MODELING NON-HEME IRON HALOGENASES – DISCUSSION QUESTIONS

1. Compare the proposed mechanism for α-ketoglutarate-dependent oxidases (https://www.researchgate.net/figure/Mechanism-of-oxidation-by-FeII-ketoglutarate-dependent-dioxygenases-Intermediate-G_fig2_5904017) with that proposed for α-ketoglutarate-dependent halogenases (https://www.nature.com/articles/nature04544, see Figure 4). In what ways are they similar? How are they different?

2. Why would scientists want to synthesize model complexes of a metalloprotein active site? Why in particular α-ketoglutarate-dependent halogenases?

3. The model complex, whose structure is shown in Figure 1, has the formula $[Fe^{IV}(O)(TQA)(Cl)]^{+}$, where TQA = tris-(quinolyl-2-methyl)amine. Why do you think this ligand works well as a mimic of the iron active site?

4. From Table 1 and Figure 1, the absorption features for the Cl and Br species are blue-shifted relative to MeCN (acetonitrile). Does this match your expectations? Why or why not?

5. Why did the authors perform resonance Raman and Mössbauer spectroscopy?

6. How did the authors test the reactivity of their complex? What types of products and product distributions did they observe? (Hint: Table 2)

7. What reasoning do the authors give for the "chemoselectivity" of their complex? (Hint: next to last paragraph) Does the explanation likely extend to the protein system also?