"**Redox-Active Iron-Oxo Complexes Containing Fe_4O_4-Cubanes; the Search for a Needle in a Haystack, or an Electron in a Multinuclear Cluster**"

Raphael G. Raptis, Department of Chemistry and Biochemistry, Florida International University, Miami, FL 33199. E-mail: rraptis@fiu.edu

The presence of an Fe_4O_4-cubane in the active-center of a protein has been suggested by an iron K-edge XAS study.[1] We will present structural, electrochemical and spectroscopic studies of a family of octanuclear complexes, $[Fe_8(\mu_4\text{-}O)_4(\mu\text{-}4\text{-}R\text{-}pz)_{12}X_4]$ -- R = H, Cl, Br, Me, Et; X = Cl, Br, NCS, OPh -- containing a redox-active Fe_4O_4-cubane, which can be reversibly reduced in four consecutive steps from an all-ferric to an all-ferrous state.[2] The close spacing of those redox steps makes the Fe_4O_4-cubane a more efficient electron-transfer agent than the corresponding Fe_4S_4-cubanes. This, in turn, raises the possibility that an electron-transfer protein based on a Fe_4O_4 active-center may exist, as yet unrecognized, in Nature. The $Fe_8(\mu_4\text{-}O)_4$-motif of our complexes is similar (by X-ray and ^{57}Fe-Mössbauer analysis) to those found in the minerals maghemite, ferrihydrite and magnetite, which might serve a sources for the Fe-O core of such a protein. Spectroscopic analysis of the redox-modified, mixed-valent ($Fe^{II/III}$) species indicate partial charge delocalization.[3, 4] Current efforts to fully characterize, structurally, spectroscopically (electronic, vibrational, Mössbauer, XPS) and magnetically the Fe_4O_4-cubane in all its possible oxidation states will be presented.[5] Recent work has tackled the issue of double-exchange in a multinuclear system for the first time and has provided fresh insights into the controversy of the "Verwey transition". We have recently described a redox-induced spin-crossover in a mixed-valent complex with a $Fe_3(\mu_3\text{-}O)$ core.[6]

1. P. Frank et al., *Inorg. Chem*. **2006**, *45*, 3920.
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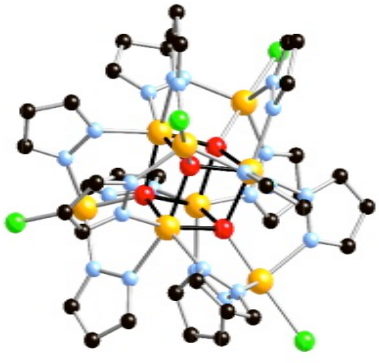
3. R. G. Raptis et al., *Inorg*. Chem. **2008**, *47*, 11734.
4. R. G. Raptis et al., *Inorg*. Chem. **2011**, *50*, 1021.
5. R. G. Raptis et al., *Dalton Trans*. **2014**, *43*, 11269.
6. R. G. Raptis et al., *Angew Chem. Int. Ed.* **2017**, *563*, 582.



Ball-and-stick diagram of $[Fe_8(\mu_4\text{-}O)_4(\mu\text{-}pz)_{12}Cl_4]$.