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**Synthesis and Characterisation of a new Schiff-Base like
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Synthesis and Characterisation of a new Schiff-Base like Ligand and it's Iron(II) Complexes**Birgit Weber*, Jaroslava Obel****Keywords:** Iron; Magnetic properties; Schiff base; Hydrogen Bonds

ABSTRACT

The reaction of iron(II) acetate with the tetradentate Schiff base like ligand H₂L ((E,E)-[{diethyl 2,2'-[4,5-dihydroxy-1,2-phenylenebis-(iminomethylidene)]bis[3-oxobutanato}}]) leads to the formation of the octahedral N₂O₄ coordinated complex [FeL(MeOH)₂]·MeOH (**1**). Conversion of **1** with N-meim leads to the N₄O₂ coordinated complex [FeL(N-meim)₂]·MeOH (**2**). Both complexes are pure HS compounds that were characterised using magnetic measurements and X-ray crystallography. A special attention was given to the role of the two hydroxyl groups at the phenyl ring on the formation of a hydrogen bond network and the influence of this network on the magnetic properties.

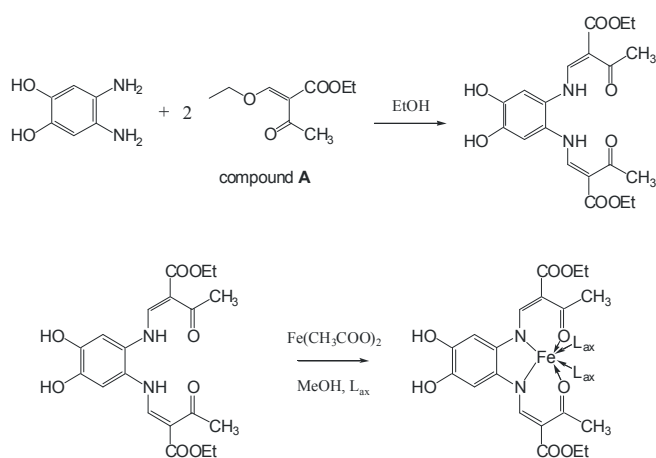
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Introduction

The bistability of spin transition complexes (spin crossover, SCO) is one of the most promising for new electronic devices in molecular memories and switches as it may be controlled by different physical perturbations as temperature, pressure or light.^[1, 2] Of the possible types of spin transition (gradual, abrupt, with hysteresis, step wise, incomplete), much of the interest is focused on the bistability in highly cooperative systems (hysteresis or memory effect) as such compounds can exist in two different electronic states depending on the history of the system. With regard to this we recently characterised an iron(II) spin crossover complex with a 70 K wide thermal hysteresis loop around room temperature based on a 2D network of hydrogen bonds between the complex molecules.^[3] Systematic investigations on the magnetic properties of iron(II) complexes of this ligand systems demonstrated that hydrogen bonds are also the foundation for long range magnetic ordering.^[4] As consequence of this finding we designed a new ligand based on 4,5-diaminocatechol with two additional hydroxyl groups at the phenyl ring that can act as H-bond donors/acceptors. In Scheme 1 the general procedure for the synthesis of the new ligand and its iron(II) complexes is given. In this paper we present the synthesis and characterisation of two octahedral iron(II) complexes of H₂L with methanol and N-methylimidazole (N-meim) as axial ligand.



Scheme 1. General procedure for the synthesis of the new ligand H₂L and its iron(II) complexes with L_{ax} = MeOH or N-meim (N-methylimidazole).

Results and Discussion

Starting point for the synthesis of the new ligand H₂L is 4,5-diaminocatechol that was prepared as described previously by Rosa *et al.*^[5] starting with the commercially available veratrol. Condensation with two equivalents of the keto-enol-ether (compound A^[6]) results in the formation of the desired ligand that was characterised by elemental analysis, IR, mass and NMR spectroscopy. In Figure 1 the

¹H NMR spectrum of H₂L is given with the signal assignment at the left. Conversion of the ligand with 1.3 equivalents iron(II) acetate in methanol gives the iron(II) complex [FeL(MeOH)₂] \cdot MeOH (**1**). The corresponding N-meim diadduct [FeL(N-meim)₂] \cdot MeOH (**2**) is obtained by dissolving **1** in a N-meim/MeOH mixture followed by slow crystallisation. Both complexes were fully characterised by elemental analysis, IR and mass spectroscopy as well as *T*-dependent magnetic measurements and X-ray crystallography.

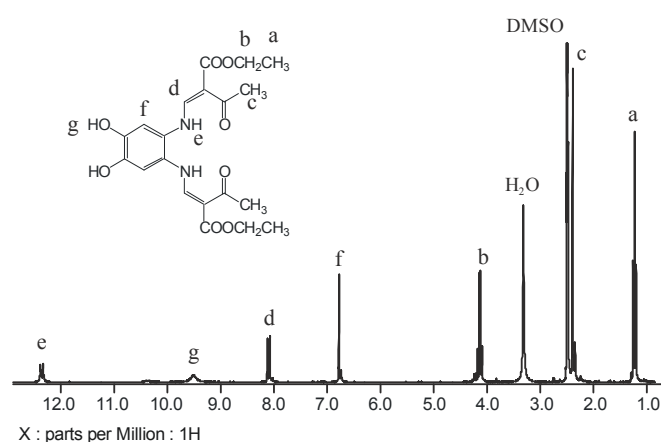


Figure 1. ¹H NMR spectrum of H₂L with the signal assignment given at the left.

Description of the X-ray structures

Crystals suitable for X-ray structure analysis were obtained for both complexes. The crystallographic data are summarized in Table 1. Figures 2 and 3 display an ORTEP drawing of the asymmetric units of the two complexes. Selected bond lengths and angles within the first coordination sphere are summarized in Table 2. In both cases an additional methanol molecule is included in the crystal packing.

