

# Mössbauer investigation of Schiff base iron(III) coordination compounds

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**Abstract** We synthesised a series of seven mononuclear Schiff base coordination compounds. The symmetric pentadentate N<sub>3</sub>O<sub>2</sub>-donating ligands were prepared by the condensation of *N*-(2-aminoethyl)-1,2-ethanediamine with either 5-bromosalicylaldehyde or 5-chlorosalicylaldehyde. The octahedral coordination sphere is completed by different pseudohalide monodentate N-donating ligands. All complexes have been analysed by Mössbauer spectroscopy, ESI-MS and IR spectroscopy. The Mössbauer spectra at room temperature 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

Under certain conditions, an external stimulus (temperature, pressure, irradiation, etc.) to specific coordination compounds can lead to a change of the ground state multiplicity. These - so called - spin crossover (SCO) coordination compounds are mostly complexes of iron(II), iron(III) or cobalt(II) [1–3]. These compounds promise a vast range of applications in the fields of sensor technology, data storage, and even in medicine.

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For iron(III) compounds a coordination sphere with an  $N_4O_2$  donor set was found to be fortunate for a possible spin transition [4]. Krüger et al. developed an asymmetric pentadentate ligand derived from salicylaldehyde derivatives and *N*-(2-aminoethyl)-1,3-propanediamine [5]. We recently presented a series of iron(III) complexes with symmetric ligands using *N*-(3-aminopropyl)propan-1,3-diamine [6]. 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 ( $\chi L^5$ ) were made of the condensation of *N*-(2-aminoethyl)-1,2-ethanediamine 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.

## 2 Experimental

We followed the synthetic route described in the literature [6, 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 MIMOSII device from the Johannes Gutenberg-Universität Mainz with a  $^{57}Co/Rh$  source. The isomer shifts are given relative to  $\alpha$ -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.

$[Fe(\chi L^5)(Cl)]$ :

5-chlorosalicylaldehyde or 5-bromosalicylaldehyde (14 mmol), respectively, were dissolved in 70  $cm^3$  methanol. 0.75  $cm^3$  of *N*-(2-aminoethyl)-1,2-ethanediamine (7 mmol) was added. The yellow solution was boiled under reflux for 90 minutes,  $FeCl_3 \cdot 6H_2O$  (7 mmol) in 40  $cm^3$  methanol was added and the mixture was further boiled for 2 h. After cooling to room temperature the volume of the solution was reduced to 50 % under reduced pressure and stored in a fridge for 16 h. The product was filtered off, washed with cold methanol and dried at room temperature.

$[Fe(BrL^5)(Cl)]$ :

$C_{18}H_{17}FeN_3O_2Br_2Cl$  ( $[M-Cl^-]^+ = 520.8954$ ); IR (KBr):  $\nu(CH) = 2918\text{ cm}^{-1}$ ,  $\nu(C=N) = 1641\text{ cm}^{-1}$ ,  $1622\text{ cm}^{-1}$ ,  $\nu(C=C\text{ arom.}) = 1528\text{ cm}^{-1}$ ,  $\delta(=C-H, \text{ out-of-plane}) = 824\text{ cm}^{-1}$ .

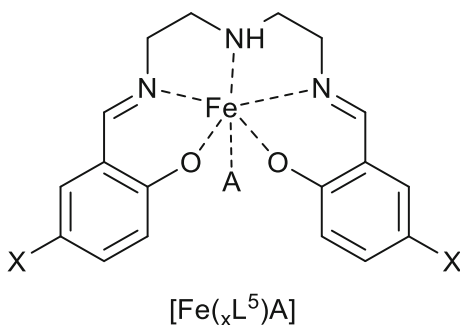
$[Fe(ClL^5)(Cl)]$ :

$C_{18}H_{17}FeN_3O_2Cl_3$  ( $[M-Cl^-]^+ = 432.7367$ ); IR (KBr):  $\nu(N-H) = 3138\text{ cm}^{-1}$ ,  $\nu(C-H) = 2930\text{ cm}^{-1}$ ,  $\nu(C=N) = 1641\text{ cm}^{-1}$ ,  $1622\text{ cm}^{-1}$ ,  $\nu(C=C\text{ arom.}) = 1533\text{ cm}^{-1}$ ,  $\delta(=C-H, \text{ out-of-plane}) = 824\text{ cm}^{-1}$ .

