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Structure and Magnetic Properties of Iron(II/III) Complexes with $N_2O_2^{2-}$ Coordinating Schiff Base Like Ligands

Birgit Weber*[a] and **Ernst-G. Jäger**[b][†]

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An overview on the structure–reactivity relationship of iron(II/III) complexes with Schiff base like N_2O_2 coordinating ligands is given. The high flexibility of the ligands results in a wide range of possible applications from model complexes for the reaction with small biomolecules such as nitric oxide to molecular switching materials either as a result of the occurrence of the spin-crossover phenomenon or the spontaneous long-range magnetic ordering.

Introduction

Iron is an inimitable biometal with a wide variety of metabolic functions.[1] Many of these functions are linked to heme as the active centre with the porphyrinato macrocycle as N_4^{2-} coordinating ligand. The continued interest in this important class of molecules is reflected in a countless number of papers, reviews and handbooks on this topic.[2] Besides the synthetic porphyrins, their tetrabenzotetraaza derivatives – the phthalocyanines – and related N_4 coordinating macrocycles, complexes of tetradentate $N_2O_2^{2-}$ coordinating ligands of *N*,*N*-bridged salicylaldimins (the best-known example is the "salen" ligand) have attracted the interest of chemists working in this field of research. Complexes of this type of ligands were, in part, quite successful as models for the active site of heme proteins. For example, the reversible uptake of dioxygen – the main function of hemoglobin – was first realised with a [Co(salen)] [salen = *N*,*N*-bis(salicylidene)ethylenediamine] complex,[3] and the first catalyst of technical relevance for cytochrome-P450-like oxygenation reaction is a derivative of [Mn(salen)].[4]

Besides their function as model compounds for biological systems, iron complexes of Schiff base ligands and their derivatives often exhibit interesting magnetic properties. For example, for iron(III) complexes with a N_3O_2Cl donor set, admixed electronic ground states were observed,[5] whereas examples with N_4O_2[6] or N_3O_2[7] donor set show spin-crossover activity. Furthermore, these complexes can be used as building blocks for the synthesis of larger systems. As a result of the studies on several dinuclear species with μ-oxo,[8] μ-azido,[9] μ-tolylimido[10] or *p*-

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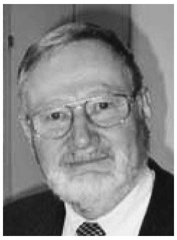
[a] Department Chemie und Biochemie, Ludwig-Maximilians-Universität München,
Butenandtstr. 5–13 (Haus F), 81377 München, Germany
Fax: +49-89-2180-77407
E-mail: bwmch@cup.uni-muenchen.de
[b] Institut für Anorganische und Analytische Chemie, Universität Jena,
August-Bebel-Str. 2, 07743 Jena, Germany
[†] Deceased.

Birgit Weber was born in 1977 in Erfurt, Germany, and received her Ph.D. in 2002 from the University of Jena, Germany, under the supervision of Prof. E.-G. Jäger. In 2003, she moved to the University of Munich to start an independent research group. Her research interests include molecular materials, in particular molecular magnets and spin-crossover systems.



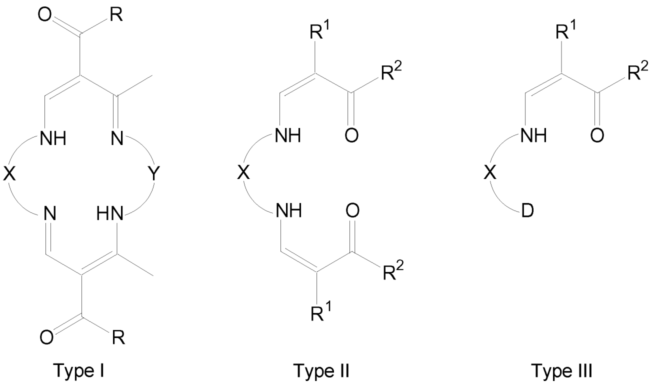
Ernst-Gottfried Jäger was born in 1936 near Leipzig and recieved his Ph.D. in 1962 from the University of Leipzig. In 1970, he was appointet as associate professor at the University of Jena, and in 1990, he was visiting professor at Technical University Darmstadt. From 1993 to 2001, he was full professor of Chemistry at Jena University and from 1995 to 1997 Pro-Rector of the University. In 2006, he died at the age of 70 years. His research interests included metal complexes of biorelevant 3d elements with [N4] macrocycles, the structure–reactivity relationship of complexes with Schiff base like ligands and coordinatively unsaturated neutral complexes of tridentate ligands.

quinone[11] bridges, special attention was drawn to the possibility of preparing molecular wheels or chains with interesting magnetic properties.[12]

In this article, an overview of the properties of iron complexes of Schiff base like ligands with an N_2O_2 coordination sphere is given. These investigations started in the research group of the late Prof. E.-G. Jäger. These complexes serve as candidates as building blocks for larger systems with interesting magnetic properties or as model complexes for biological systems.

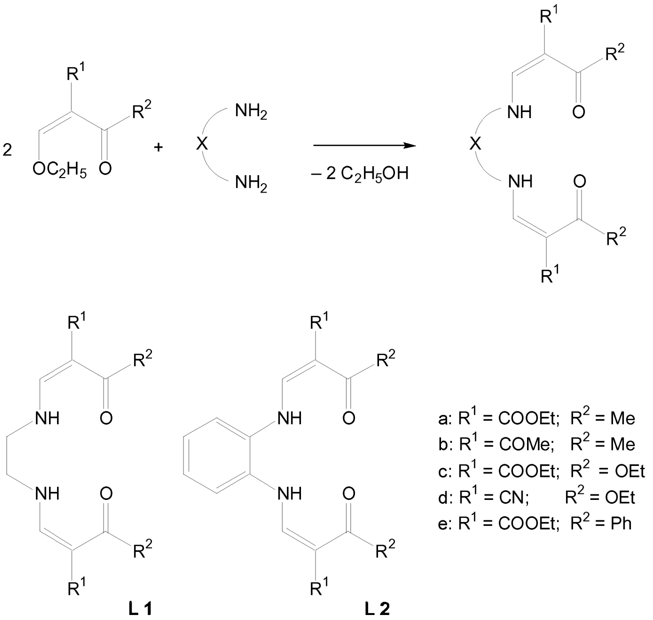
The Ligand System

Over the last years we investigated a ligand system that can be subdivided into the three basic structures given in Scheme 1.[13,14] Type I is formally most related to the porphyrins with a tetradentate macrocycle and a N_4^{2-} donor atom set. Indeed, the properties of these iron complexes are closely related to the porphyrins, but some special features can be observed as well.[15] Type II encompasses tetradentate open chain ligands with an $N_2O_2^{2-}$ coordination sphere. The properties of these iron(II/III) complexes will be the subject of this paper. Type III structures are tridentate ligands that promote the formation of oligonuclear structures similar to those found in biological systems.[16] Previous investigations on copper, cobalt and nickel complexes of this ligand system have already shown that the variation in the *N*,*N′*-bridges X and Y and the substituents $R^{1/2}$ can be used to control the properties of the metal centre, such as (i) the electronic state of the central atom,[17] (ii) the redox potential,[18] (iii) the affinity of vacant axial coordination sites towards additional ligands[19] and (iv) the binding and activation of small molecules such as dioxygen or carbon dioxide.[20]



Scheme 1. Basic structure of the ligand types I, II and III.

Scheme 2 gives the general synthetic route for the ligands discussed in this work and the substituents used. The ligands are obtained by condensation of the desired diamine (*o*-phenylenediamine or ethylenediamine) with an oxymethylene derivative. The preparation of the latter and its reaction with amines was first described by Claisen.[21] In contrast to classic Schiff base like ligands (e.g. salen), the equilibrium between the two tautomeric structures enol–imine and keto–enamine appears to be shifted towards the keto–enamine form. One indication is the ^{1}H-NMR spectra, where a NH–CH coupling constant in the region of 12 Hz is observed. The results from an X-ray structure analysis lead to similar results. In Figure 1, the molecular



Scheme 2. General route for the synthesis of the Schiff base like ligands discussed in this work with the substituents used and abbreviations.

