

Mössbauer investigation of novel pentadentate schiff base complexes

L. Heyer¹ · B. Dreyer^{1,2} · A. Preiss¹ · M. Menze¹ ·
S. Klimke¹ · M. Jahns¹ · R. Sindelar² · G. Klingelhöfer³ ·
B. F. O. Costa⁴ · F. Renz¹

© Springer International Publishing Switzerland 2016

Abstract We synthesised a series of seven mononuclear and two trinuclear Schiff base coordination compounds. All nine complexes have been analysed by Mössbauer and IR spectroscopy. The Mössbauer spectra reveal a doublet, which are related to the high spin state ($S = 5/2$) of the iron(III) centres.

Keywords Schiff base · High spin · Iron complexes · Pseudohalide · Mössbauer

1 Introduction

Certain transition metal complexes may change their electronic structure due to external stimuli (e.g. temperature, pressure, irradiation, etc.). These - so called - spin crossover (SCO) coordination compounds mostly consist of iron(II), iron(III) or cobalt(II) centres [1–3]. These compounds may be used in electric storage devices or sensors by external stimuli due to the so affected spin transition.

This article is part of the Topical Collection on *Proceedings of the International Conference on the Applications of the Mössbauer Effect (ICAME 2015), Hamburg, Germany, 13–18 September 2015*

✉ F. Renz
renz@acd.uni-hannover.de

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

² Faculty II, University of Applied Science Hannover, Ricklinger Stadtweg 120, 30459 Hannover, Germany

³ Institute of Inorganic and Analytic Chemistry, Johannes Gutenberg-Universität Mainz, Duesbergweg 10-14, 55128 Mainz, Germany

⁴ Physics Department, University of Coimbra, 3004-516 Coimbra, Portugal

Table 1 Mössbauer parameters of the discussed compounds from Figs. 1–9 relative to α -Fe, with deviations in brackets

Compound	$\delta_{IS}/mm \cdot s^{-1}$	$\Delta_{EQ}/mm \cdot s^{-1}$	Spin state	Figure
[Fe(BrL^5)Cl]	0,45 ($\pm 0,06$)	0,79 ($\pm 0,01$)	HS	Fig. 1
[Fe(BrL^5)N ₃]	0,33 ($\pm 0,10$)	0,83 ($\pm 0,17$)	HS	Fig. 2
[Fe(BrL^5)NCS]	0,45 ($\pm 0,08$)	1,01 ($\pm 0,12$)	HS	Fig. 3
[Fe(BrL^5)NCSe]	0,31 ($\pm 0,08$)	0,01 ($\pm 0,13$)	HS	Fig. 4
[Fe(ClL^5)Cl]	0,42 ($\pm 0,06$)	1,19 ($\pm 0,10$)	HS	Fig. 5
[Fe(ClL^5)NCS]	0,37 ($\pm 0,03$)	1,02 ($\pm 0,05$)	HS	Fig. 6
[Fe(ClL^5)NCSe]	0,40 ($\pm 0,02$)	0,76 ($\pm 0,03$)	HS	Fig. 7
Dendr.-[Fe(BrL^5)]	0,40 ($\pm 0,03$)	0,76 ($\pm 0,05$)	HS	Fig. 8
Dendr.-[Fe(ClL^5)]	0,39 ($\pm 0,01$)	0,76 ($\pm 0,01$)	HS	Fig. 9

A suitable coordination sphere for iron(III) was found to be of N_4O_2 -donating ligands [4]. Krüger *et al.* [5] developed an asymmetric pentadentate ligand out from the salicylaldehyde derivatives and N-(2-aminoethyl)-1,3-propanediamine. We synthesised a series of Schiff base iron(III) coordination compounds which have been analysed via Mössbauer and IR spectroscopy as well as ESI-MS. For this the symmetric pentadentate N_3O_2 -donating ligands (X -salten = χL^5) were made by the condensation of N-(3-aminopropyl)propane-1,3-diamine with either 5-bromosalicylaldehyde (BrL^5) or 5-chlorosalicylaldehyde (ClL^5). The octahedral coordination sphere is completed by the pseudohalide monodentate N-donating ligands azide, seleno- and thiocyanate as well as the precursor chloride.