$[Fe(ClL^5)(A)]$ :

0.2 g  $[Fe(ClL^5)(Cl)]$  (0.43 mmol) was dissolved in 150  $cm^3$  methanol. A solution of KNCS or KNCS<sub>e</sub> (0.45 mmol), respectively, in 20  $cm^3$  methanol was added to the filtrate. This mixture was stirred for 5 minutes and left in a beaker for precipitation at room temperature for 7 days.

**Fig. 1** Structural formula of the target compounds  $[\text{Fe}_x\text{L}^5\text{A}]$  with  $X = \text{Cl}$  or  $\text{Br}$  and  $\text{A} = \text{NCS}$ ,  $\text{NCSe}$  or  $\text{N}_3$



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

$\text{C}_{19}\text{H}_{17}\text{FeN}_4\text{O}_2\text{Cl}_2\text{S}$  ( $[\text{M}-\text{NCS}^-]^+ = 432.8540$ ); IR (KBr):  $\nu(\text{N-H}) = 3267 \text{ cm}^{-1}$ ,  $\nu(\text{C-H}) = 2943 \text{ cm}^{-1}$ ,  $\nu(\text{NCS}) = 2056 \text{ cm}^{-1}$ ,  $2044 \text{ cm}^{-1}$ ,  $\nu(\text{C=N}) = 1628 \text{ cm}^{-1}$ ,  $\nu(\text{C=C arom.}) = 1533 \text{ cm}^{-1}$ ,  $\delta(\text{=C-H, out-of-plane}) = 835 \text{ cm}^{-1}$ .

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

$\text{C}_{19}\text{H}_{17}\text{FeN}_4\text{O}_2\text{Cl}_2\text{Se}$  ( $[\text{M}-\text{NCSe}^-]^+ = 432.8540$ ); IR (KBr):  $\nu(\text{N-H}) = 3163 \text{ cm}^{-1}$ ,  $\nu(\text{C-H}) = 2918 \text{ cm}^{-1}$ ,  $\nu(\text{NCSe}) = 2037 \text{ cm}^{-1}$ ,  $2043 \text{ cm}^{-1}$ ,  $\nu(\text{C=N}) = 1622 \text{ cm}^{-1}$ ,  $1643 \text{ cm}^{-1}$ ,  $\nu(\text{C=C arom.}) = 1531 \text{ cm}^{-1}$ ,  $\delta(\text{=C-H, out-of-plane}) = 823 \text{ cm}^{-1}$ .

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

0.5 g  $[\text{Fe}(\text{BrL}^5)(\text{Cl})]$  (0.9 mmol) was dissolved in  $150 \text{ cm}^3$  methanol. A solution of KNCS, KNCSe or  $\text{NaN}_3$  (0.95 mmol), respectively, in  $20 \text{ cm}^3$  methanol was added to the filtrate. This mixture was stirred for 5 minutes and left in a beaker for precipitation at room temperature for 7 days.

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

$\text{C}_{19}\text{H}_{17}\text{FeN}_4\text{O}_2\text{Br}_2\text{S}$  ( $[\text{M}-\text{NCS}^-]^+ = 520.8787$ ); IR (KBr):  $\nu(\text{N-H}) = 3271 \text{ cm}^{-1}$ ,  $\nu(\text{C-H}) = 2940 \text{ cm}^{-1}$ ,  $\nu(\text{NCS}) = 2056 \text{ cm}^{-1}$ ,  $2042 \text{ cm}^{-1}$ ,  $\nu(\text{C=N}) = 1628 \text{ cm}^{-1}$ ,  $\nu(\text{C=C arom.}) = 1530 \text{ cm}^{-1}$ ,  $\delta(\text{=C-H, out-of-plane}) = 833 \text{ cm}^{-1}$ .

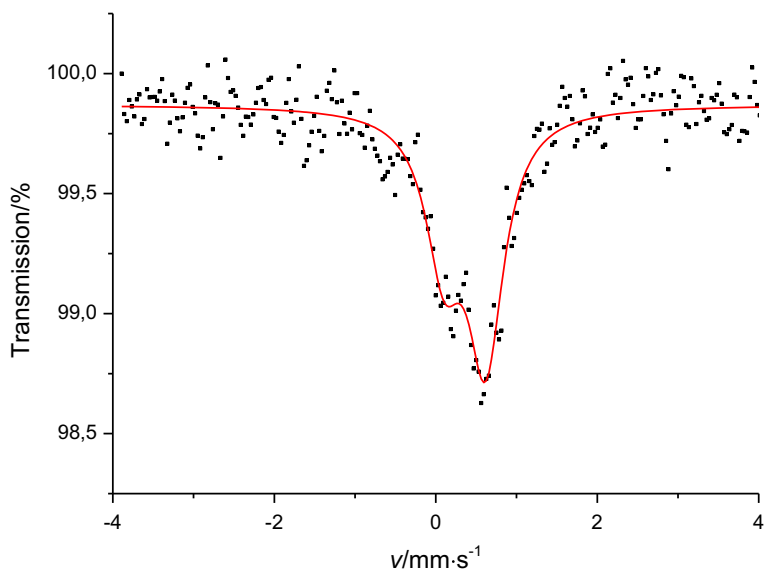
$[\text{Fe}(\text{BrL}^5)(\text{NCSe})]$ :

