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Maximilian Seydi Kilic, Isabel Mae Merchant, Erika Elliott, Justus Pawlak, Jules Brehme, Arthur Sander, Taisei Suzuki, Takuya Shiga, Masayuki Nihei, Franz Renz

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Abstract

The phenomenon which is called spin crossover is known to occur in some coordination compounds with an octahedral ligand field and electron configurations from 3d⁴ to 3d⁷. Thereby, a reversible transition between spin states (high spin and low spin state) is possible, through several external stimuli. Iron(II) triazole complexes exhibit this phenomenon at a wide range of temperatures depending on the ligands and anions used. For this reason, they are often considered for several possible practical applications. It is also possible to combine ligands or anions to modify the transition temperature. The latter of which was rarely discussed in the past. In this study we synthesized a series of iron(II)-4-Aminotriazole complexes, with different ratios of chloride- and tetrafluoroborate-anions, of the formula [Fe(Atrz)₃]Cl₂-X(BF₄)_X. We show that the combination of these anions leads to transition temperatures between those of their corresponding pure anion complexes. We furthermore present that a simple modification of the synthesis leads to a possible easy way of fine-tuning transitions temperatures.

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Modification of the Spin Transition Properties in Hetero-Anionic Iron(II)-Triazole Complexes

Maximilian Seydi Kilic,^[a] Isabel Mae Merchant,^[a] Erika Elliott,^[a] Justus Pawlak,^[a, b] Jules Brehme,^[a, b] Arthur Sander,^[a] Taisei Suzuki,^[c] Takuya Shiga,^[c] Masayuki Nihei,^[c] and Franz Renz^{*[a, b]}

The phenomenon which is called spin crossover is known to occur in some coordination compounds with an octahedral ligand field and electron configurations from $3d^4$ to $3d^7$. Thereby, a reversible transition between spin states (high spin and low spin state) is possible, through several external stimuli. Iron(II) triazole complexes exhibit this phenomenon at a wide range of temperatures depending on the ligands and anions used. For this reason, they are often considered for several possible practical applications. It is also possible to combine

ligands or anions to modify the transition temperature. The latter of which was rarely discussed in the past. In this study we synthesized a series of iron(II)-4-Aminotriazole complexes, with different ratios of chloride- and tetrafluoroborate-anions, of the formula $[\text{Fe}(\text{Atrz})_3]\text{Cl}_{2-x}(\text{BF}_4)_x$. We show that the combination of these anions leads to transition temperatures between those of their corresponding pure anion complexes. We furthermore present that a simple modification of the synthesis leads to a possible easy way of fine-tuning transitions temperatures.

Introduction

The phenomenon of spin crossover (SCO) was first observed by Cambi et al. in the 1930s. Since then, a large variety of SCO compounds have been discovered.^[1,2] Both mono- and polynuclear compounds with this property were investigated.^[3] The influence of the particle size on the effect was also taken into account.^[4] The research on SCO coordination compounds has been approached from many more perspectives, including with regard to their possible applications.^[5,6] Among other complexes, iron(II) complexes with SCO effects have often been discussed.^[7] Thermal transitions between high-spin state (HS) and low-spin state (LS) with a wide hysteresis were observed, as well as complexes with a wide range of transition temperatures.^[8] In addition, compounds have been discovered which also have switching effects in response to light irradiation.^[9,10] Complexes in the category of iron(II)-triazole-complexes for instance are known to exhibit SCO effects around room temperature and through other possible stimuli. For

example, complexes of the 4-Amino-triazole ligand are known to show photothermal effects.^[11] 1,2,4-triazole complexes that are substituted at the 4-position are further known to form 1D-Chain structures. These structures are schematically presented in Figure 1.

These triazole complexes of the formula $[\text{Fe}(\text{Rtrz})_3]\text{A}_2$, with Rtrz being a 1,2,4-triazole with a variable rest R and monovalent anion A, are also known for their high chemical flexibility and stability.^[12] These properties can be explained through their $\text{Fe}^{\text{II}}-\text{N}-\text{Fe}^{\text{II}}$ bonds and the subsequent angle of these bonds. Thereby, the Fe^{II} centers are triple connected by so called N^1, N^2 -triazole bridges.^[12,13] These bridges bring very little ring strain to the coordination chains due to the $\text{M}-\text{N}-\text{N}$ angles of 125.6° which is very close to the regular angle of the donor electrons of 126° for the five-membered rings. This results in the formerly mentioned high chemical stability.^[12] The SCO properties and

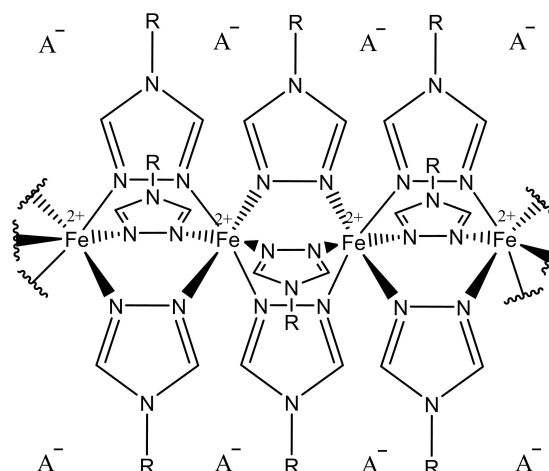


Figure 1. One-dimensional iron(II) triazole coordination chain with R being a variable rest and A being a monovalent anion.

[a] M. S. Kilic, I. M. Merchant, E. Elliott, J. Pawlak, J. Brehme, A. Sander, F. Renz
Institute of inorganic Chemistry, Leibniz Universität Hannover, Callinstrasse
7, 30167 Hannover, Germany
E-mail: franz.renz@acd.uni-hannover.de

[b] J. Pawlak, J. Brehme, F. Renz
Hannover School for Nanotechnology, Laboratorium für Nano- und Quanten-
engineering (LNQE), Leibniz Universität Hannover, Schneiderberg 39,
30167 Hannover, Germany

[c] T. Suzuki, T. Shiga, M. Nihei
Graduate School of Pure and Applied Sciences, University of Tsukuba,
Tennodai 1-1-1, Tsukuba, Ibaraki 305-8577, Japan