In a second pathway we synthesised a dendritic complex system based on polyamine dendrimers functionalized in their periphery with the halogenated salicylaldehydes to form multicentered Schiff base coordination compounds. We started with tris(2-aminoethyl)amine and extended it to the first generation dendrimer (G1) in 2 steps by adding acrylonitrile and reducing it with DIBAL-H [6].

2 Experimental

We followed the synthetic route described in the literature [5, 7]. The educts were obtained from Sigma Aldrich and used without any further purification.

The Mössbauer spectra have been collected at room temperature on a MIMOSIIa device from the Johannes Gutenberg-Universität Mainz with a $^{57}Co/Rh$ source. The isomer shifts are given relative to α -iron. The IR-Spectra have been collected on a Tensor27 from Bruker and the ESI-mass spectra were recorded on a Q-ToF Premier mass spectrometer from Micromass.

[Fe(χL^5)(Cl)]:

N-(3-aminopropyl)propane-1,3-diamine (10 mmol) and 5-chlorosalicylaldehyde or 5-bromosalicylaldehyde (20 mmol), respectively, were dissolved in 120 cm³ methanol. The solution was boiled under reflux for 2 h, $FeCl_3 \cdot 6H_2O$ (10 mmol) in 25 cm³ methanol was added and the mixture was further boiled for 1 h. After cooling in a fridge for 24 h, the product was filtered off and dried at room temperature.

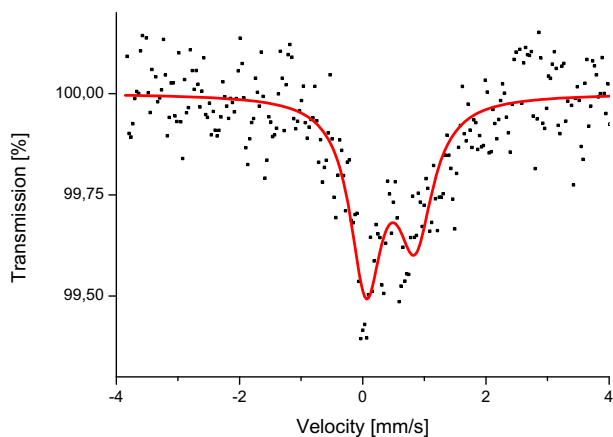


Fig. 1 The Mössbauer spectrum of the complex $[\text{Fe}(\text{BrL}^5)\text{Cl}]$ with an isomer shift (relative to αFe) $\delta_{\text{IS}} = 0.45$ mm/s and quadrupole splitting $\Delta_{\text{EQ}} = 0.79$ mm/s which are typical for iron(III) centre in high spin state

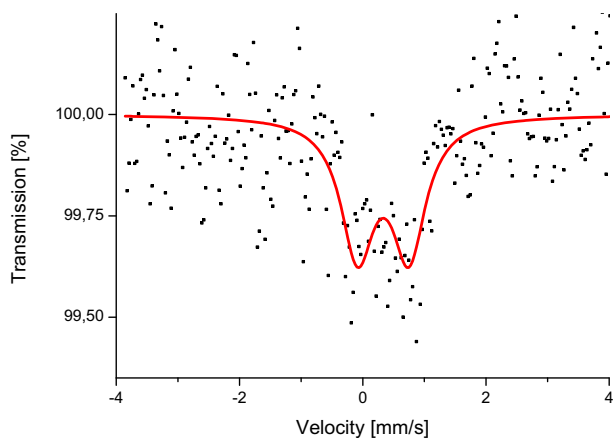


Fig. 2 The Mössbauer spectrum of the complex $[\text{Fe}(\text{BrL}^5)\text{N}_3]$ with an isomer shift (relative to αFe) $\delta_{\text{IS}} = 0.33$ mm/s and quadrupole splitting $\Delta_{\text{EQ}} = 0.83$ mm/s

$[\text{Fe}(\text{BrL}^5)(\text{Cl})]$:

$\text{C}_{20}\text{H}_{21}\text{FeN}_3\text{O}_2\text{Br}_2\text{Cl}$ ($[\text{M}-\text{Cl}^-]^+ = 551.053$); IR (KBr): $\nu(\text{N-H}) = 3260$ cm^{-1} , $\nu(\text{C-H}) = 2924, 2858$ cm^{-1} , $\nu(\text{C=N}) = 1616, 1610$ cm^{-1} , $\nu(\text{C=C arom.}) = 1528$ cm^{-1} , $\delta(\text{=C-H, out-of-plane}) = 820$ cm^{-1} .

