

Synthesis, characterization and ligand binding modes in β -enamine carbonyl complexes of iron(III)

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β -enamine carbonyl compounds have been employed in the preparation of catalysts,¹ in studies of magnetic properties,² and in the synthesis of volatile organometallic compounds for chemical vapor deposition.^{3,4} This work explored the different coordination modes of three proligands, 4-[(2-hydroxyethyl)amino]pent-3-en-2-one (H₂L-a), ethyl 3-[(2-hydroxyethyl)amino]but-2-enoate (H₂L-b), and 4-[(pyridin-2-ylmethyl)amino]pent-3-en-2-one (HL-c) towards iron(III). All syntheses were carried out using Schlenk techniques, under N_{2(g)}. The reaction between the proligands and the binuclear complex [Fe₂(μ -OMe)₂(dpm)₄] (Hdpm = dipivaloylmethane) was performed under reflux in 1,2-dimethoxyethane (glyme) for 15 min. The iron(III) precursor was chosen because the bridging methoxide groups could promote the single deprotonation of the proligands; these, in turn, could bind the remaining “Fe(dpm)₂” units coming from the starting material. Reddish-orange crystalline solids were isolated from the reactions with H₂L-a and H₂L-b (products **1** and **2**, respectively) at -20 °C, and a reddish-brown amorphous material from the reaction with HL-c (product **3**). All products were obtained in yields around 20% and were oxygen and moisture-sensitive. Single-crystal X-ray diffraction analysis carried out for **1** and **2** revealed similar structures with an overall molecular formula [Fe₂(μ -HL-x)₂(dpm)₄], where x = a or b. In both products, the alkoxide moiety of the β -enamine carbonyl ligands bridges the iron(III) centers of the “Fe(dpm)₂” units. The FTIR spectra of all products showed bands around 1610, 1580 and 1050 cm⁻¹, assigned to ν (C=O), ν (C=C) and ν (C-O), respectively. This reinforces the results obtained by single-crystal X-ray diffractometry for products **1** and **2**, and suggests the presence of the HL-c ligand coordinated to the “Fe(dpm)₂” unit in product **3**. Crystals of the known [Fe(dpm)₃] complex, characterized by both single-crystal X-ray diffractometry and FTIR, were obtained together with those of products **1** and **2**, possibly because of a small excess of the iron(III) starting material in the reaction mixture, or of a low equilibrium constant for the formation of the new dimers. The next steps consist in optimizing these syntheses to isolate a single product, and carrying out reactions with starting materials capable of promoting the double deprotonation of H₂L-a and H₂L-b, together with the investigation of the binding modes of the β -enamine carbonyl ligands towards lanthanide(III) starting materials.

¹Tseng, H. *et al.*, *Dalton Trans.* **2015**, 44, 11763; ²Maeda, Y. *et al.*, *Inorg. Chem.* **1986**, 25, 2958; ³Lim, S. *et al.*, *Chem. Mater.* **2002**, 14, 1548; ⁴Lim, S. *et al.*, *J. Organomet. Chem.* **2004**, 689, 224.