Iron-Oxo pyrazolates as Electron Transfer Agents and possible MRI Contrast Agents.

Peter Baran,1 Indranil Chakraborty,2 Dalice Piñero2 and Raphael G. Raptis2

1Chemistry Department, Juniata College, and 2Chemistry Department, University of Puerto Rico.

There is a structural parallel between transition metal carboxylates, Mₙ(OCOR)ₓ, and the corresponding pyrazolates, Mₙ(pz)ₓ, pz = pyrazolate (C₃H₃N₂⁻), or substituted pyrazolate. Exploring this parallel with regard to iron-oxo chemistry, we have prepared and characterized some tri-, octa- and nonanuclear complexes.

The paramagnetic [Fe₃(µ₃-O)(µ-4-O₂N-pz)₆Cl₃]²⁻ contains an Fe₂O-core with the same Fe-O and Fe-Fe distances as the well studied [Fe₃(µ₃-O)(µ-OCOR)₆L₃]³⁺ analogues, but the antiferromagnetic exchange constant of the former is almost twice as large as that of the latter. The octanuclear Fe₈(µ₄-O)₄(µ-pz)₁2Cl₄ in contrast has a diamagnetic ground state and a μₐ of 6.52 B.M. at ambient temperature.

The octanuclear complexes Fe₈(µ₄-O)₈(µ-4-R-pz)₁₂X₄, R = H, Cl, Br, Me, X = Cl, Br, NCS, OC₆H₅, contain a redox-active Fe₄O₄-cubane, which can be reversibly reduced in four consecutive steps from an all-ferric to an all-ferrous state. The close spacing of those redox steps makes the Fe₄O₄-cubane a more efficient electron-transfer agent than the corresponding Fe₄S₄-cubanes. This, in turn, raises the possibility that an electron-transfer protein based on a Fe₄O₄ active-center may exist, as yet unrecognized, in Nature. Efforts to fully characterize, structurally, spectroscopically (electronic, vibrational, Mössbauer) and magnetically the Fe₄O₄-cubane in all its possible oxidation states, currently in progress, will be presented.

The unusual kinetic stability of the octanuclear complexes has prompted the investigation of their MRI contrast enhancing properties. Appropriately derivatized water-soluble octanuclear clusters have shown significant image enhancement at millimolar concentrations in MRI phantom experiments.