$[\text{Fe}(\text{ClL}^5)(\text{Cl})]$:

$\text{C}_{20}\text{H}_{21}\text{FeN}_3\text{O}_2\text{Cl}_3$ ($[\text{M}-\text{Cl}^-]^+ = 462.151$); IR (KBr): $\nu(\text{N-H}) = 3208$ cm^{-1} , $\nu(\text{C-H}) = 2978, 2944$ cm^{-1} , $\nu(\text{C=N}) = 1624$ cm^{-1} , $\nu(\text{C=C arom.}) = 1530$ cm^{-1} , $\delta(\text{=C-H, out-of-plane}) = 821$ cm^{-1} .

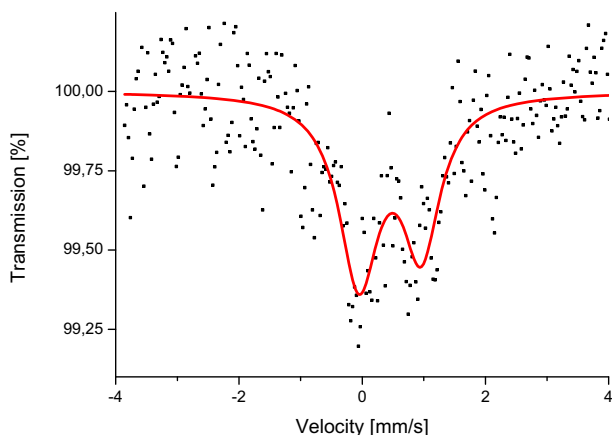


Fig. 3 The Mössbauer spectrum of the complex $[\text{Fe}(\text{BrL}^5)\text{NCS}]$ with an isomer shift (relative to αFe) $\delta_{\text{IS}} = 0.45$ mm/s and quadrupole splitting $\Delta_{\text{EQ}} = 1.01$ mm/s

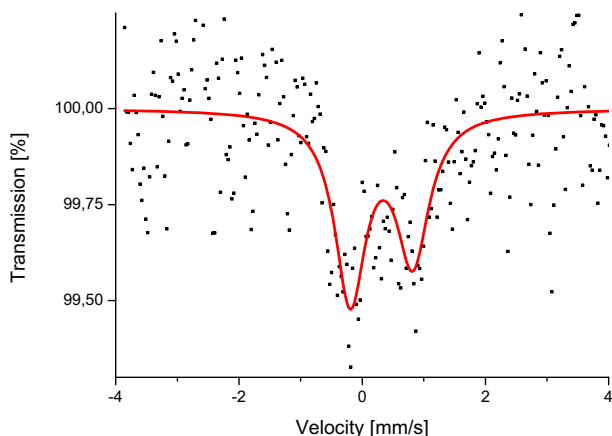


Fig. 4 The Mössbauer spectrum of the complex $[\text{Fe}(\text{BrL}^5)\text{NCSe}]$ with an isomer shift (relative to αFe) $\delta_{\text{IS}} = 0.31$ mm/s and quadrupole splitting $\Delta_{\text{EQ}} = 1.01$ mm/s

$[\text{Fe}(\text{ClL}^5)(\text{A})]$:

$[\text{Fe}(\text{ClL}^5)(\text{Cl})]$ (1mmol) was dissolved in 200 cm^3 methanol under reflux. After 15 minutes the mixture was filtered of and a solution of KNCS or KNCS_e (1 mmol), respectively, in 30 cm^3 methanol was added to the filtrate. This mixture was boiled for an additional 15 minutes and left in a beaker for precipitation at room temperature for 7 days.

