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Molecular switching in iron complexes bridged via tin-cyanides observed by Mössbauer and ESR spectroscopy

S Jung¹, F Renz^{1*}, M Klein¹, M Menzel², R Boča³ and R Stößer⁴

¹Leibniz University Hannover, Institute of Inorganic Chemistry, Callinstr. 9, D-30167 Hannover, Germany,

²Federal Institute for Materials Research and Testing (BAM) Richard-Willstätter-Str. 11, D-12489 Berlin, Germany

³Slovak Technical University, Institute for Inorganic Chemistry, Bratislava, Slovakia,

⁴Humboldt University, Institute of Chemistry, Brook-Taylor-Str. 2, D-12489 Berlin, Germany

* corresponding author: E-mail: Franz.Renz@acd.uni-hannover.de

Abstract. The precursor $[\text{Fe}^{\text{III}}(\text{L})\text{Cl}]$ ($\text{LH}_2 = \text{N,N}'\text{-bis}(2'\text{-hydroxy-3}'\text{-X-benzyliden})\text{-1,6-diamino-3-N-hexane}$) is a high-spin ($S = 5/2$) complex (with $\text{X} = \text{-CH}_3, \text{-O-CH}_3$). This precursor is combined with the bridging unit $[\text{Sn}^{\text{IV}}(\text{CN})_4]$ to yield star-shaped pentanuclear clusters, $[(\text{L-X-Fe}^{\text{III}})_4\text{Sn}(\text{CN})_4]\text{Cl}_4$. ^{57}Fe -Mössbauer, $^{119\text{m}}\text{Sn}$ -Mössbauer, and ESR spectroscopy are used to study our samples. For $\text{X} = \text{-CH}_3$ the ^{57}Fe -Mössbauer data show a multiple spin transition between iron(III) in the high-spin and low-spin state. Changing the functional group from $\text{X} = \text{-CH}_3$ to $\text{X} = \text{-O-CH}_3$ turns the switchability off.

1. Introduction

Molecular switching is one of the major targets in various disciplines, such as technology, biology and medicine. One approach is to develop multistable molecules, i.e. chemically and physically induced transitions between electronic states. In some transition metal complexes such a multistability has been discovered in 1931 and labelled spin transition phenomenon [1]. Spin transitions are rare for multinuclear compounds [1].

Our systematic approach [2-13] enabled us to apply chemical tuning on pentadentate ligand Fe(III) complexes as building units $[\text{LFe}^{\text{III}}\text{-X}]$ ($\text{L} = \text{bis}(3\text{-salicylidene aminopropyl})\text{ amine}$) and show multistability, e.g. multiple thermally induced transitions between low-spin (LS) $^2\text{T}(\text{O}_h)$ and high-spin (HS) $^6\text{A}(\text{O}_h)$ in various star-shaped compounds: tetranuclear [4], heptanuclear [3, 5, 6, 7, 8, 9], nonanuclear [2, 3, 6, 7, 8, 9], and dodecanuclear [10].

In the present work we extend this approach and introduce a novel pentanuclear system. With tin we introduce a main-group element as star-shaped center [14] and coincidental we modify the salicylidene-component with other functional groups. Such pentanuclear Fe_4Sn compounds may be capable of performing 4 spin transitions in one cluster, e.g. between 4 and 20 unpaired electrons.