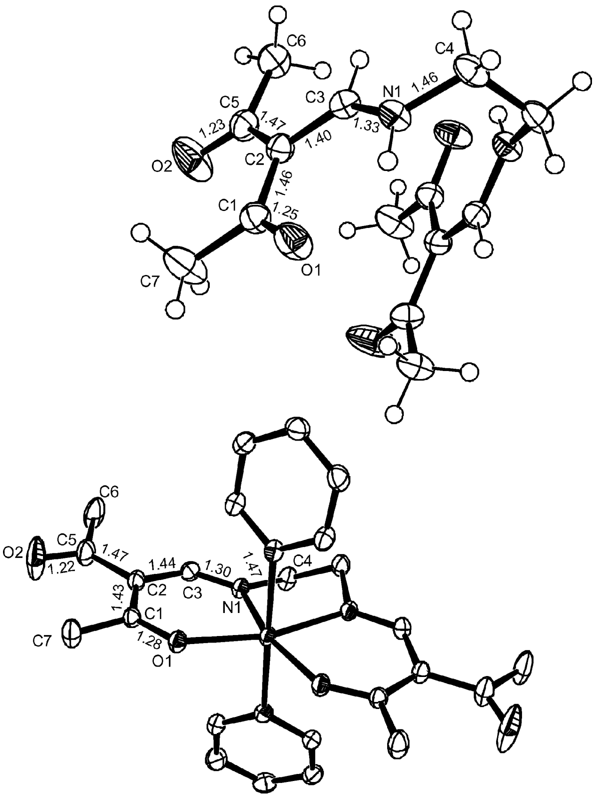


Figure 1. Molecular structure of the ligand L1b (top) and the iron complex [FeL1b(py)$_2$] (bottom) with selected bond lengths.

structure of the free ligand L1b and its iron(II) complex with pyridine (py) as axial ligand is given, and selected bond lengths are indicated.[22] For the iron complex, a equilibrium between the two tautomeric structures is obtained; the negative charge is clearly delocalised over the chelate six-membered ring. For the free ligand, the bond lengths indicate a preference for the keto–enamine structure. For this reason the ligands are always represented in this way.

In the following, selected complex classes of this ligand type are presented with emphasis on their magnetic properties or their relevance as model compounds for biological systems.

Iron(II) Complexes

Complexes with Methanol as Axial Ligands

The starting material for the synthesis of most of the complexes reviewed in this article are the corresponding iron(II) complexes with methanol as axial ligands. These complexes were first described in the late 1980s,[23] detailed investigations of the magnetic properties were carried out about 20 years later.[13,24] The complexes are obtained by conversion of the desired equatorial ligand with iron(II) acetate in methanol. From concentrated solutions, in some cases, the solvent-free square-planar complex precipitates; mostly, however, [FeL(MeOH)$_2$] is obtained as the reaction product. In Figure 2, the X-ray structure and results from magnetic measurements on the complex [FeL2b(MeOH)$_2$] is given as a typical representative.[24c] At room temperature, the $\chi_M T$ product for all complexes has a value of about 3.5 cm^3 K mol^{-1}, which is in the region typical for iron(II) in the high-spin (HS) state. Upon cooling, a slight decrease in the $\chi_M T$ product is observed, typical for weak antiferromagnetic interactions, which is in agreement with the negative Weiss constant Θ. Below 10 K, spontaneous weak magnetisation is observed that can be explained by spin canting.[24c]

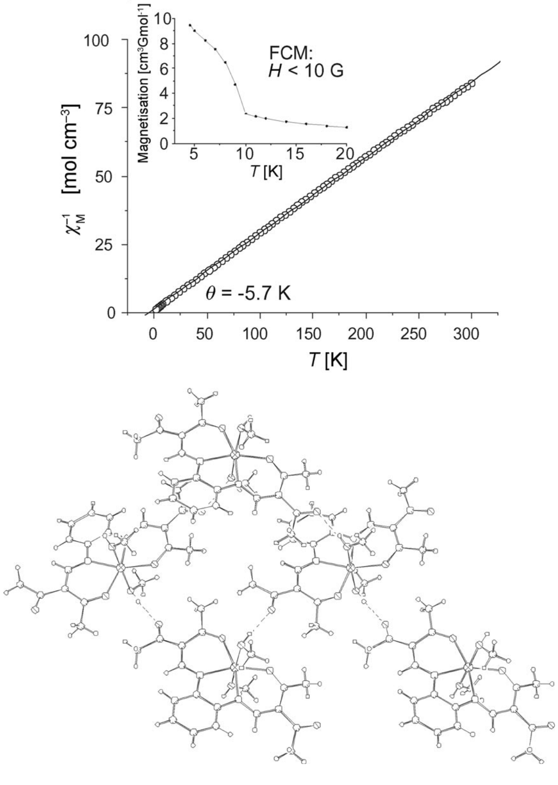


Figure 2. Top: Reciprocal molar susceptibility, χ_M^{-1}, as a function of temperature T and the fit according to the Curie Weiss law, $\chi_M = C/(T - \Theta)$, with the parameters Θ = –5.7 K, C = 3.62 cm^3 K mol^{-1}. The inset shows the field-cooled magnetisation (FCM) vs. T plot measured under a weak magnetic field of $H <$ 10 G for both compounds. Bottom: Layer of the hydrogen-bond-linked molecules projected along 001.[24c]

The complexes [FeL2a(MeOH)$_2$][24a] and [FeL2e(MeOH)$_2$][24c] show a very similar behaviour with a weak spontaneous magnetisation below 10 K. For the complex [FeL1a(MeOH)$_2$], significantly stronger interactions are observed with a critical temperature of T_C = 31 K.[24b] A satisfactorily explanation for this strong difference in the magnetic properties is not available. Probably, the sterically less demanding ethylene bridge results in a closer packing of the molecules, and therefore stronger intermolecular interactions are possible. In Table 1 selected bond lengths of the three structurally characterised complexes [FeL1a(MeOH)$_2$], [FeL2a(MeOH)$_2$] and [FeL2b(MeOH)$_2$] are given.

Table 1. Selected bond lengths [Å] and angles [°] of the methanol adducts [FeL1a(MeOH)$_2$], [FeL2a(MeOH)$_2$] and [FeL2b(MeOH)$_2$].

Compound	Fe–N$_{ax}$	Fe–O$_{ax}$	Fe–O$_{eq}$	O$_{eq}$–Fe–O$_{eq}$
[FeL1a(MeOH)$_2$]	2.079(2)	2.023(2)	2.267(2)	111.1(1)
[FeL2a(MeOH)$_2$]	2.102(2)	2.031(2)	2.223(2)	110.7(1)
	2.110(2)	2.035(2)	2.219(2)	
[FeL2b(MeOH)$_2$]	2.101(2)	2.028(1)	2.203(2)	111.98(5)
	2.107(2)	2.033(1)	2.205(1)	

Complexes with N-Heterocycles as Axial Ligands

Iron complexes with N-heterocycles as axial ligands are of special interest for several reasons. On the one side they may serve as model complexes for biological systems, on the other side, especially for octahedral complexes, magnetic switching behaviour might be observed as already reported for iron(III)(salen) complexes with imidazole (Him) or nitric oxide as the axial ligand.[6,7] The first example where both possibilities was realised is the pair [FeL2a(Him)] and [FeL2a(Him)$_2$].[13,24a,24b,25] In Figure 3, the molecular structure of the two complexes is given, and the results from the magnetic measurements of the diadduct, together with the packing of the molecules in the crystal, are presented in Figure 4.