$\text{C}_{19}\text{H}_{17}\text{FeN}_4\text{O}_2\text{Br}_2\text{Se}$  ( $[\text{M}-\text{NCSe}^-]^+ = 520.8848$ ); IR (KBr):  $\nu(\text{N-H}) = 3273 \text{ cm}^{-1}$ ,  $\nu(\text{C-H}) = 2936 \text{ cm}^{-1}$ ,  $\nu(\text{NCSe}) = 2054 \text{ cm}^{-1}$ ,  $2045 \text{ cm}^{-1}$ ,  $\nu(\text{C=N}) = 1626 \text{ cm}^{-1}$ ,  $\nu(\text{C=C arom.}) = 1530 \text{ cm}^{-1}$ ,  $\delta(\text{=C-H, out-of-plane}) = 833 \text{ cm}^{-1}$ .

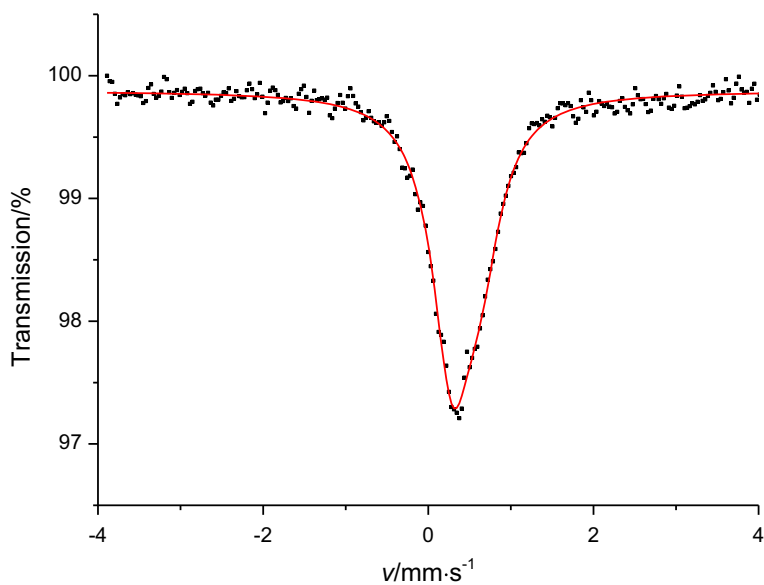
$[\text{Fe}(\text{BrL}^5)(\text{N}_3)]$ :

$\text{C}_{18}\text{H}_{17}\text{FeN}_6\text{O}_2\text{Br}_2$  ( $[\text{M}-\text{N}_3^-]^+ = 520.8427$ ); IR (KBr):  $\nu(\text{N-H}) = 3233 \text{ cm}^{-1}$ ,  $\nu(\text{C-H}) = 2926 \text{ cm}^{-1}$ ,  $\nu(\text{N}_3) = 2066 \text{ cm}^{-1}$ ,  $\nu(\text{C=N}) = 1641 \text{ cm}^{-1}$ ,  $1624 \text{ cm}^{-1}$ ,  $\nu(\text{C=C arom.}) = 1526 \text{ cm}^{-1}$ ,  $\delta(\text{=C-H, out-of-plane}) = 826 \text{ cm}^{-1}$ .

