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

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There is a structural parallel between transition metal carboxylates, $M_x(OCOR)_y$, and the corresponding pyrazolates, $M_x(pz)_y$, pz = pyrazolate ($C_3H_3N_2^-$), 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 $[Fe_3(\mu_3\text{-}O)(\mu\text{-}4\text{-}O_2N\text{-}pz)_6Cl_3]^{2-}$ contains an Fe_3O-core with the same Fe-O and Fe-Fe distances as the well studied $[Fe_3(\mu_3\text{-}O)(\mu\text{-}OCOR)_6L_3]^{n+}$ analogues, but the antiferromagnetic exchange constant of the former is almost twice as large as that of the latter. The octanuclear $Fe_8(\mu_4\text{-}O)_4(\mu\text{-}pz)_{12}Cl_4$ in contrast has a diamagnetic ground state and a μ_{eff} of 6.52 B.M. at ambient temperature.

The octanuclear complexes $Fe_8(\mu_4\text{-}O)_4(\mu\text{-}4\text{-}R\text{-}pz)_{12}X_4$, R = H, Cl, Br, Me, X = Cl, Br, NCS, OC_6H_5, contain 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. 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. Efforts to fully characterize, structurally, spectroscopically (electronic, vibrational, Mössbauer) and magnetically the Fe_4O_4-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.