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Pyridazine–derived N5 and N6 ligands as a rigid back bones for Fe (II) Spin Crossover complexes

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Abstract: Novel pyridazine-based tridentate ligands 3-(6-(3-aryl-1H-pyrazol-1-yl) pyridin-2-yl) pyridazines (**3**) were synthesized, characterized and utilized for the synthesis of iron (II) spin-crossover complexes of the type [Fe (**3**)$_2$] $(ClO_4)_2$. All newly prepared compounds were characterized by ^{1}H, ^{13}C {^{1}H} NMR and UV-Vis spectroscopy, CHN elemental analysis and ESI-TOF mass-spectrometry. Single crystals were grown for X-ray diffraction study using the diffusion strategy.

Some of these complexes show transition from the low-spin state (LS) to high-spin state (HS) at ambient temperature and above ($T_{½}$ = 311 K), associated with a change in coordination number (CN) from CN 6 to CN 8. This leads to a significant reduction in the equilibrium rate for the SCO equilibrium.

Keywords: Spin crossover, Iron complexes, Pyridazine

Introduction:

Spin-crossover (SCO) systems have gained much concern during the past few years, as they can change their spin state by external perturbation, *e.g.* change of temperature or pressure, light irradiation or guest molecules, and their promising applications in data storage, molecular switches or sensors and others *(S. Heider et al. 2013, Weber. 2009, J. A. Real et al. 2005, J. F. Létard et al. 2005 and O. Kahn et al. 1998).* Iron (II) complexes are the more predominant candidates as they show the most significant changes in their spin states from the paramagnetic high spin (HS, S = 2) to the diamagnetic low-spin (LS, S = 0) state, a phenomenon known as spin crossover (SCO) *(Holm Petzold et al. 2011).* These changes are accompanied by substantial changes in bond lengths between the central metal atom and the ligand donor atoms in octahedral iron (II) complexes, which may be transferred to neighboring molecules in the crystal lattice leading to hysteresis *(P. Guionneau et al. 2004).* For practical applications, the

mere occurrence of SCO itself is not an adequate grantee to success. For example, room temperature bistability conditions are required associated with an abrupt spin transition showing a broad hysteresis loop in the case of switching devices, whereas additional color change is necessary for displays *(Philipp Gutlich et al. 2000)*. This leads to the need to design ligand systems that can be tuned precisely to obtain SCO in a defined temperature range. Synthesis of multidentate ligand systems to met these requirements and allows such fine tuning is not an easy task.

In addition, solution studies are a useful tool for gaining more information about the factors that may affect the stability of the respective spin states *(Silvio Heider et al. 2013)*.

In this work, we aim to report the design of new hexadentae N6 ligand systems along with their iron (II) complexes that are capable to show spin crossover near room temperature in solution.

Experimental Section:

General: All reactions handling sensitive chemicals were carried out under argon using standard Schlenk and cannula techniques. NMR spectra were recorded with a Bruker Avance III 500 spectrometer; chemical shifts for ^{1}H and ^{13}C are referenced to deuterated solvents. Elemental analyses were recorded using a Thermo FlashAE 1112 analyzer. Mass spectra were recorded with a Bruker micrOTOF-QIIa mass spectrometer operating in ESI mode. UV-Vis was measured in Varian 50 Conc UV–visible spectrophotometer over the wavelength range 200–800 nm.

Materials: Tetrahydofurane (THF) and diethyl ether were purified by distillation from sodium/benzophenone ketyl. Ethanol was purified by distillation from magnesium and acetonitrile followed by distillation from calcium hydroxide. N,N/-dimethylformamide diethyl acetal, hydrazine hydrate, 2-acetyl pyridine, 2,6-dibromopyridine, n-butyl lithium, pyridazine, pyrazole, potassium tertiary butoxide, were purchased from different companies, and used without further purification. 3-phenyl-1H-pyrazole was prepared as reported in the literature *(F. Gärtner et al. 2011)*.

All reagents used within these studies were of analytical grade. Other solvents were dried by standard methods if necessary. TLC was carried out on aluminum sheets pre-coated with silica gel 60F254 (Merck). Preparative column chromatography was carried out on Alox.

