

New Fe(II) Complexes with anion dependent Spin Crossover

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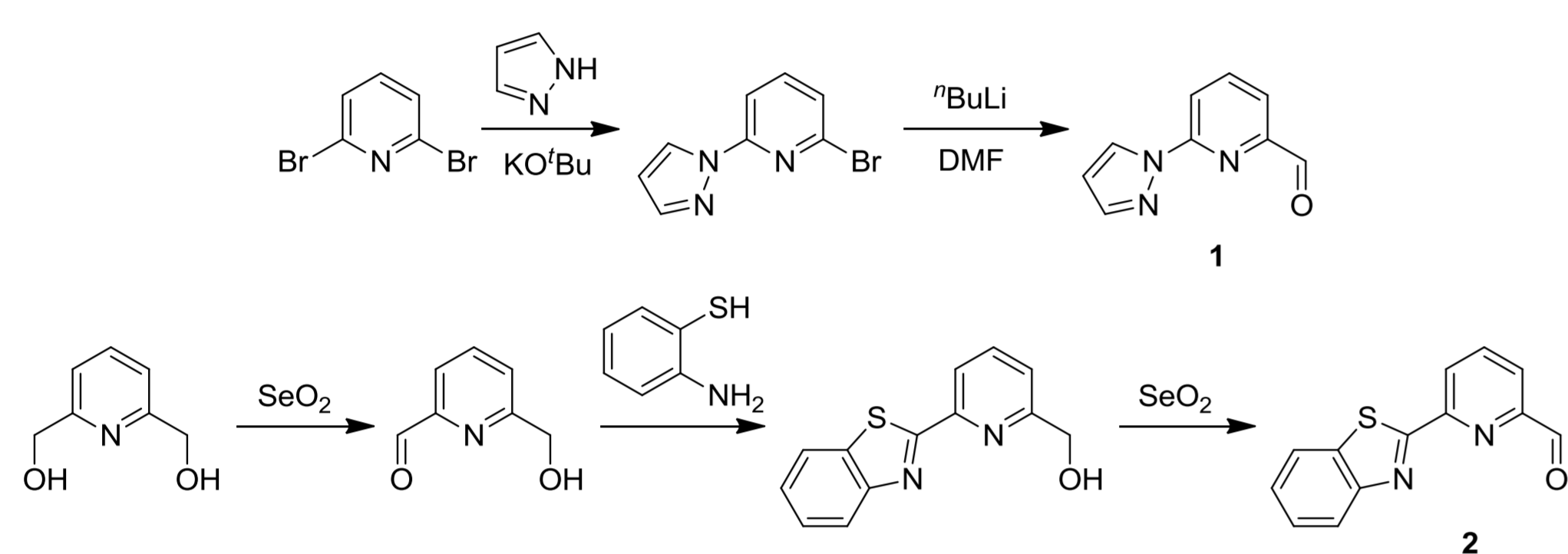
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Introduction