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transition temperatures of these systems are dependent on the choice of ligands or rest at the 4-position, and the choice of the corresponding anion.^[14,15] It is also possible to modify the SCO properties of these 1,2,4-triazole systems by combining ligands or anions.^[11] These complexes are described as molecular alloys.^[18] Ligands like Htrz (4-*H*-1,2,4-triazole) and Atrz (4-Amino-1,2,4-triazole) for example, were combined in previous studies.^[16] A modification of the SCO properties by adding a second metal-ion is also a possible method. This was shown by Lavrenova et al. and others.^[17] Combining anions was rarely reported on for 4-Amino-triazole complexes. A hetero-anionic triazole complex was first described by Kahn et al. in 1998 with the anions BF₄⁻ and NO₃⁻ in a single complex.^[18] Another study several years later involved the influence of the combination of SO₄²⁻ anions and NO₃⁻ anions on the spin transition temperature. In that case the corresponding pure complexes [Fe(Atrz)₃]SO₄ and [Fe(Atrz)₃](NO₃)₂ show SCO temperatures in a comparable range.^[19] Another mixed anionic Amino-triazole complex was just recently discussed by Yang et al.^[20] In our current study we used the monovalent anions Cl⁻ and BF₄⁻ as their corresponding mono-anion complexes show SCO properties at very different temperatures (above and below ambient temperature).^[12] Some of these complexes were first attempted to be produced as part of a master thesis, but have not yet been fully analyzed or published.^[21] We show that it is precisely possible to obtain complexes that exhibit SCO behavior in the range of these anions, exhibiting a trend where higher SCO temperatures are related to an increased chloride content. Therefore, we synthesized a series of mixed anionic complexes with different tetrafluoroborate and chloride anion ratios and compared their properties. As a first indicator of a successful synthesis, infrared spectroscopy was performed. To further verify the success of the synthesis CHN elemental analysis, UV/vis spectroscopy, Powder X-ray diffraction (PXRD) and Mössba-

uer spectroscopy were additionally performed. EDX was carried out to see an estimated trend of the chloride anions in the sample. A change of the SCO properties was observed through SQUID magnetometer measurements.

Materials and Methods

General

The obtained complexes were synthesized with the following chemicals without purifying them after the purchase: Iron(II)Chloride tetrahydrate (FeCl₂·4H₂O) (>99%) from Sigma-Aldrich (St. Louis, MO, USA); Iron(II)Tetrafluoroborate hexahydrate (Fe(BF₄)₂·6H₂O) (97%) from Sigma-Aldrich (St. Louis, MO, USA); L-Ascorbic acid (>99%) from Carl Roth; 4-Amino-1,2,4-triazole (99%) purchased from Thermo Scientific (Waltham, MA, USA).

Synthesis of [Fe(Atrz)₃]Cl_{2-x}(BF₄)_x Complexes

The synthesis used for the complexes was inspired by a synthesis by Piedrahita-Bello et al.^[22] which was then further modified as previously.^[21,23] Solution mixtures of FeCl₂·4H₂O and Fe(BF₄)₂·6H₂O and 25 mg of L-Ascorbic acid combined together in water were prepared and then added to a solution of 4-Amino-1,2,4-Triazole in water (molecular excess). The amounts of water were chosen depending on the masses of ligands and iron salts used. Comparable concentrations of iron(II) and 4-Amino-1,2,4-triazole were used in every reaction. The solution was then stirred for 1 h. The white precipitate formed was then three times washed with Ethanol by centrifugation at 6000 rpm for 10 min and dried overnight. Some of the obtained products showed a change of color during the washing with ethanol from white to pink. These were the samples that should have included a higher amount of chloride anions. For comparison the synthesis for [Fe(Atrz)₃]Cl₂ and [Fe(Atrz)₃](BF₄)₂ were also carried out similarly with only the corresponding iron salts. Table 1 shows the respective amounts of the iron salts used in the syntheses and the amount of the ligand

Table 1. Used amounts of FeCl₂·4H₂O, Fe(BF₄)₂·6H₂O and 4-Amino-1,2,4-Triazole for the synthesis of the complexes.

Complex	FeCl ₂ ·4 H ₂ O	Fe(BF ₄) ₂ ·6H ₂ O	Atrz	Yield
[Fe(Atrz) ₃]Cl ₂	0.589 g (2.962 mmol) in 1.25 mL H ₂ O	–	0.746 g (8.87 mmol) in 1.25 mL H ₂ O	1.031 g (91.84%)
[Fe(Atrz) ₃]Cl _{1.8} (BF ₄) _{0.2}	0.265 g (1.332 mmol) in 1.25 mL H ₂ O	0.049 g (0.145 mmol) in 1.25 mL H ₂ O	0.373 g (4.43 mmol) in 1.25 mL H ₂ O	0.544 g (94.61%)
[Fe(Atrz) ₃]Cl _{1.5} (BF ₄) _{0.5}	0.220 g (1.106 mmol) in 0.625 mL H ₂ O	0.125 g (0.370 mmol) in 0.625 mL H ₂ O	0.373 g (4.43 mmol) in 0.625 mL H ₂ O	0.506 g (84.71%)
[Fe(Atrz) ₃]Cl(BF ₄)	0.147 g (0.739 mmol) In 1.25 mL H ₂ O	0.249 g (0.739 mmol) in 1.25 mL H ₂ O	0.373 g (4.43 mmol) in 1.25 mL H ₂ O	0.613 g (96.37%)
[Fe(Atrz) ₃]Cl _{0.5} (BF ₄) _{1.5}	0.062 g (0.312 mmol) in 0.625 mL H ₂ O	0.317 g (0.939 mmol) in 0.625 mL H ₂ O	0.373 g (4.43 mmol) in 0.625 mL H ₂ O	0.536 g (93.92%)
[Fe(Atrz) ₃]Cl _{0.2} (BF ₄) _{1.8}	0.029 g (0.125 mmol) in 0.625 mL H ₂ O	0.380 g (1.127 mmol) in 0.625 mL H ₂ O	0.373 g (4.43 mmol) in 0.625 mL H ₂ O	0.476 g (80.59%)
[Fe(Atrz) ₃](BF ₄) ₂	–	0.501 g (1.481 mmol) in 1.25 mL H ₂ O	0.746 g (8.87 mmol) in 1.25 mL H ₂ O	0.613 g (85.92%)

and solvent used. The yields are given in regards to the molecular sum of the iron(II) salts and the complexes expected sum formula without crystalized water. The respective results of the infrared measurements and elemental analyses are listed down below.

[Fe(Atrz)₃]Cl₂ : Analytically found (calculated) with CHN elemental analysis for FeC₆H₁₂N₁₂Cl₂·2.7H₂O (molar mass 427.628 g mol⁻¹): C, 16.91 (16.85); H, 3.47 (4.10); N, 38.98 (39.31). Mid-infrared (MIR) (in cm⁻¹): 659 (w), 700 (w), 825 (w), 852 (m), 864 (m), 891 (m), 1001 (s), 1029 (m), 1062 (m), 1099 (s), 1219 (s), 1313 (w), 1338 (w), 1355 (w), 1398 (w), 1489 (w), 1541 (m), 1616 (s), 1662 (s), 3014 (w), 3080 (s), 3111 (s), 3197 (m), 3261 (s), 3300 (s), 3394 (s)

