respect to tetramethylsilane ($Si(CH_3)_4$, δ=0), and referenced internally with respect to the protio solvent impurity. Carbon (^{13}C) chemical shifts are reported in parts per million (δ) with respect to tetramethylsilane ($Si(CH_3)_4$, δ=0), and referenced internally with respect to the solvent ^{13}C signal (either $CDCl_3$ or DMSO-d_6). Deuterated NMR solvents were obtained from Cambridge Isotope Laboratories, Inc., Andover, MA, and used without further purification. All other materials were obtained from Aldrich Chemical Company, St. Louis, MO and were used as received. Solvents were dried through a commercial solvent purification system (SG Water, Inc.). Electrospray mass spectra were recorded on an Agilent 6210 LC TOF mass spectrometer using electrospray ionization and processed with an Agilent MassHunter Operating System. MALDI mass spectra were obtained using a PE Biosystems DE-STR MALDI TOF spectrometer operating in refractive mode at 2100 eV. GCMS data was collected on an Agilent Technologies 6890N Network GC system with an Agilent Technologies 5973 inert Mass Selective Detector (column phase: EC-5, length: 30 m, ID: 0.25 mm). Molecular modeling (semi-empirical calculations) were performed using the Hartree-Fock force field using SPARTAN. Cavitands **5** and **6** were synthesized according to the procedure in reference 1. All oxidation products were assigned by comparison (spectrometric or spectroscopic) to authentic samples.

2. Experimental Details

General Oxidation Procedures:

In a 2 mL scintillation vial, catalyst (3.77×10^{-3} mmol, 10 mol%) was dissolved in 0.150 mL solvent (water:acetonitrile or water:propionitrile 1:1). Oxidant (0.377 mmol) and substrate (3.77×10^{-2} mmol) were added, and the reaction was stirred for 24 h (25˚C or 60˚C). Aliquots (75µL) were taken and passed through a silica/magnesium sulfate plug with 1.5 mL ether before being analyzed by GCMS. The reactions were performed in triplicate, and the average yield is reported. All yields are based on recovered starting material.

Analysis of Recovered Catalyst 6•Fe•SO$_4$/6•Fe$_2$•(SO$_4$)$_2$

The oxidation procedure was performed as described above, using ^{t}BuOOH as oxidant and cyclooctane as substrate. Ether (5 mL) was added to the system and the insoluble cavitand precipitate recovered by filtration, dried and analyzed by MALDI-MS.

