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Spin Crossover

The First 1,3,4-Oxadiazole Based Dinuclear Iron(II) Complexes Showing Spin Crossover Behavior with Hysteresis

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Dedicated to Professor Marius Andruh on the occasion of his 60th birthday

Abstract: Three new dinuclear complexes $[Fe^{II}_2(\mu\text{-}\mathbf{L})_2]X_4$ (**L** is the bis-tridentate ligand 2,5-bis{[(2-pyridylmethyl)amino]-methyl}-1,3,4-oxadiazole and X = ClO_4^-, BF_4^- and $CF_3SO_3^-$) have been synthesized and fully characterized by single-crystal X-ray diffraction, Mössbauer spectroscopy and magnetic susceptibility measurements. Upon cooling, a trapped [high-spin–low-spin] state of the iron(II) centres is detected. Depending on the counterion, a pronounced thermal hysteresis is found. In one case, it was possible to observe a space group change that accompanies the spin transition. This is the first system showing spin crossover based on an oxadiazole ligand.

Introduction

Whether a spin state of an octahedral 3d transition metal complex with the electronic configuration d^4 to d^7 shows high spin [HS] or low spin [LS], strongly depends on the ligand field strength of the coordinating ligand.[1] At the threshold of the ligand field splitting, a transition between the two spin states can be induced by a change in temperature, pressure or the irradiation with light (LIESST).[2] This effect is called spin crossover (SCO). It is an extensively studied field due to the large potential in electronic applications.[3,4] One of the most investigated metal ions showing this phenomenon is iron(II).[5] Here, a key feature is the drastic change of the magnetic properties from a diamagnetic to a paramagnetic state, which is easily detected. Additionally, a change in color (thermochromism) is giving an easy way to observe the transition.[6]

In the solid state the SCO strongly depends on the cooperative interactions between the metal centers by intermolecular contacts between the complexes. This is mostly achieved by hydrogen bonds or π–π interactions between aromatic moieties of the ligand system.[7] A more pronounced communication of the metal centers leads to a more abrupt transition and, eventually, to a hysteresis.[8] However, mononuclear compounds are limited to these intermolecular interactions. In comparison, the intramolecular metal–metal interaction in polynuclear compounds is more easily controllable due to the close proximity of the metal centers to each another.[9] In dinuclear complexes a mixed [HS-LS] spin state can occur additionally as a third state to the diamagnetic [LS-LS] and the paramagnetic [HS-HS] state. A prominent example is the dinuclear iron(II) PMAT complex by the group of Brooker.[10] This is the first system where a mixed [HS-LS] state has been confirmed by X-ray diffraction. Inspired by this work, our group explored the behavior of the analogous thiadiazole. While in the former example the dinuclear compounds remain in the [HS-LS] state and do not switch to the fully diamagnetic [LS-LS] state, we recently reported the synthesis and characterization of a 1,3,4-thiadiazole based dinuclear iron(II) [LS-LS] complex showing incomplete SCO around room temperature.[11] This and the work of other groups demonstrated the large influence of the heteroatom in the backbone of the structure.[12] We consequently investigated the effect of an oxadiazole backbone regarding the spin transition properties.

In the present study we now report the first set of novel oxadiazole based dinuclear iron(II) compounds showing spin crossover. By magnetic susceptibility measurements and Mössbauer spectroscopy an abrupt spin transition around 150 K is observed. Using single-crystal X-ray diffraction at various temperatures a mixed [HS-LS] state below 150 K is confirmed. Additionally, we observe large differences in the connectivity between the counterions and the cations, leading to a hysteresis of 26 K for one of the compounds.