Synthesis of 2-(1H-pyrazol-3-yl) pyridine (1c). N,N'-dimethylformamide diethyl acetal (5.90 g, 6.6 ml) and 2-acetylpyridine (3 g, 2.77 ml) were mixed and refluxed overnight. After completion of the reaction the excess of *N,N'*-dimethylformamide

diethyl acetal was removed in vacuum. The solid product obtained was collected and washed with a mixture of n-hexane- diethyl ether in the ratios of 2:1 (v/v) and then dissolved in ethanol. Hydrazine hydrate (1.40 ml, 28.8 mmol) was then added in a single portion and the mixture was refluxed for 3 h. All volatiles were removed in vacuum, and the solid product obtained was washed with water, filtered and dried. Yield 3.168 g. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.8 (s, 1H), 7.77 (dt, *J* = 8.2, 1.7 Hz, 2H), 7.61 (d, *J* = 2.1 Hz, 1H), 7.44 – 7.38 (m, 2H) 7.36 – 7.31 (m, 1H), 6.62 (d, *J* = 1.8 Hz, 1H).

Improved synthetic method for the synthesis of 3-(6-bromopyridin-2-yl) pyridazine (2). A solution of 2,6-dibromopyridine (1 g, 4.22 mmol) in 10 ml of THF was added dropwise to a solution of ^{n}BuLi (1.7 ml, 4.22 mmol) dissolved in 10 ml of THF under nitrogen at -78°C. The mixture was stirred for 1 h and then pyridazine (0.3 ml, 4.22 mmol) dissolved in THF was added. The resulting mixture was allowed to warm to ambient temperature. Afterwards, the reaction mixture was quenched by addition of 1 ml of ethanol and stirred with 5 g of manganese dioxide (MnO_2) overnight. Then it was filtered, and all volatiles were evaporated in vacuum. Column chromatography of the obtained residue on Al_2O_3 as stationary phase using a 1:1 dichloromethane/ diethyl ether mixture (ratio 1:1, /v) as the eluent gave the title molecule in pure form. Yield: 40 % based on 2,6-dibromopyridine. Anal. (cald.) for $C_9H_6BrN_3$: C 45.79, H 2.56, N 17.80; Found: C 46.09, H 2.59, N 17.62.

Synthesis of 3-(6-(1H-pyrazol-1-yl) pyridin-2-yl) pyridazine (3a). Pyrazole (0.173 g, 2.54 mmol) was dissolved in 3 ml of THF and this solution was transferred into a Schlenk tube. Then potassium tertiary butoxide (0.213 g, 1.9 mmol) was added in a single portion and the reaction mixture was stirred for 1 h. All volatiles were then removed in vacuum and compound 2 (0.3 g, 1.27 mmol) was added. This mixture was heated to 180 °C for 2 h. The obtained solid product was then washed with water and extracted with dichloromethane. The organic layer was dried over anhydrous $MgSO_4$. The solvent was then removed and the product was purified by extraction with diethyl ether and precipitation of 3a from this solvent. Yield: 44 % based on pyrazole. Anal. (cald.) for $C_{12}H_9N_5$: C 64.56, H 4.06, N 31.37; Found: C 64.36, H 4.03, N 31.25. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.26 (dd *J* = 4.9, 1.6 Hz, 1H), 8.68 (dd, *J* = 2.6, 0.6 Hz, 1H), 8.64 – 8.59 (m, *J* = 7.6, 6.5, 1.1 Hz, 2H) 8.12 (dd, *J* = 8.1, 0.8 Hz, 1H), 8.04 (t, *J* = 7.9 Hz, 1H), 7.79 (d, *J* = 1.0 Hz, 1H), 7.68 (dd, *J* = 8.5, 4.9 Hz, 1H), 6.52 (dd, *J* = 2.5, 1.7 Hz, 1H).

Synthesis of 3-(6-(3-phenyl-1H-pyrazol-1-yl) pyridin-2-yl) pyridazine (3b). A solution of 3-phenyl-1H-pyrazole (1b) (0.34 g, 2.35 mmol) in THF was added to K^{t}OBu (0.197 g, 1.76 mmol) and this mixture was stirred under nitrogen for 30 min. Then all

volatiles were removed in vacuum, and compound 2 (0.277 g, 1.17 mmol) was added in a single portion. The appropriate reaction mixture was heated to 180 °C for 1 h. The obtained crude product was washed with water, extracted with dichloromethane and dried over anhydrous $MgSO_4$. Upon removal of the organic solvent, the product precipitated. It was then washed with diethyl ether and dried in air. Yield: 73 % based on 3-phenyl-1H-pyrazole. Anal. (cald.) for $C_{18}H_{13}N_5$: C 72.23, H 4.38, N 23.40; Found: C 72.02, H 4.50, N 23.53. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.24 (dd, *J* = 4.9, 1.7 Hz, 1H), 8.71 (d, *J* = 2.6 Hz, 1H), 8.61 – 8.58 (m, *J* = 8.5, 1.7 Hz, 2H), 8.22 (dd, *J* = 8.1, 0.7 Hz, 1H), 8.04 (t, *J* = 7.9 Hz, 1H), 7.97 – 7.94 (m, 2H), 7.65 (dd, *J* = 8.5, 4.9 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.40 - 7.36 (m, 1H), 6.84 (d, *J* = 2.6 Hz, 1H).