[Fe(Atrz)₃]Cl_{1.8}(BF₄)_{0.2} : Analytically found (calculated) with CHN elemental analysis for FeC₆H₁₂N₁₂Cl_{1.8}B_{0.2}F_{0.8}·2.8H₂O (molar mass 439.701 g mol⁻¹): C, 16.42 (16.39); H, 3.64 (4.03); N, 37.78 (38.23). Mid-infrared (MIR) (in cm⁻¹): 655 (w), 700 (w), 825 (w), 852 (w), 864 (m), 891 (m), 995 (s), 1026 (s), 1060 (s), 1099 (s), 1219 (s), 1313 (w), 1338 (w), 1357 (w), 1394 (w), 1487 (w), 1546 (m), 1616 (s), 1660 (s), 3008 (m), 3078 (s), 3107 (s), 3197 (s), 3259 (s), 3296 (s), 3396 (s)

[Fe(Atrz)₃]Cl_{1.5}(BF₄)_{0.5} : Analytically found (calculated) with CHN elemental analysis for FeC₆H₁₂N₁₂Cl_{1.5}B_{0.5}F₂·3H₂O (molar mass 458.711 g mol⁻¹): C, 15.89 (15.71); H, 3.58 (3.96); N, 36.18 (36.64). Mid-infrared (MIR) (in cm⁻¹): 657 (w), 694 (w), 883 (m), 995 (s), 1022 (s), 1056 (s), 1091 (s), 1219 (s), 1296 (w), 1338 (w), 1361 (w), 1396 (w), 1487 (w), 1543 (m), 1622 (s), 1656 (s), 3005 (m), 3061 (s), 3103 (s), 3201 (s), 3228 (s), 3298 (s), 3390 (s)

[Fe(Atrz)₃]Cl(BF₄) : Analytically found (calculated) with CHN elemental analysis for FeC₆H₁₂N₁₂ClBF₄·3.1H₂O (molar mass 486.190 g mol⁻¹): C, 15.33 (14.82); H, 3.22 (3.77); N, 34.06 (34.57). Mid-infrared (MIR) (in cm⁻¹): 653 (w), 692 (w), 889 (m), 995 (s), 1022 (s), 1056 (s), 1089 (s), 1219 (s), 1292 (w), 1338 (w), 1371 (w), 1394 (w), 1485 (w), 1546 (m), 1622 (s), 3001 (m), 3061 (s), 3103 (s), 3131 (s), 3230 (s), 3338 (s), 3392 (s)

[Fe(Atrz)₃]Cl_{0.5}(BF₄)_{1.5} : Analytically found (calculated) with CHN elemental analysis for FeC₆H₁₂N₁₂Cl_{0.5}B_{1.5}F₆·2.2H₂O (molar mass 495.654 g mol⁻¹): C, 14.77 (14.54); H, 2.58 (3.34); N, 33.58 (33.91). Mid-infrared (MIR) (in cm⁻¹): 655 (w), 690 (w), 889 (m), 995 (s), 1020 (s), 1056 (s), 1089 (s), 1219 (s), 1292 (w), 1338 (w), 1373 (w), 1392 (w), 1546 (m), 1627 (s), 3001 (m), 3062 (s), 3103 (s), 3140 (s), 3230 (s), 3317 (s), 3358 (s), 3603 (m)

[Fe(Atrz)₃]Cl_{0.2}(BF₄)_{1.8} : Analytically found (calculated) with CHN elemental analysis for FeC₆H₁₂N₁₂Cl_{0.2}B_{1.8}F_{7.2}·1.5H₂O (molar mass 498.450 g mol⁻¹): C, 14.55 (14.46); H, 2.51 (3.03); N, 33.28 (33.72). Mid-infrared (MIR) (in cm⁻¹): 655 (w), 692 (w), 758 (w), 767 (w), 794 (w), 887 (m), 995 (s), 1018 (s), 1055 (s), 1091 (s), 1219 (s), 1292 (w), 1338 (w), 1371 (w), 1394 (w), 1596 (m), 1631 (s), 3001 (m), 3066 (s), 3138 (s), 3242 (s), 3309 (s), 3361 (s), 3614 (m)

[Fe(Atrz)₃](BF₄)₂ : Analytically found (calculated) with CHN elemental analysis for FeC₆H₁₂N₁₂B₂F₈·H₂O (molar mass 499.713 g mol⁻¹): C, 14.84 (14.42); H, 2.37 (2.82); N, 33.25 (33.64). Mid-infrared (MIR) (in cm⁻¹): 651 (w), 690 (w), 758 (w), 794 (w), 887 (m), 995 (s), 1018 (s), 1056 (s), 1091 (s), 1219 (s), 1290 (w), 1338 (w), 1373 (w), 1392 (w), 1546 (m), 1633 (s), 3005 (m), 3066 (s), 3138 (s), 3244 (s), 3311 (s), 3365 (s), 3614 (m)

Characterization

IR spectroscopy was performed for each synthesized product to gain information on the molecular bonds of each of the complexes. A Shimadzu IR-Affinity-1 was used with the ATR method. The range of the measurements was between 650 and 4000 cm⁻¹.

The CNH elemental analysis data was collected using a Perkin-Elmer 2400 II CHN analyzer to verify successful synthesis.

UV/Vis spectroscopy was performed to further confirm the presence of distinct products and not mixtures using a Perkin Elmer Lambda 650S from 800 to 250 nm in 1 nm steps. The analyzed complexes were positioned in the reflectance sample holders of the 150 mm integrating sphere.

PXRD was performed for the structural analysis and to confirm the homogeneity and uniformity of the obtained complexes. Therefore, a Bruker D2 phaser was used. The samples were scanned from 5°–60° 2θ and steps of 0.05° using Cu–Kα (λ = 1.5406 Å) radiation.

To further analyze the containing anions of the samples, EDX measurements were performed using a Shimadzu EDX-7000.

For the analysis of the spin states and oxidation states of the compounds at room temperature Mössbauer measurements were carried out in transmission geometry with a modified miniaturized Mössbauer Spectrometer MIMOS II (Space and Earth Science Instrumentation). ⁵⁷Co nuclei in an Rh matrix were used the radiation source and the measurements were recorded at 14.4 keV. All isomer shifts were given relative to α-Fe.

To gather information about the SCO temperatures and hysteresis and to verify that the obtained complexes were individual complexes with mixed anions instead of mixtures of corresponding complexes of both anions magnetic susceptibility measurements were performed. Therefore, the samples were measured with a Quantum Design MPMS-5XL SQUID magnetometer under an applied magnetic field of 1000 Oe. The samples were wrapped in Al foil and fixed in Al cups. The temperature dependence was measured at 2 K increments with a sweeping rate of 2 K/min. Data was corrected for the paramagnetic contribution of the sample holder as background data and the diamagnetic contribution of the sample calculated from Pascal's constants. The values of the transition temperatures T_{1/2} were determined using the linear regression tool of the software Origin 2022 (Origin Labs).