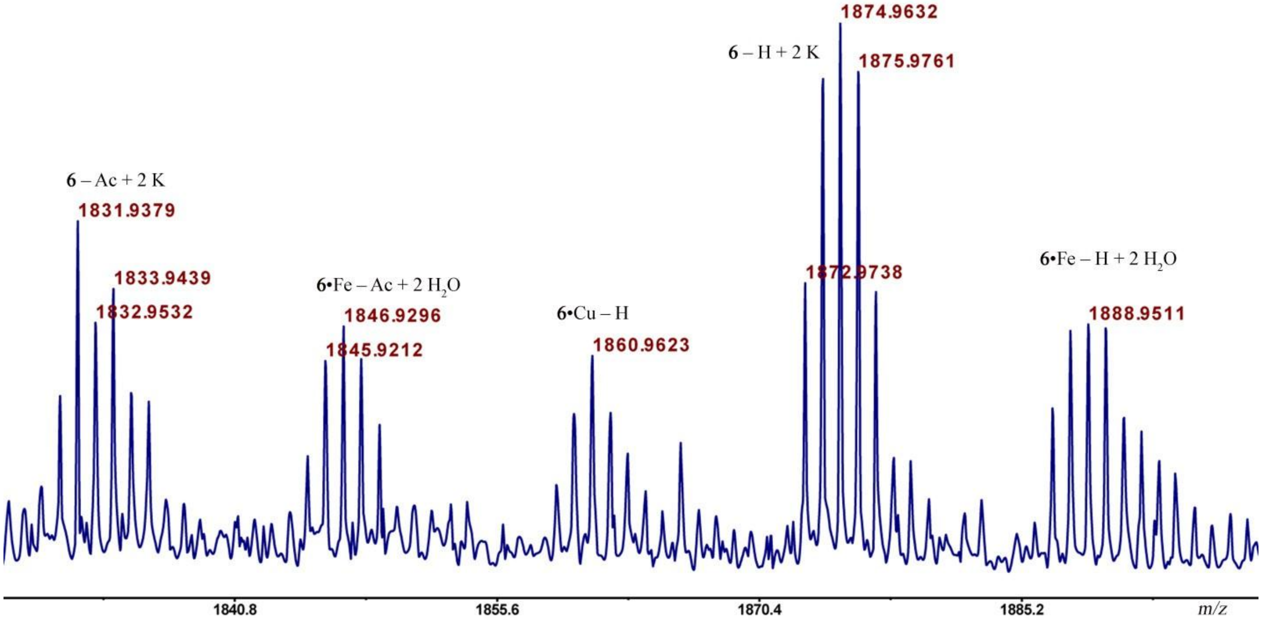

Figure S-1. MALDI spectrum of reclaimed **6•Fe** showing that iron is still coordinated to the cavitand.

3. Synthesis and Characterization of New Compounds

Synthesis of 5•Fe$_2$•(SO$_4$)$_2$

In a 20 mL scintillation vial, cavitand **5**[1] (0.375 g, 0.24 mmol) and iron (II) sulfate (0.370 g, 1.43 mmol) were sonicated in 15 mL of methanol for 20 minutes until a yellow precipitate formed. The precipitate was collected by vacuum filtration, rinsed with 3 x 50 mL portions of methanol, and dried under vacuum. The product was collected as a yellow solid (0.460 g, 99%). The product did not have sufficient solubility to obtain ^{13}C NMR data in a realistic amount of time. MS (MALDI) *m/z* calculated for $C_{84}H_{83}Fe_2N_{16}O_{22}S$ $(M + H_2O + OH – SO_4)^+$ 1811.4287; found 1812.9724. $\chi_{mol} = 1.49 \times 10^{-2}$ cm^3mol^{-1}.

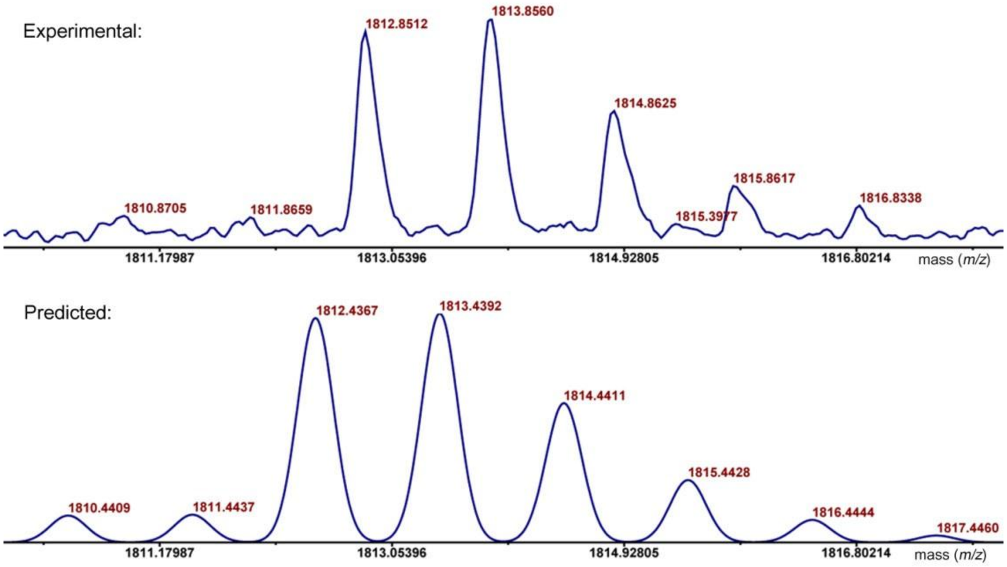

Figure S-2. MALDI spectrum of **$5\bullet Fe_2\bullet(SO_4)_2$** $(M + H_2O + OH – SO_4)^+$; experimental vs. predicted spectra.

