

SYNTHESIS, STRUCTURES AND PROPERTIES OF Fe(III) COMPLEXES WITH DIHYDRAZONE LIGAND

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The pentadentate N₃O₂ Schiff base ligand, H₂L = 2,6-diacetylpyridine bis(picolinoylhydrazone), has been used for the synthesis of two mononuclear iron(III) complexes: [Fe(H₂L)(H₂O)₂](NO₃)₃·2.5H₂O (**1**) and [Fe(H₂L)(H₂O)₂](ClO₄)₃·2.5H₂O (**2**), which were characterized by IR spectroscopy and X-ray diffraction. The crystal structures of these complexes contain mononuclear cations - [Fe(H₂L)(H₂O)₂]³⁺, NO₃⁻/ClO₄⁻ anions, and water molecules. The Schiff base ligand in both compounds is coordinated in the form of a double zwitterions [1]. It was found that in cation complex of **1** and **2** there are protons transfer from the N atoms of the amide groups to N atoms of the pyridine rings. This migration of protons was confirmed by IR spectroscopy. The band ν(NH), observed in the free ligand at 3324 cm⁻¹, is absent in the IR spectra of complexes **1** and **2**. The broad absorption in the region of 3650-2600 cm⁻¹ could be explained by the joining of hydrogen bonds due to their lengths into several groups and the broad bands of weak intensity might be PyH⁺ oscillations.

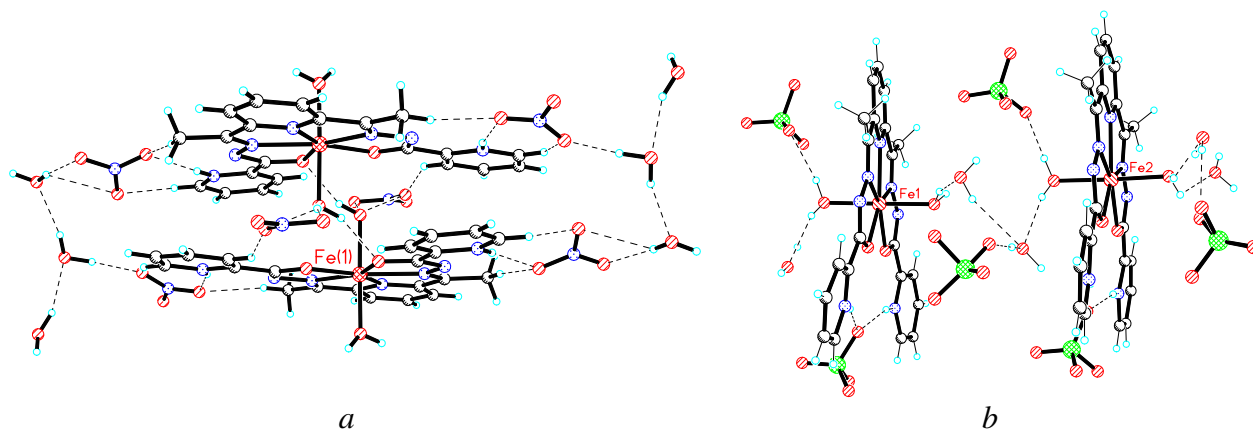


Figure 1. Fragments of crystal packings in **1**(a) and **2**(b)

The crystal structures of compounds **1** and **2** are stabilized by hydrogen bonding that give rise to a supramolecular 3D-networks *via* coordinated and crystallization water molecules, NO₃⁻ or ClO₄⁻ anions and NH⁺ (PyH⁺) (Figure 1).

The hydrogen bond mediated intermolecular magnetic couplings in mononuclear high spin iron(III) Schiff base complexes have been studied by **TB2J** python package used for calculating the magnetic interaction parameters in Heisenberg models from Density Functional Theory [2].

The photoluminescence study was performed on both samples and luminescence excitation was carried out by pulse nitrogen laser (337.1 nm) at a temperature of 300 K. The weak photoluminescence was observed in the 350 - 750 nm spectral range with maxima in the red (1.9 eV), yellow (2.1 eV) and blue (2.6 eV) spectral regions.

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[1] O. DANILESCU, I. BULHAC, P.N. BOUROSH, L. CROITOR. Anion-assisted Fe(III)-coordination supramolecular systems based on 2,6-diacetylpyridine dihydrazone. *Polyhedron*. **2022**, volume 215, page 115679.

[2] X. HE, N. HELBIG, M.J. VERSTRAETE, E. BOUSQUET. TB2J: a python package for computing magnetic interaction parameters. *Computer Physics Communications*. **2021**, page 107938.