Results and Discussion

The obtained products had colors from white to pink at ambient temperature. A trend was visible with the ratios of the applied iron salts in the synthesis. For comparison [Fe(Atrz)₃](BF₄)₂ was white at room temperature as expected and known to the literature, as the complex is expected to be in HS state. [Fe(Atrz)₃]Cl₂ for comparison had a pink color at ambient temperatures and is expected to be in LS state at RT.^[12] A transition is observed at higher temperatures. For the different ratios the observed trend was to a white product at RT with an increased amount of BF₄⁻ in the samples. The products for [Fe(Atrz)₃]Cl_{1.8}(BF₄)_{0.2} and [Fe(Atrz)₃]Cl_{1.5}(BF₄)_{0.5} and were pink solids, while [Fe(Atrz)₃]Cl(BF₄), [Fe(Atrz)₃]Cl_{0.5}(BF₄)_{1.5} and [Fe(Atrz)₃]Cl_{0.2}(BF₄)_{1.8} were white solids at room temperature. Whereby [Fe(Atrz)₃]Cl(BF₄) had a slight pink tinge. This was an indication of a partial LS state at room temperature, which was confirmed by the subsequent characterization. The colors of the compounds at RT can be seen in an image in the Supporting Information (Figure S1). Thereby, it can be mentioned that [Fe(Atrz)₃]Cl(BF₄) and [Fe(Atrz)₃]Cl_{0.5}(BF₄)_{1.5} showed a color change from white to pink in a fridge at -20 °C, which was a first indicator of the SCO properties for these compounds. As

this was above the transition temperature of the complex $[\text{Fe}(\text{Atrz})_3](\text{BF}_4)_2$, which stayed at white color (HS) at -20°C , it could be assumed that hetero-anionic complexes were present in these cases. When the products with a supposed higher amount of chloride anions were heated in comparison to $[\text{Fe}(\text{Atrz})_3]\text{Cl}_2$, they showed a change of color at lower temperatures than $[\text{Fe}(\text{Atrz})_3]\text{Cl}_2$ with $[\text{Fe}(\text{Atrz})_3]\text{Cl}_{1.8}(\text{BF}_4)_{0.2}$ showing a transition at a higher temperature than $[\text{Fe}(\text{Atrz})_3]\text{Cl}_{1.5}(\text{BF}_4)_{0.5}$. Furthermore, $[\text{Fe}(\text{Atrz})_3]\text{Cl}_{1.5}(\text{BF}_4)_{0.5}$ showed a color change at lower temperatures than $[\text{Fe}(\text{Atrz})_3]\text{Cl}_{1.8}(\text{BF}_4)_{0.2}$. This trend is visible in Figure 2 and was the first confirmation that different products had been obtained.

This first assumption was confirmed by further analyses. To determine that the complexes had hetero anions within their structures and were not just mixtures of $[\text{Fe}(\text{Atrz})_3](\text{BF}_4)_2$ and $[\text{Fe}(\text{Atrz})_3]\text{Cl}_2$, EDX, IR, CNH elemental analysis, UV/Vis spectroscopy, PXRD and Mössbauer spectroscopy were performed for the products.

The measured UV/Vis spectra proved that the obtained complexes must have been distinguishable products. These spectra are given in Figure 3 and confirmed the assumptions made when observing the obtained products at room temperature.

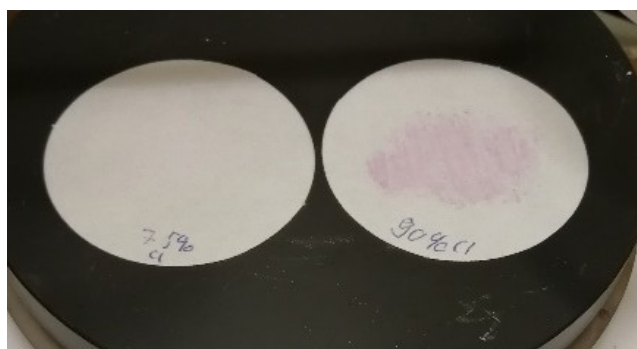


Figure 2. Comparison of $[\text{Fe}(\text{Atrz})_3]\text{Cl}_{1.5}(\text{BF}_4)_{0.5}$ (75% Cl left) and $[\text{Fe}(\text{Atrz})_3]\text{Cl}_{1.8}(\text{BF}_4)_{0.2}$ (90% Cl right) applied on filter paper and heated up to 323 K.

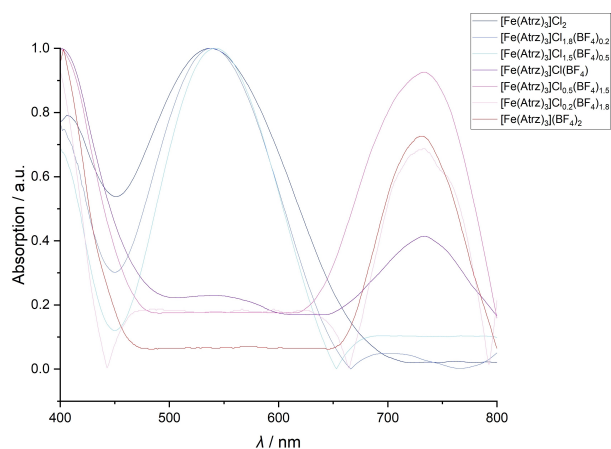


Figure 3. UV/Vis spectra of the $[\text{Fe}(\text{Atrz})_3]\text{Cl}_{2-x}(\text{BF}_4)_x$ complexes measured at room temperature.

In the 540 nm range, it was possible to recognise that a peak was visible if more chloride anions should have been present in the complexes. This occurred in the measurements of the samples that were pink at RT and was also slightly noticeable in the case of $[\text{Fe}(\text{Atrz})_3]\text{Cl}(\text{BF}_4)$. This can be attributed to these complexes being in the LS state at RT and $[\text{Fe}(\text{Atrz})_3]\text{Cl}(\text{BF}_4)$ not completely being in the HS state at room temperature. The absence of the peak in the samples with higher amounts of tetrafluoroborate anions can be explained by the HS state. Contrary to this, another peak at about 730 nm was observed in the complexes that were supposed to have an increased ratio of tetrafluoroborate ions. This peak was also observed for complex $[\text{Fe}(\text{Atrz})_3]\text{Cl}(\text{BF}_4)$ and was increasingly stronger with more tetrafluoroborate anions and occurred accordingly in complexes that were white (due to the HS state) at room temperature.