$[\text{Fe}(\text{ClL}^5)(\text{NCS})]$:

$\text{C}_{21}\text{H}_{21}\text{FeN}_4\text{O}_2\text{Cl}_2\text{S}$ ($[\text{M}-\text{NCS}^-]^+$ = 462.151); IR (KBr): $\nu(\text{N-H}) = 3252$ cm^{-1} , $\nu(\text{C-H}) = 2928, 2865$ cm^{-1} , $\nu(\text{NCS}) = 2063$ cm^{-1} , $\nu(\text{C=N}) = 1619$ cm^{-1} , $\nu(\text{C=C arom.}) = 1530$ cm^{-1} , $\delta(\text{=C-H, out-of-plane}) = 824$ cm^{-1} .

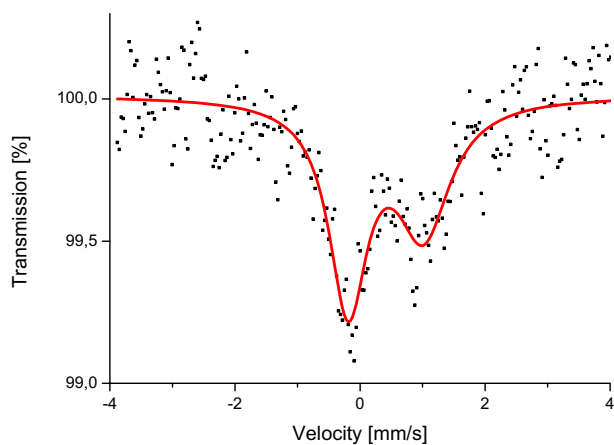


Fig. 5 The Mössbauer spectrum of the complex $[\text{Fe}(\text{C}_1\text{L}^5)\text{Cl}]$ with an isomer shift (relative to αFe) $\delta_{\text{IS}} = 0.42$ mm/s and quadrupole splitting $\Delta_{\text{EQ}} = 1.19$ mm/s

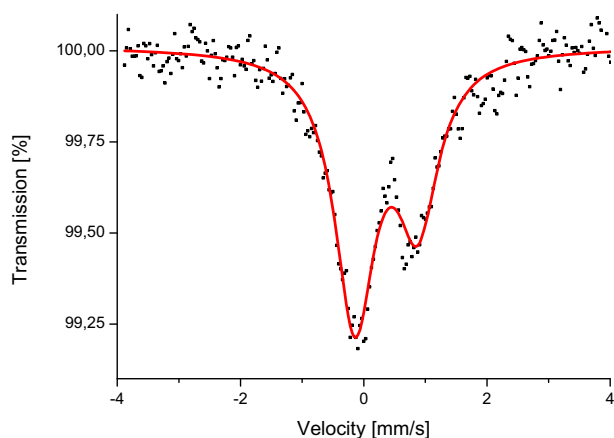


Fig. 6 The Mössbauer spectrum of the complex $[\text{Fe}(\text{C}_1\text{L}^5)\text{NCS}]$ with an isomer shift (relative to αFe) $\delta_{\text{IS}} = 0.37$ mm/s and quadrupole splitting $\Delta_{\text{EQ}} = 1.02$ mm/s

$[\text{Fe}(\text{C}_1\text{L}^5)(\text{NCSe})]$:

$\text{C}_{21}\text{H}_{21}\text{FeN}_4\text{O}_2\text{Cl}_2\text{Se}$ ($[M\text{-NCSe}^-]^+ = 462.151$); IR (KBr): $\nu(\text{N-H}) = 3249$ cm^{-1} , $\nu(\text{CH}) = 2929, 2868$ cm^{-1} , $\nu(\text{NCSe}) = 2067$ cm^{-1} , $\nu(\text{C=N}) = 1616$ cm^{-1} , $\nu(\text{C=C arom.}) = 1529$ cm^{-1} , $\delta(\text{=C-H, out-of-plane}) = 823$ cm^{-1} .

$[\text{Fe}(\text{BrL}^5)(\text{A})]$:

$[\text{Fe}(\text{BrL}^5)(\text{Cl})]$ (0.85 mmol) was dissolved in 200 cm^3 methanol under reflux. After 15 minutes the mixture was filtered off and a solution of KNCS, KNCSe or NaN_3 (0.85 mmol), respectively, in 25 cm^3 methanol was added to the filtrate. This mixture was boiled for an additional 15 minutes and left in a beaker for precipitation at room temperature for 7 days.

