

## Thiolate-Bridged Diiron(III) Complex with Spin-Crossover Behaviour

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Dedicated to Professor Georg Brauer on the Occasion of his 90th Birthday

**Abstract.** The reaction of the ligand  $\text{HL} \cdot (\text{HCl})_2$  ( $\text{HL}$  = 2,6-di(aminomethyl)-4-*tert*-butyl-thiophenol) with  $\text{MCl}_2$  in methanol in the presence of sodium methanolate and air affords the dinuclear complexes  $[\text{L}_3\text{M}_2][\text{ClO}_4]_3$  ( $\text{M} = \text{Fe}$ : **2**,  $\text{Co}$ : **3**) in 85% and 68% yield, respectively. Both complexes were characterized by infrared spectroscopy, magnetic susceptibility measurements, and  $^1\text{H}$ -NMR spectroscopy. By temperature-variable  $^{57}\text{Fe}$  Mössbauer spectroscopy diamagnetic **2** is shown to exhibit a gradual spin transition between the species  $[\text{L}_3(\text{low-spin-Fe})_2]^{3+}$  ((ls,ls)-**2**) and  $[\text{L}_3(\text{high-spin-Fe})_2]^{3+}$  ((hs,hs)-**2**). At room temperature the relative concentrations of both species are nearly equal. Well resolved quadrupole

doublets at all temperatures for both (ls,ls)-**2** ( $\Gamma$  in the range  $0.22(1)$ – $0.28(1)$  mm s $^{-1}$ ) and (hs,hs)-**2** ( $\Gamma$  in the range  $0.48(1)$ – $0.53(2)$  mm s $^{-1}$ ) are indicative of a spin conversion time longer than the half-life of the  $I = 3/2$  state of  $^{57}\text{Fe}$ . Cyclic voltammetry and square wave voltammetry of **2** in  $\text{CH}_3\text{CN}$  solution reveal four quasi-reversible one-electron transfer processes. The first two processes were assigned to metal-centered reductions of (hs,hs)-**2** and (ls,ls)-**2**, respectively, to yield the mixed-valent species  $[\text{L}_3\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}]^{3+}$ .

**Keywords:** Dinuclear Iron Complex / Amine-Thiolate Ligand / Spin-Crossover / Mössbauer Spectroscopy

## Thiolat-verbrückter Dieisen(III)-Komplex mit Spin-Crossover Eigenschaften

**Inhaltsübersicht.** Durch Reaktion des Liganden  $\text{HL} \cdot (\text{HCl})_2$  mit  $\text{MCl}_2$  in Methanol in Gegenwart von Natriummethanolat und Luftsauerstoff entstehen die zweikernigen Komplexe  $[\text{L}_3\text{M}_2][\text{ClO}_4]_3$  ( $\text{M} = \text{Fe}$ : **2**,  $\text{Co}$ : **3**) in Ausbeuten von 85 bzw. 68%. Die Komplexe wurden durch Infrarotspektroskopie, magnetische Suszeptibilitätsmessungen und durch  $^1\text{H}$ -NMR Spektroskopie charakterisiert. Durch  $^{57}\text{Fe}$ -Mößbauer Spektroskopie bei 77, 180 und 293 K wurde ein gradueller Spinübergang zwischen zwei Formen des diamagnetischen Komplexes **2**,  $[\text{L}_3(\text{low-spin-Fe})_2]^{3+}$  ((ls,ls)-**2**) und  $[\text{L}_3(\text{high-spin-Fe})_2]^{3+}$  ((hs,hs)-**2**) nachgewiesen. Die relativen Konzentrationen

beider Spezies sind bei Raumtemperatur nahezu gleich. Die jeweils gut aufgelösten Quadrupol-Dubletts für (ls,ls)-**2** ( $\Gamma = 0.22(1)$ – $0.28(1)$  mm s $^{-1}$ ) und (hs,hs)-**2** ( $\Gamma = 0.48(1)$ – $0.53(2)$  mm s $^{-1}$ ) deuten auf eine Spinübergangszeit hin, die länger als die Lebensdauer des  $I = 3/2$  Zustands von  $^{57}\text{Fe}$  ist. Durch zyklische Voltammetrie und Square Wave-Voltammetrie können für Lösungen von **2** in  $\text{CH}_3\text{CN}$  vier quasi-reversible Ein-Elektronentransferprozesse beobachtet werden. Die ersten beiden Prozesse werden den metallzentrierten Reduktionen von (hs,hs)-**2** bzw. (ls,ls)-**2** zugeordnet, die jeweils die gemischtvalente Spezies  $[\text{L}_3\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}]^{2+}$  ergeben.

### Introduction

Octahedral transition-metal complexes with the configurations  $d^4$ ,  $d^5$ ,  $d^6$  and  $d^7$  are expected to exhibit

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spin-crossover behaviour when the energy difference between the low-spin and high-spin ground states is in the range of  $kT$  [1]. Since this requirement is very restrictive, only a few classes of transition-metal complexes featuring low-spin high-spin equilibria are known. At present, spin-crossover behaviour is well documented for various transition metal ions with the above mentioned configurations, however, these are in general mononuclear compounds. Higher nuclearity spin-crossover complexes are fewer, these are in general complexes of the type LM–B–ML in which two spin-crossover transition-metal fragments LM are assembled via a bridging ligand B [2–13].