The PXRD measurements performed resulted in diffractograms, which also proved that distinguishable products were obtained. The measured diffraction patterns can be found in the supporting information. (Figure S2) Apart from a reflection at about $8-10^\circ$, which occurred in each of the measured complexes, it was not possible to determine exactly whether one of the two structures of the pristine monoanionic complexes is preferentially favoured in the heteroanionic complexes due to the broadening of the other reflections. Through the similar reflection at $8-10^\circ$, it can be stated that the structures must have been at least roughly similar. It should also be mentioned, nonetheless, that reflections which can be clearly identified as such in the diffraction pattern of $[\text{Fe}(\text{Atrz})_3]\text{Cl}_2$, at 25° and 28° , are also recognizable up to $[\text{Fe}(\text{Atrz})_3]\text{Cl}(\text{BF}_4)$ (50% Cl-anions). These reflections at least allow to assume that these cases have similar structures to $[\text{Fe}(\text{Atrz})_3]\text{Cl}_2$. There was also no significant shift in these reflections in comparison. However, it can be seen from the broadening in the diffraction patterns that a combination of anions leads to apparently more amorphous products. Only the complex $[\text{Fe}(\text{Atrz})_3]\text{Cl}_{1.8}(\text{BF}_4)_{0.2}$ showed less broadening of the reflexes than the other heteroanionic complexes and its pattern showed slight similarity to $[\text{Fe}(\text{Atrz})_3]\text{Cl}_2$ in the range of above 10° . It can therefore be assumed that higher ratios of tetrafluoroborate anions lead to lower crystallinity in the heteroanion complexes.

The success of the synthesis was further proven by the carried out CHN elemental analysis. Through CNH elemental analysis it was possible to suggest the tentative compositions that were given above for the obtained products. The precision of the given compositions fits the range of the method with smaller differences between the found and calculated values than in the given comparable literature^[22] and in addition, the results of the other measurements support the postulated tentative compositions. However, it should be noted that although the synthesis used here was inspired by the literature, it differed in that metal salts were used instead of ligands as in the synthesis of Piedrahita-Bello et al.^[22] The concentrations chosen were also different. According to the results of the elemental analysis, water molecules were included in the obtained products, which is typical for this kind of material, and

was reported in regards to hetero-anionic complexes before.^[19,20]

With EDX measurements the iron and chloride contents of the products were estimated. It was possible to observe that an increase of chloride in the educts of the syntheses could also be observed through EDX in regards to the obtained complexes. For comparison with the pristine non-hetero anionic complexes, EDX was also measured for the complexes $[\text{Fe}(\text{Atr}z)_3](\text{BF}_4)_2$ and $[\text{Fe}(\text{Atr}z)_3]\text{Cl}_2$. The observed trend is shown in Figure 4 by a graph of the measured percentage of chloride anions in the EDX against the supposed percentage of chloride anions in each product in regards to the total anions in the sample.

Thereby, it is important to mention that the only other detected element was iron. Additionally, it must be stated that the method has a certain detection limit of elements that influenced the measurement. It is necessary for a certain quantity to be present for detection to be possible. It is generally more a qualitative than a quantitative method. Therefore, there could have been difficulties for the detection of the chloride content in the sample of $[\text{Fe}(\text{Atr}z)_3]\text{Cl}_{0.2}(\text{BF}_4)_{1.8}$ as the chloride anions account for less than 10% of the total molar fraction in the total sample. The corresponding sample of $[\text{Fe}(\text{Atr}z)_3]\text{Cl}_{1.8}(\text{BF}_4)_{0.2}$ on the other hand, which has an increased chloride ratio, is distinguishable from $[\text{Fe}(\text{Atr}z)_3]\text{Cl}_2$. A difference in the measured amount of chloride was also seen in the other complexes respectively.

Infrared spectroscopy was used to further confirm the success of the synthesis and gain further information about the bonds occurring in the products. The measured infrared spectra for each of the compounds showed characteristic bonds of iron(II) triazole complexes. Some weak bonds occurred at roughly 650 cm^{-1} to 690 cm^{-1} which can be assigned to the ring deformation of the triazole ring. Furthermore, bonds were visible at around 890 cm^{-1} and 995 cm^{-1} that can be assigned the out-of-plane vibrations of the C–H-bonds and to the C–H-bend vibrations.^[24] A group of significant bonds in all of the measured infrared spectra besides the one of $[\text{Fe}(\text{Atr}z)_3]\text{Cl}_2$ can be seen at about 1022 cm^{-1} and around 1091 cm^{-1} , these can be assigned to the BF_4^- anions which were only supposed to be

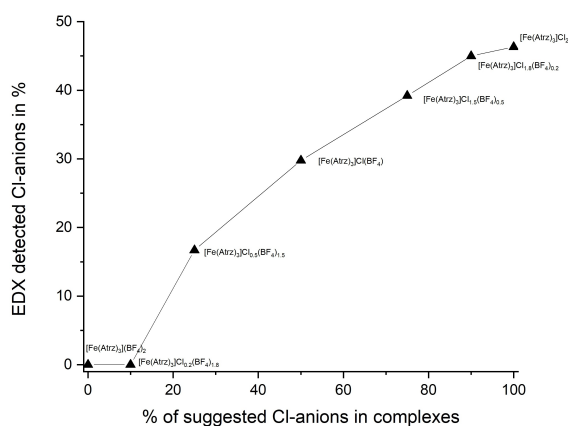


Figure 4. EDX detected chloride anions in percent relative to the other detected elements in contrast to the suggested percentage of chloride anions in the obtained complexes.

part of these products.^[20] This bond shows a trend with slight deviations of stronger bonds that are accompanied by a higher amount of expected BF_4^- anions in each sample obtained. A direct comparison of the IR spectra of the complexes $[\text{Fe}(\text{Atr}z)_3]\text{Cl}_{1.5}(\text{BF}_4)_{0.5}$ and $[\text{Fe}(\text{Atr}z)_3]\text{Cl}_{0.5}(\text{BF}_4)_{1.5}$ is shown in Figure 5.

This trend and the characteristic bonds of the ligand are representative for the success of the synthesis of the expected hetero-anionic complexes.

To investigate the spin state of the complexes at room temperature and in order to ensure that the products were hetero-anionic and no mixtures of $[\text{Fe}(\text{Atr}z)_3]\text{Cl}_2$ and $[\text{Fe}(\text{Atr}z)_3](\text{BF}_4)_2$, Mössbauer measurements were performed. The Mössbauer spectra were measured at room temperature and are shown in Figure 6, the measured Mössbauer parameters are given in Table 2.

It could be determined that the percentage of iron(II) in the LS state was higher with an increased supposed amount of chloride anions. On the other hand the spin state distribution showed a majority of iron(II) in HS with more BF_4^- anions. Both states were visible in the product to $[\text{Fe}(\text{Atr}z)_3]\text{Cl}(\text{BF}_4)$ as before assumed through the measured UV/vis spectra. This trend is also in consistency with the one already observed by the colors at ambient condition and by the cooling of the products that were white at room temperature. The spectra of the products

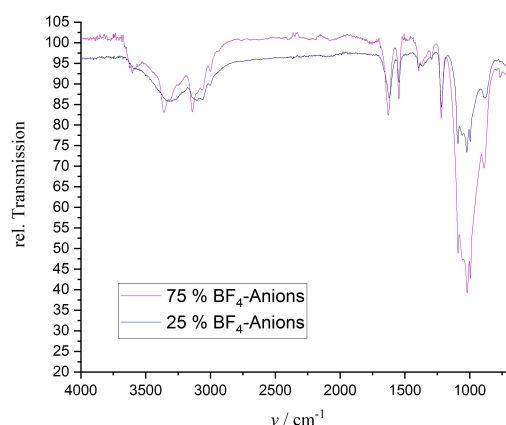


Figure 5. Infrared spectra of $[\text{Fe}(\text{Atr}z)_3]\text{Cl}_{1.5}(\text{BF}_4)_{0.5}$ (25 % BF_4) and $[\text{Fe}(\text{Atr}z)_3]\text{Cl}_{0.5}(\text{BF}_4)_{1.5}$ (75 % BF_4).