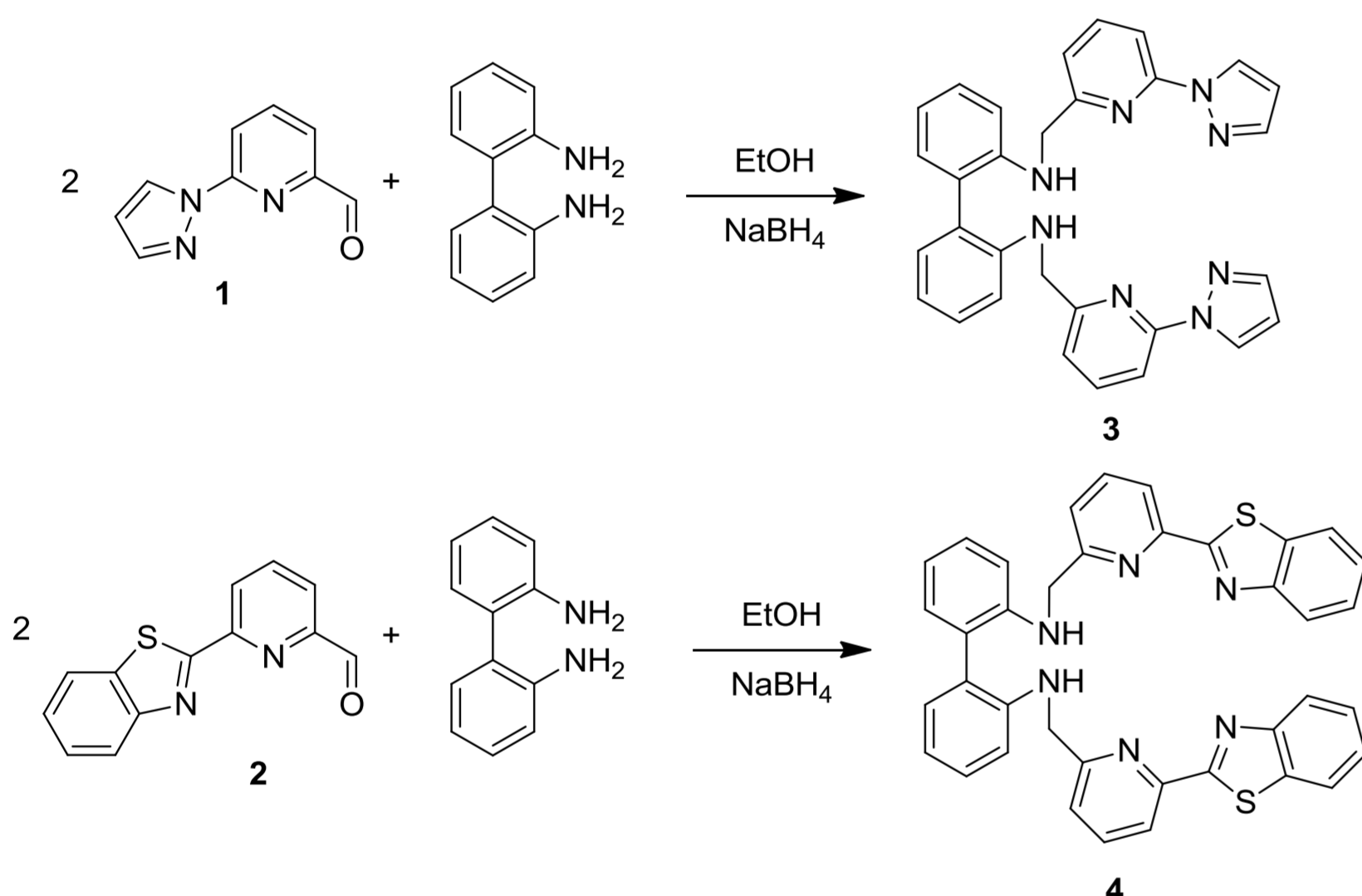
Due to their d^6 electron configuration octahedral Fe^{2+} complexes can exist in a diamagnetic low-spin or a paramagnetic high-spin form. In the last 50 years many examples of complexes have been studied, which can change their spin state. Accompanied with the spin state also the color and other physical properties change. This can be triggered by external stimuli like temperature, pressure, light irradiation etc.^[1] These so called Spin Crossover (SCO) complexes have ever since been promising candidates for several applications as data storage, new displaying devices or for sensors. Recently, we found a facile synthesis of a new group of Fe^{2+} SCO complexes and we could show the influence of the substitution pattern on the SCO transition temperature in solution.^[2] The SCO transition temperature $T_{1/2}$ for these complexes was found to be above room temperature. For further studies we aimed to synthesize complexes which show a spin transition at lower temperature. Therefore the terminal donors of the ligand set were modified and weaker ligands were introduced. The obtained Fe^{2+} SCO complexes and their properties are presented below.

