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Tuning spin transitions of iron(II)-dpp systems

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Abstract Chemical modifications of the yet reported iron(II) compound $[Fe(dpp)_2(NCS)_2]\cdot Py$ (dpp = dipyrido[3,2a:2'3'c]phenazine, Py = pyridine) which shows abrupt spin crossover below room temperature with large hysteresis have been made. The purpose was to stabilize different spin states at room temperature as well as to adjust the spin crossover in temperature and hysteresis width. We modified the bidentate ligand dpp by substituting hydrogens at the phenazine by different functional groups. In addition, we substituted the thiocyanate monodentate ligands by $NCSe^-$. The spin states of these compounds have been investigated by Mössbauer spectroscopy at two temperatures and temperature depending IR spectroscopy. These methods indicating that the chemical modifications are influencing the observed spin configuration of the complexes alongside the spin crossover behavior which changed to gradual and incomplete transitions. These promising results offer interesting possibilities for chemical adjustments of the shown spin crossover systems.

Keywords Spin crossover · Hysteresis · Iron complexes · Mössbauer spectroscopy · dpp

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1 Introduction

Coordination compounds showing a change of spin state triggered by external stimuli are named spin crossover compounds and are considered to enhance future electronic devices. The transition is depending on physical (*e.g.* temperature, pressure, electromagnetic radiation, etc.) and chemical (*e.g.* solvent, ligand exchange, pH, etc.) influences. With the change of spin state arise a change of physical properties (*e.g.* magnetic moment, bond length, color, etc.), which can be detected by various methods. Mössbauer spectroscopy is one of them and popularly used for iron compounds to gain information about spin and oxidation states [1–5]. For many possible applications, an abrupt spin transition near room temperature including a wide hysteresis is desired. The spin crossover compound $[Fe(dpp)_2(NCS)_2]\cdot py$ (dpp = dipyrido[3,2a:2'3'c]phenazine, py = pyridine) shows an abrupt transition with a wide hysteresis of about 40 K at temperatures below 200 K [6–9].

We modified the bidentate dpp ligands by substituting one or two hydrogens with methyl groups or chlorine atoms and changed the monodentate ligand NCS^- with $NCSe^-$ (Fig. 1). The purpose was to adjust the transition temperature as well as the hysteresis. The synthesized compounds were analyzed by ESI-MS, IR-spectroscopy and elemental analysis. Spin states and possible spin transitions were verified by temperature depending IR- and Mössbauer spectroscopy.

2 Experimental

dpp-R_1R_2 The different ligands were synthesized according to literature methods [10–12].

1,10-phenanthroline-5,6-dione (5 mmol) and a modified o-phenylenediamine (5 mmol) were dissolved ethanol and heated under reflux for 4 h. The solution was evaporated under reduced pressure until the respective product precipitated. The product was separated and recrystallized in methanol. ^{1}H-NMR-, ESI-MS- and IR-data are provided in the Electronic Supplementary Material.

$[Fe(dpp)_2\ (NCSe)_2]$ The complex $[Fe(dpp)_2(NCSe)_2]$ was synthesized according to literature methods [7, 8, 13].

The synthesis was carried out under inert atmosphere. $FeCl_2\cdot 4H_2O$ (0.25 mmol) and a trace amount of ascorbic acid were dissolved in a solution of pyridine (2 ml) and water (30 ml). KSeCN (0.5 mmol) in water was added to the solution. The mixture was stirred for 1 h at room temperature. The precipitation was collected by filtration and dissolved in pyridine while heated to 80 °C. A hot solution of dpp (0.5 mmol) in pyridine was added slowly under vigorous stirring. The mixture was stirred for another 30 minutes at 80 °C. The solvent was evaporated under reduced pressure until the product precipitated. It was filtered of and dried in vacuum. ESI-MS-, IR- and elemental analysis-data are provided in the Electronic Supplementary Material.