Both complexes are obtained by conversion of the methanol adduct [FeL2a(MeOH)$_2$] with imidazole in methanol.[24b,25] The monoadduct, a pentacoordinate HS complex, is obtained if the stoichiometric ratio of iron complex/imidazole is about 1:2. This complex resembles well the co-

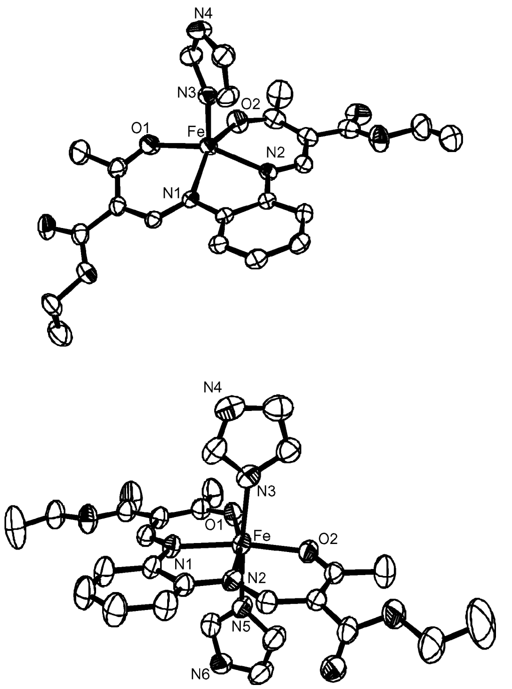


Figure 3. Molecular structure of the imidazole monoadduct [FeL2a(Him)] (top) and the diadduct [FeL2a(Him)$_2$] (bottom).[13]

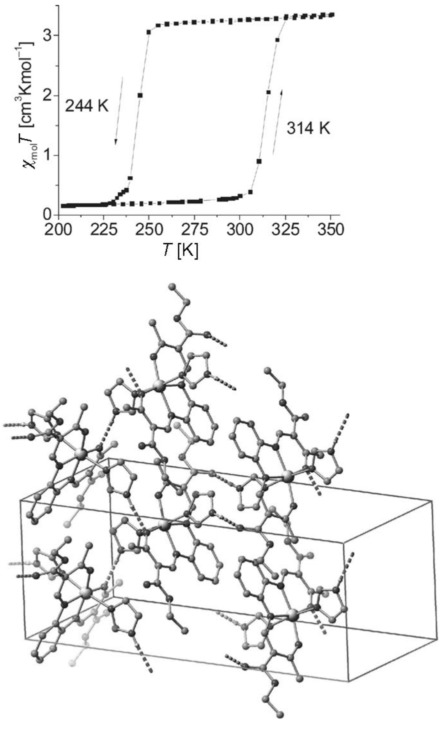


Figure 4. Spin crossover of [FeL2a(Him)$_2$] with a 70-K wide thermal hysteresis loop at about room temperature (top), and packing of the molecules in the crystal (bottom).[25]

ordination sphere of iron(II) in hemoglobin with respect to the spin state, the distances to the equatorial donor atoms (2.00/2.00/2.07/2.10 Å) and to the single strongly bound axial imidazole (Fe–N$_{Him}$ 2.12 Å) and the displacement of the central atom from the plane of the equatorial donors (Fe–Ct$_{N2O2}$ 0.38 Å). The diadduct is obtained when a large excess of imidazole is used (25-fold or higher). Depending on previous treatments, the complex is either paramagnetic (HS) or diamagnetic (low spin, LS) at room temperature. Crystals suitable for X-ray structure analysis were obtained in the HS state. Temperature-dependent magnetic measurements reveal a spin crossover with a 70-K wide thermal hysteresis loop. Reasons for these cooperative interactions are most likeably the strong intermolecular H-bridges as illustrated at the bottom of Figure 4.[25]

Thermal-induced spin transitions (spin crossover, SCO) without a change in the coordination number at the central atom are often quoted to be one of the most spectacular examples of molecular bistability. The change in the properties during the phase transition is of technological interest, and several applications such as data storage devices can be imagined.[26,27] The combination of the Schiff base like equatorial ligands L2a and L2b with N-heterocycles, especially pyridine derivatives, as axial ligands appears to be highly suitable for the synthesis of iron(II) SCO complexes. The octahedral complexes can be obtained either as described for the imidazole complex, or in a one-pot reaction, where the free equatorial ligand is converted with iron(II) acetate and excess axial ligand in a suitable solvent, in most cases methanol. In some cases. only pentacoordinate species are obtained regardless of the excess axial ligand used. One example is the combination of the ligand L2b with imidazole as the axial ligand, for which, so far, only the pentacoordinate monoadduct was obtained. In Table 2, an overview of the characterised octahedral complexes is given, and in Tables 3 and 4, selected bond lengths and angles of the structurally characterised octahedral and pentacoordinate complexes are given.

Table 2. Overview of octahedral mononuclear iron(II) complexes of the ligands L2a and L2b and their magnetic properties; 4-phenylpyridine = phpy, cnpy = 4-cyanopyridine, dmap = 4-dimethylaminopyridine, 1-meim = 1-methylimidazole, $T_{1/2}$ = temperature at γ_{HS} = 0.5.

	L2a	L2b
py	[FeL2a(py)$_2$] $T_{1/2}$ = 220 K, gradual	[FeL2b(py)$_2$] $T_{1/2}$ = 190 K, hysteresis 2 K
phpy	[FeL2a(phpy)$_2$] $T_{1/2}$ = 234 K, hysteresis 4 K	[FeL2b(phpy)$_2$](phpy) $T_{1/2}$ ≈ 290 K, gradual
cnpy	[FeL2a(cnpy)$_2$](cnpy)$_{0.25}$ $T_{1/2}$ = 265 K, 114 K, step wise	[FeL2b(4-cnpy)$_2$] $T_{1/2}$ ≈ 340 K, gradual
dmap	[FeL2a(dmap)$_2$] HS	[FeL2b(dmap)$_2$] $T_{1/2}$ = 179 K, hysteresis 9 K
1-meim	[FeL2a(1-meim)$_2$] HS	[FeL2b(1-meim)$_2$](1-meim) $T_{1/2}$ = 178 K, hysteresis 2 K [FeL2b(1-meim)$_2$] $T_{1/2}$ = 179 K, abrupt [FeL2b(1-meim)$_2$](dmf) $T_{1/2}$ ≈ 80 K, incomplete

As a general rule, it can be said that the more electron-withdrawing substituents c and d of the equatorial ligand stabilise the HS state. The same applies to the more basic axial ligands (dmap and 1-meim), where lower transition temperatures are obtained or the complex remains in the HS state over the whole temperature range investigated.

Table 3. Selected bond lengths [Å] and angles [°] within the first coordination sphere of octahedral iron(II) complexes with the spin state *S*.