2. Experimental

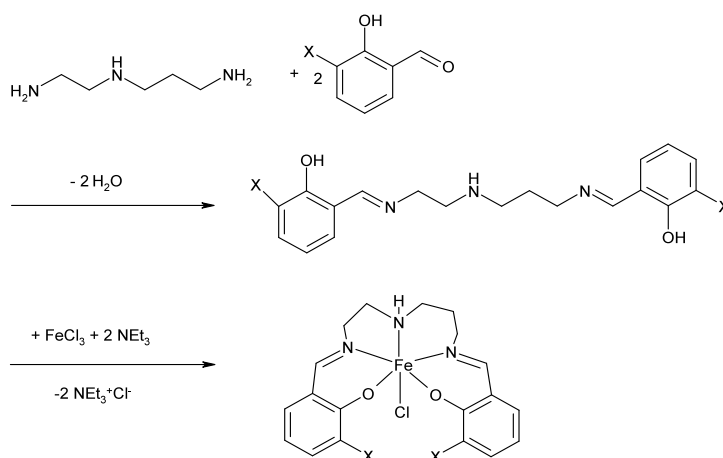


Figure 1. Synthesis of the $[\text{Fe}(\text{L})\text{Cl}]$ precursor (with $\text{X} = -\text{CH}_3, -\text{OCH}_3$)

The ligand $\text{LH}_2 = \text{N,N}'\text{-bis}(2'\text{-hydroxy-3}'\text{-X-benzylidene})\text{-1,6-diamino-3-N-hexane}$ is prepared. Complexation with Fe(III) gives the used iron precursor $[2,3/\text{H}/\text{Sal-3X}/\text{Fe}/\text{Cl}]$. This building brick, $[\text{Fe}^{\text{III}}(\text{L})\text{Cl}]$, is a high-spin ($S = 5/2$) complex (see Figure 1). This precursor is combined with the bridging unit $[\text{Sn}^{\text{IV}}(\text{CN})_4]$ to yield a star-shaped pentanuclear cluster, $[(\text{LFe}^{\text{III}}\text{-NC})_4\text{Sn}^{\text{IV}}]\text{Cl}_4$ (see Figure 2).

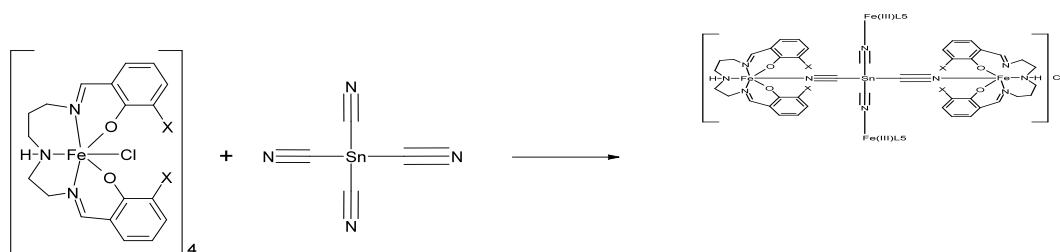


Figure 2. Synthesis of the $[(\text{LFe}^{\text{III}}\text{-NC})_4\text{Sn}^{\text{IV}}]\text{Cl}_4$ cluster

2.1. Precursor

The precursor was prepared as described in literature [2]. The dark brown powder was characterized by IR.

2.2. Tin cyanides

The tin cyanides were prepared with their analogous compound of tin chloride and potassium cyanide in acetone under nitrogen atmosphere. The mixtures stirred for six days under reflux.

2.3. Complexes

The complexes were prepared in analogy to the literature [2]. The reaction solution stirred for 30 minutes and then was cooled for 5 days. The products were characterized by IR- and Mössbauer spectroscopy, ESI-MS and ESR-spectroscopy.

2.4. IR-spectroscopy

A Tensor 27 by Bruker Optics IR-spectrometer with a 5000 – 200 cm^{-1} visual appearance and with an ATR-supplement is used at ambient temperatures.