Results and Discussion

Synthesis

Scheme 1 shows the synthesis of the ligand system 2,5-bis{[(2-pyridylmethyl)amino]methyl}-1,3,4-oxadiazole (**L**). The precursor 2,5-bis(chloromethyl)-1,3,4-oxadiazole is prepared by an intramolecular condensation reaction of 1,2-bis(chloroacetyl)hydrazine.[13] By treating the product with 2-(aminomethyl)pyridine in a nucleophilic substitution, the desired ligand **L** is synthesized.[14]

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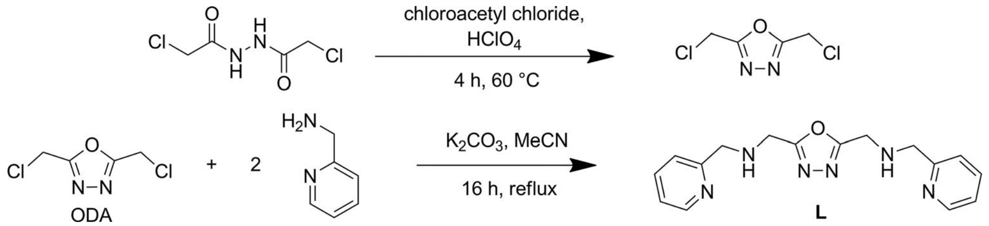

Scheme 1. Synthesis of **L**.

Depending on the counteranion, various techniques were used to obtain dinuclear complexes. In the case of perchlorate, single crystals of $[Fe^{II}_2\mathbf{L}_2](ClO_4)_4{\cdot}4MeCN$ (**1**) formed after mixing solutions of ligand and metal salt in acetonitrile. For other counteranions vapor diffusion with diethyl ether and THF was used to obtain single crystals of $[Fe^{II}_2\mathbf{L}_2](BF_4)_4{\cdot}2MeCN$ (**2**) and $[Fe^{II}_2\mathbf{L}_2](CF_3SO_3)_4{\cdot}2MeCN$ (**3**).

Crystal Structures

X-ray diffraction was performed for compounds **1** and **3** at 193 K, for compound **2** at 173 K. For crystallographic data in more detail, see the Supporting Information. Compound **1** crystallizes in the monoclinic space group *I*2/*a*, **2** and **3** in the triclinic group $P\bar{1}$. The cations of all three structures contain two Fe^{II} atoms, which are doubly μ_2-bridged by the 1,3,4-oxadiazole backbone of the two chelating ligands **L**. They are arranged in a way that both pyridyl groups of one ligand are directed either up or down. This gives in all three cases a distorted octahedral N_6 coordination sphere for both of the metal centers. In addition, there are four non-coordinating counteranions (**1**: ClO_4^-; **2**: BF_4^-; **3**: $CF_3SO_3^-$) as well as four solvent molecules in the perchlorate structure **1** and two solvent molecules in **2** and **3**. As expected for iron(II) in [HS], the average Fe–N bond lengths in **1**, **2**, and **3** are 2.180 Å, 2.1976 Å and 2.190 Å, respectively. More detailed Fe–N bond lengths are summarized in Table 1.

The N–Fe–N *cis* angles show an average of 90.7° for all compounds, even though they actually range from 74.6 to 119.9°. The average *trans* angles are 162.5°, which is far from the ideal angle of 180°. The so-called octahedral distortion parameter Σ adds up the absolute differences of the ideal octahedral *cis* angle of 90° from the actual *cis*-N–Fe–N angles of the compound. It gives values of 121.0° for **1**, 126.1° for **2** and 125.5° for **3**. This difference from an ideal octahedral geometry also shows the [HS] nature of the metal centers.[15] An important aspect to be considered is the introduction of an oxygen atom in the heterocyclic ring of the ligand. This has two effects: on the one side, it changes the electronic structure in the heterocycle. As a more electronegative atom it decreases the electron density at the nitrogen donor atoms. This results in a smaller ligand field splitting Δ, making the [HS] state more favorable. Additionally, the angle between the two nitrogen donor atoms in the oxadiazole and the amine nitrogen donor atom changes. In the analogous thiadiazole complex recently published by our group, this angle is nearly linear. This gives the system a larger flexibility compared to that of the triazole. Here, the smaller radius of the heteroatom reduces that angle to an average of 168.0°, making the structure of the ligand more rigid. A large deviation of the octahedral geometry is therefore expected.