Complex	*S*	Fe–N$_{eq}$	Fe–O$_{eq}$	Fe–N$_{ax}$	O1–Fe–O2	N$_{ax}$–Fe–N$_{ax}$	∠ L1, L2[a]	Ref.
[FeL2a(py)$_2$]	2	2.062(4) / 2.053(4)	2.017(4) / 1.990(3)	2.256(5) / 2.195(4)	106.3(1)			[24b]
	0	1.923(3) / 1.918(2)	1.962(2) / 1.955(2)	2.025(3) / 2.023(3)	92.4(1)			
[FeL2b(py)$_2$]	2	2.061(2) / 2.074(1)	1.992(1) / 2.009(1)	2.226(2) / 2.269(2)	106.99(5)	175.6(1)	16.7	[29]
	0	1.894(1) / 1.906(1)	1.930(1) / 1.948(1)	2.007(2) / 2.025(2)	89.98(5)	176.1(1)	15.4	
[FeL2c(py)$_2$]	2	2.109(2) / 2.102(2)	2.046(1) / 2.048(1)	2.239(2) / 2.262(2)	112.04(6)		43.4	[30]
[FeL2d(py)$_2$](py)	2	2.100(4) / 2.141(6)	2.083(4) / 2.050(4)	2.262(5) / 2.246(4)	108.0(2)		53.9	[31]
[FeL2a(phpy)$_2$]	2	2.078(2) / 2.081(3)	2.000(2) / 2.009(2)	2.229(3) / 2.289(3)	107.25(8)	174.47(9)	61.3	[32]
	0	1.921(4) / 1.922(3)	1.952(3) / 1.967(3)	1.989(4) / 2.009(3)	89.5(1)	174.7(1)	73.6	
[FeL2b(phpy)$_2$](phpy)	0	1.902(2) / 1.910(2)	1.950(2) / 1.952(2)	2.013(3) / 2.015(3)	89.11(8)	174.84(9)	81.1	[32]
[FeL2a(dmap)$_2$]	2	2.082(4) / 2.097(4)	2.017(3) / 2.018(3)	2.220(4) / 2.304(4)	111.2(1)	169.1(2)	16.2	[33]
[FeL2b(dmap)$_2$]	2	2.085(4) / 2.090(4)	2.008(3) / 2.025(3)	2.231(4) / 2.272(5)	109.1(2)	171.4(2)	74.6	[29]
[FeL2a(cnpy)$_2$](cnpy)$_{0.25}$	0, 0	1.895(2) / 1.899(2), 1.899(2) / 1.909(2)	1.942(2) / 1.947(2), 1.933(2) / 1.938(2)	1.979(2) / 1.985(2), 2.008(2) / 2.009(2)	90.23(6), 89.89(6)	174.7(1), 176.1(1)	80.1, 7.7	[34]
	2, 0	1.911(2) / 1.911(2), 2.034(2) / 2.040(2)	1.944(1) / 1.951(1), 1.967(2) / 1.973(2)	1.999(2) / 2.007(2), 2.228(2) / 2.231(2)	91.70(5), 102.74(6)	174.4(1), 175.9(1)	80.3, 6.6; 77.3	
	2, 2	2.061(2) / 2.068(2), 2.029(2) / 2.037(2)	1.978(1) / 1.982(1), 1.970(1) / 1.992(1)	2.289(2) / 2.285(2), 2.177(2) / 2.238(2)	105.39(6), 103.61(6)	176.1(1), 173.8(1)	77.6, 7.7	
[FeL2a(1-meim)$_2$]	2	2.113(2) / 2.125(2)	2.050(2) / 2.080(2)	2.204(2) / 2.211(2)	115.36(7)	172.4(1)	7.1	[35]
[FeL2b(1-meim)$_2$](1-meim)	2	2.080(2) / 2.075(2)	2.000(2) / 2.011(2)	2.252(3) / 2.281(3)	106.80(8)	179.23(8)	59.6	[36]
	0	1.892(3) / 1.899(3)	1.934(2) / 1.940(2)	2.012(3) / 2.016(3)	88.36(9)	178.97(11)	56.5	
[FeL2b(1-meim)$_2$](dmf)	2	2.089(2) / 2.108(2)	2.008(2) / 2.034(2)	2.259(2) / 2.302(2)	107.59(6)	177.3(1)	57.1	[35]
[FeL2a(2-meim)$_2$]	2	2.113(2) / 2.113(2)	2.040(2) / 2.059(2)	2.235(2) / 2.239(2)	113.99(6)	164.93(7)	86.9	[35]
[FeL2a(Him)$_2$]	2	2.088(3) / 2.078(3)	2.011(3) / 2.048(3)	2.198(4) / 2.239(4)	108.04(11)	173.92(12)	32.1	[25]
[FeL1a(py)$_2$]	2	2.105	2.044	2.271	114.4	179.1		[30]
[FeL1b(py)$_2$]	2	2.114(1)	2.046(1)	2.259(1)	113.87(6)	177.04(7)	28.5	[22]

[a] Angle between the planes of the axial ligands.

Table 4. Selected bond lengths [Å] and angles [°] within the first coordination sphere of pentacoordinate iron(II) complexes; 2-meim = 2-methylimidazole.

Complex	Fe–N$_{eq}$	Fe–O$_{eq}$	Fe–N$_{ax}$	O1–Fe–O2	Fe–Ct$_{N2O2}$[a]	Ref.
[FeL2a(Him)]	2.0742(17)/2.0967(19)	1.9951(17)/1.9988(16)	2.115(2)	101.5(1)	0.38	[24b]
[FeL2b(Him)]	2.08/2.09	2.00/2.01	2.11	106.9	0.28	[30]
[FeL2d(Him)][b]	2.117(3)/2.127(3)	2.092(3)/2.102(2)	2.134(3)/2.170(3) (CN)	108.79(10)	0.08	[37]
[FeL2a(2-meim)](MeOH)$_{0.5}$	2.06	2.00	2.10	97	0.44	[35]
[FeL2b(1-meim)]	2.071(2)/2.076(2)	1.982(1)/2.010(1)	2.097(2)	103.81(5)	0.33	[35]
[FeL2b(cnpy)](MeOH)	2.07/2.07	1.99/1.96	2.15	104.5	0.29	[30]

[a] Displacement of the central atom from the plane of the equatorial donors. [b] Coordination polymer with the CN substituent of the equatorial ligand as sixth ligand.

The influence of the substituents of the equatorial ligand L2 on the overall ligand field strength, which increases in the order d < c < a ≈ b, correlates well with the Fe$^{II/III}$ redox potentials of the iron(II) complexes (values E_{SCE} from ref.[28] converted to E_H with $E_H = E_{SCE} + 0.24$ V) in pyridine or dmf (Table 5).

Table 5. Redox potentials of the base iron(II) complexes from ref.[28]

Complex	FeL2a	FeL2b	FeL2e	FeL2c	FeL2d	FeL1b	FeL1e[a]
E_H(py) [V]	0.42	0.38	0.44	0.46	>0.6	0.30	≈0.34
E_H(dmf) [V]	0.25	0.24	0.28	0.27	0.41	0.14	≈0.27

[a] Estimated value.

Interestingly, the redox potential of the ligand L1e implies that the ethylene-bridged ligands are also suitable for the synthesis of spin-crossover complexes. In contrast to this, so far, only pure HS complexes have been obtained. A comparison of the X-ray structures of the pair [FeL1b(py)$_2$][22] and [FeL2b(py)$_2$][29] reveals that the bond lengths within the FeNCCN chelate five-membered ring are significantly longer for the ethylene bridge. The values are 2.11, 1.47, 1.53, 1.47, and 2.11 Å (Fe–N, N–C, C–C, C–N, and N–Fe, respectively) for the ligand L1b and 2.06, 1.42, 1.41, 1.42, and 2.06 Å for the ligand L2b. The reason for the contraction of the bond lengths by introduction of the phenylene bridge is most likeely because of the change from a sp^3-hybridised carbon to a sp^2-hybridised carbon. This results in slightly longer average bond lengths within the first coordination sphere of the iron centre for the complexes of L1 than those for L2 in the HS state. The average values for complexes of L2 in the high-spin state are 2.08 (Fe–N$_{eq}$), 2.02 (Fe–O$_{eq}$) and 2.25 Å (Fe–N$_{ax}$), relative to 2.11 (Fe–N$_{eq}$), 2.05 (Fe–O$_{eq}$) and 2.27 Å (Fe–N$_{ax}$) for complexes of L1. As the overall ligand field strength strongly depends on the Fe–L distance, those small variations might be the reason for the existence of only iron(II) SCO complexes of L2.

For the spin-crossover complexes, upon spin transition, a shortening of the bond lengths of about 10%, as discussed for other iron(II) spin-crossover complexes in literature,[26] is observed. This shortening is more pronounced for the axial than for the equatorial ligands. The average distances in the low-spin state are 1.91 (Fe–N_{eq}), 1.95 (Fe–O_{eq}) and 2.01 Å (Fe–N_{ax}). A second sensible tool for determining the spin state of these types of iron complexes is the O–Fe–O angle, the so-called bite of the ligand. It changes from an average of 108° in the high-spin state to 90° in the low-spin state. In Figure 5, a top view of the molecular structure of [FeL2b(py)$_2$], as a typical example in the high-spin and the low-spin form, is given together with the results from the magnetic measurements to illustrate the changes.[29]

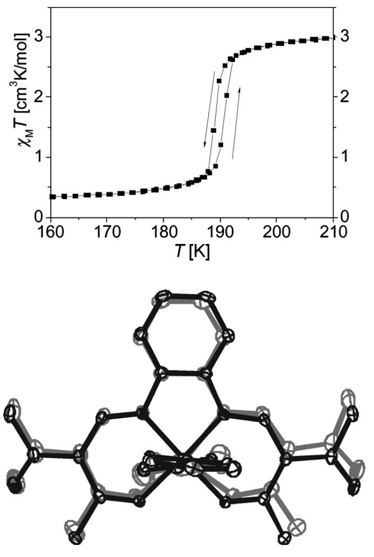


Figure 5. Thermal dependence of $\chi_M T$ (top) and schematic drawing of the top view of both the HS and LS forms of [FeL2b(py)$_2$] (bottom). The asymmetric unit at $T \cong 150$ K is the upper one; Fe–N_{eq} bonds are superimposed, the change in the O–Fe–O angle (HS: 107°, LS: 90°) is clearly visible.