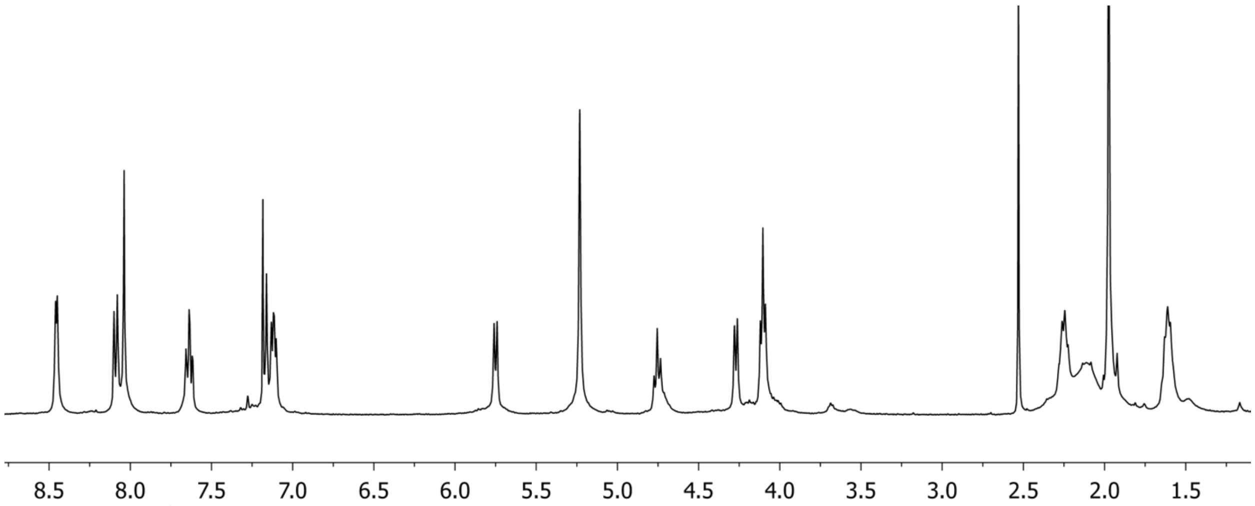

Figure S-3. ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 298K) of cavitand **5** (see ref. **1** for complete characterization).