$[Fe(dpp\text{-}R_1R_2)_2(NCS)_2]$ The complexes with the general formula $[Fe(dpp\text{-}R_1R_2)_2(NCS)_2]$ were prepared according to the synthesis described by Zhong et al. [7], Kusz et al. [8] and Suffren et al. [13]. All complexes were synthesized under inert atmosphere. $FeCl_2\cdot 4H_2O$ (0.25 mmol) and a trace amount of ascorbic acid were dissolved in a solution of pyridine (2 ml) and water (30 ml). KSCN (0.5 mmol) in water was added and the resulting mixture was stirred for 1 h at room temperature. The precipitation was collected by filtration, dissolved in pyridine and heated to 80 °C. The respective ligand (0.5 mmol) was dissolved in hot pyridine and slowly added to the first solution. The mixture was heated under reflux for 1 h. The solution was cooled to room temperature and the solvent was evaporated under reduced pressure

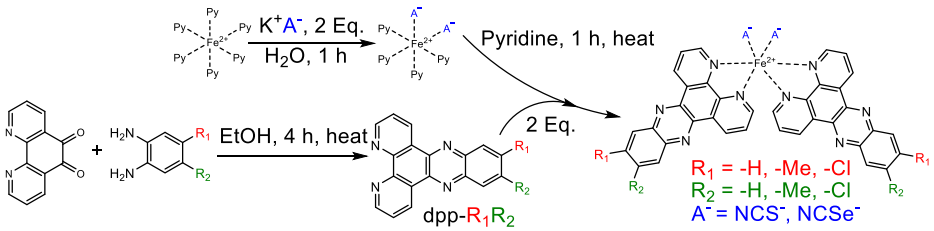

Fig. 1 Graphical Illustration of the synthesis reported in this work for chemical modifications of the spin crossover compound $[Fe(dpp)_2(NCS)_2]\cdot Py$

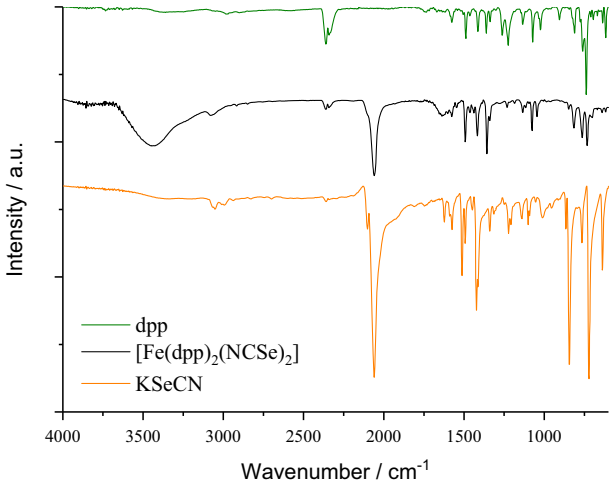

Fig. 2 IR spectroscopy of $[Fe(dpp)_2(NCSe)_2]$, the ligand dpp and KSeCN at room temperature

until the product precipitated. It was collected by filtration and dried in vacuum. ESI-MS-, IR- and elemental analysis-data are provided in the Electronic Supplementary Material.

IR spectroscopy was performed at variable temperatures on a Bruker Tensor 27 in transmission mode using potassium bromide as matrices and an Advanced Research Systems closed cycle cryocooler. ESI-MS measurements were taken on a Micromass Q-Tof Premier spectrometer, NMR spectroscopy was measured at Bruker DPX 400X spectrometer at room temperature. Mössbauer spectroscopy at room temperature was performed using a MIMOS II in transmission mode with silicon pin photodiodes. For the Mössbauer measurements at 80 K a WissEl Mössbauer spectrometer was used. In both cases a ^{57}Co(Rh) source was used. All spectra were analyzed and fitted applying the software RECOIL 1.03, whereas isomer shifts are presented related to α-iron. Due to the different measurement setups the statistical noises may vary between the measurements at room temperature and 80 K.

3 Results & discussion

The synthesized complexes were characterized by IR and ESI-MS. The IR spectra (example Fig. 2, other spectra can be found in the Electronic Supplementary Material) indicate a high similarity between ligands and complexes in the spectra. In addition, characteristic

