A Promising New Schiff Base-like Ligand for the Synthesis of Octahedral Iron(II) Spin Crossover Complexes

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Dedicated to Professor Rolf W. Saalfrank on the occasion of his 70th birthday

A new tetradentate Schiff base-like ligand H_2L (**1**) ((*E,E*)-dimethyl-2,2′-[1,2-phenylenebis(aminomethylidyne)]bis[3-oxobutanoate]) was synthesised and structurally characterised. Its reaction with iron(II) acetate leads to the formation of the octahedral N_2O_4-coordinated complex $[FeL(MeOH)_2]$ (**2**). The complex is a pure high-spin (HS) compound as is evident from magnetic measurements and X-ray crystallography.

Key words: Schiff Base-like Ligand, Iron Complexes, Magnetic Properties

Introduction

The bistability of spin transition complexes (spin crossover, SCO) is one of the most promising possibilities for new electronic devices in molecular memories and switches as it may be controlled by different physical perturbations such 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]. In order to more deeply understand the role of hydrogen bonds for cooperative effects in spin crossover systems we designed a new ligand with two ethyl groups substituted by methyl groups – a comparatively small modification that can, however, significantly influence the magnetic properties. 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 the free ligand H_2L and its octahedral iron(II) complex with two methanol molecules as axial ligands. This is the first example of this type of complexes, where we were able to analyse the X-ray structure of both, the free ligand and its iron complex.

Results and Discussion

Synthesis

Scheme 1 gives the general synthetic route to the tetradentate Schiff base-like ligand H_2L (**1**) and its octahedral iron(II) complex $[FeL(MeOH)_2]$ (**2**). The synthesis of the ligand is an adaptation of Claisen [4], who first described the preparation of oxymethylene derivatives and their reaction with amines in the late 19th century, and of Jäger and Wolf [5], who first described the preparation of this type of ligand in the 1960s. The synthesis of H_2L is carried out in two independent steps. At first the methoxymethylene derivative **1a** is directly synthesised by oxymethylation of methyl acetoacetate using trimethyl orthoformate in acetic anhydride. Contrary to literature it is essential to use trimethyl orthoformate instead of triethyl orthoformate, in order to prevent the substitution of the methoxy ester group by an ethoxy ester group. The second step is the condensation of **1a** with 1,2-*ortho*-phenylenediamine (stoichiometric ratio 2 : 1) in methanol as solvent, which gives **1** (H_2L) as a yellow precipitate. The synthesis of the octahedral complex **2** ($[FeL(MeOH)_2]$), where L^{2-}, the deprotonated form of H_2L, acts as an equatorial ligand

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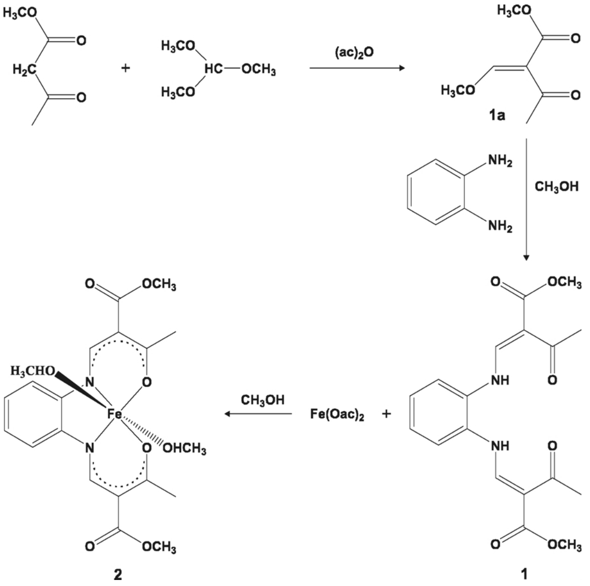


Scheme 1. General route for the synthesis of the Schiff base-like ligand **1** (H_2L) and its octahedral iron(II) complex **2** ($[FeL(MeOH)_2]$).