Synthesis

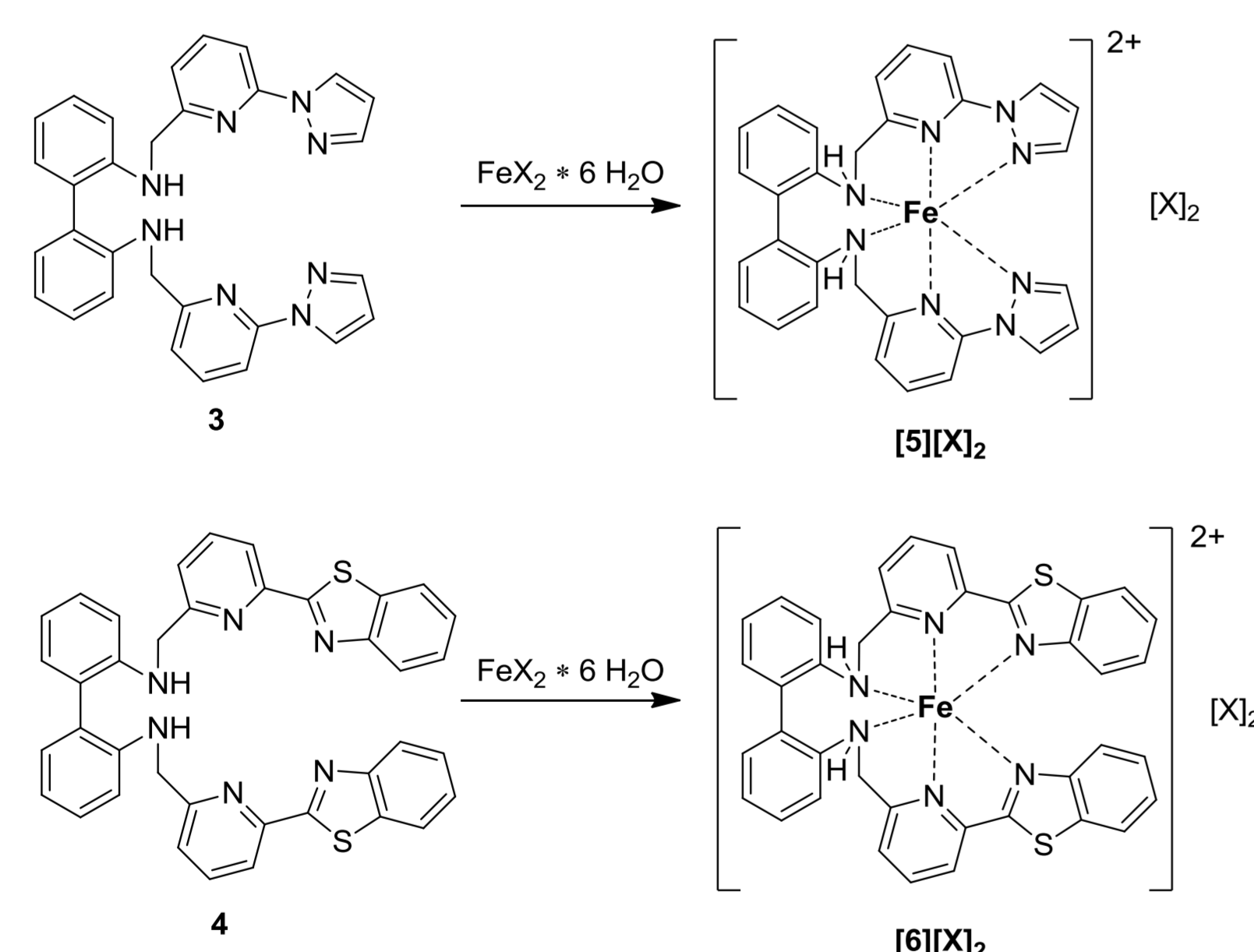
In the first step aldehydes **1** and **2** had to be synthesized. For the pyrazolyl derivative **1** a new simplified synthetic protocol was developed with superior yield compared to the published procedures.^[3] The benzothiazolyl derivative **2** was synthesized according to Bünzli *et al.*^[4]



Then aldehydes **1** and **2** were used for a reductive amination with biphenylene-2,2'-diamine^[2] yielding hexadentate amines **3** and **4**.