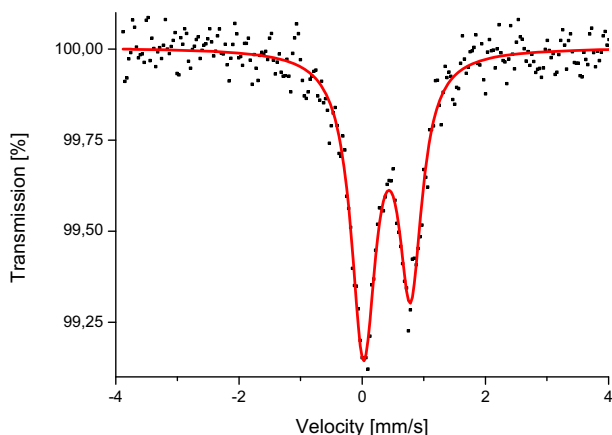


Fig. 7 The Mössbauer spectrum of the complex $[\text{Fe}(\text{C}_1\text{L}^5)\text{NCS}]$ with an isomer shift (relative to αFe) $\delta_{\text{IS}} = 0.40$ mm/s and quadrupole splitting $\Delta_{\text{EQ}} = 0.76$ mm/s

$[\text{Fe}(\text{BrL}^5)(\text{NCS})]$:

$\text{C}_{21}\text{H}_{21}\text{FeN}_4\text{O}_2\text{Br}_2\text{S}$ ($[\text{M}-\text{NCS}^-]^+$ = 551.053); IR (KBr): $\nu(\text{N-H}) = 3260$ cm^{-1} , $\nu(\text{C-H}) = 2928, 2868$ cm^{-1} , $\nu(\text{NCS}) = 2056$ cm^{-1} , $\nu(\text{C=N}) = 1638, 1610$ cm^{-1} , $\nu(\text{C=C arom.}) = 1525$ cm^{-1} , $\delta(=\text{C-H, out-of-plane}) = 835$ cm^{-1} .

$[\text{Fe}(\text{BrL}^5)(\text{NCSe})]$:

$\text{C}_{21}\text{H}_{21}\text{FeN}_4\text{O}_2\text{Br}_2\text{Se}$ ($[\text{M}-\text{NCSe}^-]^+$ = 551.053); IR (KBr): $\nu(\text{N-H}) = 3260$ cm^{-1} , $\nu(\text{C-H}) = 2928, 2868$ cm^{-1} , $\nu(\text{NCSe}) = 2056$ cm^{-1} , $\nu(\text{C=N}) = 1638, 1610$ cm^{-1} , $\nu(\text{C=C arom.}) = 1526$ cm^{-1} , $\delta(=\text{C-H, out-of-plane}) = 835$ cm^{-1} .

$[\text{Fe}(\text{BrL}^5)(\text{N}_3)]$:

$\text{C}_{20}\text{H}_{21}\text{FeN}_6\text{O}_2\text{Br}_2$ ($[\text{M}-\text{N}_3^-]^+$ = 551.053); IR (KBr): $\nu(\text{N-H}) = 3244$ cm^{-1} , $\nu(\text{C-H}) = 2928, 2910, 2868$ cm^{-1} , $\nu(\text{N}_3) = 2052$ cm^{-1} , $\nu(\text{C=N}) = 1638, 1610$ cm^{-1} , $\nu(\text{C=C arom.}) = 1524$ cm^{-1} , $\delta(=\text{C-H, out-of-plane}) = 822$ cm^{-1} .

Dendritic- $[\text{Fe}(\text{C}_1\text{L}^5)(\text{Cl})]_3$:

The first generation of the polyamine dendrimer (1.13 mmol, $M = 488.8$ g/mol) and 5-chlorosalicylaldehyde (6.79 mmol) or 5-bromosalicylaldehyde (6.79 mmol), respectively, were dissolved in 75 cm^3 methanol. The solution was boiled under reflux for 30 minutes, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (3.39 mmol) in 25 cm^3 methanol was added and the mixture was further boiled for 2 h. After cooling in a fridge for 24 h, the product was filtered off and dried at room temperature.

