

## Effect of pseudohalides in pentadentate-iron(III) complexes studied by DFT and Mössbauer spectroscopy

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**Abstract** Mononuclear iron complexes in which the iron(III) ion is coordinated by a pentadentate Schiff base ligand  $L^5$  with two phenolate, two imino and one amino group can exhibit a spin crossover. In this contribution experimental results are presented for complexes with cyanate and thiocyanate as co-ligands. Furthermore, theoretical results of quantum chemical calculations of energies and entropies for the low-spin and high-spin state are shown and compared with Mössbauer results. We also demonstrate how the ligand field of the monodentate co-ligand influences the spin crossover energies and entropies in  $[Fe^{III}L^5NCY]$  complexes.

**Keywords** Spin crossover · DFT calculations · Schiff base ligand

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## 1 Introduction

Density Functional Theory (DFT) calculations are important for the calculation of large close shell molecules (hydrocarbons, organic and biological compounds like alcohols, sugars, proteins, fats, oils) because DFT is faster than post Hartree-Fock methods. However, it is difficult to calculate open shell systems with DFT. Furthermore, there are inaccuracies in the prediction of molecular properties like total energies, electronic energy levels, geometries in comparison to wave function methods (Hartree-Fock, MP2) [1–5] and unsystematic errors in the calculation of energy differences between the different spin states of the same molecule. On the other hand broken symmetry description is required to calculate low spin states like  $\text{Fe}^{\text{III}}_{\text{LS}}$ . For that reason the complexes  $[\text{FeL}^5\text{NCY}]$  (with  $\text{Y} = \text{O}, \text{S}, \text{Se}$ ) have been calculated in their high-spin (HS) ( ${}^6\text{A}_{1\text{g}}$ ) and low-spin (LS) ( ${}^3\text{T}_{2\text{g}}$ ) states. The experimental results are shown for  $[\text{Fe}(\text{o-methoxy})_2\text{L}^5\text{NCO}]$  (**1**) in the case of  $[\text{FeL}^5\text{NCO}]$  and  $[\text{Fe}(\text{otBu})_2\text{L}^5\text{NCS}]$  (**2**) in the case of  $[\text{FeL}^5\text{NCS}]$  [6]. The pentadentate Ligand  $\text{L}^5$  was prepared by the Schiff base reaction of salicylaldehyde and 3-aminopropyl-2-aminoethylamine which has been reported so far in some examples [6–11].

Wang et al. experimentally and theoretically investigated the spin crossover of the Manganese complex  $\text{Mn}^{\text{III}}\text{L}^{6(+)}$  with the hexadentate Ligand  $\text{L}^6$  (Fig. 1a) [12]. The calculated results of this workgroup are well in accordance with the experimental results. The theoretical calculated differences in bond lengths between HS and LS state ( $\Delta R_i$ ) for  $\text{MnN}_{\text{imino}}$ ,  $\text{MnN}_{\text{amino}}$ ,  $\text{MnO}_{\text{phenolate}}$  are 0.21 Å, 0.12 Å, -0.02 Å; the experimental results are in the same order (0.12 Å, 0.09 Å, -0.01 Å). The experimental and theoretical outcome underlined that the LS ( $S = 1$ ) state is energetically more stable than the HS ( $S = 2$ ) state [12].

Hai-Bao et al. calculated the energy gap between the HOMO and the LUMO of the iron(III) Schiff Base complexes  $\text{Fe}^{\text{III}}(\text{L}^3)^{2+}$  and  $\text{Ni}^{\text{II}}(\text{L}^3)_2$  with the tridentate Ligand  $\text{L}^3$  with DFT (Fig. 1b, c) [13]. The group used also the time dependent Hartree-Fock methods to calculate the optical transitions and the second order non-linear optics coefficient [13].

