Spin states of Mn(II) and Fe(III) complexes with thiosemicarbazone

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The ligand **HL** (*E*)-2-(1-(thiazol-2-yl)ethylidene)hydrazine-1-carbothioamide) was synthetized 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 H**L** with metal salt $Fe(BF_4)_2 \cdot 6H_2O$ in a molar ratio 1:1 in methanol results in the formation of bis Fe(III) complex with composition $[Fe\mathbf{L}_2]BF_4H_2O$ (**1**) (**Scheme 2**). The reaction of the H**L** ligand with the metal salt $MnCl_2 \cdot 4H_2O$ in a molar ratio 1:1 in methanol/water mixture results in the formation of bis Mn(II) complex (**2**) with composition $[Mn\mathbf{L}_2]$ (**Scheme 3**).

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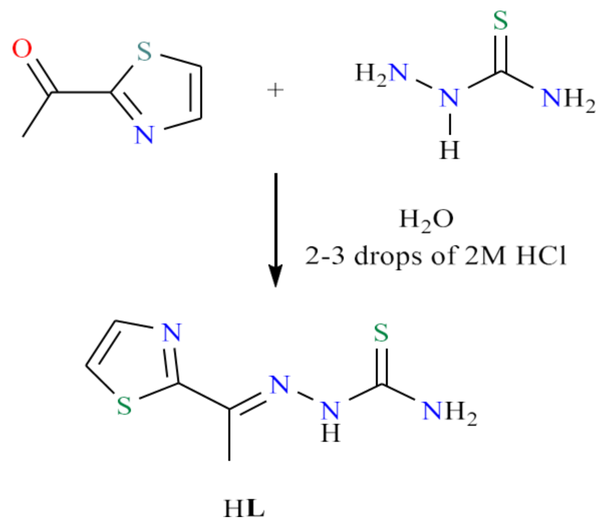
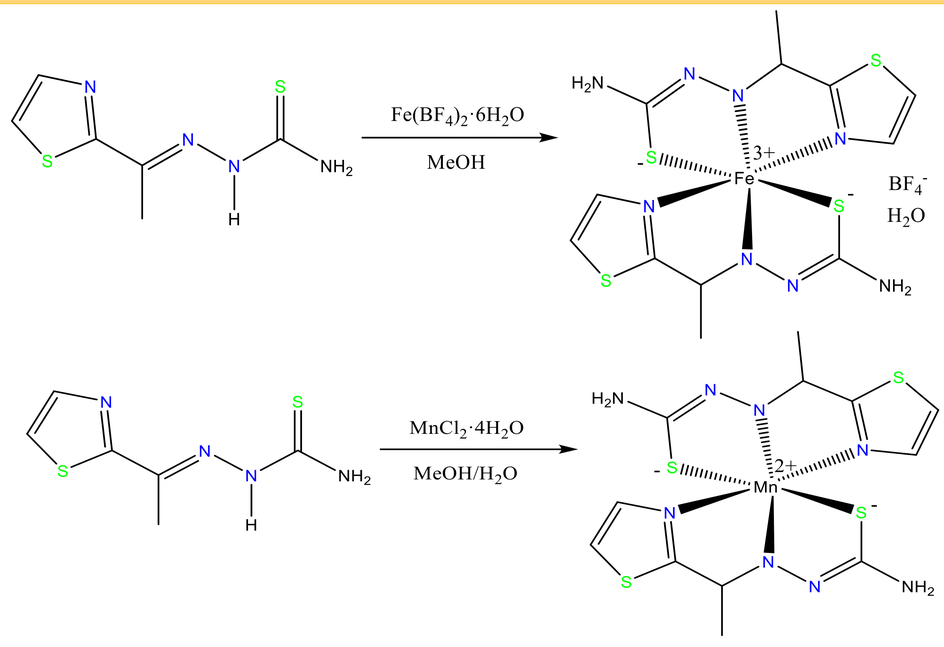


Scheme 1. Synthesis of ligand **HL**



Scheme 2. Synthesis of complexes $[Fe(\mathbf{L})_2]BF_4 \cdot H_2O$ (**1**) and $[Mn(\mathbf{L})_2]$ (**2**)