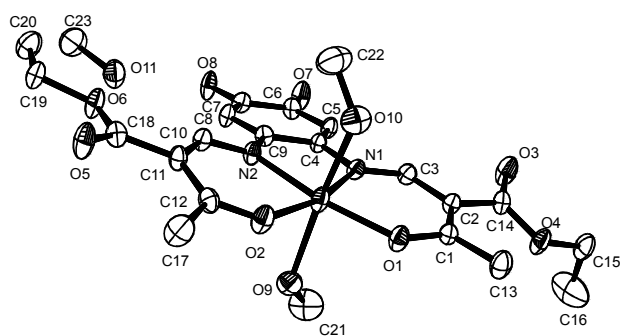


Figure 2. ORTEP drawing of the asymmetric unit of **1**. Hydrogen atoms were omitted for clarity. Thermal ellipsoids are shown at the 50% probability level.

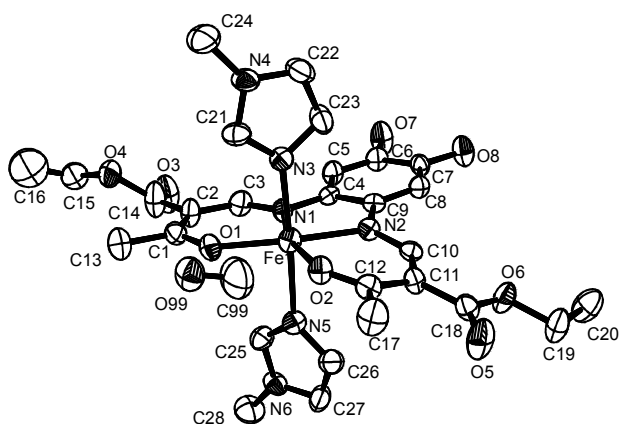


Figure 3. ORTEP drawing of the asymmetric unit of **2**. Hydrogen atoms were omitted for clarity. Thermal ellipsoids are shown at the 50% probability level.

In both complexes the iron centre is located in a distorted octahedral coordination sphere with a N_2O_4 surrounding in the case of **1** and a N_4O_2 surrounding in the case of **2**. The bond lengths and angles within the first coordination sphere are within the region reported for HS iron(II) complexes of the same ligand type.^[7] The average bond lengths are 2.09 Å (Fe- N_{eq}), 2.02 Å (Fe- O_{eq}) and 2.24 Å (Fe- L_{ax}). A characteristic tool for the determination of the spin state of this type of iron(II) complexes is the O-Fe-O angle that changes from about 110° in the HS state to about 90° in the LS state.^[8] For the complexes reported here, the angle is with 109° clearly in the region typical for the HS state. The bond lengths within the FeOCCCN chelate six ring cannot be assigned to single and double bonds indicating the delocalisation of the negative charge of the ligand over the chelate six ring. The average values are 1.27 Å, 1.42 Å, 1.43 Å, 1.31 Å (O-C, C-C, C-C, and C-N; respectively).

Table 1. Crystallographic data of the iron complexes discussed in this work.

Complex	1	2
empirical formula	C ₂₃ H ₃₄ FeN ₂ O ₁₁	C ₂₉ H ₃₈ FeN ₆ O ₉
formula weight	570.37	670.492
temperature /K	200(3)	200(3)
crystal size /mm	0.37×0.22×0.16	0.23×0.18×0.15
crystal system	triclinic	triclinic
space group	P -1	P -1
λ / Å	0.71069	0.71073
a / Å	9.984(3)	9.715(6)
b / Å	10.495(5)	11.754(7)
c / Å	14.100(6)	15.016(15)
α /°	76.07(4)	100.93(7)
β /°	69.42(3)	97.62(6)
γ /°	71.47(3)	91.81(5)
V / Å ³	1297.5(9)	1666(2)
Z	2	2
ρ_{calc} /g/cm ³	1.460	1.337
μ /mm ⁻¹	0.643	0.511
$F(000)$	600	704
Θ range /°	3.92 – 26.11	3.73-24.21
index ranges	-12 – 12	-11 – 11
	-12 – 12	-13 – 13
	-17 – 17	-17 – 17
reflections collected	21612	19832
reflections unique	5027	5163
Data/restraints/parameters	5027/0/351	5163/0/436
$R1$ (all)	0.0377 (0.0614)	0.0464 (0.0988)
$wR2$	0.0931 (0.1053)	0.0933 (0.1127)
$Goof$	1.008	0.946

Table 2. Selected bond lengths [\AA] and angles [degree] within the first coordination sphere of the iron complexes discussed in this work.

	Fe-N _{eq}	Fe-O _{eq}	Fe-L _{ax}	O1-Fe-O2	L _{ax} -Fe-L _{ax}
1	2.076(2), 2.091(2)	1.996(2), 2.009(2)	2.229(2), 2.237(2)	108.77(7)	168.83(7)
2	2.101(3), 2.108(3)	2.025(3), 2.050(3)	2.208(4), 2.276(4)	109.3(1)	176.6(1)

For a better understanding of the magnetic properties it is necessary to investigate the hydrogen bond network in the crystal packing. Previous investigations on this substance class did demonstrate that H-bonds influence the strength of cooperative interactions in spin transition complexes^[3] or can introduce long range magnetic ordering.^[4] With regard to this it is interesting to observe how the two additional hydroxyl groups introduced in H₂L influence the H-bond network. In Table 3 selected intermolecular distances of the complexes discussed in this work are summarized. In Figures 4 and 5 the packing of the two complexes in the crystal is displayed.