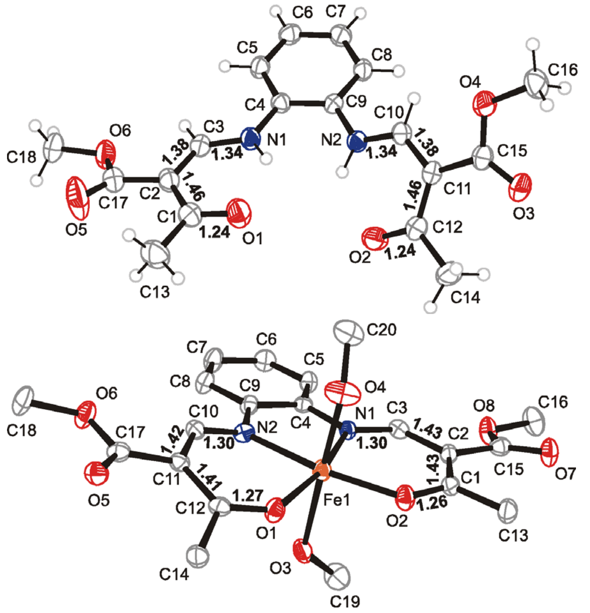


Fig. 1. ORTEP drawing of the asymmetric units of ligand **1** (top) and complex **2** (bottom) with selected bond lengths. For clarity reasons the hydrogen atoms have been omitted for **2**. Displacement ellipsoids are shown at the 50 % probability level.

and the methanol molecules as axial ligands, is carried out in a one-pot reaction by treatment of **1** with a slight excess of anhydrous iron(II) acetate in methanol.

Table 1. Crystal structure data for **1** – **2**.

	1	2
Formula	$C_{18}H_{20}N_2O_6$	$C_{20}H_{26}N_2O_8Fe$
M_r	360.36	478.28
Crystal size, mm^3	0.35 × 0.25 × 0.20	0.36 × 0.20 × 0.15
Crystal system	orthorhombic	monoclinic
Space group	*Pbca*	$P2_1$
λ, Å	0.71073	0.71069
T, K	200(2)	173(2)
a, Å	15.0360(2)	8.9590(6)
b, Å	8.60200(10)	7.4730(5)
c, Å	27.3832(4)	15.840(3)
β, deg	90	92.96(1)
V, Å^3	3541.73(8)	1059.1(2)
Z	8	2
D_{calcd}, g cm^{-3}	1.35	1.50
$\mu(\text{Mo}K_\alpha)$, mm^{-1}	0.1	0.8
θ, deg	3.3 – 25.0	4.3 – 26.4
$F(000)$, e	1520	500
hkl range	$-17 \le h \le +17$ $-10 \le k \le +10$ $-32 \le l \le +32$	$-11 \le h \le +9$ $-6 \le k \le +9$ $-19 \le l \le +18$
Refl. measured	18940	4371
Refl. unique / R_{int}	3124 / 0.0297	3094 / 0.0247
Param. refined	239	286
$R(F)$ / $wR(F^2)^{\text{a}}$ (all refl.)	0.0476 / 0.1199	0.0392 / 0.0603
x(Flack)	–	−0.009(15)
GoF $(F^2)^{\text{b}}$	1.072	0.942
$\Delta\rho_{\text{fin}}$ (max / min), e Å^{-3}	0.28 / −0.27	0.22 / −0.29

[a] $R1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2)+(AP)^2+BP]^{-1}$, where $P = (\text{Max}(F_o^2, 0)+2F_c^2)/3$ and A and B are constants adjusted by the program; [b] $\text{GoF} = S = [\Sigma w(F_o^2 - F_c^2)^2/(n_{\text{obs}} - n_{\text{param}})]^{1/2}$, where n_{obs} is the number of data and n_{param} the number of refined parameters.

Table 2. Selected bond lengths (Å) and angles (deg) of complex **2** with estimated standard deviations in parentheses.