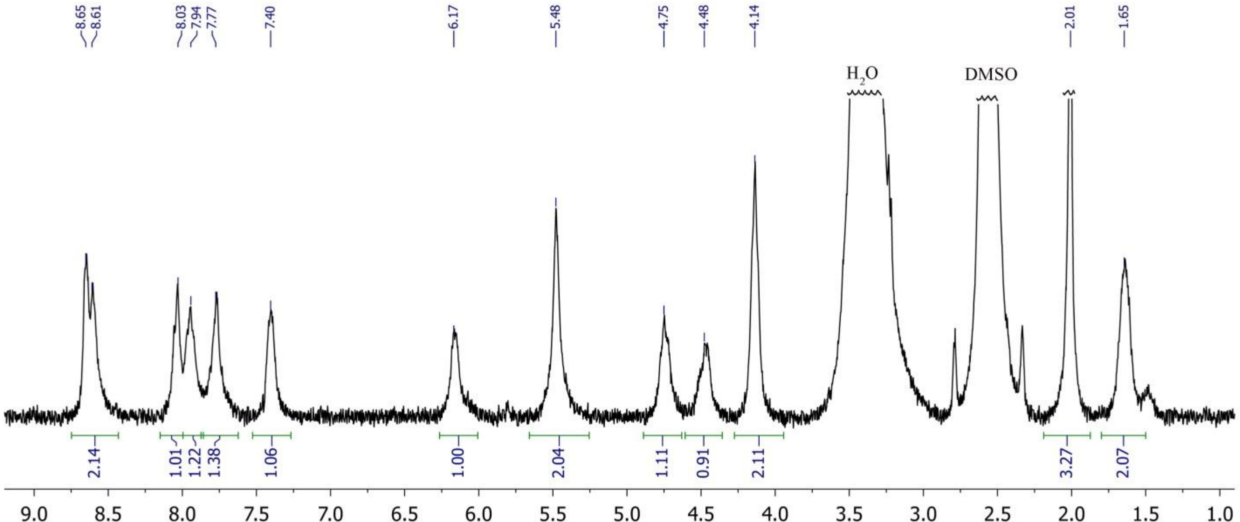

Figure S-4. ^{1}H NMR spectrum (300 MHz, DMSO-*d*$_6$, 298K) of **5•Fe$_2$•(SO$_4$)$_2$**.

Synthesis of 6•Fe•SO$_4$/6•Fe$_2$•(SO$_4$)$_2$

In a 20 mL scintillation vial, **6**[1] (0.550g, 0.31 mmol) and iron (II) sulfate (0.475g, 1.8 mmol) were sonicated in 15 mL of methanol for 20 minutes. The product was collected *via* vacuum filtration, rinsed with 3 x 50 mL excess methanol, and dried under vacuum. The product was collected as a reddish solid (0.642 g, 99%, calculation based on the mass of the bis-iron species **6•Fe$_2$•(SO$_4$)$_2$**). The NMR peaks were broad and poorly defined so no integral values or coupling constants were obtained. The product did not have sufficient solubility to obtain ^{13}C NMR data in a realistic amount of time. Due to the extremely high affinity of **6** for copper, residual copper-coordinated cavitand **6•Cu** is also observed. Copper could not be completely removed from **6** even after refluxing **6** in water with NaEDTA and then with NaSH. It should be noted that the copper-coordinated side-product **6•Cu** is observed in the MS analysis of pure **6** (NMR spectrum shown in Figure *S-7*) and has a far higher ionization potential than both **6** and **6•Fe/6•Fe$_2$**,[1] and the actual amount present in the **6•Fe/6•Fe$_2$** sample is minimal. MS (MALDI) *m/z* calculated for $C_{92}H_{91}FeN_{20}O_{20}$ (M – H – SO$_4$)$^+$ 1851.6068; found 1851.9865; and $C_{92}H_{89}Fe_2N_{20}O_{20}$ (M – 3H – 2SO$_4$)$^+$ 1905.5261; found 1905.9123. $\chi_{mol} = 1.59 \times 10^{-2}$ cm^{3}mol^{-1}