2.5. Mössbauer spectroscopy

The Mössbauer spectra were recorded using constant acceleration Mössbauer spectrometers from WissEl Electronics Starnberg (Germany) (295K and 78K) and from the Institute for Analytical Instrumentation St. Petersburg (Russia) (CM-2201, for 295K). The used Mössbauer source of ^{57}Co in chromium matrix had an average activity of about 0.4 GBq. The $^{119\text{m}}\text{Sn}$ source in CaSnO_3 matrix had an average activity of 0.35 GBq. Proportional counters (LND Inc., Ocean Side, New York, USA) were used with a voltage between 1800 V and 1950 V to detect the spectra. The sample of 33.5 mg was placed into a sealable cylindrical polyethylene sample compartment with an inner diameter of 19 mm. The ^{57}Fe Mössbauer spectra were recorded with a maximum velocity of ± 3.20 mm/s ($T=295$ K) and ± 3.6 mm/s ($T=78$ K) because no magnetic splitting could be observed. In the case of the $^{119\text{m}}\text{Sn}$ the Mössbauer spectra were recorded with a maximum velocity of ± 7.95 mm/s ($T=295$ K) and ± 6.15 mm/s ($T=78$ K). All ^{57}Fe spectra were referred to a standard α -Fe foil (Goodfellow). The $^{119\text{m}}\text{Sn}$ were referred to SnO_2 and a Sn foil.

2.6. ESR spectroscopy

The ESR spectra were measured with an ESR-spectrometer ESR 300 of the “Zentrum für wissenschaftlichen Gerätebau” (today: Magnettech GmbH), Berlin Adlershof with a test frequency of 9.426 GHz.

3. Results and Discussion

The structure of the $[\text{2,3/H/Sal-3X/Fe/Sn}(\text{CN})_4]$ complexes are shown in Figure 2. The MM+ force field structure of these clusters are shown in Figure 3. The complexes are characterized by IR-spectroscopy. On bridging the typical CN-bond stretching vibration switched from 2080 cm^{-1} to higher wavenumbers which are above 2100 cm^{-1} .

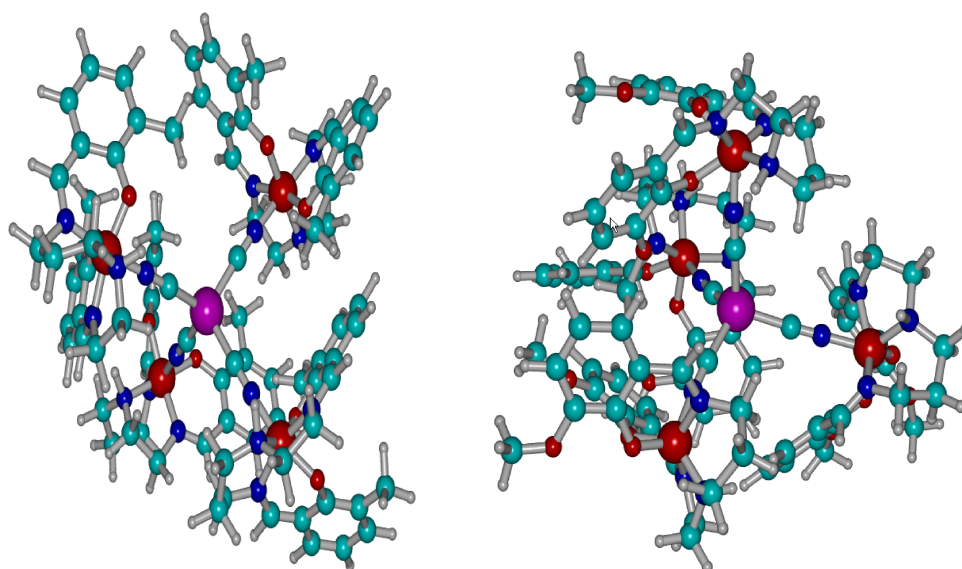


Figure 3. MM+ force field structure of $[\text{2,3/H/Sal-3Me/Fe/Sn}(\text{CN})_4]$ (left) and of $[\text{2,3/H/Sal-3MeO/Fe/Sn}(\text{CN})_4]$ (right) optimized based on standard X-ray data