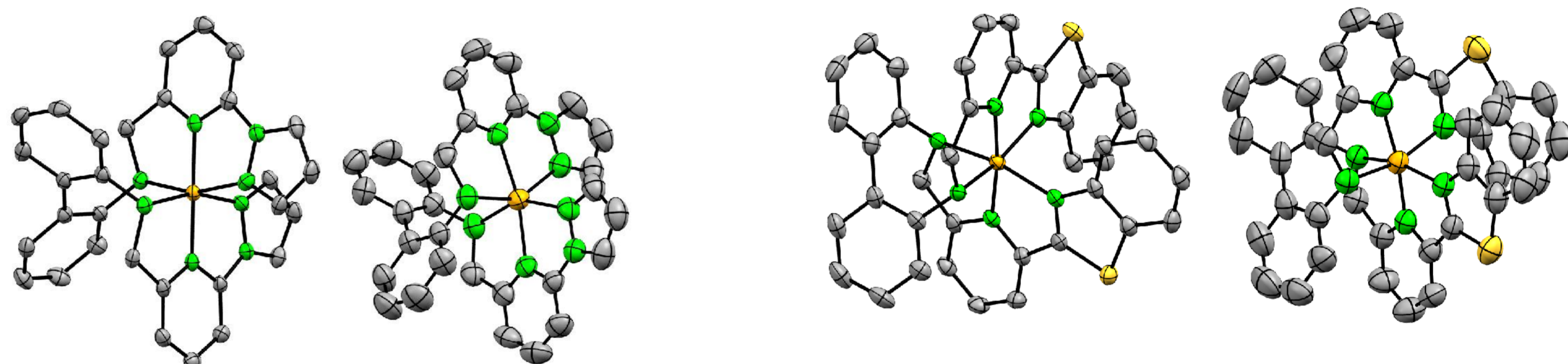
Reacting amines **3** and **4** with $FeX_2 \cdot 6 H_2O$ in acetonitrile and following precipitation with diethyl ether yielded the novel Fe(II) SCO compounds **5**[X]₂ and **6**[X]₂ (X = BF₄⁻, ClO₄⁻), respectively.



Summary

We have synthesized the new hexadentate secondary amines **3** and **4** and used those for complexation of Fe^{2+} ions leading to the different complex salts **5**[X]₂ and **6**[X]₂ (X = BF₄⁻, ClO₄⁻). These complexes show SCO behaviour below room temperature, the salts of **5**²⁺ showing different transition temperatures $T_{1/2}$ depending on the counter ion and if measured in the solid state or in solution. Similar to **5**²⁺ also **6**²⁺ reveals its high-spin form at room temperature in solution, whereas **6**²⁺ is found to be in the low-spin configuration in the solid state at this temperature. Thus all these complexes show in solution higher transition temperatures $T_{1/2}$ than in their crystalline states, where intermolecular interactions are possible. For **5**[X]₂ this was already investigated by SQUID measurements and Evans' method, for **6**[X]₂ these investigations are currently accomplished.