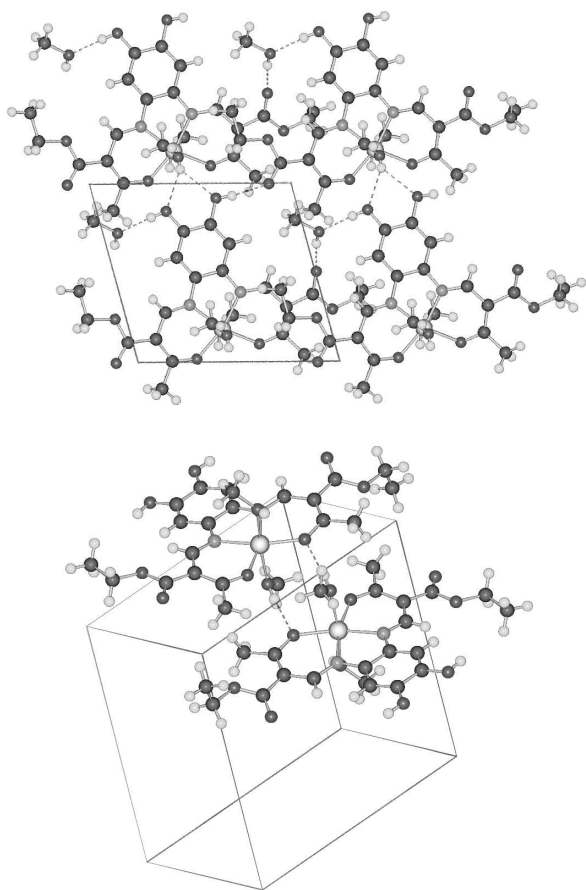
In the case of the methanol diadduct **1** the numbers of intermolecular hydrogen bonds were increased by the introduction of the hydroxyl groups. Indeed, instead of the extended 1D chain structure observed for the parent compound with no hydroxyl groups at the phenyl ring a 2D-network of linked molecules is obtained.^[4a] The two hydroxyl groups are involved in this network both as H-bond donors and acceptors participating in 4 of the 6 contacts. One of the two donor contacts (H7A) links directly two complex molecules over the OCOEt group (O5) of the neighbouring molecule. The second HO group (H8A) forms a hydrogen bond to the HO-oxygen (O11) of the additional methanol molecule included in the crystal packing. A further hydrogen bond from the HO hydrogen (H11) to the second OCOEt group (O3) leads to the next contact between two neighbouring molecules. The two oxygens O7 and O8 of the two hydroxyl groups serve as H-bond acceptors for one and the same hydrogen atom, namely H10A of one of the coordinated methanol molecules. The last hydrogen bond between the hydroxyl hydrogen of the second coordinated methanol molecule (H9) and one of the coordinated carbonyl groups of the equatorial ligand (O1) links two neighbouring molecules into a dimer unit with a very short intermolecular iron-iron distance of 5.18 \AA that is depicted at the bottom of Figure 4.

Table 3. Selected intermolecular distances [\AA] of the complexes discussed in this work resulting in an infinite 2D hydrogen bond network with the base vectors: $[0\ 1\ 0]$ and $[1\ 0\ 0]$, along the plane: $(0\ 0\ 1)$ for both compounds.

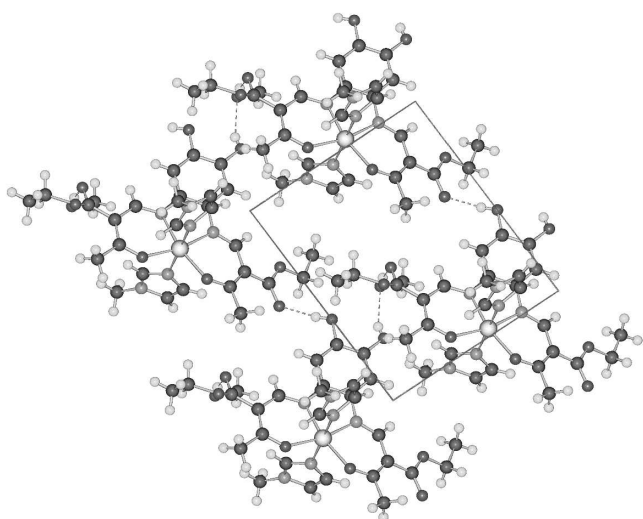
1	D-H	H \cdots A	A \cdots D	D-H \cdots A
O(7)-H(7A) \cdots O(5) ^[a]	0.82	1.97	2.775	169
O(8)-H(8A) \cdots O(11) ^[b]	0.82	1.89	2.701	171
O(9)-H(9) \cdots O(1) ^[c]	0.80	1.96	2.754	174
O(10)-H(10A) \cdots O(7) ^[d]	0.64	2.52	3.029	139
O(10)-H(10A) \cdots O(8) ^[d]	0.64	2.40	2.987	153
O(11)-H(11) \cdots O(3) ^[e]	0.82	1.91	2.726	170
C(8)-H(8) \cdots O(11) ^[b]	0.93	2.55	3.241	131
2	D-H	H \cdots A	A \cdots D	D-H \cdots A
O(7)-H(7) \cdots O(5) ^[f]	0.80	1.86	2.649	172
O(8)-H(8) \cdots O(99)	0.69	2.17	2.801	153
O(99)-H(99) \cdots O(3) ^[d]	0.86	1.94	2.786	166
C(19)-H(19) \cdots O(7) ^[g]	0.97	2.49	3.301	141
C(24)-H(24A) \cdots O(2) ^[h]	0.96	2.58	3.488	159
C(25)-H(25) \cdots O(8) ^[i]	0.93	2.57	3.355	142
C(28)-H(28B) \cdots O(8) ^[i]	0.96	2.46	3.372	158

[a] $-1+x, 1+y, z$; [b] $1-x, -y, 1-z$; [c] $2-x, 1-y, -z$; [d] $1+x, y, z$; [e] $1-x, 1-y, 1-z$; [f] $x, 1+y, z$; [g] $x, -1+y, z$; [h] $1-x, -y, 1-z$ [i] $-1+x, y, z$.