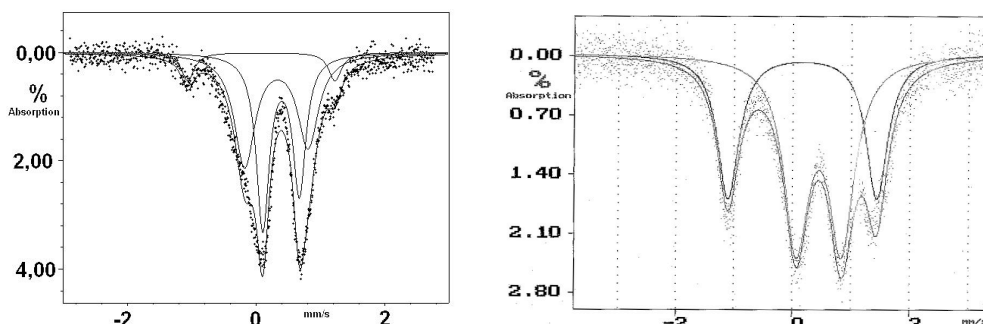


Figure 4. ^{57}Fe -Mössbauer-spectra of $[2,3/\text{H}/\text{Sal}-3\text{Me}/\text{Fe}/\text{Sn}(\text{CN})_4]$ (T=295 K (left); T=78 K (right))

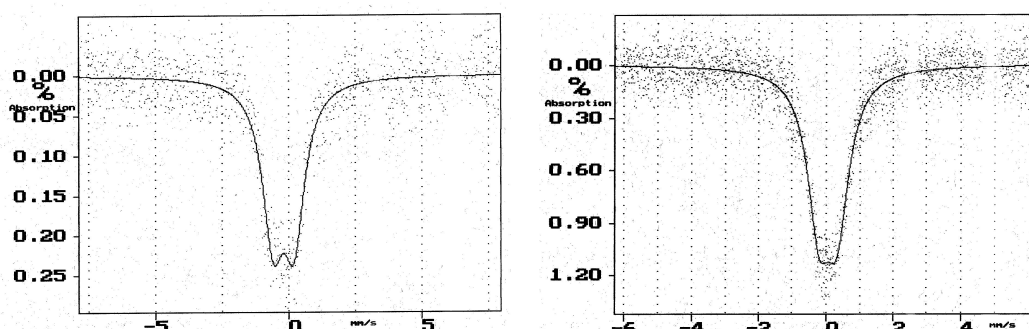


Figure 5. ^{119}Sn -Mössbauer-spectra of $[2,3/\text{H}/\text{Sal}-3\text{Me}/\text{Fe}/\text{Sn}(\text{CN})_4]$ (T=295 K (left); T=78 K (right))

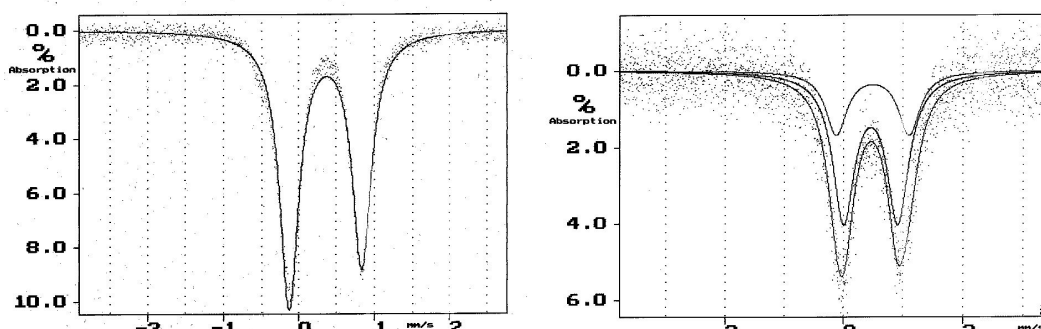


Figure 6. ^{57}Fe -Mössbauer-spectra of $[2,3/\text{H}/\text{Sal}-3\text{MeO}/\text{Fe}/\text{Sn}(\text{CN})_4]$ (T=295 K (left); T=78 K (right))