Synthesis of 3-(6-(3-(pyridin-2-yl)-1H-pyrazol-1-yl) pyridin-2-yl) pyridazine (3c). 2-(1H-pyrazol-3-yl) pyridine (1c) (0.368 g, 2.54 mmol) and K^{t}OBu (0.213 g, 1.90 mmol) were mixed and dissolved in 5 ml of THF in a Schlenk tube under nitrogen. The mixture was stirred at ambient temperature for 30 min. All volatiles were then removed in vacuum and 0.30 g (1.27 mmol) of 2 were added. The mixture was heated to melting (250°C) for 1 h. After completion of the reaction 10 ml of water was added followed by addition of 10 ml of dichloromethane. The organic layer was separated, and dried over anhydrous $MgSO_4$. The solvent was then removed and the solid product remained was collected and washed with diethyl ether. Yield 44 % Anal. (cald.) for $C_{17}H_{12}N_6$: C 67.99, H 4.03, N 27.98; Found: C 68.03, H 4.10, N 27.86. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.24 (dd, *J* = 4.9, 1.5 Hz, 1H), 8.75 (d, *J* = 2.6 Hz, 1H), 8.69 (d, *J* = 4.5 Hz, 1H), 8.63 (d, *J* = 7.6 Hz, 1H), 8.60 (dd, *J* = 8.6, 1.6 Hz, 1H), 8.25 (d, *J* = 8.0 Hz, 1H), 8.17 (d, *J* = 8.0 Hz, 1H), 8.05 (t, *J* = 7.9 Hz, 1H), 7.81 (td, *J* = 7.8, 1.4 Hz, 1H), 7.65 (dd, *J* = 8.5, 4.9 Hz, 1H), 7.29 (dd, *J* = 6.6, 5.3 Hz, 1H), 7.21 (d, *J* = 2.0 Hz, 1H).

Synthesis of Iron (II) complexes

Synthesis of $[Fe(3a)_2]$ $(ClO_4)_2$: Compound 3a (47.4 mg, 0.212 mmol) was dissolved in dichloromethane and then $[Fe(H_2O)_6](ClO_4)_2$ (21.6 mg, 0.10 mmol) dissolved in ethanol (2 ml) was added in a single portion. A red precipitate formed immediately. This solid was filtered off and recrystallized from a acetonitrile/diethyl ether mixture using the diffusion strategy. Anal. (cald.) for $C_{24}H_{18}Cl_2FeN_{10}O_8.2CH_3CN$: C 42.93, H 3.09, N 21.46, found: 42.81, H 3.10, N 21.50, ^{1}H NMR (500 MHz, CD_3CN) δ = 8.81 (d, *J* = 3.1Hz, 1H), 8.77 (dd, *J* = 7.9, 0.8Hz, 1H), 8.71(t, *J* = 8.1Hz, 1H), 8.57(dd, *J* = 5.0, 1.7Hz, 1H), 8.53 (dd, *J* = 8.6, 1.8Hz, 1H), 8.45(dd, *J* = 8.2, 0.8Hz, 1H), 7.66(dd, *J* = 8.6, 5.0 Hz, 1H), 7.07 (d, *J* = 2.1Hz, 1H), 6.50(dd, *J* = 3.0, 2.2Hz, 1H).

