

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

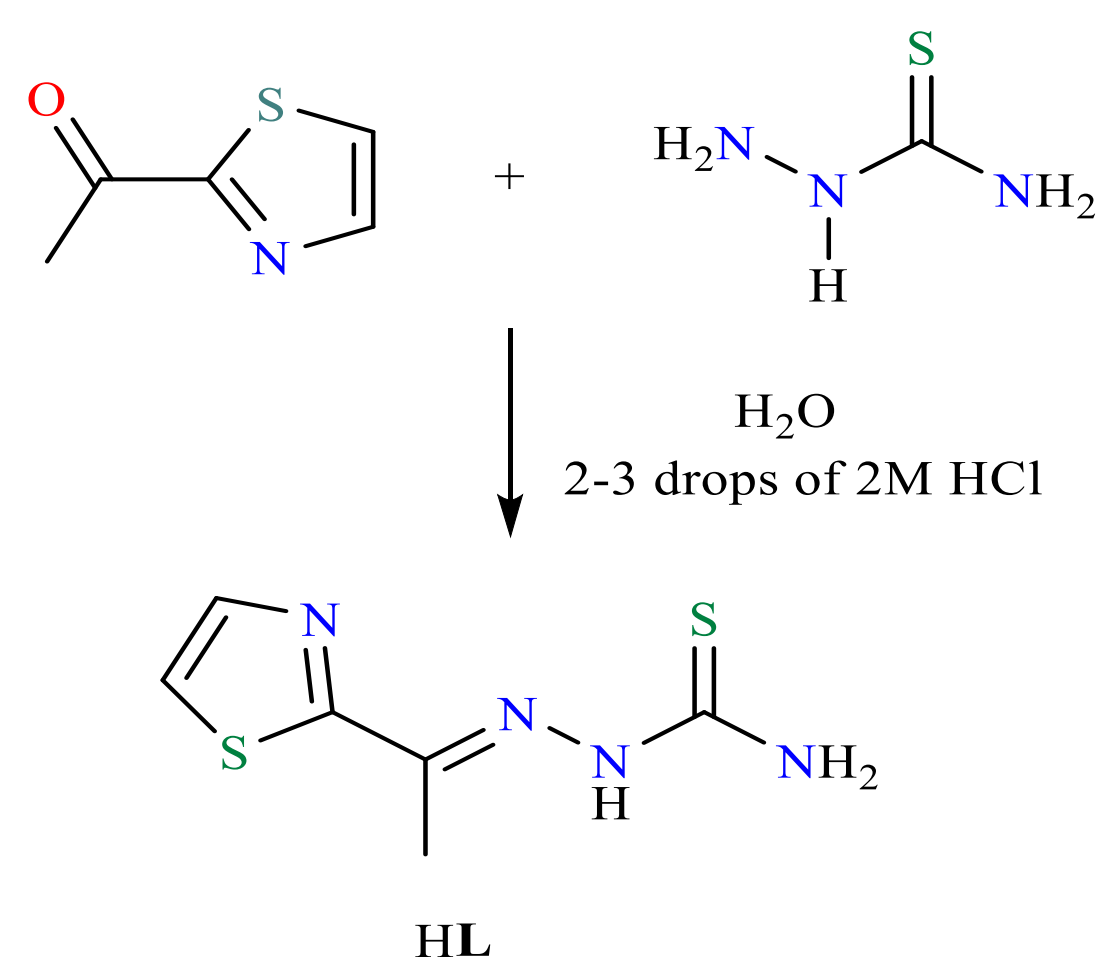


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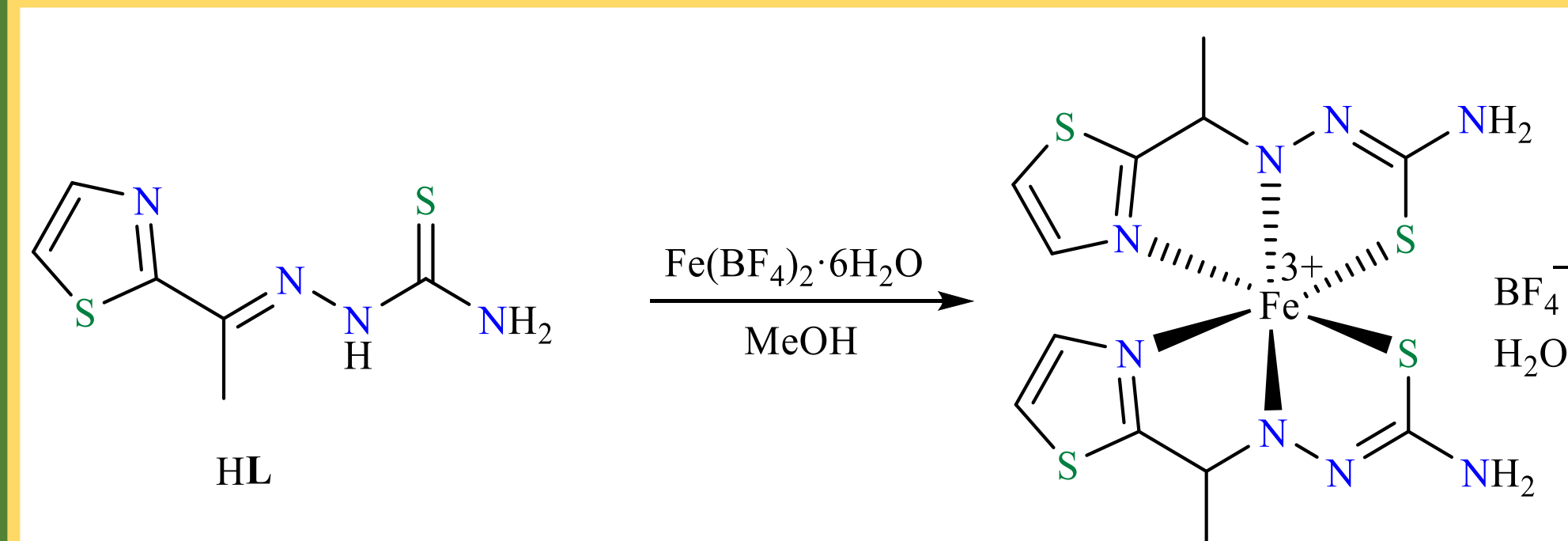
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Scheme 1. Synthesis of ligand HL

The HL ligand, (*E*)-2-(1-(thiazol-2-yl)ethylidene)hydrazine-1-carbothioamide was obtained from the condensation reaction of thiosemicarbazide and 2-acetylthiazole in water. In this complex, deprotonated hydrazone ligands were coordinated in a tridentate fashion through NNS donor set atoms (Scheme 1).



Scheme 2. Synthesis of complex $[\text{FeL}_2]\text{BF}_4\text{H}_2\text{O}$

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 $[\text{FeL}_2]\text{BF}_4\text{H}_2\text{O}$ (Scheme 2). Two deprotonated ligand molecules L coordinate the Fe(III) ion in a mer arrangement, forming a distorted octahedral complex by chelation through NNS sets of donor atoms (Fig. 1).

