

# Neutral ferric complexes of salicylaldehyde thiosemicarbazone ligands: An exceptional family of complexes exhibiting discontinuous spin transition behavior



Sébastien Floquet<sup>a,b,\*</sup>, Eric Rivière<sup>a</sup>, Kamel Boukheddaden<sup>c</sup>, Denis Morineau<sup>d,1</sup>, Marie-Laure Boillot<sup>a</sup>

<sup>a</sup> University of Paris-Sud, ICMMO-ECI, UMR CNRS 8182, 91405 Orsay, France

<sup>b</sup> University of Versailles, Institut Lavoisier de Versailles, UMR 8180, 45 avenue des Etats-Unis, 78035 Versailles, France

<sup>c</sup> University of Versailles, GEMAC, UMR 8635, 45 avenue des Etats-Unis, 78035 Versailles, France

<sup>d</sup> University of Paris-Sud, LCP, UMR 8000, 91405 Orsay, France

## ARTICLE INFO

### Article history:

Received 13 December 2013

Accepted 23 January 2014

Available online 4 February 2014

Dedicated to the Prof. Vukadin Leovac at the occasion of his 70th birthday.

### Keywords:

Thiosemicarbazone

Spin crossover

Spin transition

Iron(III)

Bistability

## ABSTRACT

Three neutral thiosemicarbazone ferric complexes of general formulas  $[\text{Fe}(\text{H5XThsa})(\text{5XThsa})]\cdot\text{H}_2\text{O}$  have been prepared and studied by magnetic susceptibility, DSC and Mössbauer measurements. The three compounds exhibit an abrupt spin transition associated with thermal hysteresis, a still rarely observed behavior for ferric complexes. DSC and Mössbauer measurements allowed confirming that these spin transition processes are coupled with a first order crystallographic phase transition whose thermodynamical parameters have been determined. Finally, it can be highlighted from the comparison of properties observed for these compounds with the literature that the synthetic procedures are a crucial point for the magnetic properties.

© 2014 Elsevier Ltd. All rights reserved.

## 1. Introduction

Transition metal complexes of thiosemicarbazones are widely studied since the sixties, especially because of their chemical and biological properties of broad interest. According to the transition metal and the parent aldehyde or ketone associated to the thiosemicarbazide moiety, the thiosemicarbazone complexes are developed for analytical chemistry [1–3], can be engaged in catalysis or pre-catalysis [4,5], or may exhibit biological properties such as antitumoral, antifungal, antibacterial or antitubercular properties [6–13]. All these peculiar properties prompt many authors to study transition metal complexes of thiosemicarbazone in order to understand the relationship between these activities and their molecular structures. Among these authors, the contribution of Leovac is of prime importance, since he published with his collaborators a number of papers from the end of the seventies until now.

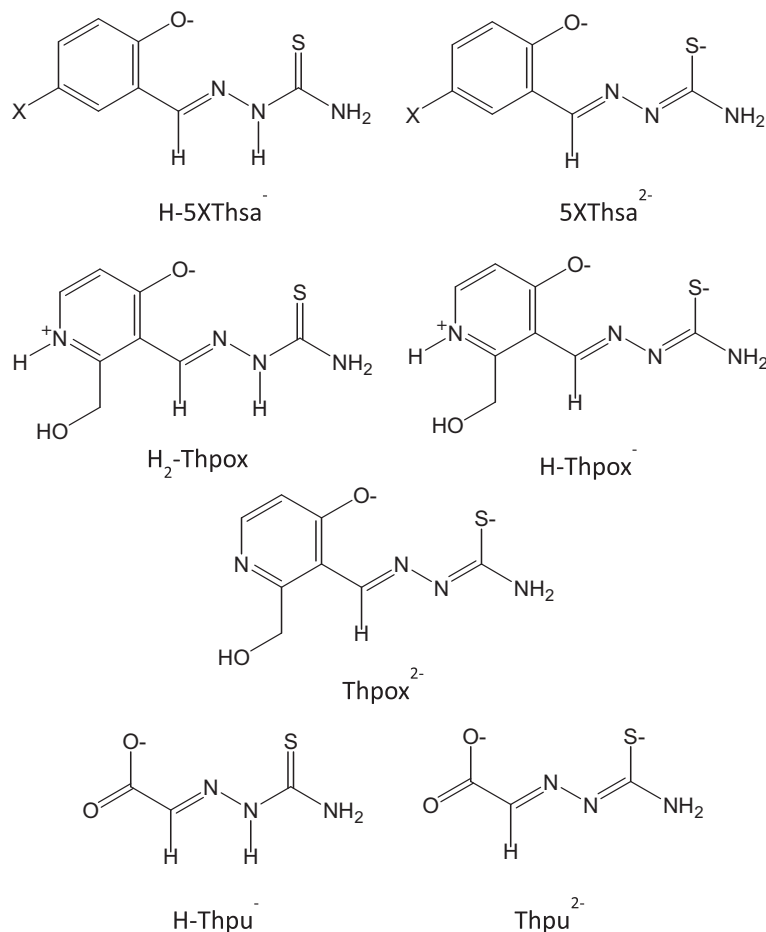
\* Corresponding author at: University of Versailles, Institut Lavoisier de Versailles, UMR 8180, 45 avenue des Etats-Unis, 78035 Versailles, France. Tel.: +33 139254379.

E-mail address: [sebastien.floquet@uvsq.fr](mailto:sebastien.floquet@uvsq.fr) (S. Floquet).

<sup>1</sup> Present address: University of Rennes 1, Institut de Physique de Rennes, UMR 6251, F-35042 Rennes, France.