One central question when dealing with spin-crossover complexes is to understand the origin of the cooperative interactions that are responsible for the occurrence of abrupt transitions and thermal hysteresis loops. For mononuclear complexes, intermolecular interactions such as van der Waals interactions, π stacking or hydrogen bonds are discussed as suitable information transmitters. An impressive example for the latter possibility is already given in Figure 4 with the complex [FeL2a(Him)$_2$].[25] For the complexes summarised in Table 2, different degrees of cooperative interactions are observed; however, on a much lower level. The properties of the spin-transition curve range from gradual {e.g. [FeL2a(py)$_2$][24b]} to abrupt with hysteresis {e.g. [FeL2b(dmap)$_2$], hysteresis width 9 K[29]}. The only possible reason for the cooperative interactions is short van der Waals contacts between the neighbouring molecules for all examples. The extent of the cooperative interactions should therefore correlate with the number of short contacts and the dimension of the built network. On first view, a comparison of the molecular packing of the different complexes gives no direct correlation between the number of intermolecular contacts and the hysteresis width.[38] Complexes with gradual spin transition {e.g. [FeL2a(py)$_2$][24b]} have a similar number of short contacts as complexes with small hysteresis {e.g. [FeL2b(py)$_2$][29]}. The complex with the widest hysteresis {[FeL2b(dmap)$_2$], 9 K[29]} does not have the highest number of short intermolecular contacts, but in the literature, the extent of cooperative interactions is always correlated with the number of contacts.[39] The reason for these discrepancies is the varying effectiveness of the contacts for the transmission of elastic interactions. For complexes of the equatorial ligand L2a, the intermolecular interactions are often mediated through the rather flexible ethoxy group of the substituents. The complexes [FeL2a(py)$_2$] and [FeL2b(py)$_2$] illustrate rather nicely that those interactions of flexible groups can have little or no relevance for the transmission of cooperative interactions.[29] Rigid and sterically demanding axial ligands such as 4-phenylpyridine are necessary to obtain enough relevant contacts. If the effectiveness of the contacts are considered, all predictions made in the literature for other systems[39] also work for our complexes, and the strength of the cooperative interactions correlate well with the number of intermolecular contacts.[38]

Results from X-ray structure analysis are very important in the understanding of cooperative interactions, but this is not the only application. They also help to understand unusual or discontinuous curve progressions obtained from the magnetic measurements. One example is the complex [FeL2a(cnpy)$_2$](cnpy)$_{0.25}$ (cnpy = 4-cyanopyridine), where an unusual wide plateau (≈100 K) at $\gamma_{HS} \approx 0.25$ (high-spin molar fraction) is observed.[34] The Mössbauer spectra in combination with results from the X-ray structure analysis clearly show that an additional distorted 4-cyanopyridine molecule is responsible for the significantly lower transition temperature of one fourth of the iron centres, which has a slightly different chemical surrounding. In solution (followed by ^{1}H NMR spectroscopy[40]), a gradual spin transition is observed.[34] In Figure 6, the molecular structure of the complex is represented together with the results from susceptibility measurements and Mössbauer spectroscopy.

The combination of iron(II) complexes of L2 with N-heterocycles as axial ligands is highly suitable for the synthesis of spin-crossover complexes. The different substituents at the equatorial ligand cannot only be used to fine tune the ligand field strength, and by this vary the transition temperature, they can also be used to control the extent of the intermolecular interactions. For future work, it will be interesting to prepare more examples of hydrogen-bond–linked, spin-crossover complexes to see if the prediction that the hydrogen bonds are responsible for the wide thermal hysteresis loop is true. It will also be interesting to provide

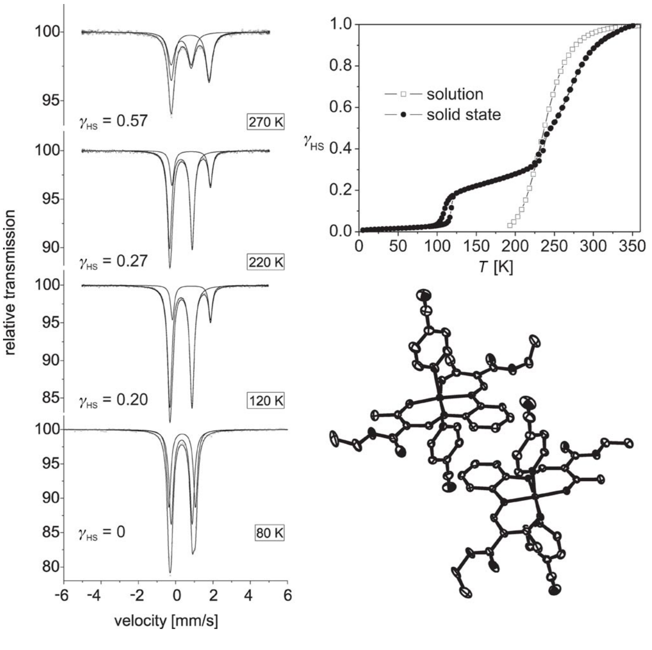


Figure 6. Left: Plot of the Mössbauer spectra of $[FeL2a(cnpy)_2]$-$(cnpy)_{0.25}$ at 80 K, 120 K, 220 K and 270 K with the high-spin molar fraction indicated. Right: Thermal dependence of $\chi_M T$ (top) and ORTEP drawing of the asymmetric unit of $[FeL2a(cnpy)_2]$-$(cnpy)_{0.25}$ at 240 K (bottom). Hydrogen atoms and solvent molecules are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level.[34]

the preconditions for π stacking. These interactions are responsible for up to 40-K wide thermal hysteresis loops in mononuclear complexes whose ligands have extended aromatic structures.[41] In other compounds with 70-K[42] or up to 92-K[43] wide thermal hysteresis loops, π stacking is also considered to play a central role; however, no X-ray structure analysis is available for those compounds.

Reaction of the Iron(II) Complexes with Nitric Oxide

The groundwork relating to current studies on nitrosyliron complexes was laid down about five decades ago when NO was used as an EPR active probe for studying the reaction of heme proteins and related derivatives with small molecules. During the last years, there has been a renewed interest in the chemistry of nitric oxide because of its many functions as a biomolecule.[44] Most of those functions are linked to iron as the active centre. As a consequence, a large variety of nitrosyliron complexes with porphyrin or non-porphyrin ligands have been synthesised and characterised in detail.[45] According to the electron-counting mechanism introduced by Enemark and Feltham,[46] they can be subdivided into $\{Fe–NO\}^6$, $\{Fe–NO\}^7$ and $\{Fe–NO\}^8$ species. While the latter is very rare,[47] numerous examples of the first two species are known.[45] The determination of the electronic structure of the $\{Fe–NO\}^{6–8}$ species has been of interest for a long time. Especially for the $\{Fe–NO\}^7$ species, which possesses an $S = 3/2$[47a,48] or 1/2[47a,49] ground state or shows an $S = 1/2 \leftrightarrow S = 3/2$ spin-equilibrium behaviour,[7,50] the assignment of spin and oxidation states is still controversial.

Due to the high variability, our ligand system is very suitable for systematic investigations on the influence of the equatorial ligand on the properties of the Fe–NO bond. Consequently, several '$\{FeNO\}^7$' nitrosyliron complexes were prepared and investigated in detail.[37,51] An overview of the results is summarised in Table 6. For comparative purposes, the results for three macrocyclic complexes of type I[37,51] are also included.

The general trends will be discussed. Table 6 shows that small changes at the ligand significantly influence the properties of the corresponding nitrosyliron complex. This can be noted in the NO stretching frequencies and is also reflected in the EPR spectra (hyperfine coupling constant),

Table 6. Overview of the properties of the $\{FeNO\}^7$ nitrosyliron complexes discussed in this work.