For compound 2 three different classical hydrogen bonds are observed. The one between the hydroxyl hydrogen H7 and the carboxyl oxygen O5 directly links two neighbouring molecules, while the second contact between two neighbouring molecules is mediated over the methanol molecule included in the crystal, similar to compound 1. Additionally some non-classical H-bonds are observed for this complex. As for 1 the number H-bonds did increase compared to the parent compound with no hydroxyl groups (from 0 to 3), as does consequently the dimension of the network.^[7b]



33 Figure 4. Top: Packing of compound 1 in the crystal; view along [0 0 1], bottom: view of the H-bond
34 linked dimer unit.
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56 Figure 5. Packing of compound 2 in the crystal; view along [0 0 1].
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Magnetic properties

Magnetic susceptibility measurements for both compounds were performed in the temperature range from 300 to 2 K. The plots of the reciprocal molar susceptibility ($1/\chi_M$) and the $\chi_M T$ product versus T are given in Figure 6 for both compounds. For compound **2** (top of Figure 6) nearly ideal Curie behaviour is observed. Upon cooling, the $\chi_M T$ product decreases from a value of $3.45 \text{ cm}^3 \text{ K mol}^{-1}$ at 295 K to a value of $2.89 \text{ cm}^3 \text{ K mol}^{-1}$ at 20 K. The susceptibility data above 20 K can be fitted very well with the Curie-Weiss law ($\chi_M = C/(T - \Theta)$) with the parameters $\Theta = -7.5 \text{ K}$ and $C = 3.50 \text{ cm}^3 \text{ K mol}^{-1}$. The Curie constant C is in a region expected for iron(II) HS complexes and the negative Weiss constant Θ in combination with the temperature-dependent decrease of the $\chi_M T$ product is an indication for weak antiferromagnetic interactions between the spin centres. For compound **1** the situation is more complex. Upon cooling, the $\chi_M T$ product decreases from a value of $3.32 \text{ cm}^3 \text{ K mol}^{-1}$ at 300 K to a value of $1.33 \text{ cm}^3 \text{ K mol}^{-1}$ at 20 K. The room temperature value is in the region typical for an iron(II) HS complex. The temperature-dependent decrease of the $\chi_M T$ product is an indication for significantly stronger antiferromagnetic interactions compared to **2**. As a consequence, the fitting of the susceptibility data using the Curie-Weiss law does not give reliable parameters. A possible explanation for the observed behaviour is antiferromagnetic interactions within the described dimer unit mediated over the hydrogen bonds. However, attempts to fit the data assuming the formula given in [9] for the magnetic interactions in a $S_1 = 2$ and $S_2 = 2$ spin system with $H = -J S_1 \cdot S_2$, were not successful (dashed line). Most likely two or more different exchange pathways give rise to the observed curve progression.

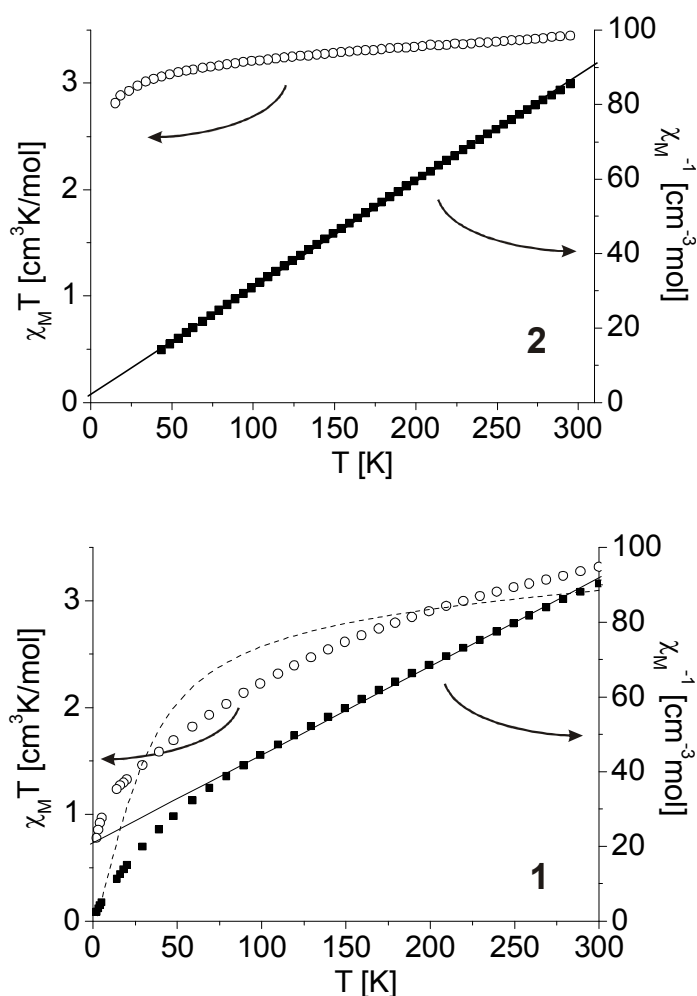


Figure 6. Reciprocal molar susceptibility, χ_M^{-1} (squares) and $\chi_M T$ product (open circles), as function of temperature T and the fits according to the Curie Weiss law, $\chi_M = C/(T - \Theta)$, with the parameters $\Theta = -88.4$ K, $C = 4.23$ cm³ K mol⁻¹ for compound 1 and $\Theta = -7.5$ K, $C = 3.50$ cm³ K mol⁻¹ for compound 2 (solid line).

Conclusions

In this paper the synthesis and characterisation of a new Schiff-base like ligand and its iron(II) complexes is presented. The influence of the two hydroxyl groups at the phenyl ring on the formation of a hydrogen bond network and the magnetic properties of the iron complexes is discussed. As attempted, the number of H-bonds as well as the dimension of the formed H-bond network was increased for both complexes compared to the analogue compounds with no hydroxyl groups at the phenyl ring. For compound **2** with N-meim as axial ligand the magnetic properties are similar to that of the analogue complex, both showing nearly ideal Curie behaviour. As no spin transition takes place no statements can be made about the influence of the H-bond network in **2** on cooperative interactions. In the case of **1**

the magnetic properties significantly differ from those of the hydroxyl group free complex. This can be explained with differences in the H-bond network.

