

Synthesis and characterization of Mn(II) and Fe(III) complexes with the condensation product of thiosemicarbazide and 2-acetylthiazole



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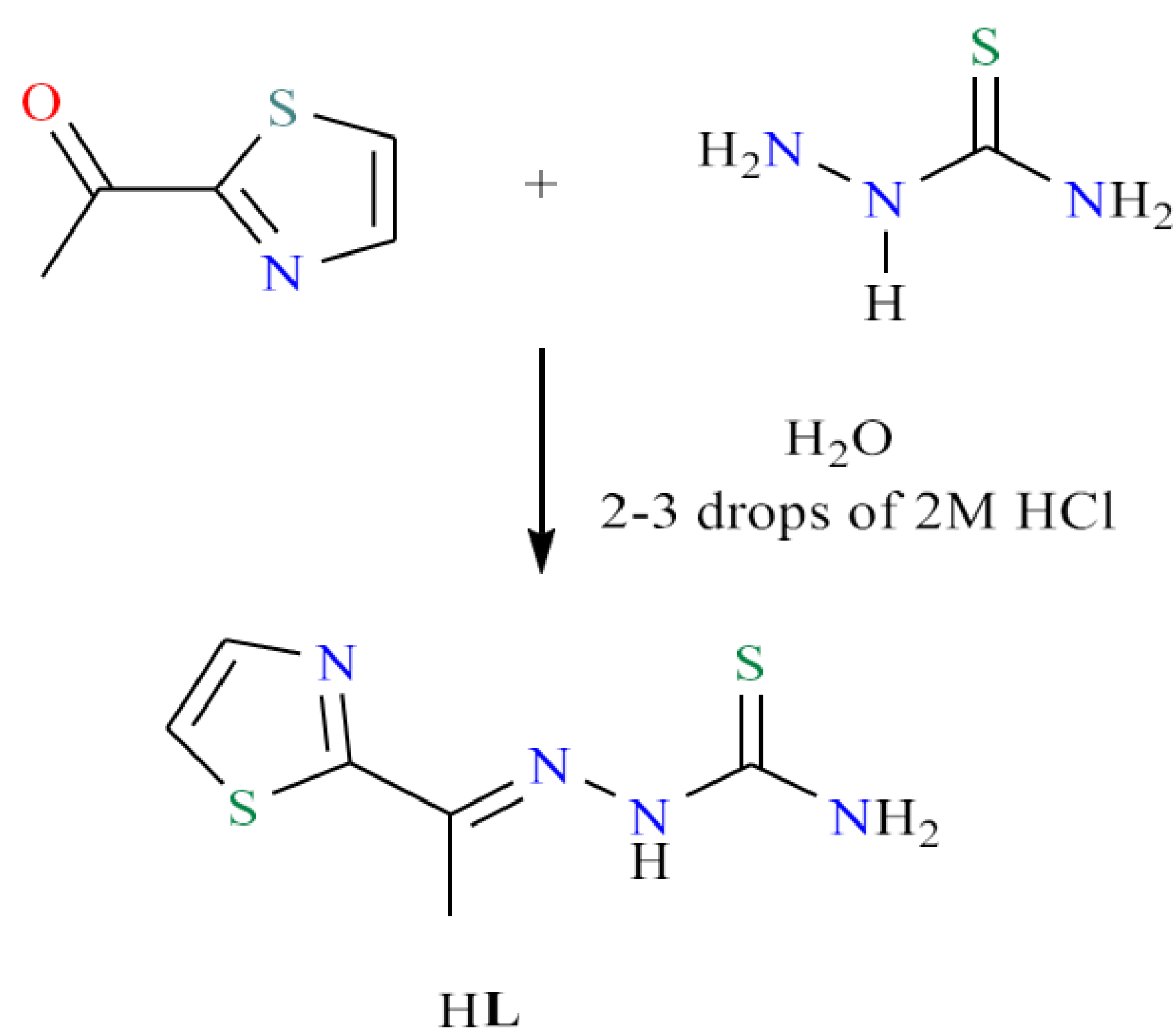
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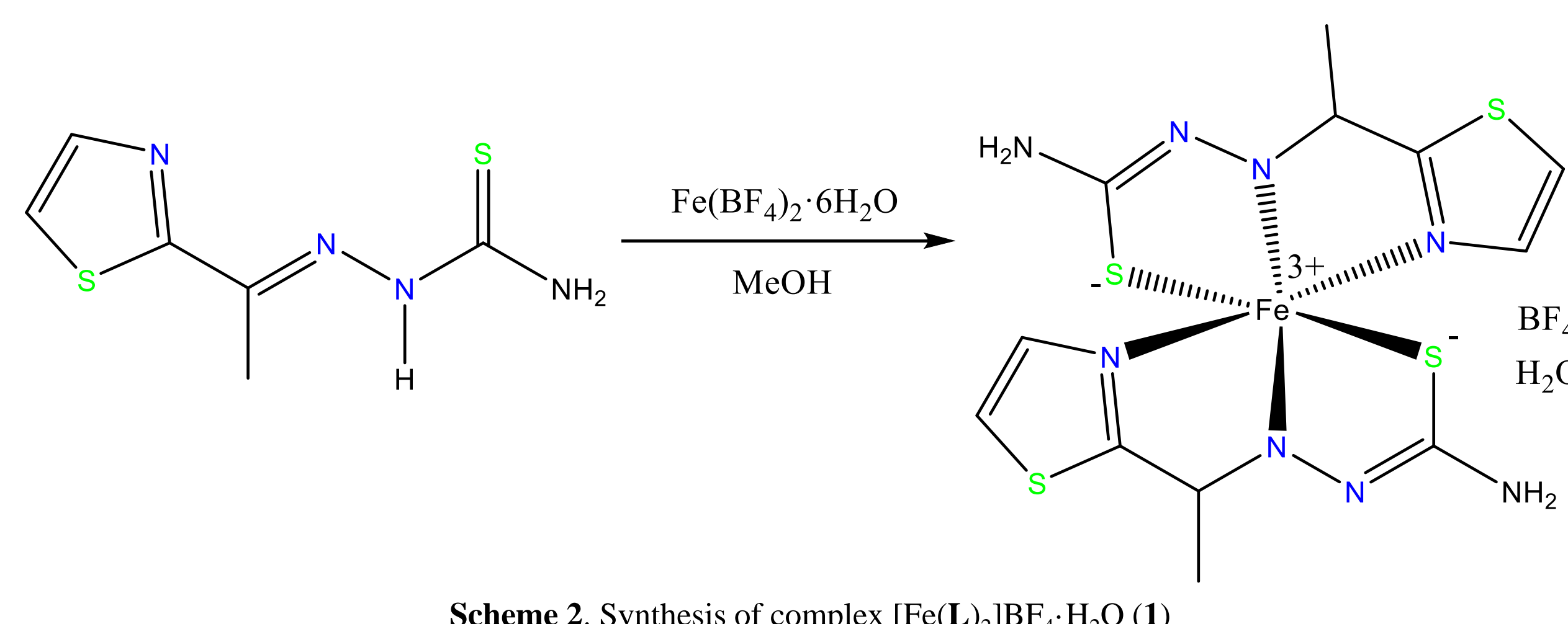
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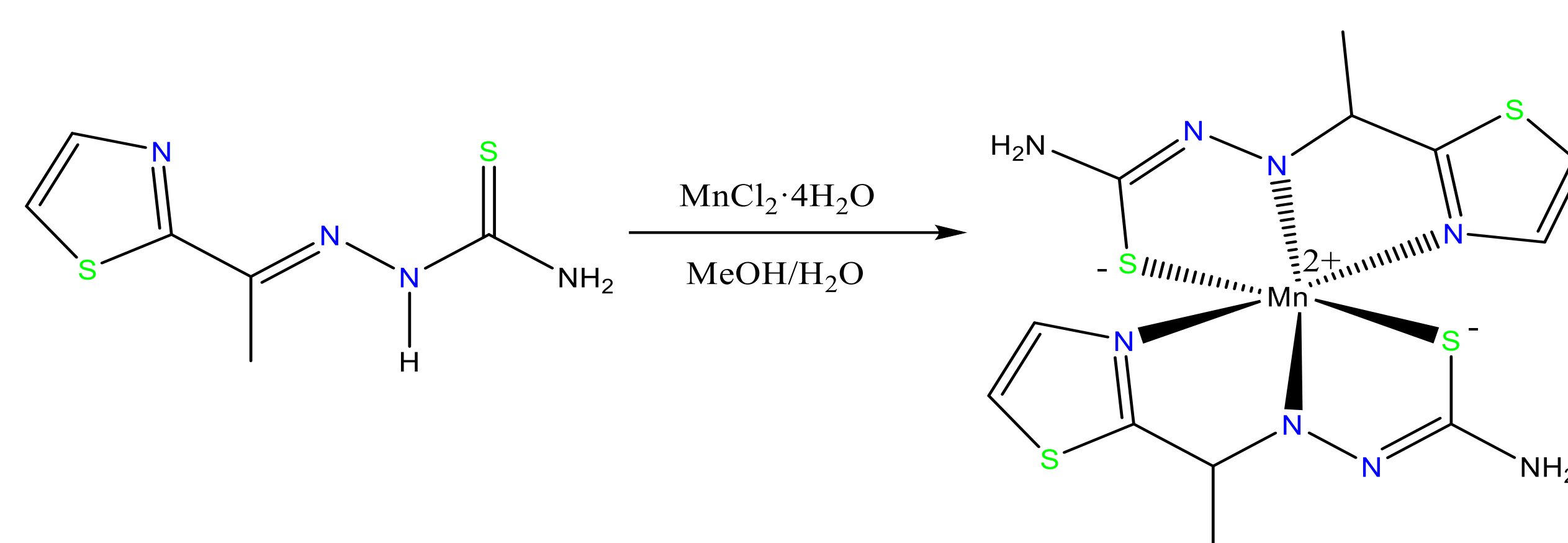
The ligand **HL** (*E*)-2-(1-(thiazol-2-yl)ethylidene)hydrazine-1-carbothioamide) was synthesized in the reaction of thiosemicarbazide and 2-acetylthiazole in molar ratio 1:1 in water, with 3 drops of 2M HCl. (**Scheme 1**). The reaction of the ligand **HL** with metal salt $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ in a molar ratio 1:1 in methanol results in the formation of bis Fe(III) complex with composition $[\text{FeL}_2]\text{BF}_4 \cdot \text{H}_2\text{O}$ (**1**) (**Scheme 2**). The reaction of the **HL** ligand with the metal salt $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ in a molar ratio 1:1 in methanol/water mixture results in the formation of bis Mn(II) complex (**2**) with composition $[\text{MnL}_2]$ (**Scheme 3**).