Complex	Solid state					Solution		
	ν(NO)[a] [cm^{-1}]	δ[b] [mm/s]	ΔE_Q[c] [mm/s]	$T_{1/2}$[d] [K]	∠ FeNO [°]	ν(NO)[e] [cm^{-1}]	$E_H(CH_2Cl_2)$[f] [V]	A^N[g] [G]
[FeL1c(NO)]	≈1660	0.269	1.840	S = 1/2		1679	–0.65	14.8
[FeL2a(NO)]	1774			S = 1/2		1779	–0.58	17
[FeL2b(NO)][h]	1790; 1717[h]	0.441/0.326[i]	0.388/1.398[i]	140[h]	167	1783	–0.58	18
[FeL2e(NO)]	1778	0.307	1.507	255		1781		18
[FeL2c(NO)(MeOH)]	1716	0.329	1.170	>r.t.	142.1(4)	1786		23
[FeL2d(NO)(MeOH)]	1744	0.711	1.087	123	149.5(3)[j]	1803	–0.37	26
[FeL2d(NO)] (CN)	1776	0.577	0.686	S = 3/2	162.6(4)			
[FeL2d(NO)]	1812			S = 3/2				
[FeLM1(NO)][k]	1629	0.102	2.151	S = 1/2	140.3(2)	1635	–1.01	13.2
[FeLM2(NO)][l]	1637	0.105	2.090	S = 1/2	145.1(2)	1648	–0.90	15.0
[FeLM3(NO)][m]	1675	0.159	1.422	S = 1/2	152.0(3)	1669	–0.76	16.0

[a] Measured as nujol mull. [b] Isomer shift at 130 K. [c] Quadrupole splitting at 130 K. [d] $S = 3/2 \leftrightarrow S = 1/2$ spin crossover. [e] Measured in CH_2Cl_2 solution. [f] Reduction in CH_2Cl_2. [g] Average value of the hyperfine coupling constant. [h] This complex was first described by Numata et al. and was characterised by König et al.[52] [i] 300 K/88.5 K. [j] Room temperature modification. [k] LM1 = {6,13-bis-(ethoxycarbonyl)-7,12-dimethyl-1,4,8,11-tetraazacyclotetradeca-5,7,12,14-tetraen}. [l] LM2 = {6,13-bis(ethoxycarbonyl)-7,12-dimethyl-benzo-[*b*]-1,4,8,11-tetraazacyclotetradeca-5,7,12,14-tetraen}. [m] LM3 = {6,13-bis(ethoxycarbonyl)-7,12-dimethyl-dibenzo-[*b*,*i*]-1,4,8,11-tetraazacyclotetradeca-5,7,12,14-tetraen}.

the Mössbauer spectra (isomer shift and quadrupole splitting) and the reduction potentials as well as in the results from the X-ray structure analysis.[37,51] For a better visualisation of the influence of the ligand on NO binding and the corresponding experimental data, the solid-state NO stretching frequencies of the complexes are plotted against the Fe–N–O angle (Figure 7).[51] With respect to the binding mode of nitric oxide, it is interesting to note that there exists a significant correlation between the NO stretching frequency and the Fe–N–O angle. This can be explained by the sp^2 hybridisation of the NO nitrogen if the nitric oxide is bound as nitroxyl anion (double bond, theoretical angle 120°) and by the sp hybridisation of the NO nitrogen if the nitric oxide is bound as NO^+ (triple bound, theoretical angle 180°). For our complexes, the angle varies from 142° up to 167°, and the stretching frequencies vary between 1629 and 1812 cm^{-1}. In both cases, this increase with increasing electron-withdrawing character of the equatorial ligand can be explained by a decreasing population of the antibonding π^* orbital and therefore by a decreasing electron transfer from iron to the nitric oxide. The plot shown in Figure 7 has been completed with the data for other pentacoordinate $\{FeNO\}^7$ complexes from the literature.[53] Both octahedral complexes show the same trend as the pentacoordinate complexes, but do not fit into linear correlation.[37,51]

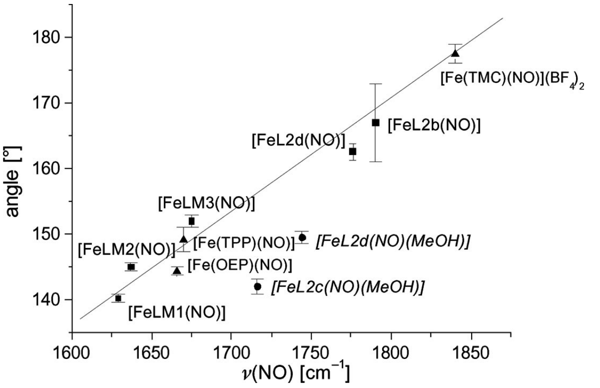


Figure 7. Correlation between the NO stretching frequency and the Fe–N–O angle in the pentacoordinate $\{FeNO\}^7$ nitrosyliron complexes with Schiff base like ligands, supplemented with other examples from the literature.[53] The octahedral derivatives [FeL2c(NO)(MeOH)] and [FeL2d(NO)(MeOH) are not included in the linear fit.

While the macrocyclic complexes can clearly be described as iron(III)–NO^- complexes, the situation is more complex for the open-chain systems under discussion here. Some of the complexes can still be described as iron(III)–NO^- {e.g. [FeL1c(NO)]}; for the others, however, the shift of the NO stretching frequency to higher values indicates that NO is probably no longer bound in its anionic form (NO^-) but as a radical. The different bonding conditions in the complexes of L1 and L2 are reflected in the stability of the iron–nitrosyl bond. The complexes of L1 or L2a and L2b are stable in solution (similar to the macrocyclic complexes) and do not decompose upon dissolving or addition of potential donor ligands (D). In contrast to this, the possibility of a NO⇔D ligand exchange is found for [FeL2c], and is even more pronounced for [FeL2d]. It can be followed by UV/Vis and EPR spectroscopy. In Figure 8, the corresponding EPR spectra of [FeL2d] in a methanol solution are given and display two cycles in which NO is added and removed.[51] The increasing delocalisation of the unpaired electron over the Fe–NO moiety with increasing electron-withdrawing character of the substituents at the equatorial ligand is also reflected in an increase in the hyperfine coupling constant A^N in the EPR spectra and an increase in the isomer shift in the Mössbauer spectra towards values more typical for iron(II) (especially for the ligand L2d).[51]

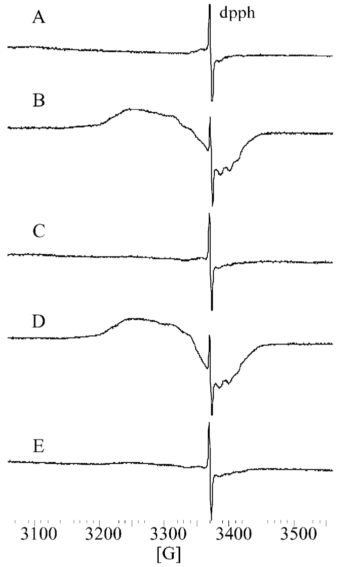


Figure 8. Reversible binding of nitric oxide to [FeL2d] followed by EPR spectroscopy with 2,2-diphenyl-1-picrylhydrazyl (dpph) as standard; spectrum A: starting iron(II) complex; spectra B and D: nitric oxide bound to the iron centre by bubbling NO through the solution; spectra C and E: bound nitric oxide is removed by bubbling argon through the solution.