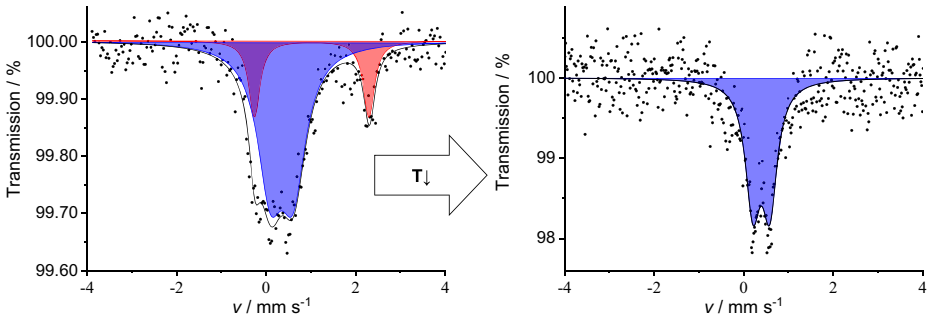

Fig. 3 Mössbauer spectra of $[Fe(dpp)_2(NCSe)_2]$ at room temperature (left) and 80 K (right). LS area marked blue and HS area marked red

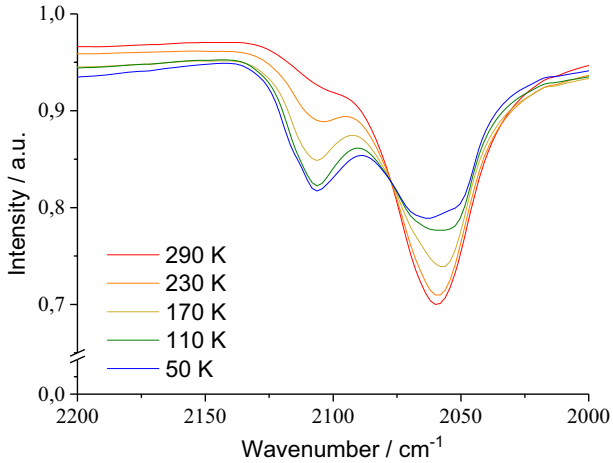

Fig. 4 Temperature depending IR spectroscopy of $[Fe(dpp)_2(NCSe)_2]$ at temperatures between 290 K and 50 K in the range of 2200 – 1900 cm^{-1}

vibrations of the respective monodentate ligands are observable. These absorptions could be assigned to carbon-nitrogen vibrations. ESI-MS measurements show characteristic complex fragments as well as fragments in which the iron is coordinated three times by the respective dpp-R ligand. In comparison to other ESI-MS studies on complexes of a similar structure, this effect was anticipated [14].

$[Fe(dpp)_2(A)_2]$ Influence of monodentate ligand exchange on the spin state and spin crossover behavior

Substitutions of the monodentate ligands by other pseudohalide anions lead to changes in the coordination sphere as well as the spin state of complexes [15]. While the compound $[Fe(dpp)_2(NCS)_2]\cdot py$ is at room temperature in high spin state (S = 2, HS) [7], the Mössbauer spectrum of $[Fe(dpp)_2(NCSe)_2]$ at room temperature (Fig. 3) indicates the presence of both the HS und the low spin (LS) state (S = 0). After cooling the sample to 80 K the Mössbauer measurement (Fig. 3) only shows a single doublet suggesting an iron(II) LS state. Temperature depending IR spectroscopy was used to investigate its spin crossover behavior (Fig. 4). A shift from 2060 cm^{-1} to 2114 cm^{-1} can be observed with

Table 1 Mössbauer data (isomer shift IS, quadrupole splitting QS, population) of the iron(II) complex. Isomer shifts related to α-iron

Compound	Temperature	IS [mms^{-1}]	QS [mms^{-1}]	Pop [%]	FWHM [mms^{-1}]
$[Fe(dpp)_2(NCS)_2]\cdot py$ [7]	RT	0.828	2.655	100	–
	80 K	0.268	0.423	100	–
$[Fe(dpp)_2(NCSe)_2]$	RT	1.016 0.345	2.558 0.514	20.2 79.8	0.15 0.35
	80 K	0.393	0.378	100	0.20

Table 2 Mössbauer data (isomer shift IS, quadrupole splitting QS, population) of dpp-substituted iron(II) complexes with the regular formula $[Fe(dpp\text{-}R_1R_2)_2(NCS)_2]$. Isomer shifts related to α-iron