Both complexes **1** and **2** with **HL** ligand are bis octahedral complexes in which two deprotonated ligand molecules coordinate in a *mer* arrangement through two NNS sets of donor atoms, through thiazole and imine nitrogens and thioenolate sulfur (**Fig. 1**; **Fig. 2**). Furthermore, the central metal ions in both cases have the same d^5 electronic configuration. However, effective magnetic moment measurements (1.95 μB for Fe(III) complex and 5.73 μB for Mn(II) complex, respectively) and analysis of the crystal geometries show that these two complexes have a different number of unpaired electrons. We rationalized the results by DFT calculations.

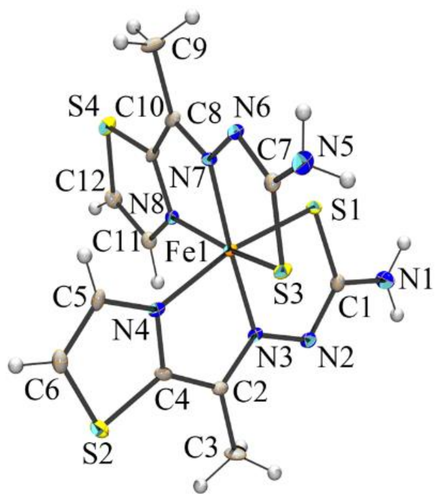


Fig. 1. The complex **1** crystallizes in the orthorhombic space group *Pbca*.
CShM (OC-6) = 1.731
CShM (TPR-6) = 11.228

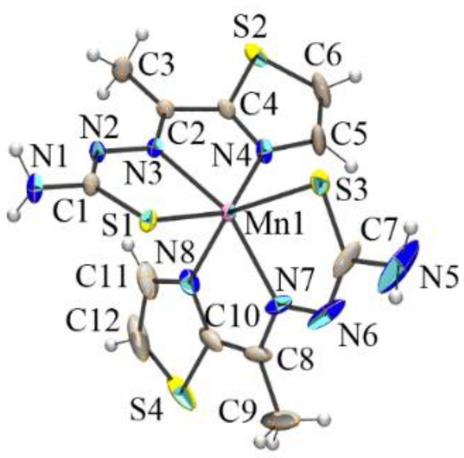


Fig. 2. The complex **2** crystallizes in the triclinic space group *P*−1.
CShM (OC-6) = 7.979
CShM (TPR-6) =6.517

Table 1. Relative spin state energies (kcal/mol) for $[Fe^{III}(\mathbf{L})_2]^+$ and $[Mn^{II}(\mathbf{L})_2]$

	$[Fe^{III}(L)_2]^+$		$[Mn^{II}(L)_2]$		
Level of theory	E_{HS-LS} (X-ray)[a]	E_{HS-LS} (opt.)[b]	E_{HS-LS}(X-ray1)[a]	E_{HS-LS} (X-ray2)[a]	E_{HS-LS} (opt.)[b]
OPBE/TZP	50.74	18.97	-51.15	-52.99	-0.15
OLYP/TZP	53.75	13.48	-44.11	-46.07	-4.59
B97-D/TZP	50.43	11.40	-46.91	-48.80	-5.41
SSB-D/TZP	43.84	8.57	-49.42	-51.23	-5.76
B3LYP*/TZP	52.53	14.03	-40.45	-42.84	-8.60
B97-D/TZP-COSMO[c]	49.08	11.58	-49.28	-51.24	-6.90
SSB-D/TZP-COSMO[c]	42.62	8.92	-51.20	-53.53	-7.00

a) single-point on X-ray geometries; for Mn(II) two crystalographically independent complexes; b) geometry optimization; c) COSMO – DMSO as solvent