For **1** X-ray diffraction was performed, additional to 193 K, at 100 K (Figure 1). Due to a pulverization of crystals in the process of cooling, no diffraction experiment for both of the other compounds could be run at 100 K. Upon cooling of compound **1**, a change of the space group to *Ia* is observed, cancelling the center of inversion relating the metal centers in the molecule at high temperature. After the phase transition, the two iron(II) atoms clearly can be distinguished. While the average bond length for Fe1–N is 2.204 Å and therefore only slightly larger than the value at 193 K, the Fe2–N bond length is with 2.025 Å much shorter than before. This is attributed to the depopulation of the antibonding e_g* orbitals.[16] The shrinking of the bonds by 7.1 % is in good agreement with the reported values for a spin crossover. Interestingly, the contraction of the N_6 coordination sphere of Fe2 has another effect: for the second metal center, all bonds are elongated. As discussed above, the backbone of the ligand system is quite rigid. This influence comes to light once more: by switching one center into the [LS] state, the second one becomes even more distorted. This

Table 1. Selected bond lengths [Å], bond angles of N–Fe–N [°] and the octahedral distortion parameter Σ [°] for compounds **1**, **2** and **3**. For compound **1**, the values from the measurements at both temperatures are included.

	1 (@ 100 K) Fe1 [HS] /Å	Fe2 [LS] /Å	**1** (@ 193 K) Fe /Å	**2** (@ 173 K) Fe /Å	**3** (@ 193 K) Fe /Å
N1–Fe/N_6–Fe	2.145(8)/2.120(8)	2.010(9)/2.017(8)	2.140(4)/2.136(4)	2.132(2)/2.154(2)	2.139(2)/2.139(2)
N2–Fe/N4–Fe	2.291(8)/2.148(9)	2.102(8)/1.943(9)	2.275(4)/2.130(4)	2.328(2)/2.137(2)	2.291(2)/2.127(2)
N3–Fe/N5–Fe	2.177(8)/2.345(8)	1.969(8)/2.107(8)	2.113(3)/2.284(4)	2.132(2)/2.302(2)	2.132(2)/2.313(2)
N–$Fe_{Average}$	2.204	2.0248	2.180	2.198	2.190
cis-N–Fe–$N_{average}$	91.2	90.1	90.7	90.7	90.7
trans-N–Fe–$N_{average}$	158.0	172.1	162.6	162.3	162.6
Σ[a]	136.7	70.2	121.0	126.1	125.5

[a] The octahedral distortion parameter Σ adds up the absolute differences of the ideal octahedral *cis* angle from the actual *cis*-N–Fe–N angles of the compound.

interplay is reflected by the change of the octahedral distortion parameters ($\Sigma_{(Fe1,[HS])}$ = 136.7°, $\Sigma_{(Fe2,[LS])}$ = 70.16°). While the average *cis* angle remains nearly constant ($\Delta_{(Fe1)}$ = 0.4°; $\Delta_{(Fe2)}$ = 0.6°), the *trans* angles change more drastically by 4.6° to 158.0° for the [HS] center and by 9.5° to 172.1° for the [LS] center. Being in that constrained geometry dictated by the rigidity of the oxadiazole, it is very unlikely for the iron(II) center in the [HS] state to undergo a spin transition as well.