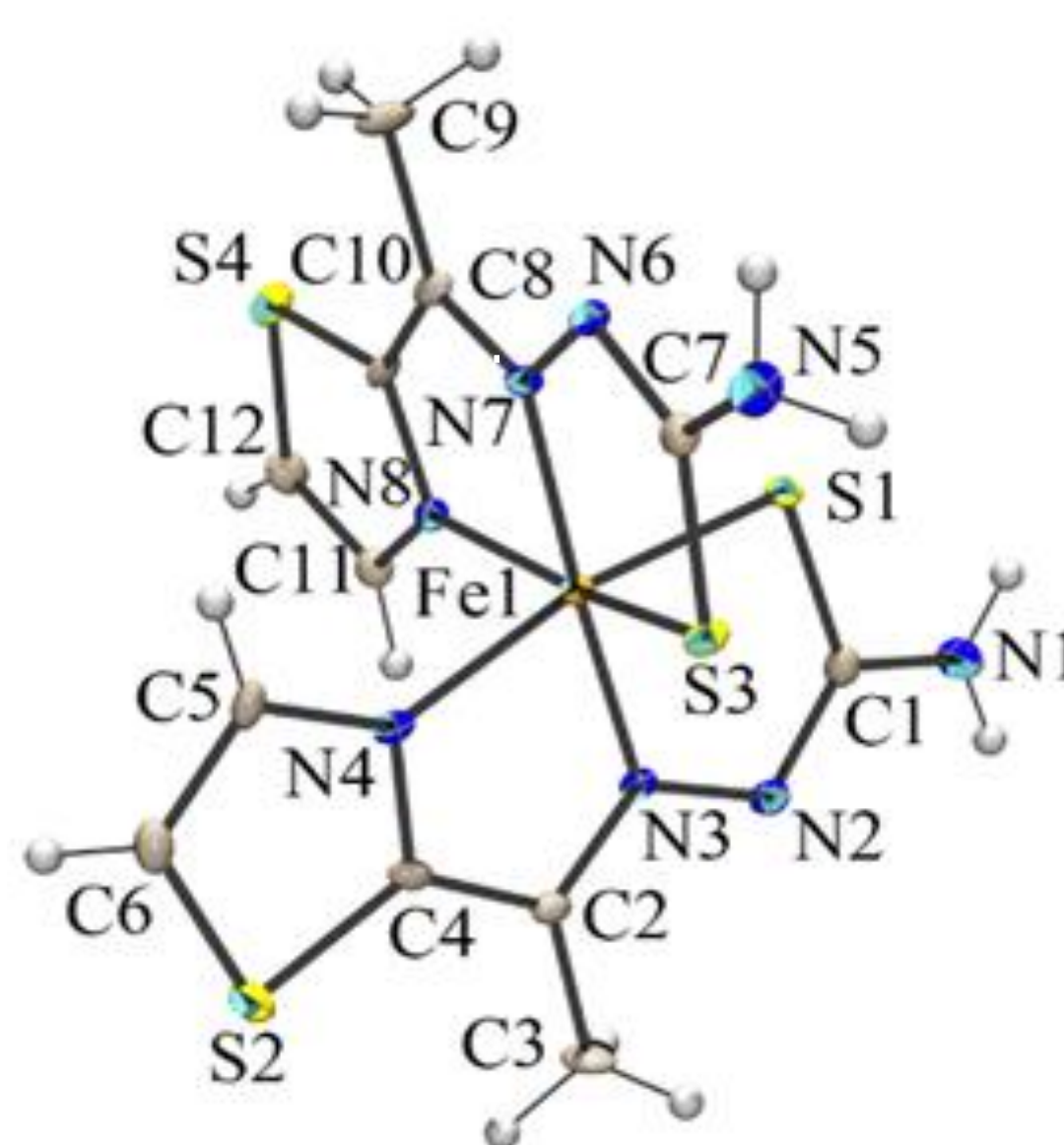
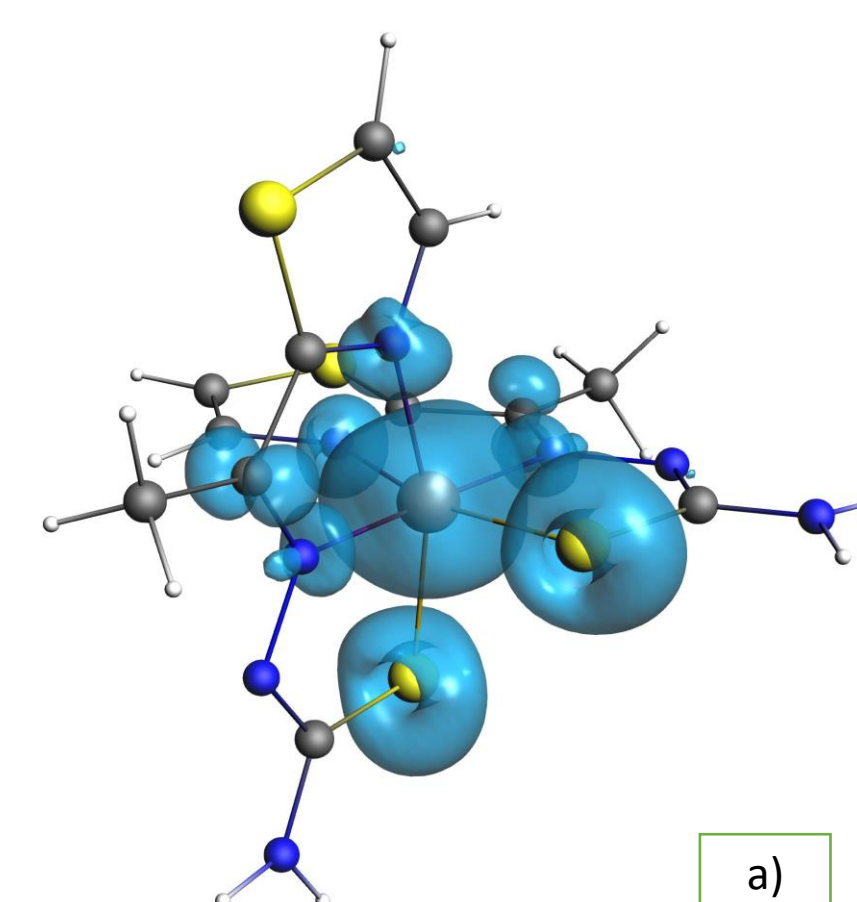