Fe1–O1	2.0113(17)	Fe1–O2	1.9904(19)
Fe1–O3	2.264(2)	Fe1–O4	2.189(2)
Fe1–N1	2.075(2)	Fe1–N2	2.0810(19)
O1–Fe1–O2	105.62(8)	O3–Fe1–O4	174.77(8)

X-Ray structure analysis

Crystals suitable for X-ray analysis of the free equatorial ligand **1** and its iron(II) complex **2** were obtained by slow crystallisation out of the mother liquor. The crystallographic data are summarised in Table 1. Fig. 1 displays the asymmetric units of **1** and **2**, respectively. Selected bond lengths and angles are summarised in Table 2. Compound **1** crystallises with the orthorhombic space group *Pbca*. The unit cell contains 8 formula units. The molecular structure of **1** is non-planar, and thus the N_2O_2 coordination sites are not in a common plane. This is indicated by the two dihedral angles, which are defined by atoms C3–N1–C4–C5 and C10–

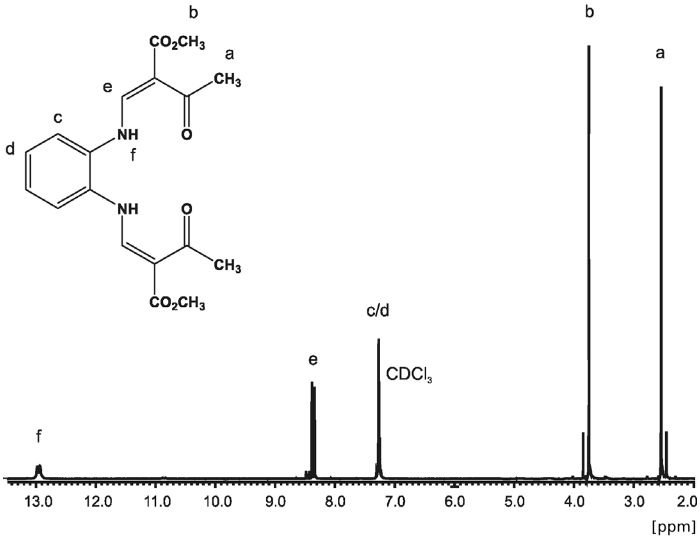
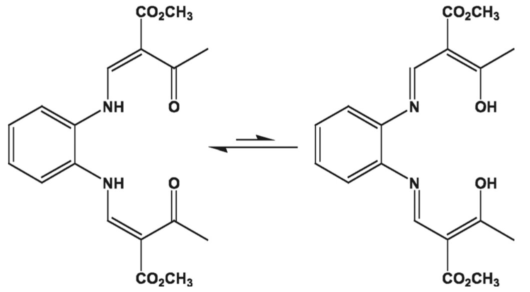


Fig. 2. ^{1}H-NMR spectrum of H_2L with the signal assignment given at the left.



Scheme 2. Possible tautomeric structures of **1**, keto-enamine (left) and enol-imine (right). The equilibrium is shifted to the keto-enamine form.

N2–C9–C8 and display the torsion of the conjugated aminomethylidene chains, which build up the chelate ring, relative to the phenylene ring. Their values are 7.6(3)° and 34.3(2)°. The average bond lengths within the conjugated π-system of the chelate ring [1.34 Å (C-N), 1.38 Å (C=C), 1.46 Å (C–C) and 1.24 Å (C=O)] are in line with literature values for similar single and double bonds. This leads to the result that the equilibrium between the two possible tautomeric structures enol-imine and keto-enamine (see Scheme 2) is shifted to the keto-enamine form, in contrast to classic Schiff base ligands (*e. g.* salen). The ^{1}H-NMR spectrum, pictured in Fig. 2, in which a CH–NH coupling constant in the range of 12 Hz is observed, supports this finding. Between the carbonyl oxygen atoms O1 and O2 of the acetyl groups and the amino groups N1–H1 and N2–H2 intramolecular hydrogen bonds are formed.

Table 3. Bond lengths (Å) and angles (deg) of intermolecular hydrogen bonds of complex **2** with $d(\mathrm{D}\cdots\mathrm{A}) < \mathrm{R(D)} + \mathrm{R(A)} + 0.50$, $d(\mathrm{H}\cdots\mathrm{A}) < \mathrm{R(H)} + \mathrm{R(A)} - 0.12$ Å, $\mathrm{D{-}H}\cdots\mathrm{A} > 100.0°$.