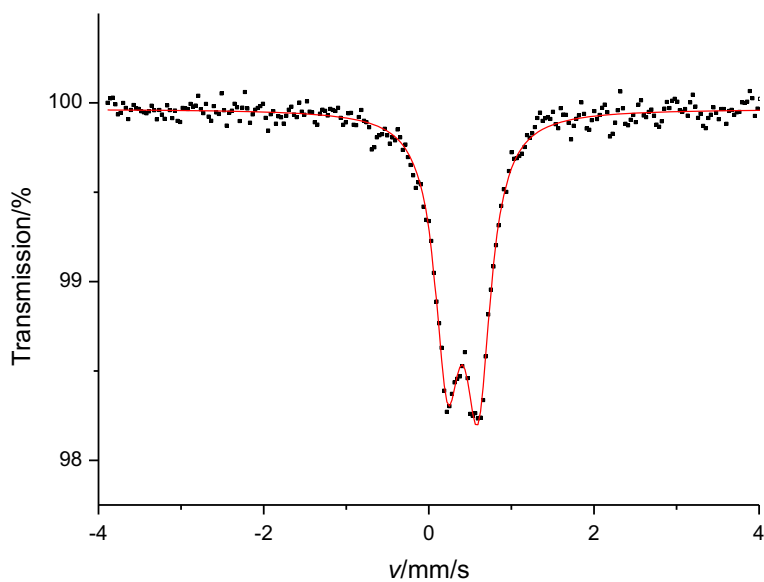
Caution notice: Working with large amounts of sodium azide may be associated with exposure to highly toxic  $\text{HN}_3$ ; therefore this reaction should be carried out in a well-ventilated fume hood (Fig. 1).



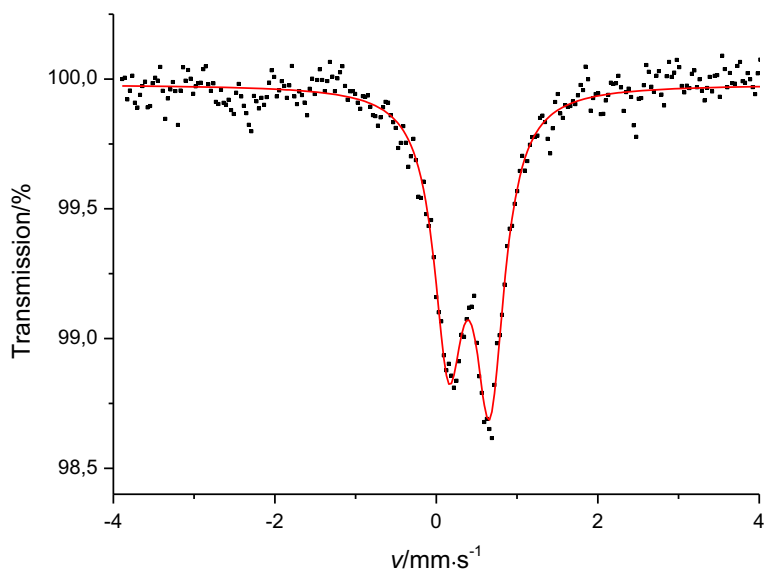
**Fig. 2** The Mössbauer spectrum of the complex  $[\text{Fe}(\text{BrL}^5)\text{Cl}]$  with an isomer shift (relative to  $\alpha\text{-Fe}$ )  $\delta_{\text{IS}} = 0.36 \text{ mm}\cdot\text{s}^{-1}$  and quadrupole splitting  $\Delta_{\text{EQ}} = 0.51 \text{ mm}\cdot\text{s}^{-1}$  which are typical for iron(III) centre in high spin state



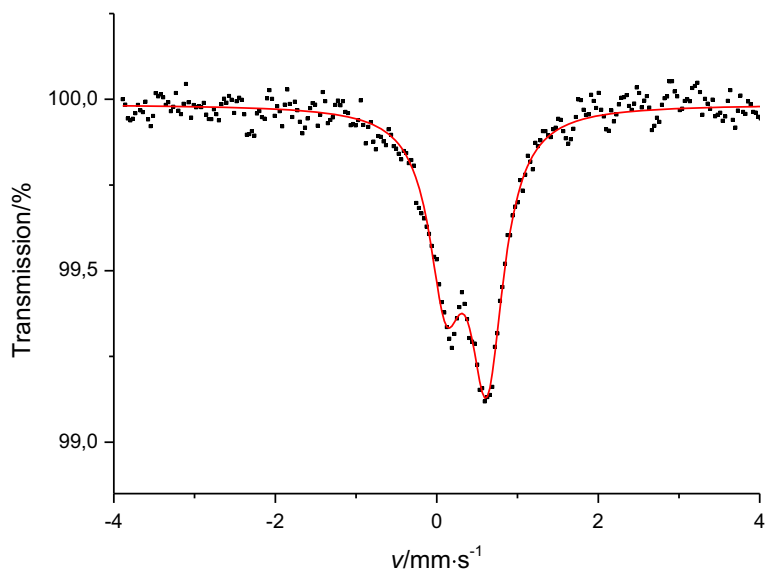
**Fig. 3** The Mössbauer spectrum of the complex  $[\text{Fe}(\text{BrL}^5)\text{N}_3]$  with an isomer shift (relative to  $\alpha\text{-Fe}$ )  $\delta_{\text{IS}} = 0.46 \text{ mm}\cdot\text{s}^{-1}$  and quadrupole splitting  $\Delta_{\text{EQ}} = 0.34 \text{ mm}\cdot\text{s}^{-1}$