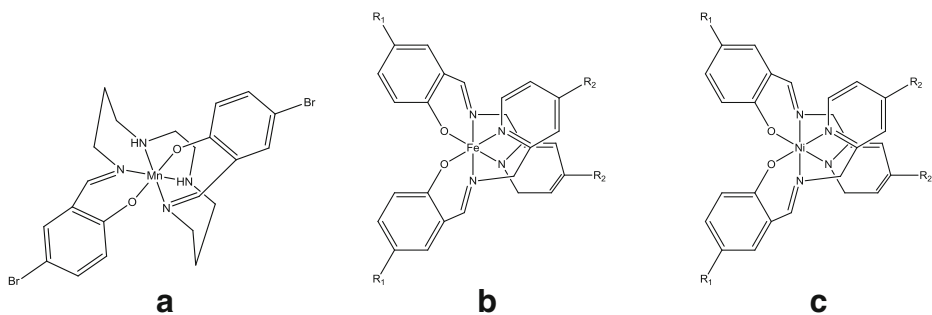
Neese et al. calculated the energies of the mononuclear metal complexes of the general formula  $\text{Fe}(\text{phen})_2\text{X}_2$  ( $\text{X}^- = \text{NCS}^-, \text{NO}^+, \text{CO}, \text{PH}_3, \text{PMe}_3, \text{NH}_3, \text{N}_2\text{H}_4$  and complexes with the 2,2'-bis(2-mercaptophenylthio)diethylamine dianion and the amino and aqua complexes  $\text{Fe}^{\text{II}}(\text{NH}_3)_6^{2+}$ ,  $\text{Fe}^{\text{II}}(\text{H}_2\text{O})_6^{2+}$ ,  $\text{Fe}^{\text{IV}}\text{O}(\text{NH}_3)_5^{2+}$  with several density functional like BP86, OPBE, TPSS, TPSSh, B3LYP, B2PLYP and compared the calculated energies of the HS, the LS states and their differences [14]. Wolny et al. calculated the geometries of those coordination compounds to determine the change in length of the bond between the metal atom (Fe) and the donor atoms (N) of the ligands and the resulting vibrational frequencies. Theoretical results of Wolny et al. are in good agreement to the experimental data [15, 16].

## 2 Results

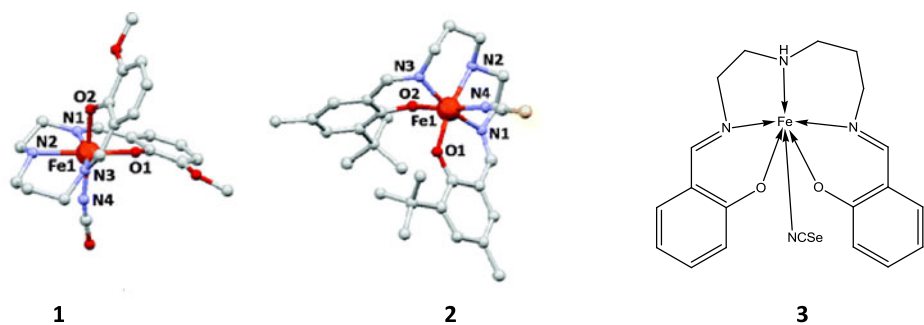
Figure 2 illustrates the crystal structure of  $[\text{Fe}(\text{o-methoxy})_2\text{L}^5\text{NCO}]$  (**1**),  $[\text{Fe}(\text{o-tBu})_2\text{L}^5\text{NCS}]$  (**2**) and a graphical scheme of the compound  $\text{FeL}^5\text{NCS}$  (**3**).

The comparison between the experimental and theoretical results shows interesting facts:

1. The calculated and experimental measured bond lengths are at the same order of magnitude (maximal deviations are between 10 and 20 % (Table 1)).
2. The calculation of the stability of the both spin states LS or HS is in good agreement with the experimental results (Table 2).
3. The entropic conditions stabilize the HS state in respect to the LS state.



**Fig. 1** Structural scheme of a Mn complex with its hexadentate ligand L<sup>6</sup> (a) [12] and a tridentate ligand L<sup>3</sup> and its corresponding Fe(III) (b) and Ni(II) (c) coordination compound [13]



**Fig. 2** Crystal structure of [Fe(o-methoxy)<sub>2</sub>L<sup>5</sup>NCO] (1) and [Fe(o-tBu)<sub>2</sub>L<sup>5</sup>NCS] (2) and a graphical scheme of FeL<sup>5</sup>NCSe (3). Reprinted with permission of [6]

Table 2 compares the experimental results and theoretically calculated energies and entropies of both spin states (HS and LS) for each compound at 300 K and 20 K. The free energies are quantitative values for the stability of both spin states for each compound and can be calculated via the Gibbs-Helmholtz-Equation. The energies are calculated with the 6–31 g\* basis set, the entropies (vibrational entropies) are calculated with the 6–31 g basis set. The absolute energies and free energies are given in kJ/mol, the absolute entropies are given in J/molK. The relative energies and free energies (energy differences) are given in kJ/mol, the relative entropies (entropy differences) in J/Kmol. The entropies and free energies are calculated at 298.15 K.