Scheme 1. Synthesis of ligand **HL**



Scheme 2. Synthesis of complex $[\text{Fe}(\text{L})_2]\text{BF}_4 \cdot \text{H}_2\text{O}$ (**1**)



Scheme 3. Synthesis of complex $[\text{Mn}(\text{L})_2]$ (**2**)

In both complexes, the thiosemicarbazone ligand is coordinated in deprotonated form through two NNS donor sets of atoms through thiazole and imine nitrogens and thioenolate sulfur (**Fig. 1**; **Fig. 2**). However, while Fe(III) complex is in the doublet ground state with distorted octahedral geometry, the coordination environment around Mn(II) is distorted trigonal-prismatic, and the sextet state is found to be the ground state. Furthermore, the central metal ions in both cases have the same d^5 electronic configuration. However, measured magnetism and analysis of the crystal geometries show that these two complexes have a different number of unpaired electrons. We rationalized the results by electronic structure calculations based on density functional theory.

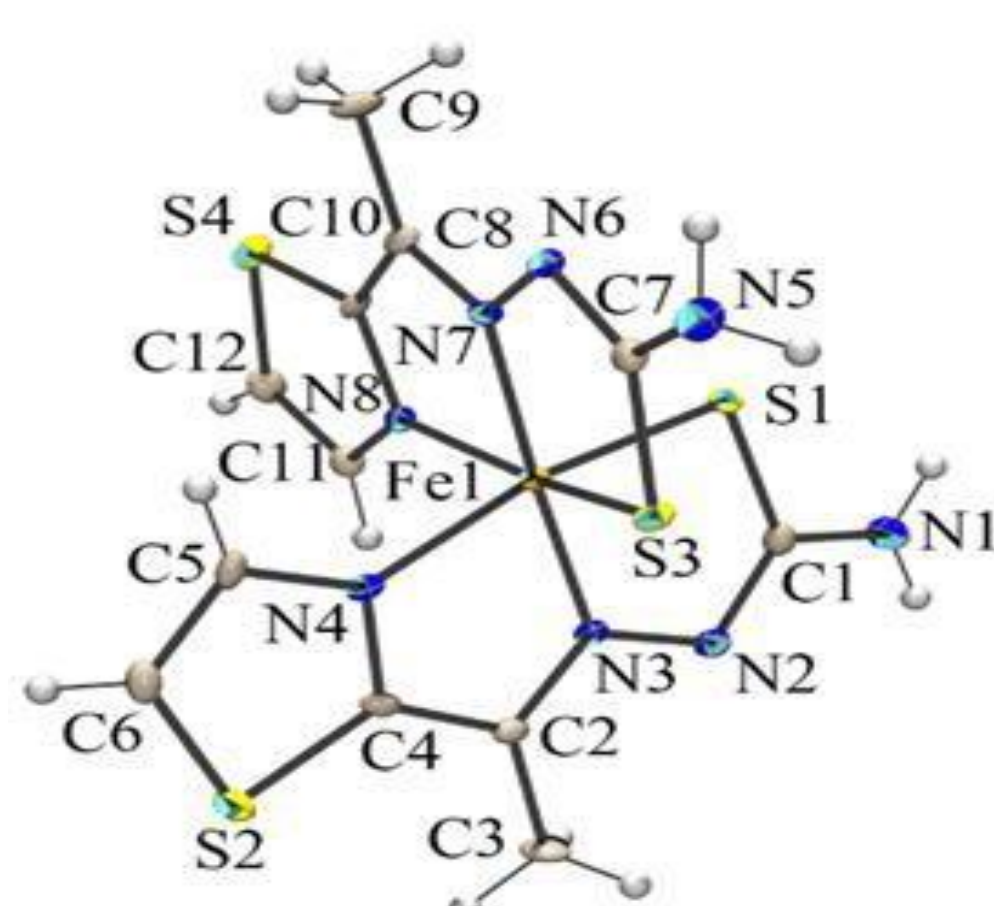


Fig 1. The ORTEP drawing of $[\text{FeL}_2]^+$ complex cation (**1**)

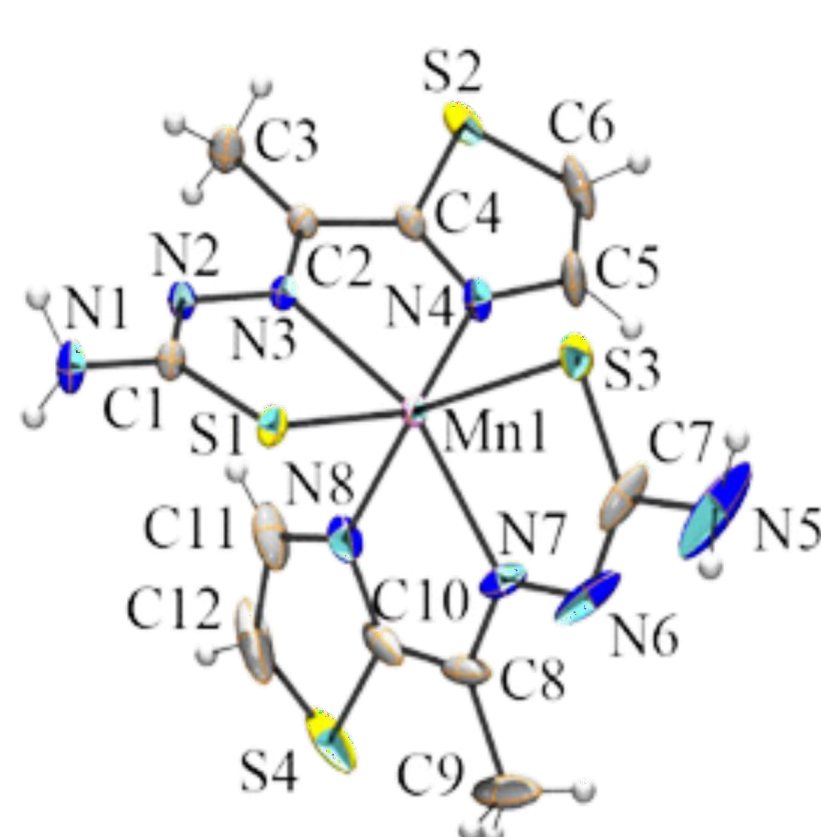


Fig 2. The ORTEP drawing of $[\text{Mn}(\text{L})_2]$ complex (**2**)

Fig. 1. The complex **1** crystallizes in the orthorhombic space group *Pbca*.

Fig. 2. The complex **2** crystallizes in the triclinic space group *P*-1.