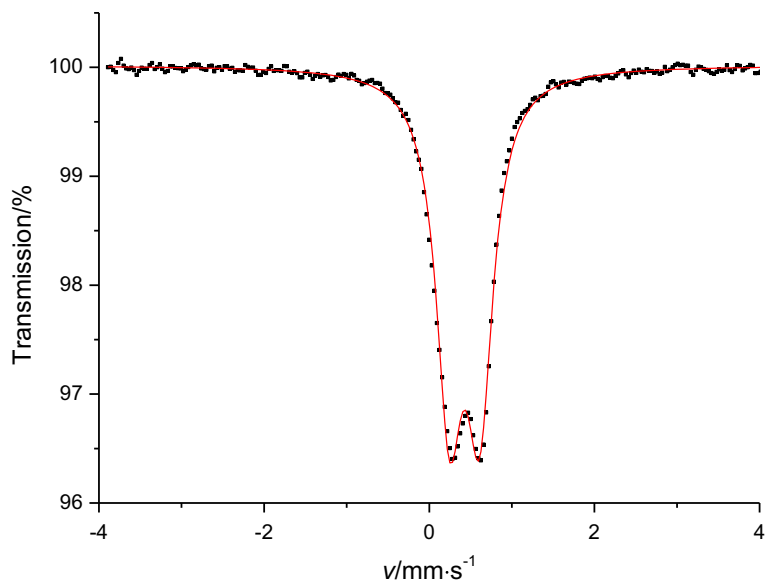
**Fig. 4** The Mössbauer spectrum of the complex  $[\text{Fe}(\text{BrL}^5)\text{NCS}]$  with an isomer shift (relative to  $\alpha\text{-Fe}$ )  $\delta_{\text{IS}} = 0.41 \text{ mm}\cdot\text{s}^{-1}$  and quadrupole splitting  $\Delta_{\text{EQ}} = 0.37 \text{ mm}\cdot\text{s}^{-1}$



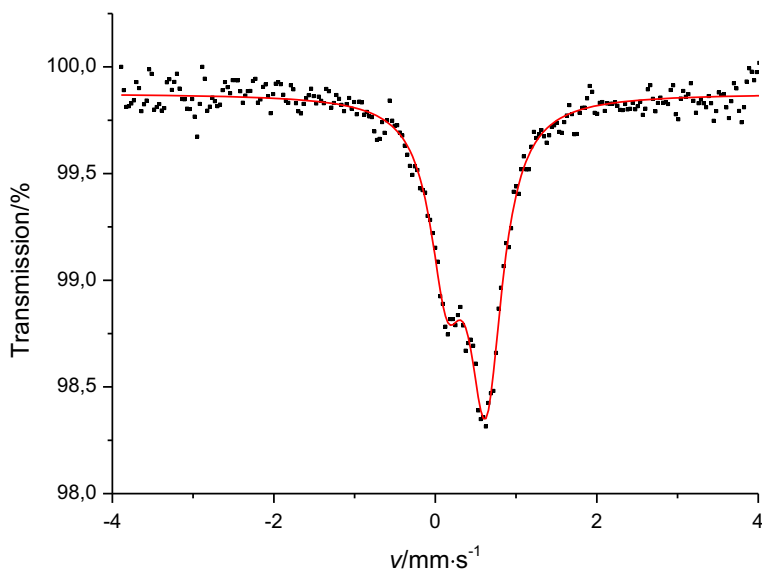
**Fig. 5** The Mössbauer spectrum of the complex  $[\text{Fe}(\text{BrL}^5)\text{NCSe}]$  with an isomer shift (relative to  $\alpha\text{-Fe}$ )  $\delta_{\text{IS}} = 0.41 \text{ mm}\cdot\text{s}^{-1}$  and quadrupole splitting  $\Delta_{\text{EQ}} = 0.51 \text{ mm}\cdot\text{s}^{-1}$