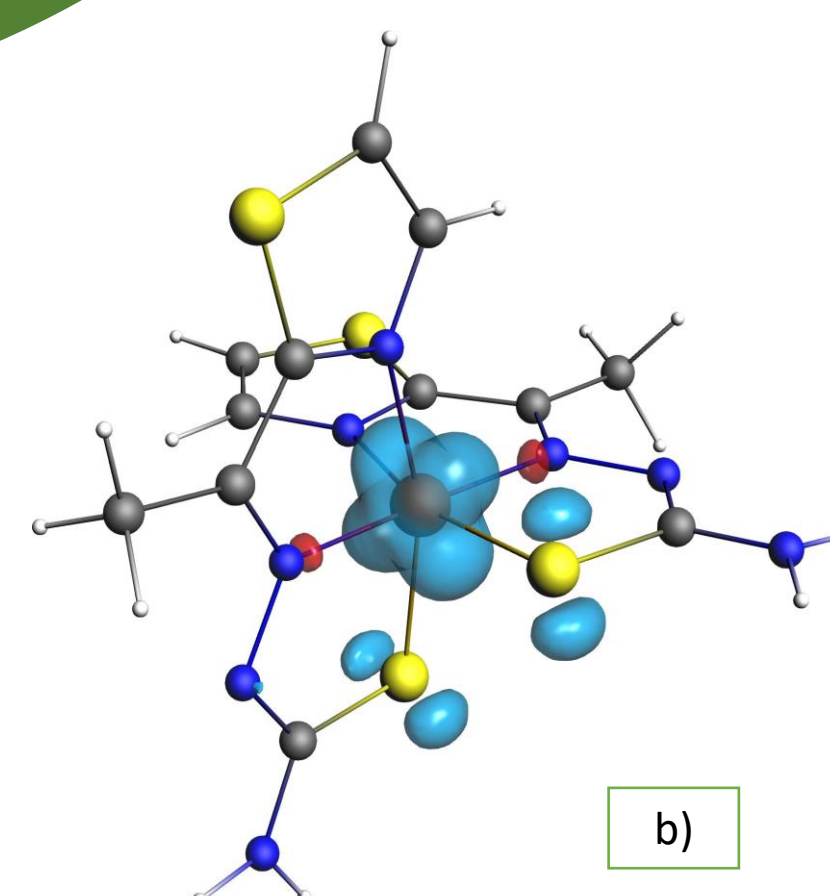