	O3–H31···O5[a]	O4–H41···O5[b]
D–H	0.84	0.84
H···A	1.93	1.92
D···A	2.763(3)	2.758(3)
D–H···A	175	173

[a] Symmetry code: $2-x, -1/2+y, -z$; [b] symmetry code: $2-x, 1/2+y, -z$.

Compound **2** crystallises in the monoclinic space group $P2_1$, with 2 formula units per cell. The bond lengths and angles around the iron atom are within the range reported for octahedral HS iron(II) complexes of the same ligand type with two axial ligands [6, 7]. The average values are 2.08 Å (Fe–N_{eq}), 2.00 Å (Fe–O_{eq}) and 2.23 Å (Fe–O_{ax}). A characteristic tool for the determination of the spin state of this type of iron(II) complexes is the O_{eq}–Fe–O_{eq} angle, which changes from about 110° in the HS state to about 90° in the LS state [6, 7]. With 105.6° compound **2** is clearly in the HS state. The average values of the bond lengths within the conjugated π-system of the chelate ring [1.30 Å (C–N), 1.43 Å (C–C), 1.42 Å (C–C) and 1.26 Å (C–O)] reveal that the negative charge of the deprotonated form of the Schiff base-like ligand L^{2-} is delocalised over the six-membered chelate ring. For the discussion of cooperative interactions or spontaneous magnetic ordering, intermolecular interactions such as hydrogen bonding or π-stacking are thought to play a central role as such contacts are necessary for long-range ordering effects. In complex **2** two different intermolecular hydrogen bonds can be found, which are listed in Table 3,

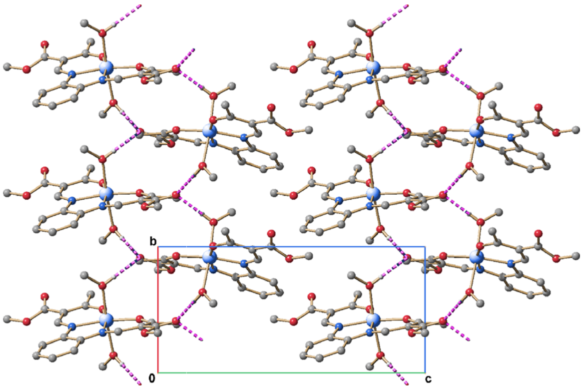


Fig. 3. Crystal structure of the hydrogen-bonded molecules of complex **2** projected along [1 0 0].

leading to an infinite one-dimensional chain with the base vector [0 1 0], as can be seen in Fig. 3. The hydroxyl oxygen atoms of both axial methanol ligands act as hydrogen bond donors. In both cases, an ester carbonyl oxygen atom O5 of the respective neighbouring complex is the acceptor.

Magnetic susceptibility data

The magnetic susceptibility of the iron(II) complex **2** was measured in the temperature range from 300 to 2 K. The plots of $\chi_M T$ and $\chi_M{}^{-1}$ *versus* T (χ_M being the molar susceptibility) are given in Fig. 4. Over the whole temperature range investigated, **2** remains in the paramagnetic high-spin state, with typical $\chi_M T$ values, considering four unpaired electrons ($S = 2$). The $\chi_M T$ product slightly decreases from a value of 3.34 cm^3 Kmol^{-1} at 300 K to 3.29 cm^3 Kmol^{-1} at 110 K, and then again rises to 3.34 cm^3 Kmol^{-1} at 20 K. The decrease of $\chi_M T$ below 20 K is due to zero field splitting. The susceptibility data above 20 K can be fitted with the Curie-Weiss law ($\chi_M = C/(T - \theta)$) with the parameters $\theta = -0.65$ K and $C = 3.33$ cm^3 K^{-1} mol^{-1}. The Curie constant C of the complex is in a region expected for iron(II) complexes in the high-spin state, and the negative Weiss constant θ together with the temperature-dependent decrease of the $\chi_M T$ product above 110 K are indications of weak antiferromagnetic interactions between the spin centres. The increase of the magnetic moment below 110 K is probably due to spin canting as observed previously for similar complexes of this ligand system [8]. A zero field-cooled (ZFCM) and a field-cooled magnetisation (FCM) measurement with $H = 30$ G was performed for compound **2**, and the result is shown at the bottom of Fig. 4. As expected from results of the magnetic susceptibility measurement only very weak indications for long-range magnetic ordering can be found. The FCM measurement exhibits no abrupt increase in the magnetisation (typical for spontaneous magnetic ordering), but only a small slope in the magnetisation curve at about 10 K. This is in line with the ZFCM measurement. However, the spontaneous magnetic ordering is significantly less pronounced compared to other iron(II) complexes of this type with methanol molecules as axial ligands and a Schiff base-like equatorial ligand [8].