Dendritic- $[\text{Fe}(\text{C}_1\text{L}^5)(\text{Cl})]_3$:

$\text{C}_{66}\text{H}_{76}\text{Fe}_4\text{N}_{10}\text{O}_8\text{Cl}_{12}$; Calculated: C 44.38 %; Found: C 41.23 %; IR (KBr): $\nu(\text{C-H}) = 2955, 2874$ cm^{-1} , $\nu(\text{C=N}) = 1614$ cm^{-1} , $\nu(\text{C=C arom.}) = 1520$ cm^{-1} , $\delta(=\text{C-H, out-of-plane}) = 827$ cm^{-1} .

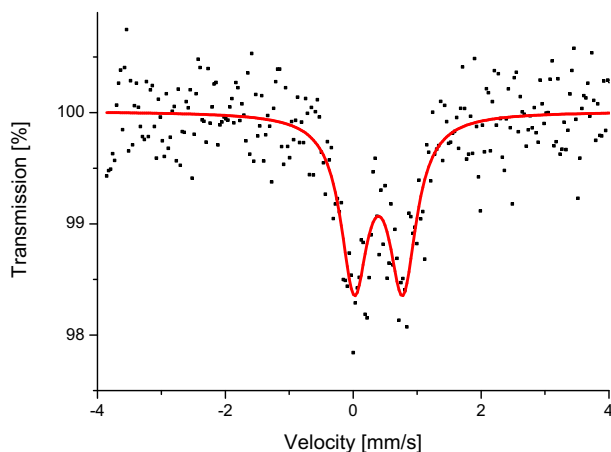


Fig. 8 The Mössbauer spectrum of the dendritic complex system with $[\text{Fe}(\text{BrL}^5)]$ -units with an isomer shift (relative to αFe) $\delta_{\text{IS}} = 0.40$ mm/s and quadrupole splitting $\Delta_{\text{EQ}} = 0.76$ mm/s

Dendritic- $[\text{Fe}(\text{BrL}^5)(\text{Cl})]_3$:

$\text{C}_{66}\text{H}_{76}\text{Fe}_4\text{N}_{10}\text{O}_8\text{Br}_6\text{Cl}_6$; Calculated: C 38.61%; Found: C 38.88 %; IR (KBr): $\nu(\text{C}-\text{H}) = 2945, 2835 \text{ cm}^{-1}$, $\nu(\text{C}=\text{N}) = 1609 \text{ cm}^{-1}$, $\nu(\text{C}=\text{C arom.}) = 1516 \text{ cm}^{-1}$, $\delta(\text{C}-\text{H, out-of-plane}) = 827 \text{ cm}^{-1}$.

3 Results and discussion

The collected Mössbauer spectra in Figs. 1–9 as well as the corresponding parameters of all compounds, listed in Table 1, are related to α -iron. To record the spectra 100 mg of the Cl-salten (ClL^5) complexes have been used within approximately 24 h and 100 mg of the Br-salten (BrL^5) complexes within approximately 48 h, respectively.

As expected, the chloride complexes $[\text{Fe}(\text{XL}^5)\text{Cl}]$ are in high spin (HS) state ($S = 5/2$). Substitution of the monodentate anionic ligand chloride with the pseudohalides thiocyanate, selenocyanate or azide did not affect the spin state at room temperature. The quadrupole splittings range from 0.76 mm/s to 1.19 mm/s and the isomer shifts from 0.31 mm/s to 0.45 mm/s. Thereby no trend is observable.

