

Synthesis, Structure and Spectroscopic Properties of Oxo-centered Carboxylate-Bridged Triiron Complexes and a Deca Ferric Wheel

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Abstract : Trinuclear oxo-centered carboxylate-bridged iron complexes, $[\text{Fe}_3(\mu_3\text{-O})(\mu_2\text{-O}_2\text{CR})\text{L-3}]^{+}/0$ (where R = alkyl or aryl; L = H₂O, ROH, Py, solvent) have attracted tremendous attention because of their interesting structural and magnetic properties, exhibit mixed-valent trapped and de-trapped states, and have bioinorganic relevance. The presence of a trinuclear iron binding center has been implicated in the formation of both bacterial and human iron storage protein, Ft. They are used as precursors for the synthesis of models for the active-site structures of non-heme proteins, hemerythrin (Hr), methane monooxygenase (MMO) and polyiron storage protein, ferritin (Ft). Used as important building blocks for the design and synthesis of supramolecules this can exhibit single molecular magnetism (SMM). Such studies have often employed simple and compact carboxylate ligands and the use of bulky carboxylates is scarce. In the present study, we employed two different type of sterically hindered carboxylates and synthesized a series of novel oxo-centered, carboxylate-bridged triiron complexes of general formula $[\text{Fe}_3(\text{O})(\text{O}_2\text{CCPh}_3)_6\text{L}_3]\text{X}$ (L = H₂O, 1; py, 2; 4-NMe₂py, 3; X = ClO₄; L = CH₃CN, 4; X = FeCl₄) and $[\text{Fe}_3(\text{O})(\text{O}_2\text{C-anth})_6\text{L}_3]\text{X}$ (L = H₂O, 5; X = ClO₄; L = CH₃OH, 6; X = Cl). Along with complex $[\text{Fe}(\text{OMe})_2(\text{O}_2\text{CCPh}_3)]_{10}$, 7 was prepared by the self-assemble of anhydrous FeCl₃, sodium triphenylacetate and sodium methoxide at ratio of 1:1:2 in CH₃OH. The Electronic absorption spectra of these complexes 1-6, in CH₂Cl₂ display weak bands at near FTIR region (970-1135 nm, $\epsilon > 15\text{M}^{-1}\text{cm}^{-1}$). For complex 7, one broad band centered at ~670nm and also an additional intense charge transfer (L→M or O→M) bands between 300 to 550nm observed for all the complexes. Paramagnetic ¹H NMR is introduced as a good probe for the characterization of trinuclear oxo - cantered iron compounds in solution when the L ligand coordinated to iron varies as: H₂O, py, 4-NMe₂py, and CH₃OH. The solution state magnetic moment values calculated by using Evans method for all the complexes and also solid state magnetic moment value of complex, 7 was calculated by VSM method, which is comparable with solution state value. These all magnetic moment values indicate there is a spin exchange process through oxo and carboxylate bridges in between two irons (d₅). The ESI-mass data complement the data obtained from single crystal X-ray structure. Further purity of the compounds was confirmed by elemental analysis. Finally, structural determination of complexes 1, 3, 4, 5, 6 and 7 were unambiguously conformed by single crystal x-ray studies.

Keywords : decanuclear, paramagnetic NMR, trinuclear, uv-visible

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