Compound	Isomeric Shift/ mm s^{-1}	Quadrupol splitting/ mm s^{-1}	Relative Area/%	Sites
$[\text{Fe}(\text{Atr}z)_3]\text{Cl}_2$	0.5391(13)	0.2786(31)	100	LS
$[\text{Fe}(\text{Atr}z)_3]\text{Cl}_{1.8}(\text{BF}_4)_{0.2}$	0.53556(98)	0.2913(22)	100	LS
$[\text{Fe}(\text{Atr}z)_3]\text{Cl}_{1.5}(\text{BF}_4)_{0.5}$	0.5436(30) 1.297(25)	0.2493(84) 3.628(50)	88.4 11.6	LS HS
$[\text{Fe}(\text{Atr}z)_3]\text{Cl}(\text{BF}_4)$	1.0669(13) 0.34068	2.9125(26) –	85.8 14.2	HS LS
$[\text{Fe}(\text{Atr}z)_3]\text{Cl}_{0.5}(\text{BF}_4)_{1.5}$	0.4979(12)	1.1735(24)	100	HS
$[\text{Fe}(\text{Atr}z)_3]\text{Cl}_{0.2}(\text{BF}_4)_{1.8}$	0.4972(19)	1.1766(38)	100	HS
$[\text{Fe}(\text{Atr}z)_3](\text{BF}_4)_2$	0.6883(12)	1.7472(24)	100	HS

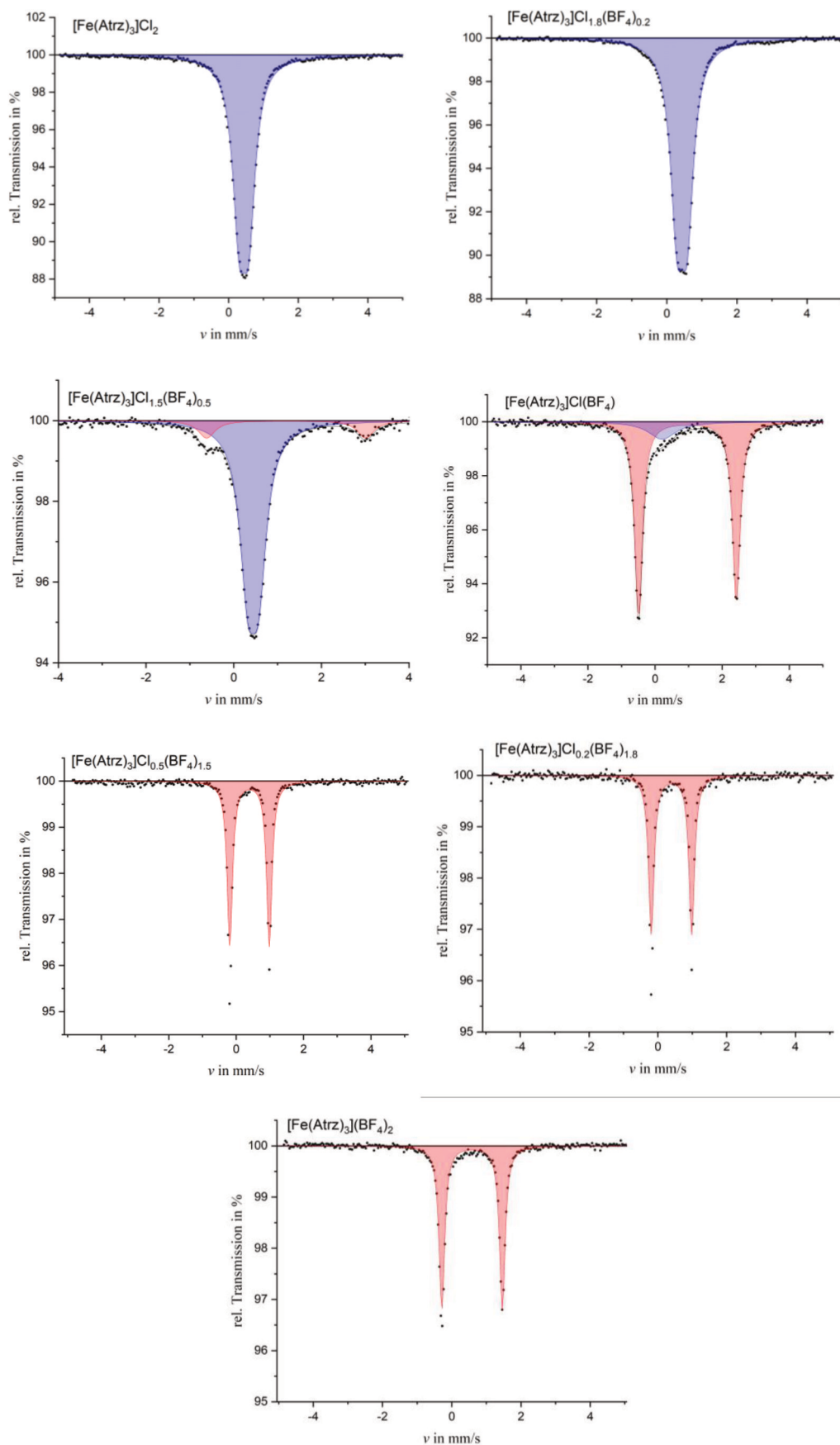


Figure 6. Mössbauer spectra of the $[\text{Fe}(\text{Atrz})_3]\text{Cl}_{2-x}(\text{BF}_4)_x$ complexes at 293 K.