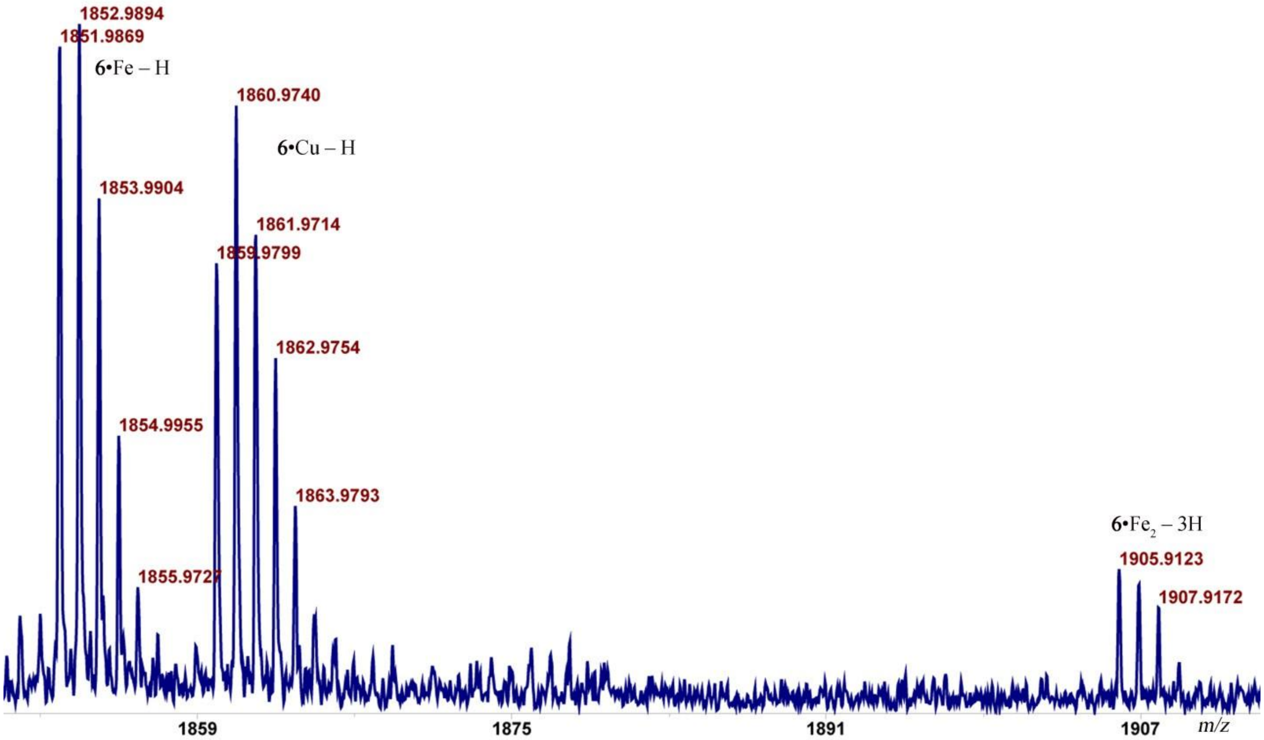

Figure S-5. MALDI-MS spectrum of **6•Fe/6•Fe$_2$**. Note that residual copper from the CuAAC synthesis of **6** is present (see discussion above).

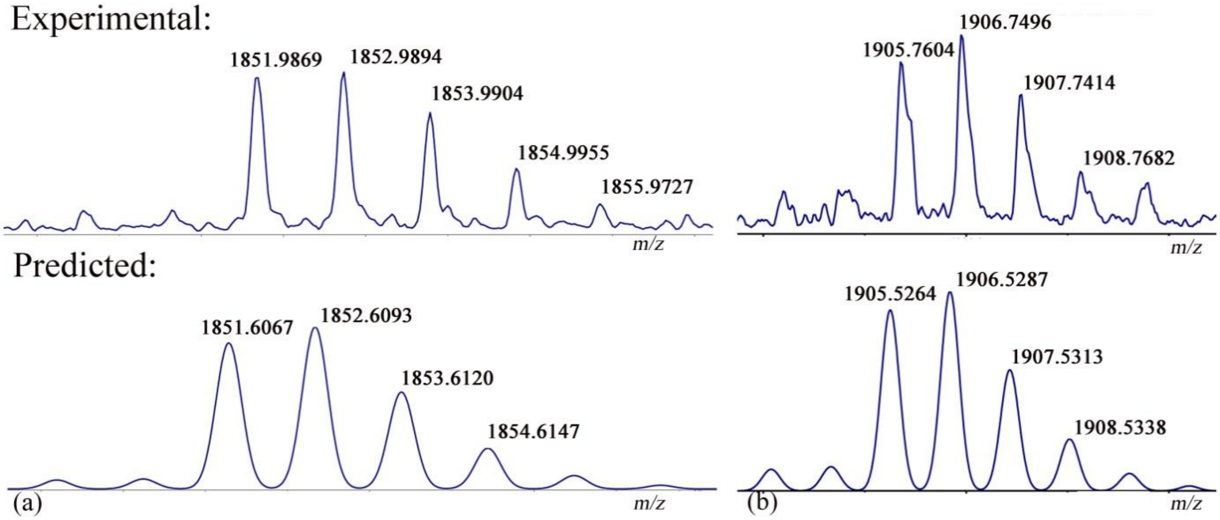

Figure S-6. Experimental vs. predicted MALDI spectra of (a) **6•Fe** $(M - H)^+$ and (b) **6•Fe$_2$** $(M - 3H - 2SO_4)^+$.