Of the possible spin states for the $\{FeNO\}^7$ systems discussed in literature, all versions could be realised with the Schiff base like ligands presented here. In Figure 9, the molecular structures of the spin-crossover complex [FeL2d(NO)(MeOH)] and the $S = 3/2$ complex [FeL2d(NO)] are given, together with the results from susceptibility measurements. The change in the spin state is also reflected in the solid-state EPR spectra, as given on the right hand side in Figure 9. For the $S = 3/2$ systems, the line widths are in the region of 2000 G. Upon spin transition, the line width decreases until a value in the region of 100–20 G (typical for $S = 1/2$ systems of this ligand type) is obtained, when the spin transition is complete. In the case of iron(II) complexes, Mössbauer spectroscopy is a valuable tool to follow the spin transition. For the nitrosyliron complexes, the spin-flipping frequency between the intermediate-spin and the low-spin state is higher than the technique frequency scale of 10^{-7} s^{-1}. Therefore, only one average signal for both species is obtained at temperatures where both species coexist.[51,52b] Similar to those in the iron(II) SCO systems, the ligands L2a–f appear to be more suitable for the synthesis

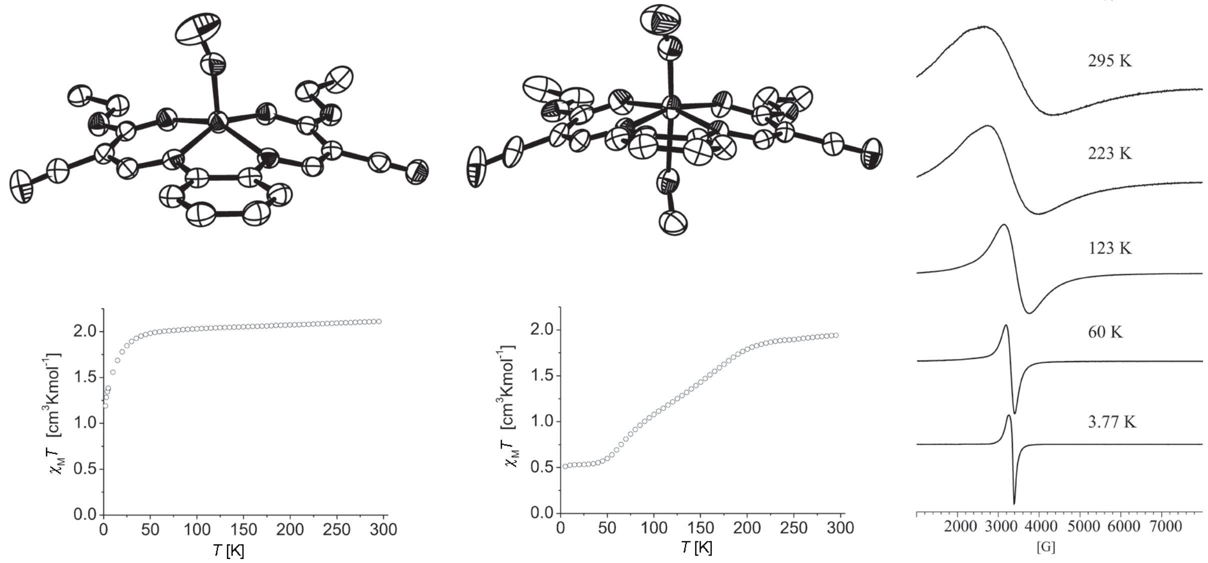


Figure 9. Left and centre: Thermal dependence of $\chi_M T$ (bottom) and ORTEP drawing of the asymmetric unit of [FeL2dNO] and [FeL2dNO(MeOH)] (top). The hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Right: Temperature dependence of the solid-state EPR spectra of [FeL2dNO(MeOH)].

of SCO complexes. However, in contrast to the octahedral iron(II) complexes here, the complex of L1 is obtained in the $S = 1/2$ low-spin state and not in the $S = 3/2$ intermediate-spin state. The ligand field strength order obtained from the redox potentials of the iron(II) complexes (Table 5) is reflected even better. For the substituents of L2, the same order as found for the iron(II) spin-crossover complexes ($d < c < b \approx a$) is obtained.

For the assignment of the spin and oxidation states of iron and nitric oxide, the overall spin state of the system has to be considered. For the $S = 1/2$ state, the discussion in the literature is still very controversial. Complexes have been described either as a low-spin ferrous species ($S = 0$) with a coordinated nitric oxide radical[48c,49d,50b] or as an intermediate-spin ferric species ($S = 3/2$) with a nitroxyl anion ($S = 1$) antiferromagnetically coupled.[47a] Although several complexes were prepared of our ligand system, the question can still not be answered satisfactorily. SCC-Xα calculations revealed that this is because of the highly covalent character of the Fe–NO bond in which the unpaired electron is localised in a common molecular orbital. This raises the question whether an assignment of the spin and oxidation state is meaningful at all.[51] In contrast to this, the best description of the electronic conditions in the intermediate-spin ($S = 3/2$) state of the nitrosyliron complexes is Fe^{III}(high spin)–NO^- ($S = 1$), antiparallel coupled. This is supported by SCC–Xα calculations,[51] but some experimental results do also point in this direction. One powerful indication is the EPR spectrum of a powder sample of [FeL2d(NO)] at 3.77 K, which is displayed in Figure 10. Several signals are observed at g = 4.28, 3.96, 3.73, 3.05, 2.05, 1.50, 1.35 and 0.98 (measured values). The g values between 2 and 4 can be assigned to the intermediate-spin state of the system. The g values below 2 are an indication of the S = 1 spin state of nitric oxide, which leads to the formulation: Fe^{III} ($S = 5/2$); NO ($S = 1$); antiferromagnetically coupled for the $S = 3/2$ state of the nitrosyliron complexes. This formulation is in good agreement with results from the literature, where the electronic structure has been established by X-ray crystallography, X-ray absorption, resonance Raman, Mössbauer and EPR spectroscopy in combination with DFT calculations.[47a,49b,54]

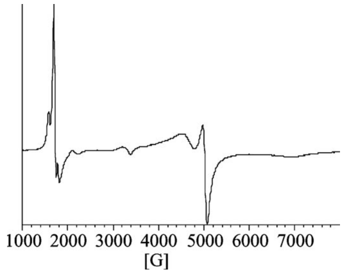


Figure 10. Solid-state EPR spectrum of [FeL2d(NO)] at 3.77 K.

There exist two borderline cases for nitric oxide binding in nature as well as for our model compounds. Some of the complexes bind nitric oxide very tightly and resemble, in this respect, the enzymes such as nitrite reductase or hydroxylamine oxidase, in which nitric oxide is an intermediate in the catalytic cycle.[1] Especially, the complexes [FeL2c] and [FeL2d] bind nitric oxide less tightly, even reversibly. They are more suitable as models for the reversible binding of nitric oxide found for the nitrophorins.[1] But, as for the iron(II) complexes with N-heterocycles as axial ligands, the complexes are not only model compounds for biological systems, they also exhibit interesting magnetic properties such as the $S = 1/2 \leftrightarrow S = 3/2$ spin transition. For a better understanding of the magnetic properties, the nature of the

Fe–NO bond and the influence of the equatorial ligand on the assignment of the spin- and oxidation states is a valuable tool.

Iron(III) Complexes

The synthetic approach for the preparation of iron(III) complexes is always the oxidation of the corresponding iron(II) complex that has been previously isolated.[24b] Iron(III) complexes of L1 are very sensitive towards hydrolysis, and, in the frame of this review, only a few selected examples of iron(III) complexes of L2 are presented. In Table 7, selected bond lengths and angles of the structurally characterised complexes discussed in this work are summarised.

µ-Oxo Iron(III) Complexes

Dinuclear µ-oxo complexes are obtained when the corresponding iron(II) complexes are exposed to oxygen (from the air). As a consequence, they are often obtained as unwanted side products (or products) if the necessary diligence required when working with air-sensitive compounds is missing. The speed of the reaction strongly depends upon the ligands {crystals of [FeL2d(py)$_2$](py) are stable for weeks} and whether a solution or a solid is used. The obtained complexes of L2 are relatively stable in air, while µ-oxo complexes of L1 decompose within a few days even as a solid with the formation of the free ligand and iron(III) oxide/hydroxide. The change in the oxidation state is often accompanied by a characteristic colour change (especially in solution), and the experienced experimentalist should be able to realise if the desired iron(II) complex decomposed.[24b]

The complexes of L2a and L2b do not show this tendency on addition of more axial ligands, which is similar to the NO adducts.[24b] In contrast to this, for the complex [FeL2d], the decomposition of the corresponding nitrosyliron complex in the presence of pyridine yielded a dinuclear complex in which one iron centre is pentacoordinate and the other iron centre is octahedral with one additional pyridine as axial ligand. The molecular structure together with the results from the magnetic measurements are presented in Figure 11.[30]

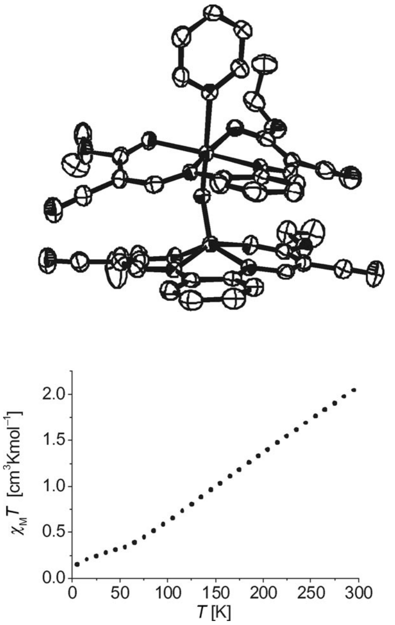


Figure 11. Thermal dependence of $\chi_M T$ (bottom) and ORTEP drawing of the asymmetric unit of µ-oxo-[FeL2d][FeL2d(py)] (top). The hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level.