Synthesis of $[Fe(3b)_2]$ $(ClO_4)_2$: To a suspension of **3b** in ethanol was added $[Fe(H_2O)_6](ClO_4)_2$ dissolved in ethanol in a single portion. This reaction mixture was

stirred for 15 min at ambient temperature. The red solid product formed was collected, washed with diethyl ether and crystallized by from a acetonitrile- diethyl ether solution at ambient temperature. Anal (cald.) for $C_{36}H_{26}Cl_2FeN_{10}O_8 \cdot CH_3CN$: C 51.03, H 3.27, N 17.23, Found: C 51.12, H 3.30, N 17.20, ^{1}H NMR (500 MHz, Acetone d^6) δ = 9.1(d, *J* = 3.0Hz, 1H), 8.98(d, *J* = 7.9 Hz, 1H), 8.91(dd, *J* = 8.5, 1.7Hz, 1H), 8.81(dd, *J* = 4.9, 1.7Hz, 1H), 8.68(t, *J* = 8.1Hz,1H), 8.44(d, *J* = 8.3Hz, 1H), 7.90(dd, *J* = 8.5, 4.9z, 1H), 7.38(t, *J* = 7.6Hz, 1H), 7.20(t, *J* = 7.8Hz, 2H), 6.77(d, *J* = 3.0Hz,1H), 6.54(dd, *J* = 8.1, 1.2Hz, 2H).

Synthesis of $[Fe(3c)_2](ClO_4)_2$: Compound **3c** (83.0 mg, 0.276 mmol) was dissolved in dichloromethane and then $[Fe(H_2O)_6](ClO_4)_2$ (35.0 mg, 0.14 mmol) dissolved in ethanol was added. A red precipitate was formed immediately. This was crystallized from acetonitrile-diethyl ether mixture at ambient temperature. Yield 89 mg. Anal. (cald.) for $C_{34}H_{24}Cl_2FeN_{12}O_8.2(CH_3CN)$: C 48.68, H 3.23, N 20.92; Found: C 49.64, H 3.23, N 20.04; ^{1}H NMR (500 MHz, Acetone; -80°C) δ 9.50 (d, *J* = 3.0 Hz, *H*7, 1H), 9.07 (dd, *J* = 6.5, 2.2 Hz, H4/6, 1H), 8.92 – 8.85 (m, *J* = 6.5, 5.7, 3.2 Hz, *H*1-*H*3-*H*4/6-*H*5, 4H), 8.25 (d, *J* = 4.2 Hz, *H*12, 1H), 7.88 (dd, *J* = 8.5, 4.9 Hz, H2, 1H), 7.78 (td, *J* = 7.7, 1.7 Hz, *H*11, 1H), 7.40 (d, *J* = 7.7 Hz, *H*9, 1H), 7.34 (dd, *J* = 7.2, 5.3 Hz, *H*10, 1H), 7.13 (d, *J* = 3.0 Hz, *H*8, 1H).

Results and Discussion

Synthetic work

Compounds **3a-c** (Figure 1) were successfully prepared starting from the 3-aryl-substituted pyrazoles **1a-c** *(F. Gärtner et al. 2011)* and 3-(6-bromopyridin-2-yl) pyridazine (**2**) (Figure 2). The C-N bond was formed by nucleophilic aromatic substitution in a melt reaction. For this purpose, pyrazoles **1** (a - c) were transformed into their potassium salts, and the respective salts along with the bromo-pyridine **2** were heated together (>150°C) in melt. No solvents were used to achieve high temperatures and high concentrations of the reactants. Although harsh reaction conditions were applied, compounds **3a-c** were isolated in good yields without elaborated workup.

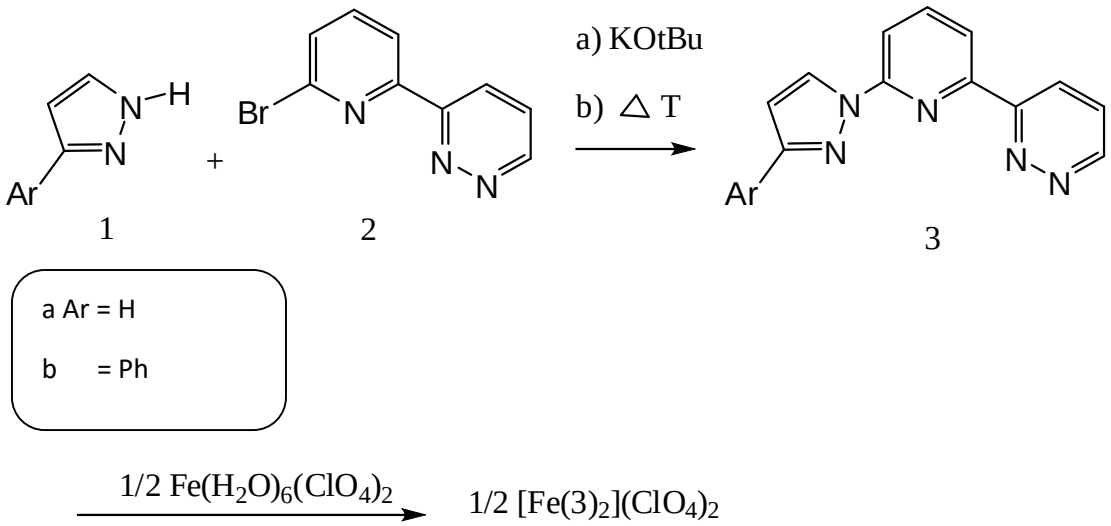

Figure 1. Synthesis of pyridazine-terminated terpy analogues of **3** (a – c) and their respective Fe^{2+} complexes.