with a higher chloride ratio did not show any notable visible high amounts of iron(II) in the HS state. In the spectrum of $[\text{Fe}(\text{Atrz})_3\text{Cl}_{1.5}(\text{BF}_4)_{0.5}]$ there is a small percentage of 11.6% in HS state which can be explained by the broadness of the hysteresis of the complex which starts slightly under room temperature. In the case of $[\text{Fe}(\text{Atrz})_3\text{Cl}_{1.8}(\text{BF}_4)_{0.2}]$, no iron(II) in HS state was observed which speaks for the synthesis of a heteroanionic product and not a mixture, as the complex $[\text{Fe}(\text{Atrz})_3(\text{BF}_4)_2]$ would show Iron(II) in HS state at room temperature. This is also consistent with the first assumptions that were made when the products were heated in comparison to $[\text{Fe}(\text{Atrz})_3\text{Cl}_2]$. The product for the complexes $[\text{Fe}(\text{Atrz})_3\text{Cl}_{0.2}(\text{BF}_4)_{1.8}]$ and $[\text{Fe}(\text{Atrz})_3\text{Cl}_{0.5}(\text{BF}_4)_{1.5}]$ furthermore showed no LS state at RT, which would be the case in the presence of two separate products including $[\text{Fe}(\text{Atrz})_3\text{Cl}_2]$. In regards to the differences of the parameters in the measured spectra, it can be stated that the quadrupole splitting of the measured LS state signals that were measured were relatively small roughly between 0.25 mm s^{-1} and 0.30 mm s^{-1} , which is typical for iron(II) triazole complexes in the LS state.^[25,26] In the case of $[\text{Fe}(\text{Atrz})_3\text{Cl}(\text{BF}_4)]$ the quadrupole splitting of the measured LS was tending towards zero. The HS only showed typical Mössbauer parameters. The other measured HS states of the complexes with higher amounts of BF_4^- showed unusually small quadrupole splitting as well as unusual isomeric shifts. This could be typical for heteroanionic iron(II) triazoles with a majority of this anion as both values seemed to be significantly larger in the spectrum of the obtained $[\text{Fe}(\text{Atrz})_3(\text{BF}_4)_2]$.

To analyze the SCO properties of the obtained complexes in detail, measurements with a SQUID magnetometer were carried out. The performed magnetic measurements showed that the obtained products had been distinguishable from each other, further confirming the results of the other methods used. The Hysteresis curves in the Figure 7 show that the products had different hysteresis curves and transition temperatures. For comparison, the hysteresis of $[\text{Fe}(\text{Atrz})_3(\text{BF}_4)_2]$ and $[\text{Fe}(\text{Atrz})_3\text{Cl}_2]$ were also measured and are also presented. The measured transition temperatures $T_{1/2\uparrow}$ and $T_{1/2\downarrow}$ are listed in Table 3 for heating and cooling in the second cycle of the measurement, respectively. The transition temperatures are furthermore presented in Figure 8 in contrast to the suggested molar fractions of chloride anions in the complexes.

A trend was observed in the SQUID measurements towards higher transition temperatures with an increased amount of

chloride anions in the product, as formerly assumed through simple heating and cooling of the complexes. It can also be said that the obtained products must have been hetero anionic complexes according to progression of the hysteresis of the samples, as there was no two-step transition observed in a second cycle which would be the case for mixtures of two complexes according to Kahn et al.^[18] It has to be mentioned that the complexes with a higher amount than 50% Chloride showed an unusual hysteresis behavior in the first cycle of heating. This can be explained by water molecules which leave the sample and do not return while cooling, which also occurs with the monoanionic complex $[\text{Fe}(\text{Atrz})_3\text{Cl}_2]$. This is most visible in the case of $[\text{Fe}(\text{Atrz})_3\text{Cl}_2]$ and $[\text{Fe}(\text{Atrz})_3\text{Cl}_{1.8}(\text{BF}_4)_{0.2}]$, because both complexes only showed a spin transition at higher temperatures, at which the crystal water presumably left the complexes. The SQUID measurements furthermore prove that even only a small ratio of anions with a lower transition temperature of their corresponding mono-anion complex will decrease the transition temperature of the hetero-anionic complex notably. This can especially be observed by the comparison of the hysteresis of $[\text{Fe}(\text{Atrz})_3\text{Cl}_{1.5}(\text{BF}_4)_{0.5}]$ and $[\text{Fe}(\text{Atrz})_3\text{Cl}_{1.8}(\text{BF}_4)_{0.2}]$ with $[\text{Fe}(\text{Atrz})_3\text{Cl}_2]$, which shows significantly higher transition temperatures. Even smaller amounts of each of the anions can also lead to differences which are visible, in the cases of $[\text{Fe}(\text{Atrz})_3\text{Cl}_{1.8}(\text{BF}_4)_{0.2}]$ and $[\text{Fe}(\text{Atrz})_3\text{Cl}_{0.2}(\text{BF}_4)_{1.8}]$ having only 10% of one of the ions present. However, the difference in hysteresis behavior of the complexes with 10% of the respective other anion is noticeably greater in the case of complex $[\text{Fe}(\text{Atrz})_3\text{Cl}_{1.8}(\text{BF}_4)_{0.2}]$. The Complex $[\text{Fe}(\text{Atrz})_3\text{Cl}_{0.2}(\text{BF}_4)_{1.8}]$ shows differences compared to $[\text{Fe}(\text{Atrz})_3(\text{BF}_4)_2]$, but these are miniscule. The second cycle showed a narrower hysteresis in each case. The complexes with an increased amount of BF_4^- showed lower transition temperatures and usual hysteresis behavior in comparison. The measured spin states of the iron(II) species within the Mössbauer measurements also agree with the performed SQUID measurements. The spin state distributions roughly align with the measured magnetic data at around ambient temperature for every obtained iron(II) triazole complex.

Conclusions

Through the performed analysis it can be stated that distinct products have been obtained which showed SCO behavior. These products were confirmed to be distinguishable hetero-anionic iron(II) triazole complexes by IR spectroscopy, UV/Vis spectroscopy, PXRD, elemental analysis, EDX and Mössbauer spectroscopy. The obtained complexes showed trends in regards to their SCO properties with a higher amount of chloride anions leading to higher transition temperatures and lower transition temperatures with a higher amount of tetrafluoroborate anions. The measured spectra of the hetero-anionic complexes showed no signs of the monoanionic complexes $[\text{Fe}(\text{Atrz})_3\text{Cl}_2]$ or $[\text{Fe}(\text{Atrz})_3(\text{BF}_4)_2]$. The analysis showed that complexes have been obtained of heteroanionic nature and were called alloys by Kahn et al.^[18] It was proven that

Table 3. Transition temperature of the $[\text{Fe}(\text{Atrz})_3\text{Cl}_{2-x}(\text{BF}_4)_x]$ complexes while heating and cooling (second cycle).