The magnetic properties of the µ-oxo iron(III) complexes are dominated by a strong intermolecular antiferromagnetic interaction mediated over the µ-oxo bridge. Upon cooling, a strong decrease in the magnetic moment is observed, and the room temperature value {$\chi_M T$ = 1.78 cm^3 K mol^{-1} for µ-oxo-[FeL2a]$_2$ and $\chi_M T$ = 2.05 cm^3 K mol^{-1} for µ-oxo-[FeL2d][FeL2d(py)]} is much smaller than the theoretically expected value for a dinuclear iron(III) complex in the intermediate-spin (IS, $\chi_M T$ = 3.56 cm^3 K mol^{-1}) or HS state ($\chi_M T$ = 8.74 cm^3 K mol^{-1}), which makes direct assignment of the spin ground state difficult.[24b]

Halide Iron(III) Complexes

The complexes [FeL2aBr] and [FeL2aI] are obtained when the corresponding iron(II) complex is converted with elemental bromine or iodine in the presence of the corresponding alkali halide.[24b] [FeL2aCl] is obtained when the corresponding iron(II) complex is suspended in CHCl$_3$ or CCl$_4$ for several days. Recrystallisation from methanol

Table 7. Selected bond lengths [Å] and angles [°] within the first coordination sphere of the iron(III) complexes discussed in this work.

Complex	Fe–N$_{eq}$	Fe–O$_{eq}$	Fe–L$_{ax}$	O1–Fe–O2	Fe–Ct$_{N_2O_2}$[a]	Ref.
[FeL2aCl]	2.046(3)/2.045(4)	1.925(3)/1.921(3)	2.205(1)	90.91(15)	0.57	[24b]
[FeL2aBr]	2.06(2)/2.06(2)	1.93(2)/1.93(1)	2.351(3)	92.0(6)	0.56	[24b]
[FeL2aI]	2.049(2)/2.042(3)	1.924(2)/1.934(2)	2.7475(5)	92.52(11)	0.54	[24b]
µ-oxo-[FeL2a]$_2$	2.07	1.96	1.78	91.9	0.60	[24b]
µ-oxo-[FeL2d][FeL2d(py)]	2.04/2.07	2.00/1.99	1.76	89.4	0.56	[30]
	2.06/2.07	2.08/2.06	1.81 (O)/2.25 (py)	106.7	0.17	
[FeL2aCl(MeOH)]	2.06/2.07	1.96/1.95	2.27 (Cl)/2.19 (MeOH)	104.6	0.20	[30]

[a] Displacement of the central atom from the plane of the equatorial donors.

yields, depending on the concentration, a pentacoordinate solvent-free complex or an octahedral complex with one additional methanol as axial ligand. In Figure 12, the molecular structure and results from the magnetic measurements are given for the octahedral complex [FeL2aCl(MeOH)]. Magnetic measurements reveal that all complexes show Curie–Weiss behaviour, except at very low temperatures. The room-temperature magnetic moment is 4.67 $cm^3 K mol^{-1}$, 4.41 $cm^3 K mol^{-1}$, 2.31 $cm^3 K mol^{-1}$ and 4.66 $cm^3 K mol^{-1}$ for [FeL2aCl], [FeL2aBr], [FeL2aI] and [FeL2aCl(MeOH)], respectively. The complexes with chloride and bromide are $S = 5/2$ HS complexes, while [FeL2aI] is one of the more rare intermediate-spin complexes. The differences in the magnetic properties are not reflected in the results from the X-ray structure analysis, as the structural variations between the three solvent-free complexes are negligible (Table 7).

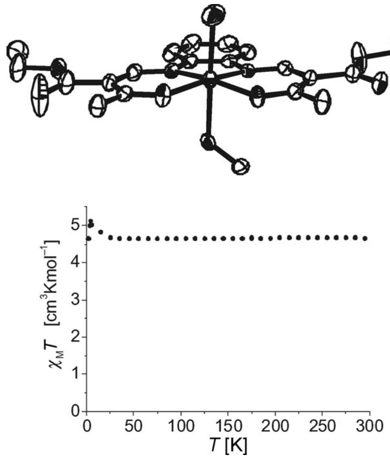


Figure 12. Thermal dependence of $\chi_M T$ (bottom) and ORTEP drawing of the asymmetric unit of [FeL2aCl(MeOH)] (top). The hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level.

Other Examples

The reaction of [FeL2a] with tetracyanoethylene (tcne) or tetracyanoquinondimethane (tcnq) leads to the formation of the two iron(III) charge-transfer complexes [FeL2a(tcne)](MeOH) and [FeL2a(tcnq)$_2$](CH_3CN), respectively. X-ray structure analyses are not available for both complexes; however, all other analytical results indicate chain-like polymer structures. Susceptibility measurements show a decrease in the magnetic moment from room temperature down to approximately 20 K, where an abrupt increase is observed. Field-cooled magnetisation measurements show a spontaneous magnetisation below 10 K. This behaviour is typical for ferromagnetic chains.[24b,55]

Conclusions and Perspectives

In 1962, E.-G. Jäger completed his Ph.D. work with the title "Coordination–Competition between Oxygen and Nitrogen in Metal Chelates of Amino Derivatives of Tricarbonylmethane Compounds".[56] His intentions were to investigate the coordination properties of Schiff bases relative to β-dicarbonyl compounds by applying ligands that theoretically offer both coordination possibilities at the same time. The characterisation of the corresponding copper(II) and nickel(II) complexes did lead to the conclusion, as expected, that N,O coordination is always preferred over O,O coordination. In the last half a century, the ligand system was expanded (especially with regard to the substituents R^1 and R^2), and the corresponding metal complexes (mainly copper, nickel, cobalt and iron) were investigated in detail. Over the years, coordination chemical problems were expanded by questions of bioinorganic or magnetochemical relevance. We now understand the ligand system fairly well. The influence of the substituents and the different bridges on the properties of the ligands and their metal complexes has been determined, and now the information can be used to fine tune the system under investigation until the desired features are obtained. This makes those ligands and their metal complexes extremely valuable for systematic investigations, regardless of the actual area of research. The two main paragraphs of this review article, the one on iron(II) complexes with N-heterocycles as axial ligands and the other on nitrosyliron complexes, both demonstrate this principle. For octahedral iron(II) complexes, the change in the substituents allows us to fine tune the ligand field strength of the complexes so as to reach the region necessary for observation of the spin-crossover phenomenon. So far, 10 SCO complexes were prepared by combining different equatorial and axial ligands, and systematic investigations on the influence of the ligands on the SCO properties, especially with regard to the occurrence of thermal hysteresis loops, were possible. For the nitrosyliron complexes, the properties of the Fe–NO moiety were modified to realise a strong (irreversible) Fe–NO bond on the one side and a loose (reversible) Fe–NO bond on the other side just by small modifications of the substituents of L2. The strong dependence of the properties of the metal complexes on comparably small variations at the ligand demonstrates the importance of such systematic investigations in order to obtain a better understanding of biological systems. In nature, small derivations of the tetrapyrrole macrocycle lead to a wide variety of biologically relevant complex classes with often completely different functions.

The beauty of this ligand system lies in the possibility that it can be expanded even further. Alone the possibility to introduce substituents at the ethylene or phenylene bridge opens a new area of research. The influence of the new substituents on the properties of the metal centre can be investigated, existing systems can be optimised even further and preconditions for the synthesis of polynuclear (mixed) metal complexes can be generated.

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