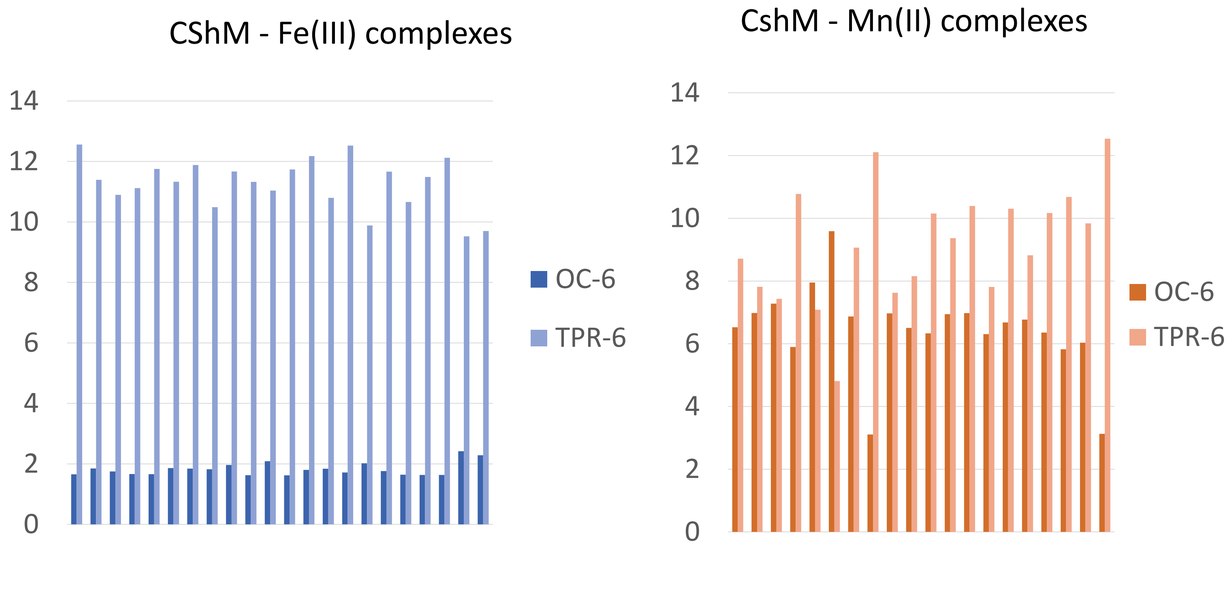


Fig 3. Continuous shape measures (CShMs) for similar Fe(III) and Mn(II) complexes

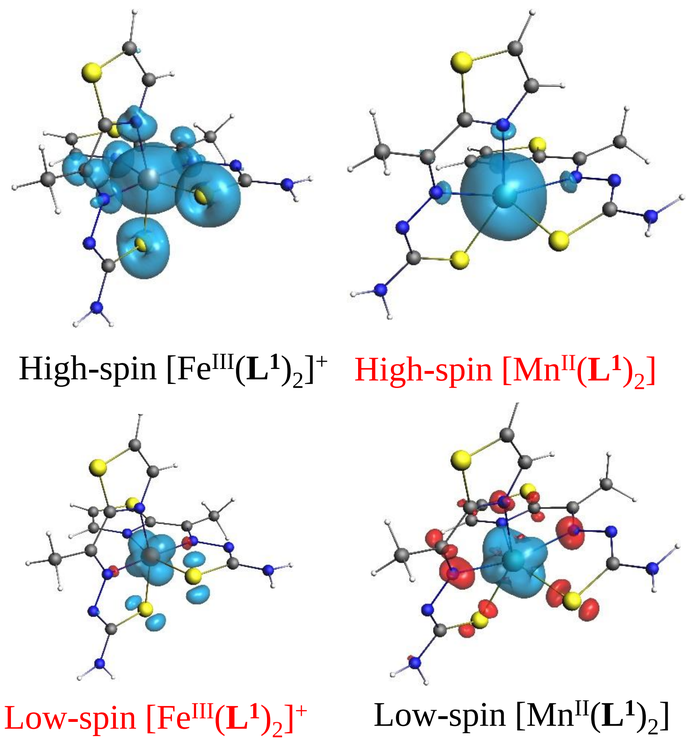


Fig 4. Spin densities (B97-D/TZP-Xray) of complexes **1** and **2**.

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