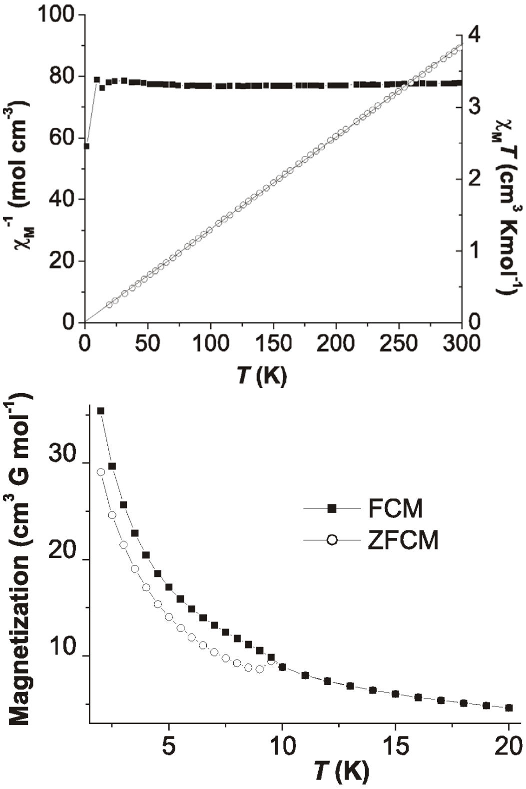


Fig. 4. Plot of the product $\chi_M T$ and of $\chi_M{}^{-1}$ *vs.* T for complex **2** between 5 and 300 K (top) and the fits according to the Curie-Weiss law, $\chi_M = C/(T - \theta)$, with the parameters $\theta = -0.65$ and $C = 3.33$ cm^3 K mol^{-1} for complex **2**. Bottom: (zero) field-cooled magnetisation ((Z)FCM) plots measured under a weak magnetic field of $H < 30$ G.

Conclusion

Compound **1** is the first example of this ligand type where the determination of the X-ray structure was possible. This enabled us to provide a further proof for the suggested keto-enol-tautomeric structure for this type of Schiff base-like ligands. Upon coordination to a metal centre the two amino nitrogens are deprotonated, and the negative charge is delocalised over the six-membered chelate ring. The magnetic properties of **2** demonstrate how small changes in the ligand structure influence the magnetic properties of the related complexes. While for other methanol diadducts of this complex type a spontaneous magnetisation due to canted antiferromagnetism is observed, for complex **2** the observed effects in the FCM/ZFCM measurements are too small to be seriously discussed any further.

Experimental Section

The synthesis of the iron(II) complex was carried out under argon using Schlenk tube techniques. The solvent methanol was purified as described in the literature [9] and distilled under argon. The synthesis of iron(II) acetate is described in the literature [10].