Experimental Section

Synthesis

All syntheses were carried out under argon using Schlenk tube techniques. All solvents were purified as described in the literature^[10] and distilled under argon. The synthesis of 4,5-diaminocatechol^[4], compound A^[5] and iron(II)acetate^[11] is described in literature.

H₂L: 0.01 mol (3.02 g) 4,5-diaminocatechol dihydrobromide and 0.02 mol (1.08 g) sodium methanolate were dissolved in 100 mL methanol. 0.02 mol (3.72 g) of compound A were given to the solution in one portion. The solution was stirred for 16 h at room temperature. After this time the precipitate was filtered off, recrystallised from ethanol and dried in vacuum. Yield: 2.1 g (50 %). C₂₀H₂₄N₂O₈ (420.41): C 56.70 (calc. 57.14); H 5.74 (5.75); N 6.55 (6.66). IR (Nujol) $\tilde{\nu}$ (C=O, COOEt) = 1704 cm⁻¹, $\tilde{\nu}$ (C=O, COMe) = 1680, 1665 cm⁻¹, $\tilde{\nu}$ (OH) = 3400 cm⁻¹(broad). MS (DEI): 420 m/z (H₂L⁺, 75%), 375 m/z (H₂L⁺-OEt, 25%). ¹H-NMR (270 MHz, DMSO-d₆, ppm) δ = 1.21 (m, 6H, CH₂-CH₃), 2.49 (s, 6H, CO-CH₃), 4.10 (m, 4H, CH₂-CH₃), 6.73 (s, 2H, CH-Aromat), 8.08 (d, 2H, CH=C), 9.5 (s, 2H, OH), 12.35 (d, 4H, NH₂).

[FeL(MeOH)₂](MeOH) (**1**): A suspension of 6.1 mmol (1.07 g) iron(II)acetate and 4.7 mmol (1.99 g) H₂L were heated to reflux for one hour in 80 mL methanol until a clear solution was obtained. After cooling black crystals of **1** were obtained that were collected and dried in vacuum. Yield: 1.65 g (61%). C₂₃H₃₄N₂O₁₁Fe (570.37): C 47.81 (calc. 48.43); H 5.72 (6.01); N 4.79 (4.91). IR (Nujol) $\tilde{\nu}$ (C=O, COOEt) = 1704 cm⁻¹, $\tilde{\nu}$ (C=O, COMe) = 1630 cm⁻¹, $\tilde{\nu}$ (OH) = 3250 cm⁻¹(broad). MS (FAB+): Basis peak: 473 m/z ([FeL]⁺, 100%), 429 m/z ([FeL-OEt]⁺, 50%).

[FeL(N-meim)₂](MeOH) (**2**): 1.01 mmol (0.58 g) [FeL(MeOH)₂](MeOH) (**1**) were dissolved in 15 mL N-meim and were refluxed for one hour. After this time 10 mL MeOH were added. Cooling the mixture to room temperature yielded a fine crystalline black precipitate of **2** that was collected and dried in vacuum. Standing of the remaining solution at 4°C produced single crystals of **2**. Yield: 0.28 g (40 %). C₂₉H₃₈N₆O₉Fe (670.49): C 52.36 (calc. 51.95); H 5.65 (5.71); N 13.35 (12.53). IR (Nujol) $\tilde{\nu}$ (C=O, COOEt) = 1673 cm⁻¹, $\tilde{\nu}$ (C=O, COMe) < 1600 cm⁻¹, $\tilde{\nu}$ (OH) = 3200 cm⁻¹(broad). MS (FAB+): Basis

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2 peak: 83 m/z (N-meim fragment ion, 100%); 474 m/z ($[\text{FeL}]^+$, 55%); 556 m/z ($[\text{FeL}(\text{N-meim})]^+$, 20%);
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4 429 m/z ($[\text{FeL-OEt}]^+$, 20%).
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7 *Magnetic measurements*

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10 Magnetic measurements of the fine crystalline samples were performed on a Quantum-Design-
11 MPMSR2-SQUID-Magnetometer in a temperature range from 2 to 300 K. The measurements were
12 carried out at two field strengths (0.02 and 0.05 T) in the settle mode. The data were corrected for the
13 magnetisation of the sample holder and diamagnetic corrections were made using tabulated Pascals
14 constants.
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18 *X-ray Crystallography*

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21 The intensity data of **1** and **2** were collected on a Oxford XCalibur diffractometer using graphite-
22 monochromated Mo-K α radiation. Data were corrected for Lorentz and polarisation effects. The
23 structure was solved by direct methods (Sir 97^[12]) and refined by full-matrix least-square techniques
24 against F02 (SHELXL-97^[13]). The hydrogen atoms were included at calculated positions with fixed
25 thermal parameters. ORTEP-III was used for structure representation.^[14] Crystallographic data are
26 summarized in Table 1. Selected distances and angles are presented in Table 2. Further details on the
27 crystal structures (CCDC-729385 for **1** and CCDC-729386 for **2**) can be obtained free of charge on
28 application to Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK
29 (Fax: int.code+(1223)336-033; e-mail fileserv@ccdc.cam.ac.uk).
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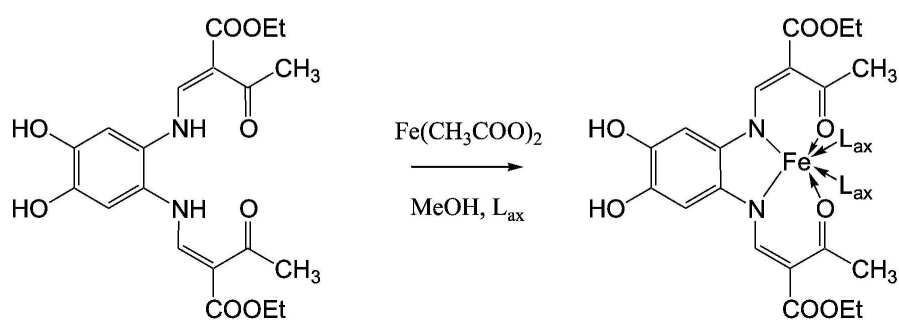
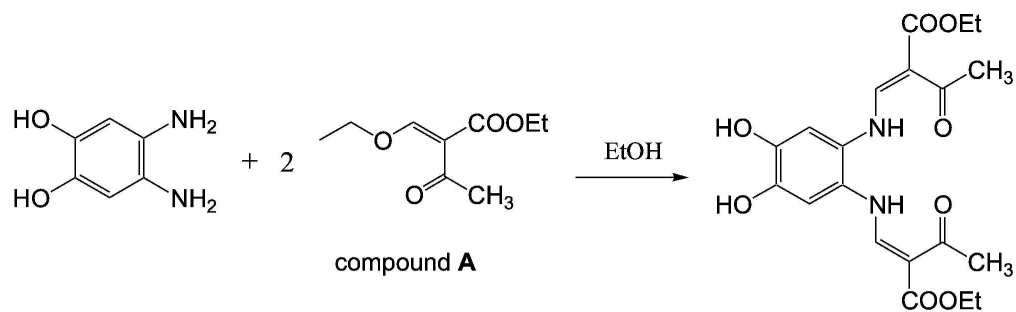
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30 General procedure for the synthesis of the new ligand H₂L and its iron(II) complexes with L_{ax} =
31 MeOH or N-meim (N-methylimidazole).
32 169x116mm (600 x 600 DPI)