An improved method for the synthesis of **2** was used. The reported synthesis of **2** is based on a Stille cross-coupling reaction *(S. De, S. Pramanik et al. 2012)*. This reaction requires the preparation of 3-bromo/chloro-pyridazine and the 6-stanyl-2-bromo-pyridine, both compounds are not commercially available. The alternative route from pyridazine and 6-lithio-2-bromopyridine afforded the expected compounds **3a-c** in a "one pot" reaction. Although the overall yield is only 20 %, the reaction is considerably faster, all starting materials are commercially available and the reaction is scalable. Although this type of reaction is well known for pyridines and especially for phenanthroline, this is the first example for pyridazines. The second component, pyrazole **1**, was prepared by literature protocols *(F. Gärtner et al. 2011)*. The obtained terpy analogues of **3a-c** were transferred into their Fe^{2+} complexes [Fe(**3a-c**)$_2$](ClO$_4$)$_2$ by treatment with [Fe(H$_2$O)$_6$](ClO$_4$)$_2$.

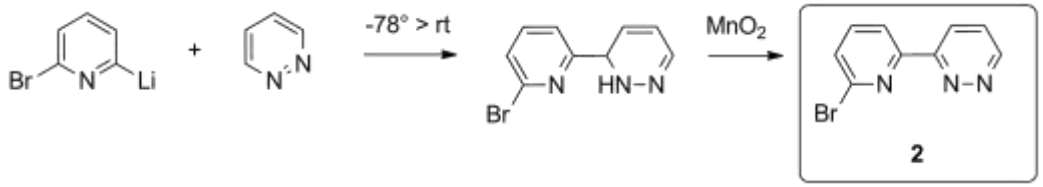

Figure 1. Improved synthesis to 3-(6-bromopyridin-2-yl) pyridazine 2.

The SCO properties of [Fe(**3a-c**)$_2$](ClO$_4$)$_2$ were investigated by ^{1}H NMR spectroscopy. The complexes [Fe(**3a-c**)$_2$](ClO$_4$)$_2$ were found in their LS-state at ambient temperature. This can be well explained by the stronger ligand field induced by replacement of the pyridine by pyridazine. Similar to the analogous series of complexes with the pyridine-

terminated ligand *(Holm Petzold et al. 2018)*, the placement of the pyridine in 3-position of the pyrazole, lead to a significant stabilization of the HS state of the Fe^{2+} ion. In variance to the pyridine analogues, the midpoint ($T_{1/2}$ = 311 K) for the transition from the LS state to HS state is found above ambient temperature and [Fe(**3c**)$_2$](ClO$_4$)$_2$ is found in an equilibrium between the HS and LS state in acetonitrile solution at ambient temperature. The transition between the LS and HS state in this complex is associated with a change in the coordination number (CN) from CN 6 to CN 8. That leads to a significant reduction in the equilibration rate for the SCO equilibrium. ^{1}H NMR spectra, recorded at -45°C, of [Fe(**3c**)$_2$](ClO$_4$)$_2$ in acetonitrile solution show sub-spectra of both spin states (Figure 3)