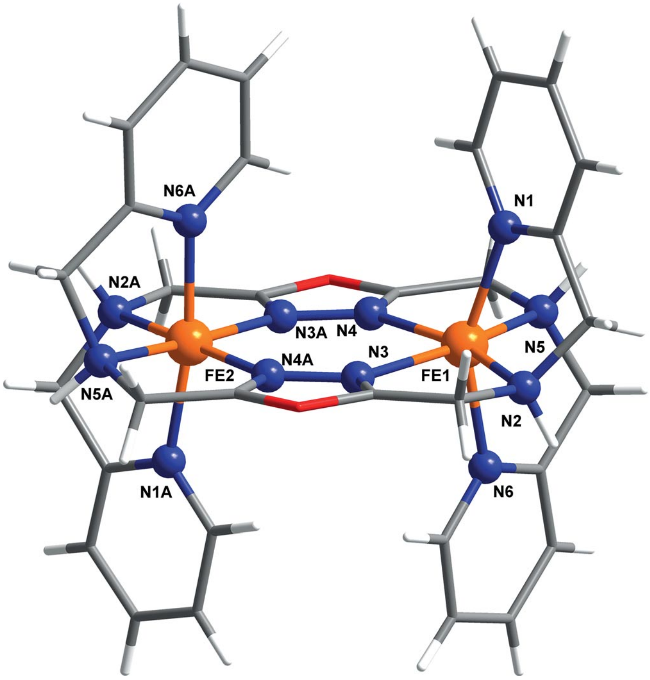

Figure 1. Crystal structure of [**1**]$^{4+}$ measured at 100 K. Solvent molecules and counteranions have been omitted for clarity. Nitrogen and iron atoms have been highlighted and labelled. Color code: iron is orange, nitrogen blue, oxygen red, carbon gray, and hydrogen white.

Figure 2 shows a cutout of the molecular packing in compound **3**.

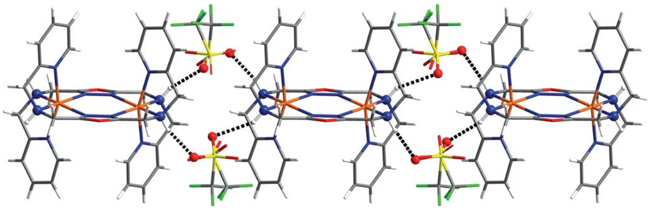

Figure 2. Representation of the hydrogen bonds in compound **3** (black dashed lines). Solvent molecules and some counteranions have been omitted for clarity. Selected atoms have been highlighted. The disorder of the counterions occurs alternating. Hydrogen bonds are shown as dashed lines for only one of the disordered position each.

A very important role is attributed to the intermolecular interaction between the complexes. Here the counteranions and solvent molecules can become crucial, because they are linking the cations through hydrogen bonds. The cooperativity, which is introduced this way, has enormous effects on the resulting spin crossover properties, such as $T_{1/2}$, sharpness of a transition and the occurrence of a hysteresis.[14] It is straightforward that the intermolecular interaction has the largest influence when it is mediated directly to the transition active centers. An ideal position in our system is the amine proton at the nitrogen donor atom. It is the most direct way to shift the electron density at the metal center.

In all three compounds, the solvent molecules do not form any hydrogen bonds that affect the amine group. However, they are necessary for the integrity of the crystal structure, and loss of solvent molecules results in the absence of spin crossover.

More important in the present compounds is to discuss the role of the counteranions. Close examination of compound **2** shows four BF_4^- anions enclosing the cation. However, no NH–μ_2-BF_4^-–NH connections are observed. All bonds from amine protons to counterions tend to form a bridge between the NH group and an aromatic or an aliphatic proton.

The picture is different in compound **1**. Here, every cation is twisted to its next neighbor. The square planes of two molecules, each generated by the four oxadiazole nitrogen and the four amine nitrogen atoms, show a dihedral angle of 81.3°. One of the amine protons and its symmetry equivalent build a hydrogen bond towards an oxygen atom of the ClO_4^- anion. The same oxygen atom binds to the other amine proton in the next cation, which is oriented the other way. In this manner a twisted grid is formed, where all of the amine protons are μ_2-bridged to one another by the same oxygen atom from one of the counteranions.