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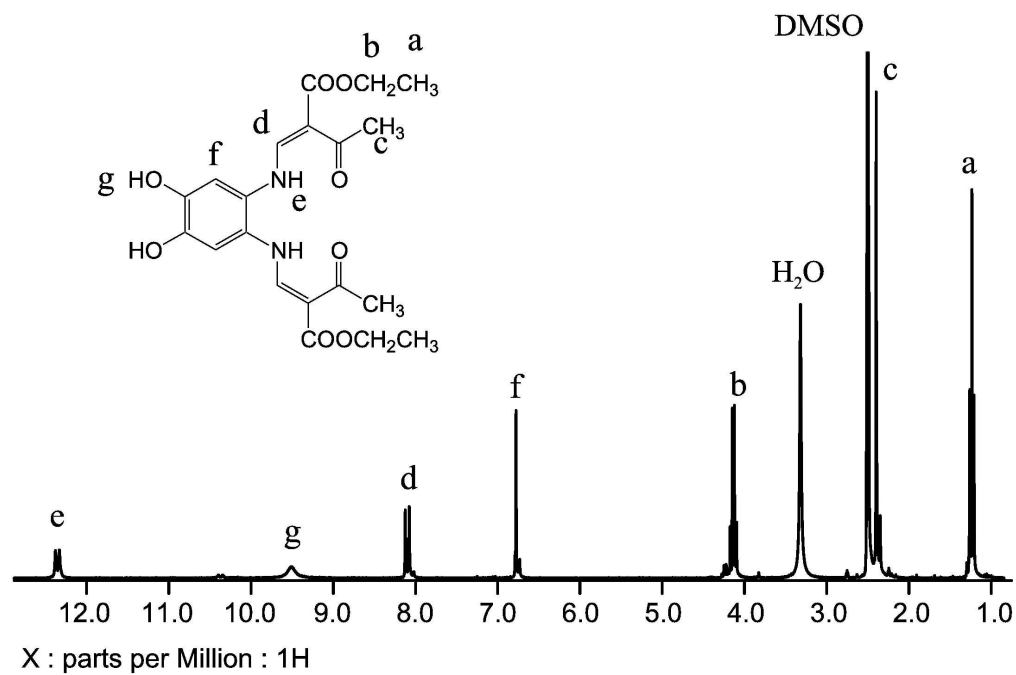


Figure 1. ¹H NMR spectrum of H₂L with the signal assignment given at the left.
183x120mm (600 x 600 DPI)

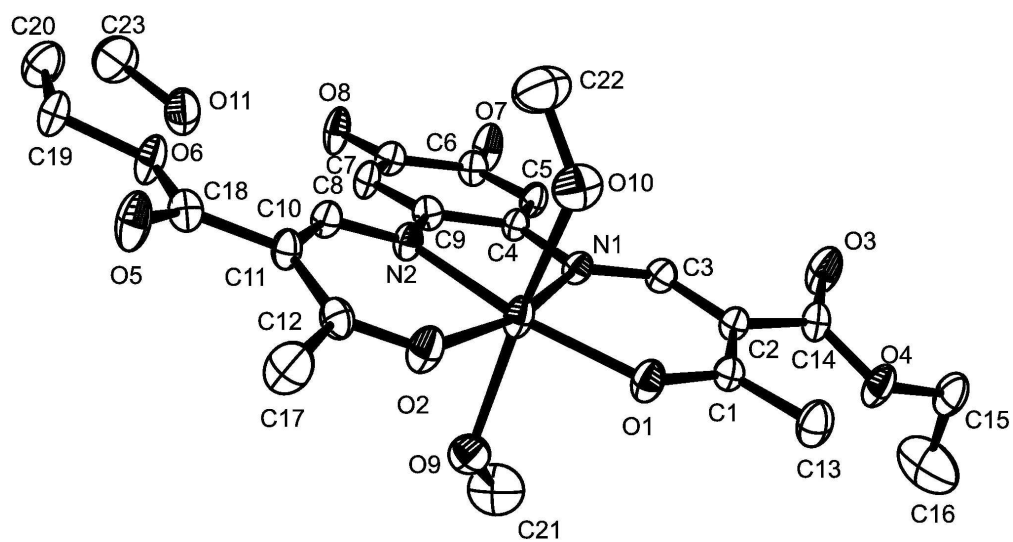


Figure 2. ORTEP drawing of the asymmetric unit of 1. Hydrogen atoms were omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. 171x89mm (600 x 600 DPI)