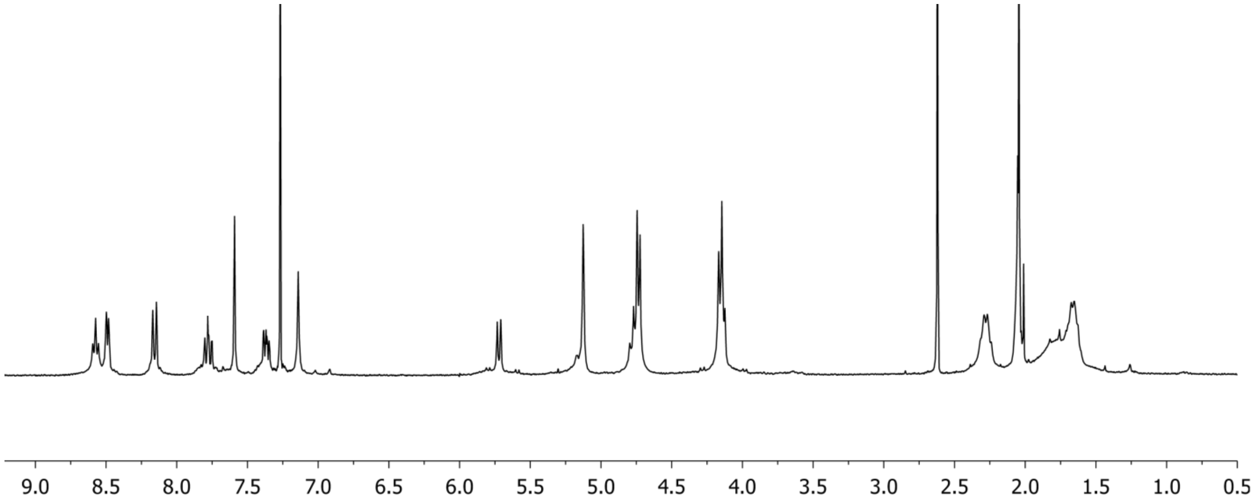

Figure S-7. ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 298K) of cavitand **6** (see ref. 1 for complete characterization).

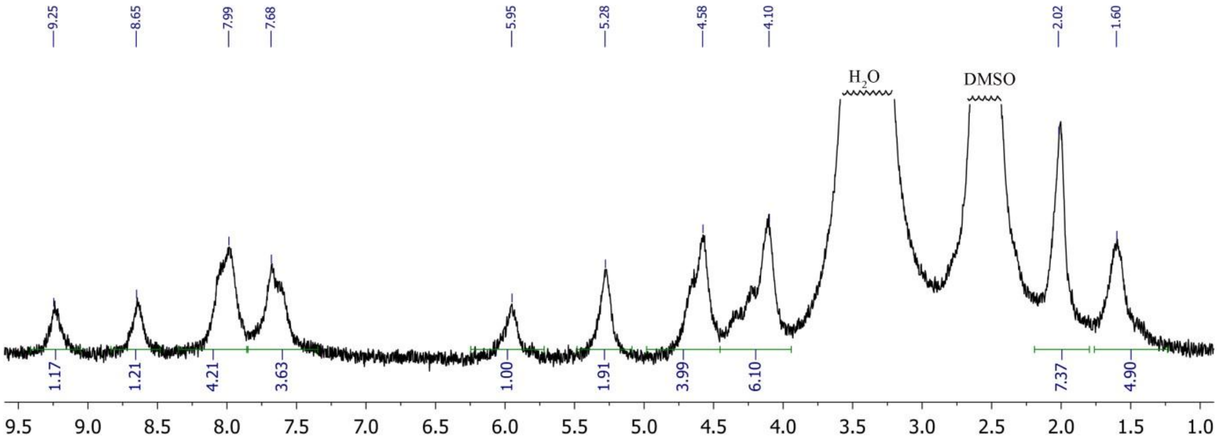

Figure S-8. ^{1}H NMR spectrum (300 MHz, DMSO-d_6, 298K) of the mixture of **$6{\bullet}Fe{\bullet}SO_4/6{\bullet}Fe_2{\bullet}(SO_4)_2$**.