In compound **3** the cations form a linear chain. They are bridged by hydrogen bonds mediated through the counteranions. Two opposing amine protons are connected to an oxygen atom from two $CF_3SO_3^-$ anions. A second oxygen atom from the same anion builds hydrogen bonds to the NH group from the neighboring cation. This arrangement shows the largest cooperativity. Every disturbance of the ligand field of any iron(II) center is transmitted directly to the next molecule, where it has the same effect due to the similar order of the cations.

Magnetic Measurements and Mössbauer Spectroscopy

Variable-temperature magnetic measurements were carried out on freshly prepared crystalline samples of **1**, **2** and **3** with an external magnetic field of 1 kOe in a temperature range from 10 to 300 K. For compounds **1** and **2**, a sweep mode was used with a scan rate of 5 K/min in the temperature range from 10 to 100 K and from 200 to 300 K. Between 100 and 200 K, the sweep velocity was 1 K/min. For the measurement of compound **3**, a settle mode was used with a scan rate of 1 K/min, except in the ranges, where the spin transition occurs; here, the scan rate was 0.5 K/min (from 158 to 149 K and from 170 to 180 K).

At 300 K compound **1** shows a value for $\chi_m T$ of 7.14 $cm^3\,K\,mol^{-1}$ (Figure 3). Upon cooling, the susceptibility decreases slightly to 6.55 $cm^3\,K\,mol^{-1}$ at 170 K. At this point, a rapid decline is observed, which comes to a halt at 126 K, where $\chi_m T$ settles at 3.80 $cm^3\,K\,mol^{-1}$. Further lowering of the temperature has no effect on the magnetic susceptibility in a range from 100 to 50 K. Only below 50 K does $\chi_m T$ start to decrease slightly again to reach 3.29 cm^3 K mol^{-1} at 10 K. This lowering of the χ_mT value at low temperature probably arises from intermolecular interactions, saturation and contributions from zero-field splitting. Increasing the temperature leads again to the same plateau value for the magnetic moment of 3.80 cm^3 K mol^{-1}. Once again a rapid increment of the susceptibility is monitored with the same shape as in the cooling process. Upon reaching a temperature of 170 K, the slope shows again a very small gradient. The magnetic moment of 6.58 cm^3 K mol^{-1} is slightly higher than the values during cooling. Raising the temperature again to 300 K leaves the sample with a value of 7.18 cm^3 K mol^{-1}.

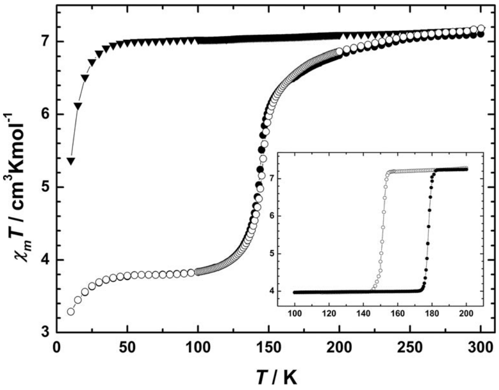

Figure 3. χ_mT vs. T data for compound **1** (solid circles: cooling; open circles: heating) and **2** (triangles) and compound **3** (small picture). The data is per dinuclear complex molecule.

For compound **2**, the variable temperature magnetic data revealed no spin transition. At 300 K, the χ_mT value of 7.14 cm^3 K mol^{-1} is similar to that of compound **1**. Decreasing the temperature has no effect on the magnetic susceptibility until 50 K is reached, where χ_mT declines to a final value of 5.37 cm^3 K mol^{-1} at 10 K. This behavior is proof for us, that the change of χ_mT at a temperature below 50 K here and as well as in compound **1** is not caused by a spin transition of the second iron(II) atom.