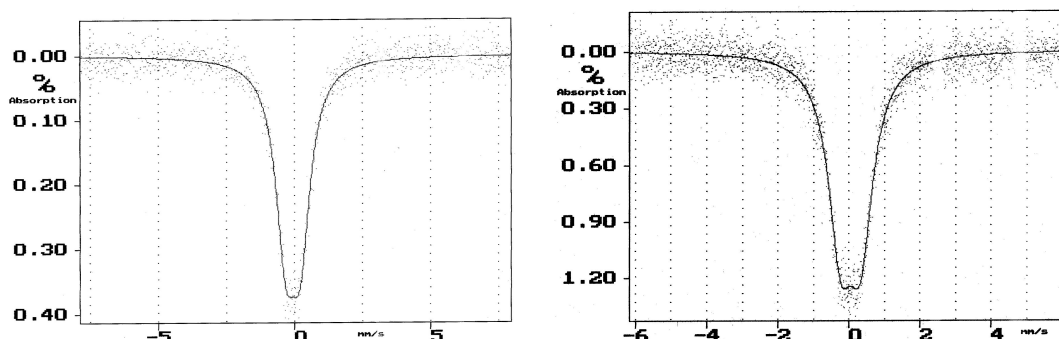


Figure 7. ^{119}Sn -Mössbauer-spectra of $[2,3/\text{H}/\text{Sal}-3\text{MeO}/\text{Fe}/\text{Sn}(\text{CN})_4]$ (T=295 K (left); T=78 K (right))

Figure 4 and 5 show the ^{119}Sn and ^{57}Fe Mössbauer spectra for the compound $[2,3/\text{H}/\text{Sal}-3\text{Me}/\text{Fe}/\text{Sn}(\text{CN})_4]$. The tin-spectra show that the oxidation state of tin is +4 at high and low temperature. For the iron-spectra there are three doublets at 295K. One with an isomeric shift (δ) of

0.388 mm/sec, a quadrupol-splitting (QS) of 0.568 mm/sec and a site population of 44.96 %, and the other with a δ of 0.315 mm/sec, a QS of 0.987 and a site population of 47.00 %. Both are characteristic for a high-spin state for Fe(III). The third one is typical for a Fe(III) low-spin state with a δ of 0.084 mm/sec, a QS of 2.288 mm/sec and a site population of 8.04%. At 78 K two doublets are presented, one with an isomeric shift of 0.177 mm/sec, a quadrupol-splitting of 2.550 mm/sec and a signal plot of 40.01 %, and the other one with an isomeric shift of 0.465 mm/sec, a QS of 0.776 mm/sec and a signal plot of 59.99 %. This indicates that the molar ratio shifts from the dominant high-spin state at room temperature towards the low-spin state at 78 K for Fe(III). Figure 6 and 7 show the ^{119}Sn and ^{57}Fe Mössbauer spectra for the compound $[2,3/\text{H}/\text{Sal}-3\text{MeO}/\text{Fe}/\text{Sn}(\text{CN})_4]$. The tin-spectra show that the oxidation state of tin is +4 at high and low temperature like before. In the iron spectra just iron(III) in high-spin state can be seen. A low-spin state cannot be verified, neither at room temperature nor at low temperature. That means by changing the functional group at the salicylidene from methyl to methoxy turns the switchability off. It shows, that some iron(III)-molecules can reversibly be converted between high-spin and low-spin state, but the switchability is addicted to their functional groups.