The experimental results of the Mössbauer measurements are shown in Table 3. The isomer shift  $\delta$  and the quadrupole splitting  $\Delta E_Q$  of all three compounds are in a good agreement with a HS state both at 20 K and 300 K.

The relative high organic/iron ratio of the complex leads to low statistics in the Mössbauer spectra and corresponds to the thickness of the sample in the ray path. Because of that there is a limit for higher statistics.

**Table 1** Experimental and calculated bond distances of **1**, **2** and **3** [10]

Compound	Fe-X-Bond	Distance [Å]	Distance [Å]	Distance [Å]
		exp. HS	calc. HS	calc. LS
<b>1</b>	Fe-O	1.939	1.919	1.875
		1.939	1.970	1.895
	Fe-N	2.080	2.130	1.953
		2.080	2.131	1.955
		2.215	2.423	2.086
Fe-NCO	2.067	2.003	1.958	
<b>2</b>	Fe-O	1.916	1.909	1.871
		1.916	1.961	1.883
	Fe-N	2.096	2.125	1.953
		2.096	2.125	1.953
		2.191	2.419	2.084
Fe-NCS	2.100	2.027	1.939	
<b>3</b>	Fe-O		1.912	1.875
			1.972	1.902
	Fe-N		2.114	1.955
			2.138	1.957
			2.345	2.097
Fe-NCSe		2.042	1.994	

**Table 2** Calculated energy, entropy and Gibbs energy differences of **1**, **2** and **3**

Compound	Calc. energy difference $\Delta E_{\text{HS-LS}}$	Calc. entropy difference $\Delta S_{\text{HS-LS}}$	Calc. Gibbs energy difference $\Delta G_{\text{HS-LS}}$
	[kJ/mol]	[J/molK]	[kJ/mol]
<b>1</b>	-4.2899	58.672	-39.976
<b>2</b>	-1.3797	15.213	-27.397
<b>3</b>	-12.0461	69.634	-38.863

**Table 3** Mössbauer data of **1**, **2** and **3** at 20 K and 300 K

Compound	Temperature [K]	$\delta$ [mm/s]	$\Delta E_Q$ [mm/s]
<b>1</b>	20	0.37 (35)	0.82 (62)
	300	0.38 (24)	0.83 (43)
<b>2</b>	20	0.39 (32)	0.84 (58)
	300	0.39 (27)	0.84 (49)
<b>3</b>	20	0.38 (23)	0.79 (42)
	300	0.38 (17)	0.78 (21)

### 3 Conclusions

The comparison of the experimental and calculated results for geometry and stability of **1** and **2** show that the calculation of the complexes with the B3LYP functional and the 6–31 g\* basis set gives a good estimation of the geometry and stability of this type of complexes. We use the relative energy of the HS state in respect to the LS state. The energy calculations show the tendency of the energy of the HS state relative to the energy of the LS state.

The comparison of the pure electronic ground state energy of both spin states shows that the electronic ground state energy differences of both spin states for the complexes FeL<sup>5</sup>-NCY (Y = O, S, Se) are well calculated with the basis set 6–31 + g\*, despite of the problems that are mentioned above in the introduction. The found electronic ground state energy differences exhibit that the HS state has a slightly lower energy than the LS state. These findings are in a good agreement with the experimental Mössbauer measurements which suggests that all three compounds are HS compounds and exhibit no thermal spin transition.

*Computational methods* In this contribution all calculations were performed using the GAUSSIAN09 package. B3LYP with the small basis set 3–21 g was applied to pre-optimize the geometry for these complexes. We optimized the geometry using the larger basis set 6–31 g\*. The frequencies are calculated with the basis set 6–31 g.

*Mössbauer measurements* The measurements were performed by a Mössbauer spectrometer from WissEl GmbH Starnberg. A Co<sup>57</sup> source in a Rh-matrix and a proportional counter were used. The Lorentzian fit and all parameters were calculated by Recoil 1.05 to the reference of alpha-iron.

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