Figure 1. The ORTEP drawing of $[\text{FeL}_2]^+$ complex cation



a)

Figure 2. Spin densities calculated at B97-D/TZP level of theory on crystal structures of $[\text{Fe}^{\text{III}}\text{L}_2]^+$ a) high spin; b) low spin



b)

Table 1. Crystal data for $[\text{FeL}_2]\text{BF}_4\text{H}_2\text{O}$	
Empirical formula	$\text{C}_{12}\text{H}_{16}\text{BF}_4\text{FeN}_8\text{OS}_4$
Formula weight	559.23
Temperature/K	199.98
Crystal system	orthorhombic
Space group	<i>Pbca</i>
<i>a</i> /Å	17.8604(10)
<i>b</i> /Å	12.1006(7)
<i>c</i> /Å	18.9002(11)

Complex $[\text{FeL}_2]\text{BF}_4\text{H}_2\text{O}$ crystallizes in the orthorhombic crystal system with space group *Pbca*. The asymmetric unit consists of a complex cation $[\text{FeL}_2]^+$, BF_4^- counter anion and one solvent water molecule. The tridentate coordination of each ligand implies the formation of two fused five-membered chelate rings Fe–N–C–C–N and Fe–N–N–C–S which are noncoplanar, as indicated by the dihedral angles of 5.3° and 3.2° for the rings fused along Fe1–N7 and Fe1–N3 bonds, respectively. The two chelation planes comprising the atoms S–N–N–Fe are nearly perpendicular. The Fe–L mean bond distances: Fe–N_{thiazole} 1.982 Å, Fe–N_{imine} 1.939 Å and Fe–S_{thiolate} 2.222 Å are in close agreement with those observed in related Fe(III)-N₄S₂ complexes with thiosemicarbazone ligands.

Conclusions:

- thiosemicarbazone ligand is coordinated in tridentate deprotonated form through NNS donor set of atoms forming a distorted octahedral complex
- complex have been characterized by X-ray crystallographic analysis, elemental analysis and IR spectroscopy.
- DFT calculations were performed to rationalize spin state preferences.

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