Powder X-ray structure determination and physical properties study on [Fe_2 (μ-O) $(DOEt)_2$] complex

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Abstract

The design and synthesis of multifunctional materials have drawn much attention in recent years. Among them, we focus on the combination of spin-crossover (SCO) and luminescence characters, which may expand the horizon of SCO-based applications especially in magneto-optical switches. In this work, the Schiff base ligand, $C_{26}H_{26}O_6N_4$ (**H_2DOEt** = diethyl-[2,2'-((phenazine-2,3-diylbis(azanediyl))bis-methaneylylidene))(2E,2'E)-bis(3-oxobutanoate)]) was synthesized by using luminescence dye 2,3-diaminophenazine (DAP). In addition, we also synthesized μ-oxo-bridge diiron(III) complex of [Fe_2 (μ-O) $(DOEt)_2$] (**1**) but no good quality of single crystal is obtained. Thus, we use Fe K-edge extended X-ray absorption fine structure (EXAFS) and powder X-ray diffraction (PXRD) to resolve the 3-D structure of complex **1**. To do *ab initio* structure determination from PXRD, the cell constants are indexed by DICVOL and N-TREOR programs first. Then, we use direct method to find the most probable structure, and use periodic-DFT calculation to obtain the best structure model. The final structure is completed by Rietveld refinement. The cell constants of complex **1** are a = 22.3992(4) Å, b = 13.8747(2) Å, c = 16.4296(2) Å, α = 90°, β = 90.294(8) °, γ = 90°. According to Rietveld refinement results, the Fe coordinated by one bridge O atom and Schiff base four atoms(2N2O) at distances of Fe-O(bridge) = 1.787(3) Å, Fe-O1 = 1.938(1) Å, Fe-O2 = 1.922(1) Å, Fe-N1 = 1.966(6) Å and Fe-N2 = 2.201(6) Å. According to Fe K-edge XANES results, we can confirm complex **1** is a ferric ion complex. Moreover, in the study of luminescence characters, solution state of **H_2DOEt** and complex **1** displayed the maximum intensity of emission spectra at λ_{em} = 529 nm and λ_{em} = 518 nm, respectively.

***Keywords*: EXAFS、PXRD、SCO**