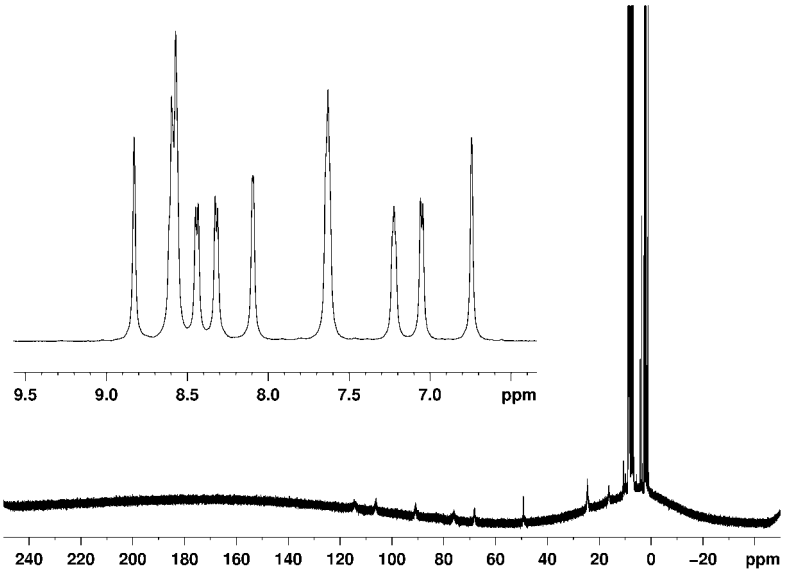

Figure 3: ^{1}H NMR spectrum of [Fe(3c)$_2$](ClO$_4$)$_2$ in d_3-acetonitrile (-45°C). The inset shows the intense signals for the LS component. The weak and low field shifted signals correspond to the HS component. ^{1}H EXSY spectroscopy confirmed this interpretation by the detection of cross peaks. The transition point $T_{1/2}$ was calculated to 311 K.

This is in contrast to known Fe^{2+} SCO complexes. It is worth to mention that the diamagnetic LS state can be converted into the HS state by irradiation with light. Due to the high quantum yield and the intensive MLCT absorption an almost complete transformation into the HS state can be achieved with visible light and relative weak intensities.

Crystals suitable for X-ray analysis were grown by diffusion of diethyl ether vapors into concentrated solutions of the complex salts [Fe(**3a-c**)$_2$](ClO$_4$)$_2$. The crystallization affords well-shaped crystals of the complexes without incorporating packing solvents. The crystal lattice of [Fe(**3c**)$_2$](ClO$_4$)$_2$ is monoclinic P21/n space group. (Figure 4)

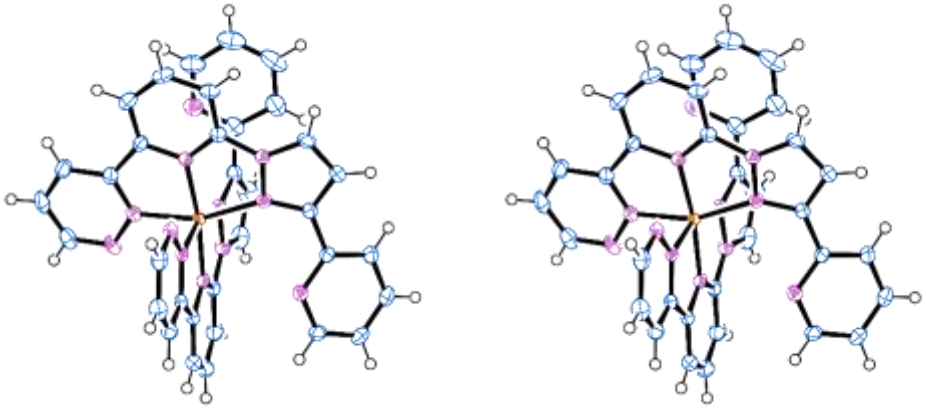

Figure 4. Stereoscopic view on the solid state structure of $[Fe(\mathbf{3c})_2](ClO_4)_2$.

Conclusion

A series of Fe^{2+} SCO complexes featuring strong field ligands **3a-c**: 3-(6-(3-aryl-1H-pyrazol-1-yl) pyridin-2-yl) pyridazines (**3**) were prepared. An alternative route to 3-(6-bromopyridin-2-yl) pyridazine (**2**) was developed, allowing a straightforward access to transition metal complexes of type $[Fe(\mathbf{3a\text{-}c})_2](ClO_4)_2$. Ligands **3a-c** are tridentate in complexes of the type $[Fe(\mathbf{3a\text{-}c})_2](ClO_4)_2$. It was found that the coordination mode of complexes **3a-c** changes from tridentate in the low-spin (LS) state to tetradentate in the high-spin (HS) state of the respective Fe^{2+} complexes. To the best of our knowledge this is the first example of a Fe^{2+} complex, showing this extreme change in the coordination mode with a 50:50 distribution close to ambient temperature. Due to the strong displacement of the HS from the LS state on the reaction coordinate the HS state is exceptional long lived, with a gain of roughly 10^3 with respect to classical Fe^{2+} SCO complexes.

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