In contrast to the curve of compound **1**, the magnetic moment vs. temperature curve for compound **3** has a much more abrupt shape. The value of 7.24 cm^3 K mol^{-1} observed at 200 K remains almost constant with decreasing temperature. At 154 K the value for χ_mT shows a steep descent until the temperature reaches 149 K, where it settles immediately to 3.97 cm^3 K mol^{-1}. Upon further cooling, the magnetic moment remains constant until 100 K. While increasing the temperature again, it attracted our attention that the magnetic moment did not rise when 149 K was reached. Instead it lasted until 174 K. At that point, a steep increase in χ_mT was found, which stopped at 182 K reaching finally the same value of 7.24 cm^3 K mol^{-1}. The divergence in the steep decrease or increase of the magnetic moment upon cooling and heating reveals a hysteresis loop with a noticeable width of 26 K. The origin of this hysteresis is probably caused by cooperative effects that arise from intermolecular hydrogen bonds as discussed above. It is expected to find this pronounced behavior only for compound **3**, as in here a distortion of the ligand field at one metal atom has the largest influence on the rest of the iron(II) centers.

Mössbauer spectroscopy was performed on a freshly prepared crystalline sample of **1** to gain insight into the nature of the local spin states of the single iron atom in the dimer complex. Spectra were recorded at 293 K and at 100 K. At high temperature, only a single doublet with an isomer shift (IS) of 0.9393(58) mm s^{-1} and a quadrupole splitting Δ (QS) of 2.128(12) mm s^{-1} was found (see Supporting Information). This indicates that both Fe^{II} ions are in the [HS] state. The crystallinity of the sample causes small texture effects, which lead to an asymmetry of the doublet. The spectrum at 100 K differs significantly (Figure 4). Again a doublet refers to the [HS] state [IS = 1.0811(55) mm s^{-1}, QS = 2.080(11) mm s^{-1}]. Additionally, however, a second signal with an IS of 0.4862(52) mm s^{-1} and a small QS of 0.1907(86) mm s^{-1} is present, which clearly can be assigned to an Fe^{II} [LS] species. Relative areas of the signals reveal a ratio of 48.7 % [LS] to 51.3 % [HS]. This proves that the decrement of the magnetic susceptibility is caused from a spin transition. Looking at the crystal structure at 100 K, it is clear that this ratio is a result of a molecule incorporating the [HS] and the [LS] state rather than a 1:1 mixture of [HS-HS] and [LS-LS] molecules.

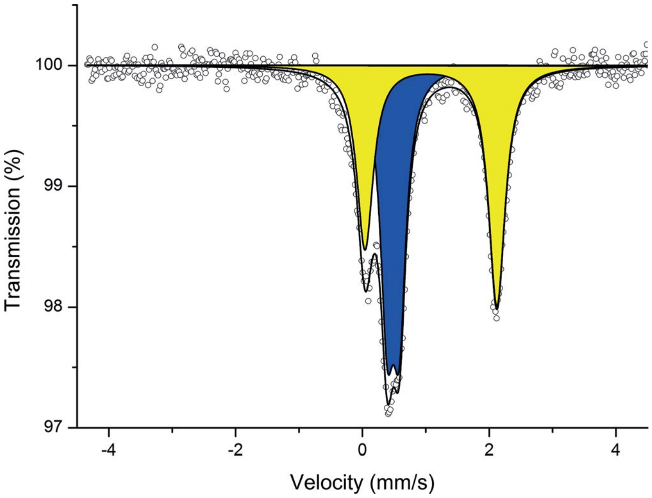

Figure 4. Mössbauer spectra of compound **1** at 100 K. The open circles are the experimental data, the black solid line shows the fit, the blue area is [LS] fraction, the yellow the [HS] fraction.

The comparable values for **3** are found to be IS = 1.0834(49) mm s^{-1}, QS = 2.4904(98) mm s^{-1} for the Fe^{II} [HS] site and IS = 0.4957(88) mm s^{-1} and QS = 0.229(11) mm s^{-1} for the Fe^{II} [LS] site at 100 K.