Compound	Temperature	IS [mms^{-1}]	QS [mms^{-1}]	Pop [%]	FWHM [mms^{-1}]
$[Fe(dpp\text{-}Me)_2(NCS)_2]$	RT	0.880 0.280	1.898 0.540	65.6 34.4	0.21 0.28
	80 K	1.078 0.457	2.715 0.672	34.6 65.4	0.22 0.41
$[Fe(dpp\text{-}Cl)_2(NCS)_2]$	RT	0.894	2.721	100	0.1
	80 K	1.074	3.100	100	0.16
$[Fe(dpp\text{-}(Me)_2)_2(NCS)_2]$	RT	0.887 0.235	2.703 0.346	35.6 64.6	0.20 0.16
	80 K	0.394	0.358	100	0.14
$[Fe(dpp\text{-}Cl_2)_2(NCS)_2]$	RT	0.997	2.031	100	0.17
	80 K	1.061 0.388	2.802 0.279	47.8 52.2	0.25 0.16

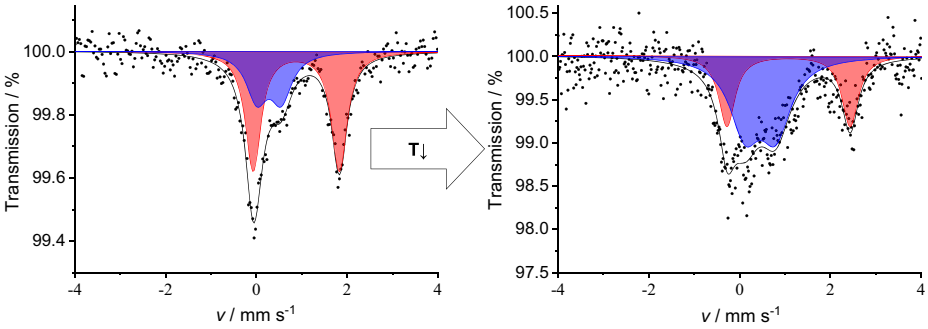

Fig. 5 Mössbauer spectra of $[Fe(dppMe)_2(NCS)_2]$ at room temperature (left) and 80 K (right). LS area marked blue and HS area marked red

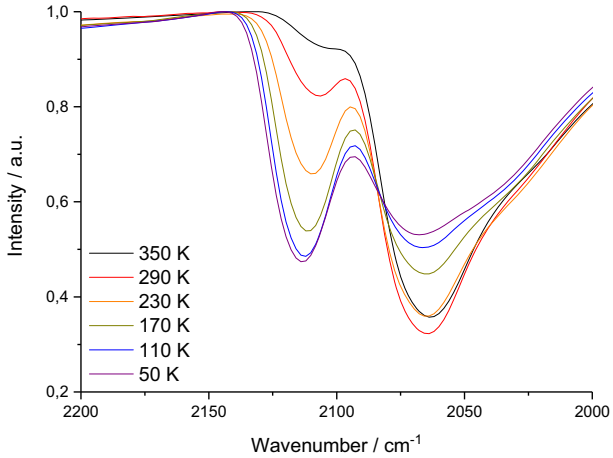

Fig. 6 Temperature depending IR spectroscopy of [Fe(dpp-Me)$_2$(NCS)$_2$] at temperatures between 350 K and 50 K in the range of 2200 – 1900 cm^{-1}

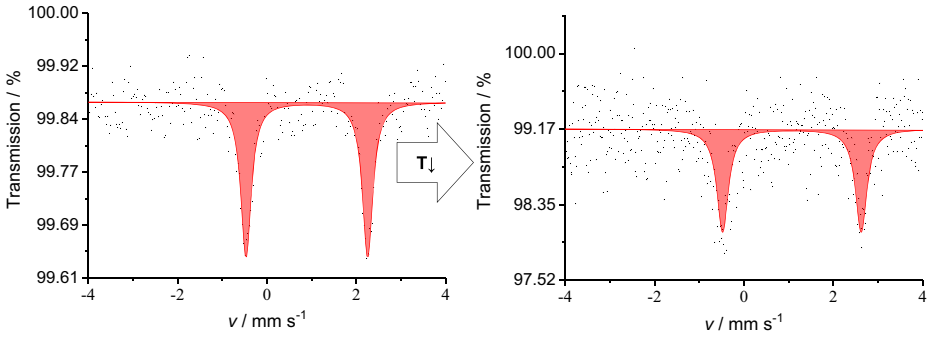

Fig. 7 Mössbauer spectra of [Fe(dppCl)$_2$(NCS)$_2$] at room temperature (left) and 80 K (right). HS area marked red

decreasing temperature. Both measurements agree that the compound [Fe(dpp)$_2$(NCSe)$_2$] is at low temperatures (80 K) in LS state while it shows an incomplete thermal spin crossover (Table 1).