4. Magnetic Susceptibility Measurements

Magnetic susceptibility measurements were performed according to the Evans method.[2] DMSO-d_6 was used as the NMR solvent, with the density of the solvent measured before and after dissolution of analyte. A reference tube was prepared by adding DMSO-d_6 into a melting point capillary, followed by flame sealing the tip. This was added to the NMR tube, and a standard ^{1}H-NMR was taken. The change was determined by looking at the difference in chemical shift between the DMSO-protio impurity peaks. In determining the magnetic susceptibility, the diamagnetic contribution of the solvent was added to compensate for the retardation of the shift caused by the solvent.[3] Because the change in density was found to be very small, the solvent correction term was omitted. As the cavitands used in making these complexes are very large, the diamagnetic contribution was expected to be quite large, and these were calculated using Pascal's constants.[4] In determining the molar susceptibilities, the molecular weight of the **$6{\bullet}Fe{\bullet}SO_4/6{\bullet}Fe_2{\bullet}(SO_4)_2$** was assumed to be from a 1:1 mixture of the mono and dimetallated species.

For **$5{\bullet}Fe_2{\bullet}(SO_4)_2$**:

$$\chi_{g(obsd)} = \frac{3\Delta\delta}{4\pi[\text{[illegible]}]} + \chi_{g(Solvent)}$$

$$\chi_{g(obsd)} = \frac{3 * -.0249}{4\pi * .00605\,g/cm^3} + -7.68 * 10^{-6} = 6.70 * \frac{10^{-6}cm^3}{g}$$

$$\chi_{M(obsd)} = \chi_{g(obsd)} * MW(\text{[illegible]})$$

$$\chi_{M(obsd)} = 6.70 * \frac{10^{-6}cm^3}{g} * 2065.58\frac{g}{mol} = 1.39 * \frac{10^{-2}cm^3}{mol}$$

$$\chi_M = \chi_{M(obsd)} + \chi_{M(Ligand)}$$

$$\chi_M = 1.39 * \frac{10^{-2}cm^3}{mol} + 1.05 * \frac{10^{-3}cm^3}{mol} = 1.49 * \frac{10^{-2}cm^3}{mol}$$

For **$6{\bullet}Fe{\bullet}SO_4/6{\bullet}Fe_2{\bullet}(SO_4)_2$**:

$$\chi_{g(obsd)} = \frac{3 * -.0238}{4\pi * .00550\,g/cm^3} + -7.68 * 10^{-6} = 6.65 * \frac{10^{-6}cm^3}{g}$$

$$\chi_{M(obsd)} = 6.65 * \frac{10^{-6}cm^3}{g} * 2217.83\frac{g}{mol} = 1.47 * \frac{10^{-2}cm^3}{mol}$$

$$\chi_M = 1.47 * \frac{10^{-2}cm^3}{mol} + 1.18 * \frac{10^{-3}cm^3}{mol} = 1.59 * \frac{10^{-2}cm^3}{mol}$$

---

5. References

1) K. E. Djernes, O. Moshe, M. Mettry, D. D. Richards and R. J. Hooley, *Org. Lett*. 2012, **14**, 788.
2) J. Loliger and R. Scheffold, *J. Chem. Educ.*, 1972, **49**, 646; E. M. Schubert, *J. Chem. Educ.*, 1992, **69**, 62.
3) S. M. Sprinkhuizen, C. J. G. Bakker, J. H. Ippel, R. Boelens, M. A. Viergever, L. W. Bartels, *Magn. Reson. Mater. Phys., Biol. Med.* 2012, **25**, 33-39.
4) G. A. Bain and J. F. Berry, *J. Chem. Educ.* 2008, *85*, 532-536.