*(E)-Methyl 2-(methoxymethylidyne)-3-oxobutanoate (**1a**)*

A mixture of 58.1 g methyl acetoacetate (0.5 mol), 53.1 g trimethyl orthoformate (0.5 mol) and 102.1 g acetic anhydride (1.0 mol) was heated to reflux for 75 min, while the colour of the reaction mixture turned to dark red. At first, under normal pressure the low-boiling side products were distilled off. At second, by fractionated vacuum distillation **1a** was isolated as a slightly yellow oil at about 90 °C (1.7 mbar) and used immediately for further synthesis. Yield: 39.5 g (50 %). – ^{1}H NMR (270 MHz, $CDCl_3$): δ = 2.30 (s, 3 H, COMe), 3.72 (s, 3 H, OMe), 3.95 (s, 3 H, CO_2Me), 7.52 (s, 1 H, CH).

*H_2L (**1**)*

To a solution of 4.56 g *ortho*-phenylenediamine (42.4 mmol) in 60 mL methanol was added drop-wise a solution of 14.7 g **1a** (93.4 mmol) in 20 mL of methanol. The reaction mixture was heated to reflux for 30 min. After cooling to r. t. light-yellow crystals formed which were recrystallised from methanol. Crystals suitable for X-ray analysis formed in the mother liquor at 4 °C within one day. Yield: 14.0 g (92 %). – M. p. 132 – 133 °C. – $C_{18}FeH_{20}N_2O_6$ (360.36): calcd. C 59.99, H 5.59, N 7.77; found C 60.07, H 5.51, N 7.73. – ^{1}H NMR (270 MHz, $CDCl_3$): δ = 2.54 (s, 6 H, COMe), 3.75 (s, 6 H, CO_2Me), 7.23 – 7.30 (m, 4 H, CH-arom), 8.36 (d, ^3J = 12.0 Hz, 2 H, CH), 12.95 (d, ^3J = 12.0 Hz, 2 H, NH). – MS ((+)-DEI), 70 eV): *m/z* (%) = 360.2 (17) $[M]^+$, 285.1 (84) $[C_{15}H_{13}N_2O_4]^+$, 253.1 (100) $[C_{14}H_9N_2O_4]^+$, 232.1 (83) $[C_{12}H_{12}N_2O_3]^+$.

*$[FeL(MeOH)_2]$ (**2**)*

2.95 g anhydrous iron(II) acetate (17.0 mmol) and 3.60 g H_2L (10.0 mmol) were dissolved in 100 mL methanol, and the mixture was heated to reflux for one hour. After two days a black fine-crystalline precipitate had formed which was filtered off, washed two times with 5 mL of methanol and dried *in vacuo*. Crystals suitable for X-ray analysis formed in the mother liquor within further two days. Yield: 4.26 g (71 %). – $C_{20}FeH_{26}N_2O_8$ (478.3): calcd. C 50.23, H 5.48, N 5.86; found C 49.80, H 4.43, N 5.85. – MS ((+)-DEI), 70 eV): *m/z* (%) = 414 (100) $[FeL1]^+$. – IR (KBr): ν = 3398 (O–H), 1702 (OC=O), 1572 (C=O), 1435, 1417, 1388, 1269, 1200, 1087 cm $^{-1}$.

Magnetic measurements

Magnetic susceptibility data were collected using a Quantum Design MPMSR-2 SQUID magnetometer under an applied field of 0.5 T over the temperature range 2 – 300 K. The samples of **2** were placed in gelatine capsules held within a plastic straw. The data were corrected for the diamagnetic magnetisation of the ligands, using tabulated Pascal's constants, and of the sample holder.

X-Ray structure determination

The intensity data of **1** were collected on a Nonius Kappa CCD diffractometer using graphite-monochromatised MoK_α radiation (λ = 0.71073 Å). The intensity data of **2** were collected on an Oxford XCalibur diffractometer likewise using graphite-monochromatised MoK_α radiation. The data were corrected for Lorentz and polarisation effects. The structures were solved by Direct Methods (SIR 97) [11] and refined by full-matrix least-squares techniques against $F_0{}^2$ (SHELXL-97) [12]. The hydrogen atoms were included at calculated positions with fixed displacement parameters. ORTEP-III [13] was used for the representation of the molecular structures, SCHAKAL-99 [14] to illustrate the crystal structures.The crystallographic data are summarised in Table 1.

CCDC 753713 (**1**) and 753714 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

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