[Fe(dpp-R$_1$R$_2$)$_2$(NCS)$_2$] Modifications of the dpp ligand and its influence on the spin states and spin crossover behavior of the complexes

The spin state of the four investigated compounds was determined by Mössbauer spectroscopy at room temperature and 80 K (Table 2). Temperature depending IR-spectroscopy was performed to confirm the spin states and to gain better insight into possible spin crossovers.

The Mössbauer measurements of [Fe(dppMe)$_2$(NCS)$_2$] (Fig. 5) indicate temperature depending changes of LS and HS states. While the HS ratio is larger at room temperature, the spin ratios are inverted at 80 K. The temperature depending IR-spectra (Fig. 6) show during the cooling process a decreasing band at 2065 cm^{-1} with an increasing band at 2114 cm^{-1}. This indicates also a spin crossover.

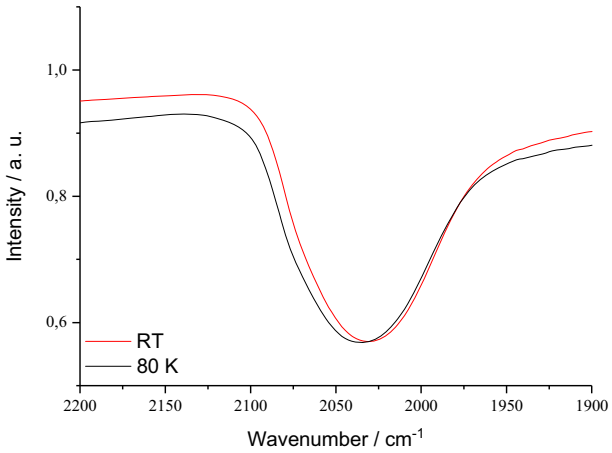

Fig. 8 Temperature depending IR spectroscopy of [Fe(dpp-Cl)$_2$(NCS)$_2$] at room temperature and 80 K in the range of 2200 – 1900 cm^{-1}

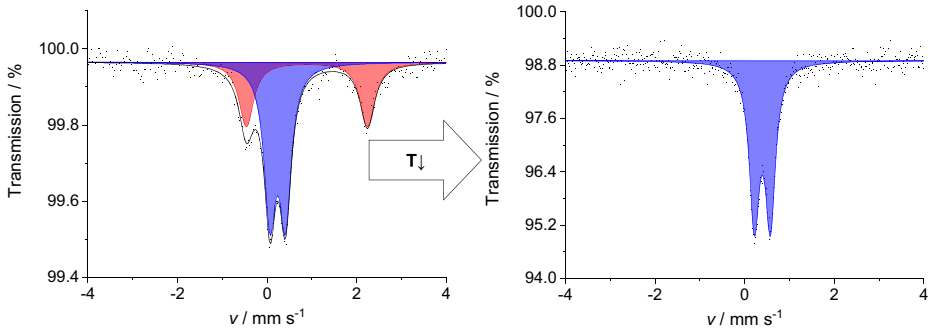

Fig. 9 Mössbauer spectra of [Fe(dpp(Me)$_2$)$_2$(NCS)$_2$] at room temperature (left) and 80 K (right). LS area marked blue and HS area marked red

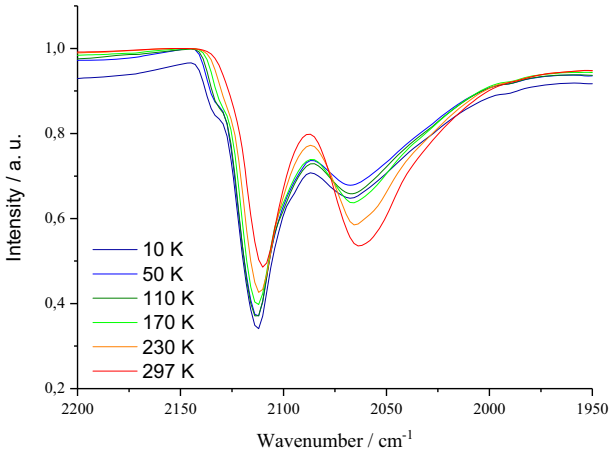

Fig. 10 Temperature depending IR spectroscopy of [Fe(dpp-(Me)$_2$)$_2$ (NCS)$_2$] at different temperatures in the range of 2200 – 1950 c m^{-1}