**Fig. 6** The Mössbauer spectrum of the complex  $[\text{Fe}(\text{C}_1\text{L}^5)\text{Cl}]$  with an isomer shift (relative to  $\alpha\text{-Fe}$ )  $\delta_{\text{IS}} = 0.37 \text{ mm}\cdot\text{s}^{-1}$  and quadrupole splitting  $\Delta_{\text{EQ}} = 0.51 \text{ mm}\cdot\text{s}^{-1}$



**Fig. 7** The Mössbauer spectrum of the complex  $[\text{Fe}(\text{C}_1\text{L}^5)\text{NCS}]$  with an isomer shift (relative to  $\alpha\text{-Fe}$ )  $\delta_{\text{IS}} = 0.43 \text{ mm}\cdot\text{s}^{-1}$  and quadrupole splitting  $\Delta_{\text{EQ}} = 0.37 \text{ mm}\cdot\text{s}^{-1}$



**Fig. 8** The Mössbauer spectrum of the complex  $[\text{Fe}(\text{ClL}^5)\text{NCSe}]$  with an isomer shift (relative to  $\alpha\text{-Fe}$ )  $\delta_{\text{IS}} = 0.38 \text{ mm}\cdot\text{s}^{-1}$  and quadrupole splitting  $\Delta_{\text{EQ}} = 0.48 \text{ mm}\cdot\text{s}^{-1}$

**Table 1** Mössbauer parameters of the discussed compounds from Figs. 1–7 relative to  $\alpha\text{-Fe}$

Compound	$\delta_{\text{IS}} / \text{mm}\cdot\text{s}^{-1}$	$\Delta_{\text{EQ}} / \text{mm}\cdot\text{s}^{-1}$	Spin State	Figure
$[\text{Fe}(\text{BrL}^5)\text{Cl}]$	0.36 ( $\pm 0.04$ )	0.51 ( $\pm 0.06$ )	HS	Fig. 2
$[\text{Fe}(\text{BrL}^5)\text{N}_3]$	0.46 ( $\pm 0.03$ )	0.34 ( $\pm 0.04$ )	HS	Fig. 3
$[\text{Fe}(\text{BrL}^5)\text{NCS}]$	0.41 ( $\pm 0.01$ )	0.37 ( $\pm 0.02$ )	HS	Fig. 4
$[\text{Fe}(\text{BrL}^5)\text{NCSe}]$	0.41 ( $\pm 0.02$ )	0.51 ( $\pm 0.02$ )	HS	Fig. 5
$[\text{Fe}(\text{ClL}^5)\text{Cl}]$	0.37 ( $\pm 0.02$ )	0.51 ( $\pm 0.03$ )	HS	Fig. 6
$[\text{Fe}(\text{ClL}^5)\text{NCS}]$	0.43 ( $\pm 0.01$ )	0.37 ( $\pm 0.01$ )	HS	Fig. 7
$[\text{Fe}(\text{ClL}^5)\text{NCSe}]$	0.38 ( $\pm 0.02$ )	0.48 ( $\pm 0.03$ )	HS	Fig. 8

### 3 Results and discussion

Figures 2, 3, 4, 5, 6, 7 and 8 show the collected Mössbauer spectra relative to the  $^{57}\text{Co}/\text{Rh}$  source. The corresponding parameters of all compounds are listed in Table 1 and related to  $\alpha\text{-iron}$ .

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  $0.34 \text{ mm}\cdot\text{s}^{-1}$  to  $0.52 \text{ mm}\cdot\text{s}^{-1}$  and the isomer shifts from  $0.36 \text{ mm}\cdot\text{s}^{-1}$  to  $0.46 \text{ mm}\cdot\text{s}^{-1}$ .

In contrast to the Mössbauer results of the previously reported complexes no trend in the quadrupole splitting is observed, as well as for the isomer shifts. The quadrupole splitting of the symmetric complexes derived from *N*-(3-aminopropyl)propan-1,3-diamine ranged from  $0.76 \text{ mm}\cdot\text{s}^{-1}$  to  $1.19 \text{ mm}\cdot\text{s}^{-1}$  and was therefore significantly higher than for the herein

presented compounds [6]. The smaller values of the quadrupole splitting indicate a lower distortion of the octahedral coordination sphere of the investigated complexes.

In conclusion, we synthesised seven mononuclear coordination compounds that are in the HS state at room temperature. Ongoing investigations are temperature dependent IR spectroscopy to possibly reveal a spin transition as well as single crystal structure analysis to possibly determine a relation between  $\Delta_{EQ}$  and a distortion of the coordination sphere.

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