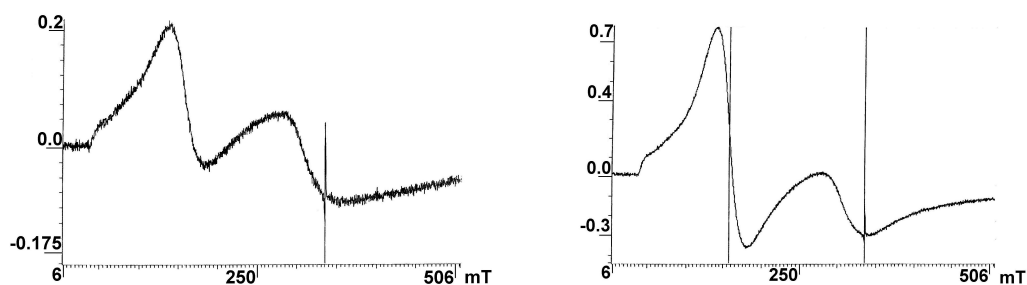


Figure 8. ESR-spectra of $[2,3/\text{H}/\text{Sal}-3\text{Me}/\text{Fe}/\text{Sn}(\text{CN})_4]$ (T=293 K (left); T=77 K (right))

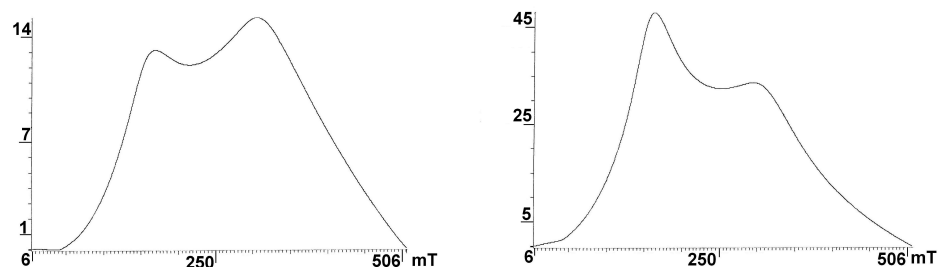


Figure 9. Integral of the ESR-spectra of $[2,3/\text{H}/\text{Sal}-3\text{Me}/\text{Fe}/\text{Sn}(\text{CN})_4]$ (T=293 K (left); T=77 K (right))

Figure 8 show the ESR-spectra of the compound $[2,3/\text{H}/\text{Sal}-3\text{Me}/\text{Fe}/\text{Sn}(\text{CN})_4]$. For 77 K a broad transition at $g \sim 4,3$ (first step) and a broad segue with a lower intensity at $g \sim 2$ (second step) can be seen. For 293K the intensity-ratio switches to the segue at $g \sim 2$. These intensity effects are clearly verified by their corresponding integrals (see Figure 9). This confirms $[2,3/\text{H}/\text{Sal}-3\text{Me}/\text{Fe}/\text{Sn}(\text{CN})_4]$ as a switching molecular complex. The analysis for the corresponding ESR-data of the compound $[2,3/\text{H}/\text{Sal}-3\text{MeO}/\text{Fe}/\text{Sn}(\text{CN})_4]$ are not straight forward. A detailed ESR-analysis will be published somewhere else.

4. Conclusion

The ^{57}Fe -Mössbauer data indicate that the $[2,3/\text{H}/\text{Sal}-3\text{Me}/\text{Fe}/\text{Sn}(\text{CN})_4]$ show multiple spin transition between Fe(III) in the high-spin and low-spin state. Changing the functional group at the salicylidene from methyl to methoxy turns the switchability off. The multiple spin transition for the 3-methyl-derivate is confirmed by the ESR-data of this compound. The results show that the compound $[2,3/\text{H}/\text{Sal}-3\text{Me}/\text{Fe}/\text{Sn}(\text{CN})_4]$ is a switching molecular complex with a main group element as central atom. This proves the usage of main group elements such as tin as central atoms in switching molecules and a continuative investigation of the influence on this switchability from functional groups in complexes. The ESR-measurement shows that this method of spectroscopy is useful to verify switching complexes and further investigations are in progress.

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