Conclusions

We prepared and characterized the novel bis-tridentate oxadiazole bridging ligand **L** and used it for the reaction with different iron(II) salts. At room temperature, iron(II) centers of three dinuclear compounds are in the HS state, demonstrated by magnetic susceptibility, Mössbauer spectroscopy, single-crystal X-ray diffraction and the absence of color of the crystal.

With lowering of the temperature, two out of three iron(II)–oxadiazole based complexes show SCO. The color change upon cooling was the first indication for SCO. Magnetic susceptibility studies revealed a magnetic moment that originates from a mixture of an iron(II) [HS] and [LS] species at low temperature. Mössbauer spectroscopy confirmed the presence of both states. Finally, X-ray diffraction ruled out a statistic iron(II) [HS-HS] and [LS-LS] mixture, but proved a distinct [HS-LS] state due to the clear differences in bond lengths, angles and octahedral distortion parameters. Furthermore, one of the compounds shows a sharp hysteresis of 26 K, which is explained by the intermolecular hydrogen bonds that lead to a large cooperativity.

Experimental Section

General Methods and Materials: All chemicals were purchased from Alfa Aesar, Deutero, Fisher Chemicals, Sigma–Aldrich and Acros Organics and used without further purification. NMR spectra were recorded at room temperature by using a Bruker DRX 400 spectrometer and analyzed with the program MestReNova.[17] Magnetic susceptibility data was collected with a Quantum Design SQUID magnetometer MPMSXL in a temperature range of 10–300 K with an applied field of 10 kOe. ^{57}Fe Mössbauer spectra were recorded at the Johannes Gutenberg University Mainz by Dr. Vadim Ksenofontov and Sergii Shylin. ESI mass spectra, FD mass spectra and elemental analyses (C, H, N, and S) were measured at the microanalytical laboratories of the Johannes Gutenberg University Mainz. X-ray diffraction data were collected at 100 and 193 K with a Bruker SMART and a STOE IPDS 2T diffractometer, respectively, at the Johannes Gutenberg University Mainz. The structures were solved with ShelXT and refined with ShelXL 2013 with the program Olex2.[18] CCDC 1434701 (for **1**·4MeCN, 100 K), 1434702 (for **1**·4MeCN, 193 K), 1434703 (for **2**·2MeCN, 100 K), and 1434704 (for **3**·2MeCN, 193 K) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre. ***Caution!*** The prepared perchlorate complexes are potentially explosive; even though no explosions occurred, only small amounts should be prepared and handled with care.

Ligand Synthesis: 1,2-Bis(chloroacetyl)hydrazine and 2,5-Bis-(chloromethyl)-1,3,4-oxadiazole were prepared as described in the literature,[13] 2,5-bis[(2-pyridylmethyl)amino]methyl-1,3,4-oxadiazol was synthesized according to a modified version of the analogous 1,3,4-thiadiazole ligand.[11]