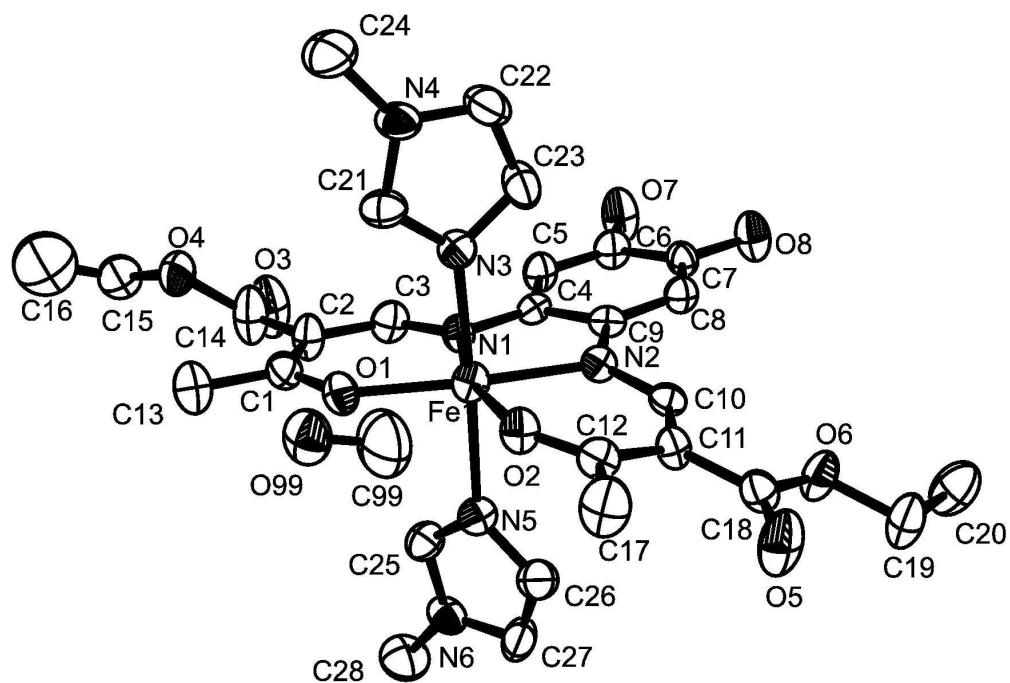


Figure 3. ORTEP drawing of the asymmetric unit of 2. Hydrogen atoms were omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. 147x99mm (600 x 600 DPI)

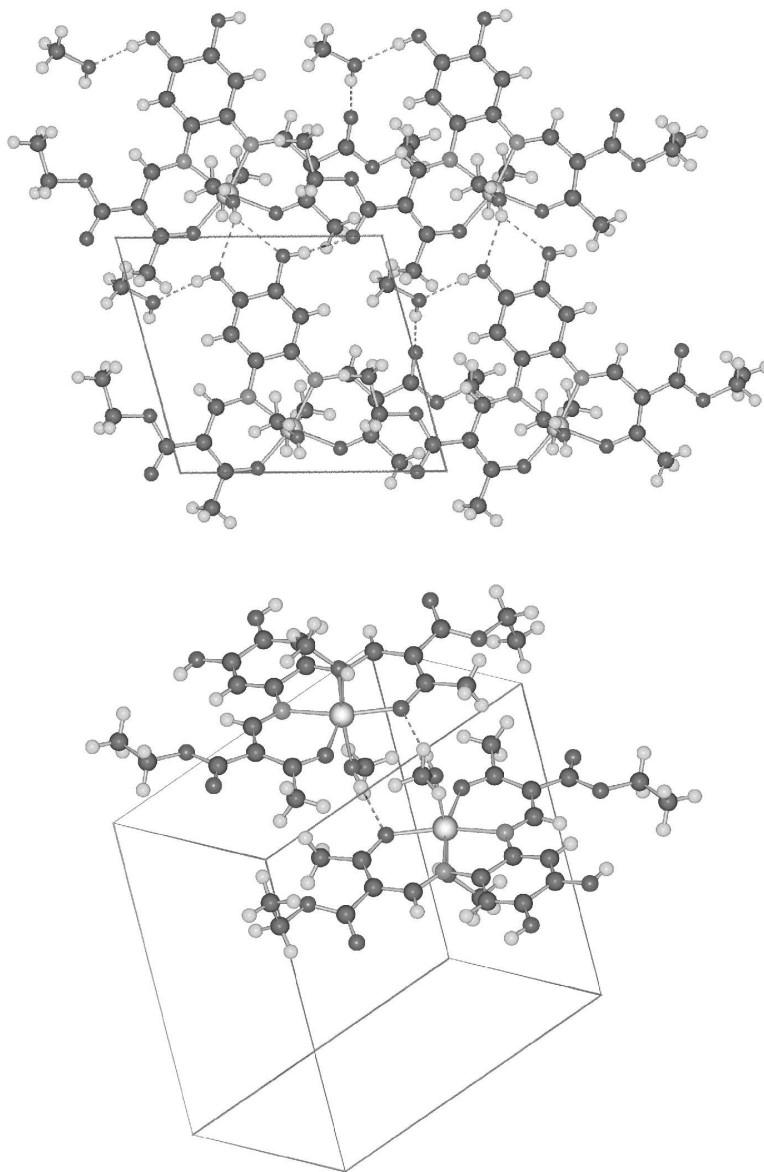


Figure 4. Top: Packing of compound 1 in the crystal; view along [0 0 1], bottom: view of the H-bond linked dimer unit.
196x274mm (600 x 600 DPI)