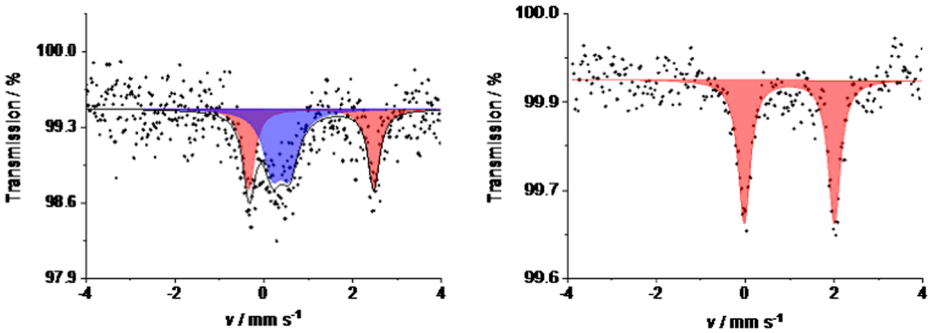

Fig. 11 Mössbauer spectra of $[Fe(dppCl_2)_2(NCS)_2]$ at room temperature (left) and 80 K (right). LS area marked blue and HS area marked red

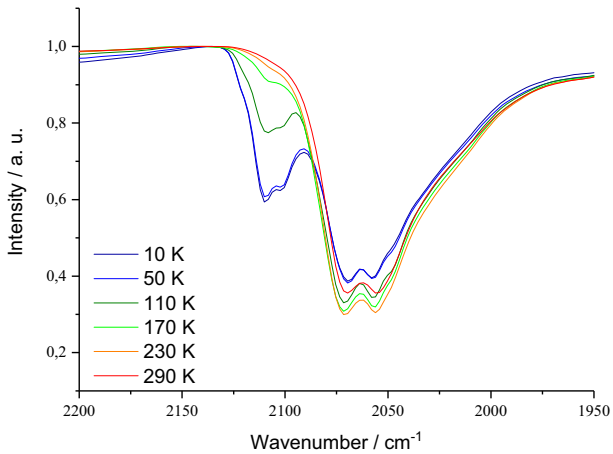

Fig. 12 Temperature depending IR spectroscopy of $[Fe(dpp\text{-}Cl_2)_2(NCS)_2]$ at temperatures between 290 K and 10 K in the range of 2200 – 1950 cm^{-1}

For the second complex $[Fe(dppCl)_2(NCS)_2]$ only the HS state could be observed by Mössbauer spectroscopy (Fig. 7). The bands between 2200 cm^{-1} and 1900 cm^{-1} of the IR-spectra (Fig. 8) at room temperature and 80 K don't change as expected from the Mössbauer data.

A change of spin state could also be observed for the compound $[Fe(dpp(Me)_2)_2(NCS)_2]$. At room temperature both the LS and the HS state are stable. Through cooling to 80 K the HS state disappears in favor of the LS state (Fig. 9). Through cooling the IR band at 2064 cm^{-1} is shrinking while the band at 2112 cm^{-1} rises (Fig. 10) which supports the Mössbauer spectra.

$[Fe(dpp(Me)_2)_2(NCS)_2]$ shows in Mössbauer spectra at room temperature only HS configuration while both can be observed at 80 K (Fig. 11). Together with the changing bands of the temperature depending IR spectroscopy (Fig. 12) the measurements also indicating a spin crossover.

4 Conclusion

Chemical modifications of the spin crossover compound $[Fe(dpp)_2(NCS)_2]\cdot Py$ by exchanging the thiocyanate ligands with cyano selenide anions and substituting one or two hydrogen atoms of the dpp ligand with methyl groups or chlorine atoms have been made. The modification directly influences the electronic configuration shown by Mössbauer spectroscopy at room temperature and 80 K. Thermal spin crossover could be shown for four of the five investigated complexes. Only for the complex $[Fe(dppCl)_2(NCS)_2]$ remained in HS state and a thermal spin crossover could not be observed. Further investigations as structure analysis and magnetic measurements on the complexes are in progress.

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Compliance with Ethical Standards

Conflict of interests The authors declare that they have no conflict of interest.

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