2,5-Bis{[(2-pyridylmethyl)amino]methyl}-1,3,4-oxadiazol (L): 2-(Aminomethyl)pyridine (3.244 g, 30.00 mmol) and potassium carbonate (6.910 g, 50.00 mmol) were suspended in acetonitrile (600 mL) and heated to 70 °C. A solution of 2,5-bis(chloromethyl)-1,3,4-oxadiazole (1.670 g, 10.00 mmol) in acetonitrile (100 mL) was added dropwise over a period of 30 min. After complete addition, the suspension was stirred and refluxed for additional 16 h. After cooling to room temperature, the white precipitate was filtered and the solvent removed under reduced pressure. The resulting brown oil was purified by column chromatography (aluminium oxide; chloroform/methanol, 9:1) to give the pure product as orange oil. Yield: 1.831 g (5.9 mmol, 59 %) ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 8.54$ (d, $J = 4.1$ Hz, 2 H, *H5*Py), 7.63 (td, $J = 7.7$, 1.7 Hz, 2 H, *H4*Py), 7.28 (d, $J = 7.8$ Hz, 2 H, *H2*Py), 7.16 (dd, $J = 6.5$, 5.1 Hz, 2 H, *H3*Py), 4.06 (s, 4 H, ODA-C*H*$_2$), 3.97 (s, 4 H, C*H*$_2$-Py), 2.50 (s, 2 H, N*H*) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): $\delta = 165.73$ (*C*, ODA), 158.55 (*C1*-Py), 149.55 (*C5*-Py), 136.71 (*C4*-Py), 122.57 (*C2*-Py), 122.37 (*C3*-Py), 54.20 (Py-*C*H$_2$), 43.37 (CH_2-ODA) ppm. FD-MS ($CHCl_3$): m/z (%) = 309.25 (11.13) [**L** – H^+], 310.26 (17.71) [**L**], 311.26 (100) [**L** + H^+], 312.23 (16.73) [**L** + 2 H^+].

$[Fe_2(\mu\text{-}L)_2](ClO_4)_4\cdot 4MeCN$ (1): A solution of **L** (0.10 mmol, 31 mg) in acetonitrile (4 mL) was added to a solution of $Fe(ClO_4)_4\cdot xH_2O$ (0.10 mmol, 25 mg) in acetonitrile (3 mL). An immediate color change from yellow to brown was observed. After a few hours, single crystals suitable for single-crystal X-ray diffraction could be obtained. Yield: 45 mg (0.034 mmol, 34 %). $C_{32}H_{38}Cl_4Fe_2N_{12}O_{19}$ {$[Fe_2(\mu\text{-}\mathbf{L})_2](ClO_4)_4\cdot H_2O$} (1145.98): calcd. C 33.47, H 3.34, N 16.64; found C 33.22, H 3.00, N 14.72.

$[Fe_2(\mu\text{-}L)_2](BF_4)_4\cdot 2MeCN$ (2): A solution of **L** (0.10 mmol, 31 mg) in acetonitrile (4 mL) was added to a solution of $Fe(BF_4)_4\cdot 6H_2O$ (0.10 mmol, 34 mg) in acetonitrile (3 mL). An immediate color change from yellow to brown was observed. Using vapor diffusion with diethyl ether, crystals suitable for single-crystal X-ray diffraction could be obtained after 24 h. Yield: 19 mg (0.016 mmol, 17 %). $C_{35}H_{40.5}B_4F_{16}Fe_2N_{13.5}O_2$ {$[Fe_2(\mu\text{-}\mathbf{L})_2](BF_4)_4\cdot 1.5MeCN$} (1141.19): calcd. C 36.84, H 3.58, N 16.57; found C 36.80, H 3.64, N 16.86.

$[Fe_2(\mu\text{-}L)_2](CF_3SO_3)_4\cdot 2MeCN$ (3): A solution of **L** (0.20 mmol, 62 mg) in acetonitrile (4 mL) was added to a solution of $Fe(CF_3SO_3)_4\cdot 6H_2O$ (0.20 mmol, 71 mg) in acetonitrile (5 mL). An immediate color change from yellow to brown was observed. After addition of tetrahydrofuran (4 mL), crystals suitable for single-crystal X-ray diffraction could be obtained after several hours. Yield: 41 mg (0.029 mmol, 14.5 %). $C_{40}H_{42}F_{12}Fe_2N_{14}O_{14}S_4$ {$[Fe_2(\mu\text{-}\mathbf{L})_2](CF_3SO_3)_4\cdot 2MeCN$} (1410.78): calcd. C 34.06, H 3.00, N 13.90, S 9.09; found C 33.91, H 3.17, N 14.09, S 9.16.

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Keywords: Spin crossover · Magnetic properties · 1,3,4-Oxadiazole · Hysteresis · Iron

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