Solid state structures

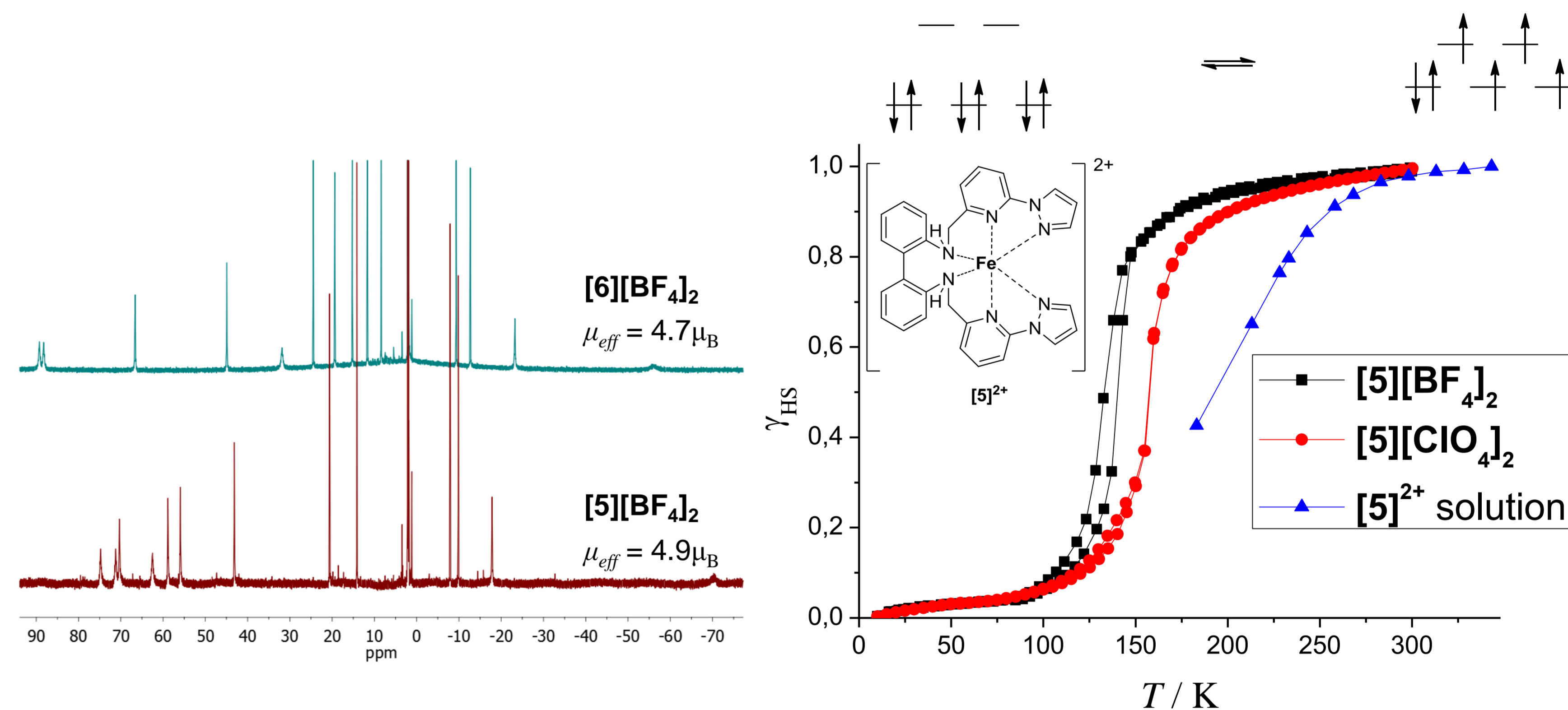


Molecular structures of the complex cation in **5**[ClO₄]₂ at 115K (left) and 298K (right), 50% probability level.

Molecular structures of the complex cation in **6**[BF₄]₂ at 115K (left) and 298K (right), 50% probability level.

Complex	Fe-N (Å)	cis-N-Fe-N (°)	Spin State
5 [ClO ₄] ₂ (115K)	1.911(2) – 2.069(3)	80.4(1) – 101.1(1)	low-spin
5 [ClO ₄] ₂ (298K)	2.118(4) – 2.252(5)	74.2(2) – 117.4(2)	high-spin
6 [BF ₄] ₂ (115K)	1.9003(1) – 2.0580(2)	80.7(3) – 104.2(1)	low-spin
6 [BF ₄] ₂ (298K)	1.9148(2) – 2.0775(2)	81.0(3) – 104.7(5)	low-spin

Magnetic behaviour



Paramagnetic ¹H NMR spectra of **5**[BF₄]₂ and **6**[BF₄]₂ at 298K in CD₃CN revealing the high-spin state.

Temperature dependent behaviour of the molar high-spin fraction of **5**[X]₂ (X = BF₄⁻, ClO₄⁻) representing the SCO.

The ¹H NMR spectra of complex salts **5**[X]₂ and **6**[X]₂ (X = BF₄⁻, ClO₄⁻) clearly show that **5**²⁺ and **6**²⁺ adopt the paramagnetic high-spin state at room temperature. For both salts of **5**[X]₂ X-Ray structure analyses could be obtained and solved at 115K and 298K, showing a low-spin complex at low temperatures and a high-spin complex at high temperatures in both cases.

The SQUID measurements for **5**[X]₂ reveal a dependency of the spin transition temperature on the counter ion. In both cases an abrupt spin change can be observed, in the case of **5**[BF₄]₂ accompanied by a narrow hysteresis ($T_{\downarrow} = 133K$, $T_{\uparrow} = 140K$), while the transition in **5**[ClO₄]₂ occurs at ca. 157K without hysteresis. Therefore the transition temperature $T_{1/2}$ can be shifted by approximately 20K through changing the counter ion. This effect is attributed to different hydrogen bonding interactions in the crystal lattices.

In solution, where these intermolecular interactions are negligible, the spin transition is observed at ca. 196K. This once more exemplifies the important role of crystal packing effects and the lattice structure for the Spin Crossover process.

As stated above, salts **6**[X]₂ also show the high-spin configuration in solution at 298K, however the crystal structure of **6**[BF₄]₂ reveals the low-spin state at 298K as well as at 115K. Thus we are on the way to further characterize the SCO behaviour of complex compounds **6**[X]₂.

References

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