The spectra of the ClL^5 -complexes reveal an increasing ligand field strength with a decreasing quadrupole splitting from monodentate ligands chloride via thiocyanate to selenocyanate:

$$\Delta_{\text{EQ}}(\text{Cl}^-) > \Delta_{\text{EQ}}(\text{NCS}^-) > \Delta_{\text{EQ}}(\text{NCSe}^-)$$

In contrast to that, the spectra of the BrL^5 -complexes reveal the opposite effect. Herein the thiocyanate has the same quadrupole splitting as the selenocyanate and, in addition, the difference between chloride and azide is only insignificantly larger:

$$\Delta_{\text{EQ}}(\text{Cl}^-) < \Delta_{\text{EQ}}(\text{N}_3^-) < \Delta_{\text{EQ}}(\text{NCS}^-) \cong \Delta_{\text{EQ}}(\text{NCSe}^-)$$

The spectra of the dendritic compounds dendritic- $[\text{Fe}(\text{ClL}^5)]$ and dendritic- $[\text{Fe}(\text{BrL}^5)]$ reveal approximately the same value for the isomer shifts and quadrupole splittings.

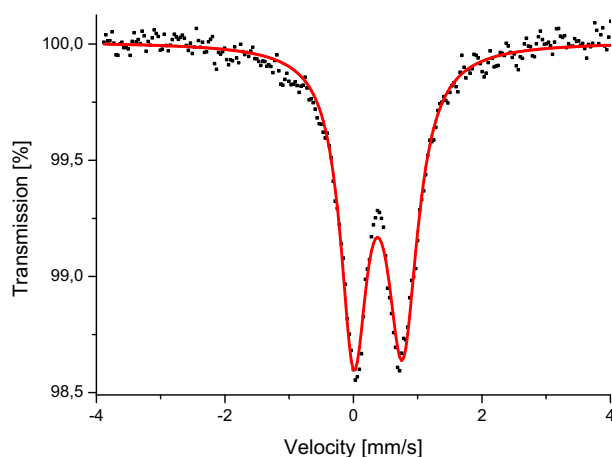


Fig. 9 The Mössbauer spectrum of the dendritic complex system with $[\text{Fe}(\text{C}_1\text{L}^5)]$ -units with an isomer shift (relative to αFe) $\delta_{\text{IS}} = 0.39$ mm/s and a quadrupole splitting $\Delta_{\text{EQ}} = 0.76$ mm/s

In conclusion, we synthesised seven mononuclear as well as two dendritic trinuclear coordination compounds that are in the HS state at room temperature. Ongoing investigations are low temperature IR spectroscopy measurements as well as further Mössbauer spectroscopy especially at low temperatures to possibly reveal a spin transition and single crystal structure analysis to possibly determine a relation between Δ_{EQ} and a distortion of the coordination sphere.

Acknowledgments We like to thank the Hannover School for Nanotechnology (hsn) and the MARIO graduate school programme as well as the Laboratory of Nano and Quantum Engineering (LNQE), the University of Applied Science Hannover and the Leibniz University Hannover (LUH).

References

1. Renz, F.: Physical and chemical induced spin crossover. *J. Phys.: Conference Series*, 217 (2010). doi:10.1088/1742-6596/217/1/012022
2. Gütlich, P., Gaspar, A.B., Garcia, Y.: Spin state switching in iron coordination compounds. *Beilstein J. Org. Chem.* **9**, 342–391 (2013)
3. Gütlich, P.: Spin crossover – quo vadis? *Eur. J. Inorg. Chem.* **2013**, 581 (2013)
4. Van Koningsbruggen, P., Maeda, Y., Oshio, H.: Iron(III) spin crossover compounds. *Topics in Current Chemistry* **233**, 259–324 (2004)
5. Krüger, C., Augustín, P., Nemeč, I., Trávníček, Z., Oshio, H., Boča, R., Renz, F.: Spin crossover in iron(III) complexes with pentadentate schiff base ligands and pseudohalido coligands. *Eur. J. Inorg. Chem.* **2013**, 902 (2013)
6. Buhleier, E., Wehner, W., Vögtle, F.: "Cascade"- and "nonskid-chain-like" syntheses of molecular cavity topologies. *Synthesis* **2**, 155–158 (1978)
7. Krüger, C., Augustín, P., Dlháň, L., Pavlik, J., Moncol, J., Nemeč, I., Boča, R., Renz, F.: Iron(III) complexes with pentadentate Schiff-base ligands: Influence of crystal packing change and pseudohalido coligand variations on spin crossover. *Polyhedron* **87**, 194–201 (2015)