We can notably cite the 59 parts of his papers entitled “Transition-Metal Complexes with the Thiosemicarbazide-Based Ligands” published between 1987 and 2012 [14,15].

The affinity of thiosemicarbazones ligands for iron and its relationship with antitumoral properties received a greater attention [16–18]. The research works were also directed to molecular magnetism. From the sixties until recently, some authors like Ablov, Turta, Gerbeleu and Zelentsov discovered and studied this class of ferric thiosemicarbazone complexes exhibiting unique spin crossover properties. Abrupt processes, sometimes associated to thermal hystereses [19–33], were reported whereas a very limited number of bistable ferric systems were known [34–38], and progressive transformations were the rule [39,40]. Related compounds were reinvestigated by several authors until very recently. In 1985, Hendrickson discovered an abrupt spin transition with hysteresis centered at 225 K for the neutral complex  $[\text{Fe}(\text{Hthpu})(\text{Thpu})]\cdot\text{H}_2\text{O}$  where  $\text{Thpu}^{2-}$  is the deprotonated form of pyruvic acid thiosemicarbazone ligand (see Scheme 1) [41]. Some years after, Mohan et al. described similar properties with the cationic ferric complexes  $[\text{Fe}(\text{HThpox})_2]\text{Cl}$  (250 K) and  $[\text{Fe}(\text{PhHthpox})_2]\text{Cl}$  (295 K) where  $\text{HThpox}^-$  and  $\text{PhHthpox}^-$  are derivatives of pyridoxal thiosemicarbazone ligands (see Scheme 1)



**Scheme 1.** Representation of thiosemicarbazone ligands found in the ferric complexes exhibiting spin crossover complexes [23,24,41,46–51].

[42,43]. Between 2001 and now, we also evidenced spin transition behavior with a large hysteresis at RT for the anionic complex  $\text{Li}[\text{Fe}(\text{5BrThsa})_2] \cdot \text{H}_2\text{O}$  ( $\text{5BrThsa}^{2-}$  = di-deprotonated 5 bromosalicylaldehyde thiosemicarbazone, see Scheme 1) [44–46] and showed how the protonation degree of the pyridoxal thiosemicarbazone ligand modulates the ligand-field strength and the spin-state energies [47]. Similar works with pyridoxal or pyridoxal derivative of thiosemicarbazone were reported by van Koningsbruggen et al. They demonstrated that a partial LS to HS conversion can be obtained by removing of the hydration water molecules [48,49]. Finally, Sato and coll. published very recently multistep spin transition behaviors for the neutral complexes  $[\text{Fe}(\text{H5ClThsa-Me})(\text{5ClThsa-Me})] \cdot \text{H}_2\text{O}$  and  $[\text{Fe}(\text{H5BrThsa})(\text{5BrThsa})] \cdot \text{H}_2\text{O}$  where the ligand  $\text{5ClThsa-Me}$  corresponds to the di-deprotonated form of the 5-chloro salicylaldehyde methylthiosemicarbazone ligand [50,51]. These two compounds compare to a series of neutral ferric complexes  $[\text{Fe}(\text{H5xThsa})(\text{5Xthsa})] \cdot \text{H}_2\text{O}$  ( $\text{X} = \text{H}, \text{Br}, \text{Cl}$ ) possessing different properties and which were obtained during the PhD work of Floquet (1998–2001) but not yet published [44]. In the present contribution, we present the syntheses, the characterizations and the studies of the magnetic properties of three neutral ferric complexes of salicylaldehyde thiosemicarbazone derivatives, namely  $[\text{Fe}(\text{H5xThsa})(\text{5Xthsa})] \cdot \text{H}_2\text{O}$  ( $\text{X} = \text{H}, \text{Br}, \text{Cl}$ ). The magnetic behaviors of these compounds are studied, completed by DSC and Mossbauer measurements and are discussed in comparison to those of the literature data.

## 2. Material and methods

### 2.1. Physical methods

Infrared spectra were recorded on a Magna 550 Nicolet spectrophotometer, using KBr pellet. NMR measurements were performed on a Bruker AC250 operating at 250 MHz for  $^1\text{H}$  in 5 mm tubes. Chemical shifts were referenced to the usual external TMS standard. Elemental analyses were performed by the service central d'analyses du CNRS, Vernaison, France and/or by the service d'analyses du CNRS, ICSN, Gif sur Yvette, France. EDX measurements were performed on a JEOL JSM 5800LV apparatus. ESI-MS experiments were performed on  $10^{-5}$  M methanol solutions with the negative ion mode and using a Thermo Scientific TSQ apparatus.

**Magnetic measurements:** The temperature dependence of the magnetic susceptibility was characterized with a Quantum Design SQUID magnetometer (MPMS5S Model) calibrated against a standard palladium sample. The independence of the susceptibility value with regard to the applied magnetic field was checked at room temperature. The heating and cooling rates were 2 and  $0.5 \text{ K min}^{-1}$  close to the abrupt spin transitions.

**$^{57}\text{Fe}$  Mössbauer measurements:** The Mössbauer spectra were recorded on a constant-acceleration spectrometer, with a 25 mCi source of  $^{57}\text{Co}$  in a rhodium matrix. The polycrystalline absorber contained 35 mg of material per  $\text{cm}^2$  (i.e., ca  $0.83 \text{ mg cm}^{-2}$  of  $^{57}\text{Fe}$ ). Variable-temperature spectra, in the 360–160 K range, were

Download English Version:

<https://daneshyari.com/en/article/1335283>

Download Persian Version:

<https://daneshyari.com/article/1335283>

[Daneshyari.com](https://daneshyari.com)