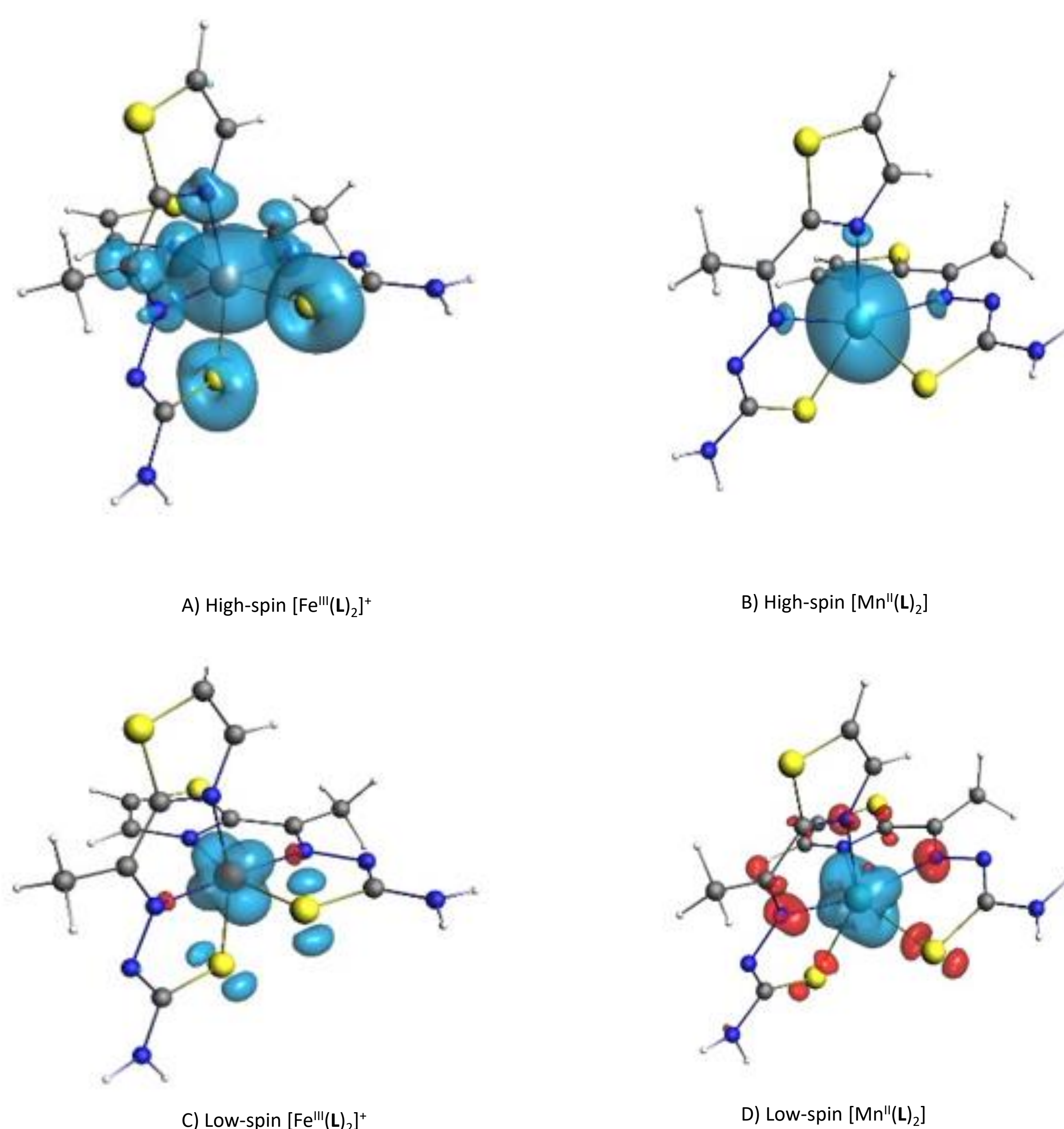


Fig 3. Spin densities calculated at B97-D/TZP level of theory on crystal structures of $[\text{Fe}^{\text{III}}\text{L}_2]^+$ (A) high spin; C) low spin) and $[\text{Mn}^{\text{II}}(\text{L})_2]$ (B) high spin; D) low spin). The ground spin state of $[\text{Fe}^{\text{III}}\text{L}_2]^+$ is low spin. The ground spin state of $[\text{Mn}^{\text{II}}(\text{L})_2]$ is high spin.

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