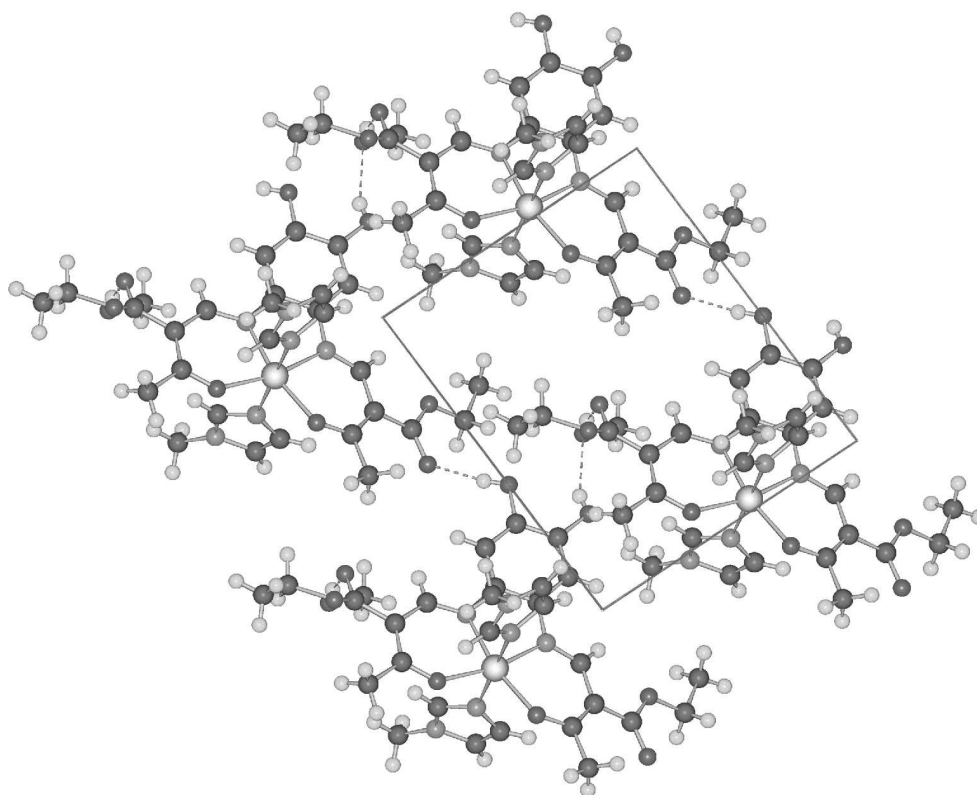


Figure 5. Packing of compound 2 in the crystal; view along [0 0 1].
200x160mm (600 x 600 DPI)

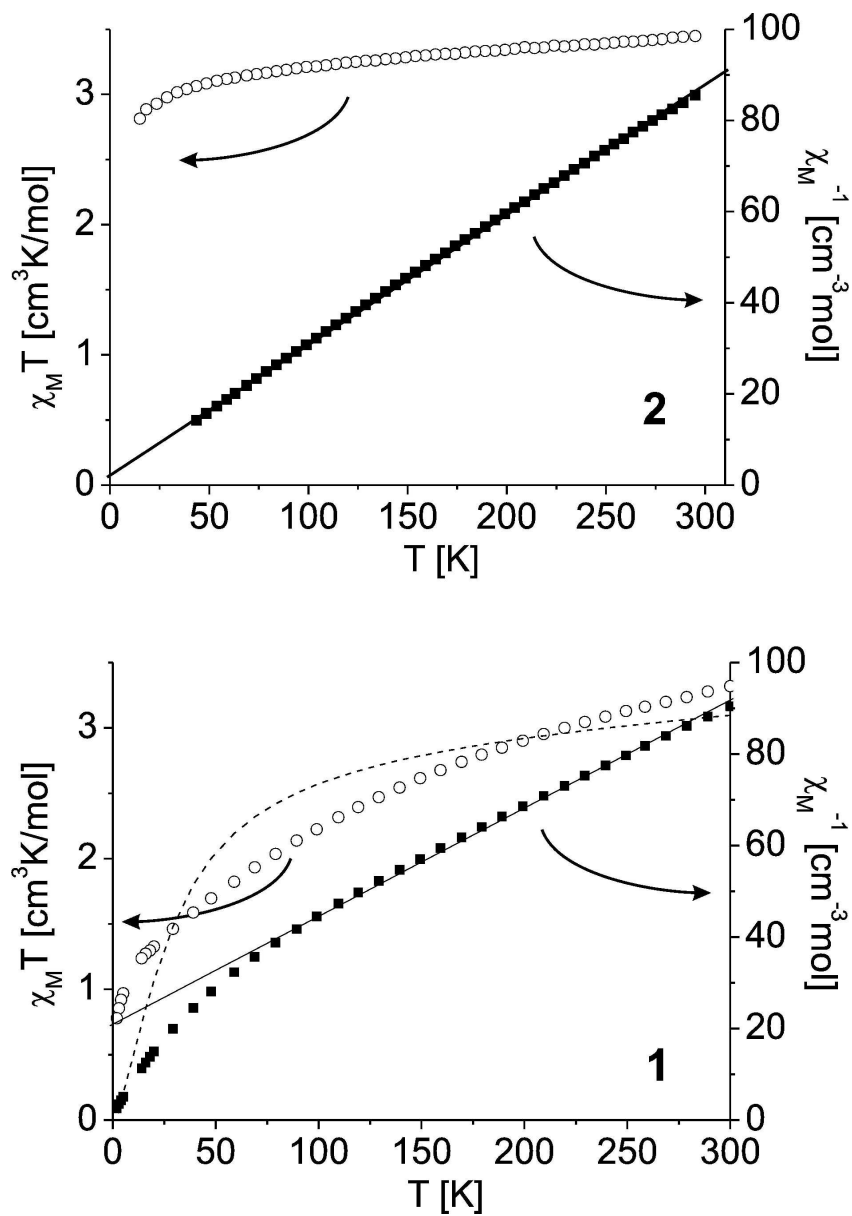


Figure 6. Reciprocal molar susceptibility, χ_M^{-1} (squares) and $\chi_M T$ product (open circles), as function of temperature T and the fits according to the Curie Weiss law, $\chi_M = C/(T - \Theta)$, with the parameters $\Theta = -88.4$ K, $C = 4.23$ cm³ K mol⁻¹ for compound 1 and $\Theta = -7.5$ K, $C = 3.50$ cm³ K mol⁻¹ for compound 2 (solid line).XXXX
160x228mm (600 x 600 DPI)