Compound	$T_{1/2\uparrow}$ in K	$T_{1/2\downarrow}$ in K
$[\text{Fe}(\text{Atrz})_3\text{Cl}_2]$	353.25(21)	342.57(13)
$[\text{Fe}(\text{Atrz})_3\text{Cl}_{1.8}(\text{BF}_4)_{0.2}]$	334.43(77)	322.25(33)
$[\text{Fe}(\text{Atrz})_3\text{Cl}_{1.5}(\text{BF}_4)_{0.5}]$	285.59(62)	284.84(27)
$[\text{Fe}(\text{Atrz})_3\text{Cl}(\text{BF}_4)]$	261.06(53)	251.21(48)
$[\text{Fe}(\text{Atrz})_3\text{Cl}_{0.5}(\text{BF}_4)_{1.5}]$	258.02(29)	247.76(32)
$[\text{Fe}(\text{Atrz})_3\text{Cl}_{0.2}(\text{BF}_4)_{1.8}]$	239.06(17)	235.36(22)
$[\text{Fe}(\text{Atrz})_3(\text{BF}_4)_2]$	239.03(26)	236.44(26)

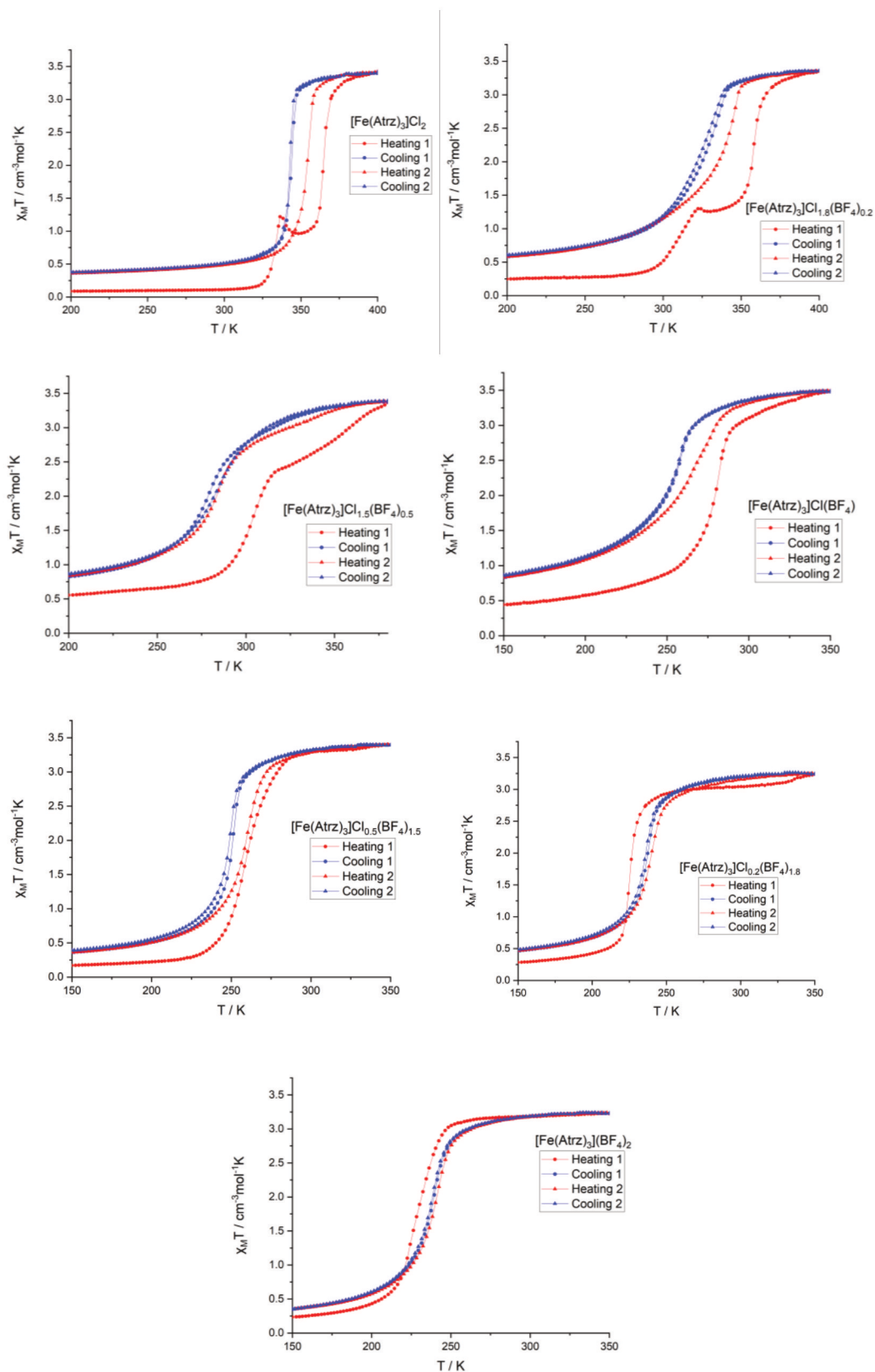


Figure 7. SQUID measurements of the $[\text{Fe}(\text{Atrz})_3]\text{Cl}_{2-x}(\text{BF}_4)_x$ complexes.

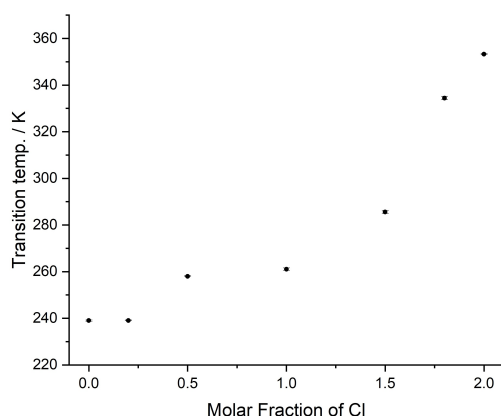


Figure 8. Measured transition temperatures ($T_{1/2}^{\uparrow}$ in K) of the second heating cycle in contrast to the molar fraction of chloride anions of the $[\text{Fe}(\text{Atzr})_3]\text{Cl}_{2-x}(\text{BF}_4)_x$ complexes.

simple adjustments to the precursors of the synthesis can have a significant influence on the SCO properties of the triazole complex. The pristine complexes have transition temperatures that are above and below ambient temperature and mixtures result in transition temperatures at ambient temperature and slightly above. In the case of $[\text{Fe}(\text{Atzr})_3]\text{Cl}(\text{BF}_4)$, it was initially assumed by the UV/vis and by mere observation that the complex is still partially in the LS state at RT, which was proven by Mössbauer spectroscopy. Even small amounts of anions, for example in the case of the complexes $[\text{Fe}(\text{Atzr})_3]\text{Cl}_{1.5}(\text{BF}_4)_{0.5}$, $[\text{Fe}(\text{Atzr})_3]\text{Cl}_{1.8}(\text{BF}_4)_{0.2}$, resulted in significant differences regarding the SCO temperature. This makes these compounds especially interesting for several applications. This was recently tested in a study by us in which we implemented one of these complexes into a polymer.^[27] Furthermore, the results show that it is possible to utilize different types of anions for the fine tuning of the SCO properties of iron(II) triazole complexes with various different ratios. This opens up the possibility to combine more anions, for example organic anions, which could solve known problems in these systems like a limited solubility in a variety of solvents while maintaining exact SCO temperature adjustments. The compatibility of more anions can therefore be tested and this can also be done in the case of other comparable triazole ligands. Anion combination and ligand combination at the same time could also lead to even better adjustments of the SCO properties in these systems.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: Triazole Complexes · Spin transition · Spin crossover · Molecular switches · Modification of properties

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