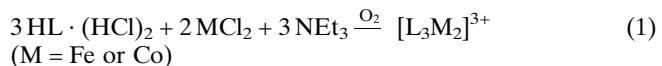
We are interested in the chemical, electronic, and magnetic properties of discrete, dinuclear amine-thiolate metal complexes of the 3d transition metals. Dinuclear amine-thiolate iron(III) complexes, for example, may exhibit spin-crossover behaviour that differs from that seen in related but mononuclear complexes. For example, Wieghardt and Trautwein and their co-workers reported on the pseudo-octahedral iron(III) compound  $[L'Fe]$  (**1**), which contains an *fac*- $N_3S_3$  donor set ( $H_3L'$  is the hexadentate ligand 1,4,7-tris(4-*tert*-butyl-2-mercaptophenyl)-1,4,7-triaza-cyclonane, Fig. 1) [14]. This complex exhibits an electronic spin equilibrium between the high-spin  $^6A_1$  state and  $^2T_2$  state of the ferric ion that is characterized by a spin conversion time shorter than the life time of the  $I = \frac{3}{2}$  state of  $^{57}\text{Fe}$  ( $\tau \approx 10^{-7}$  s).

It was of interest to study the electronic and magnetic properties of dinuclear iron(III) complexes in which two such *fac*- $N_3S_3\text{Fe}$  spin-crossover fragments are joined by the thiolate-sulphur atoms. For this purpose we have selected the new binucleating amine-thiolate ligand 2,6-di(aminomethyl)-4-*tert*-butyl-thiophenol (HL), since ligands of this type have been shown to form stable thiolate-bridged dimetal complexes [15]. Here we report on the synthesis and on the electronic and magnetic properties of  $[L_3\text{Fe}_2][\text{ClO}_4]_3$  (**2**) and  $[L_3\text{Co}_2][\text{ClO}_4]_3$  (**3**), the proposed structures of which are displayed in Figure 1. Reported are the results of temperature-variable  $^{57}\text{Fe}$  Mössbauer spectroscopy and cyclovoltammetric investigations. Finally, the high-spin (hs)-low-spin (ls)

equilibria of  $[L'\text{Fe}]$  (**1**) and  $[L_3\text{Fe}_2][\text{ClO}_4]_3$  (**2**) are compared.

## Results and Discussion

The complexes  $[L_3\text{M}_2][\text{ClO}_4]_3$  ( $\text{M} = \text{Fe}$ : **2**,  $\text{M} = \text{Co}$ : **3**) were obtained in good yields by the reaction of 3 equiv.  $HL \cdot (\text{HCl})_2$  with 2 equiv. anhydrous  $\text{MCl}_2$  and 3 equiv. of  $\text{NaOMe}$  as base in the presence of air as shown in eq. (1). In contrast, any attempts to prepare **2** from  $HL \cdot (\text{HCl})_2$  and an iron(III) source such as  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  resulted in the oxidation of the ligand. Both compounds were isolated as their perchlorate salts. Solid **2** and **3** are stable in air both in the solid state and in solution ( $\text{MeOH}$ ,  $\text{CH}_3\text{CN}$ ,  $\text{DMF}$ ).



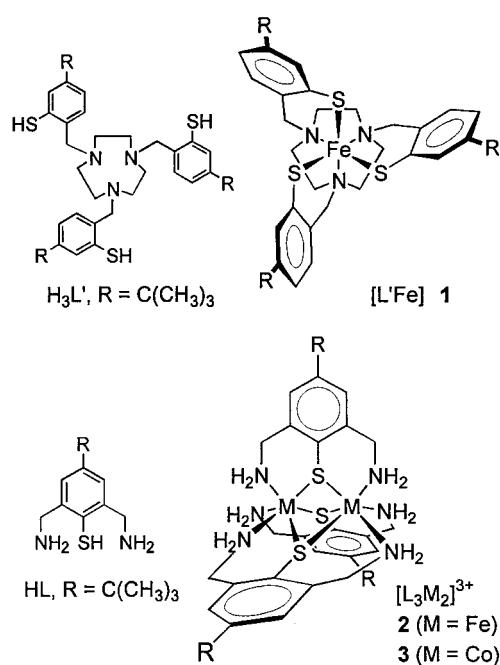
### Infrared spectroscopy of **2** and **3**

Infrared spectra of solid **2** and **3** were recorded at room temperature as KBr pellets. The positions and intensities of the infrared absorption bands (see Experimental Part) of both complexes are identical, except for the absorption at  $760\text{ cm}^{-1}$  for **3**, which appears at  $750\text{ cm}^{-1}$  for **2**. In the  $1600$ – $1000\text{ cm}^{-1}$  region both spectra are dominated by a strong absorption band at  $1086\text{ cm}^{-1}$ , which was assigned to the  $v_3(F_2)$  stretching vibration of the  $\text{ClO}_4^-$  anion [16]. The almost identical IR spectra of **2** and **3** clearly show the presence of the ligand, the presence of the perchlorate ions, and that the complexes are likely to be isostructural.

### Magnetic susceptibility measurements and $^1\text{H-NMR}$ spectroscopy of **2** and **3**

The magnetic susceptibility measurements revealed that complex **3** is diamagnetic at room temperature as are related cobalt(III) complexes featuring a *fac*- $N_3S_3$  coordination [17, 18]. However, the diamagnetism of compound **2** at room temperature is in striking contrast to paramagnetic **1** ( $2.9\ \mu_B$  at 300 K). This result is consistent with the proposed structure for **2** if both iron(III) ions are strongly antiferromagnetically coupled.

Due to their diamagnetism both complexes could be investigated by  $^1\text{H}$  NMR spectroscopy. The  $^1\text{H}$  NMR spectrum of the cobalt(III) complex **3** in  $\text{CD}_3\text{OD}$  solution displays a simple pattern. Characteristic features are as follows: the singlet at 7.48 ppm for the aromatic protons; the two doublets at 3.98 and 3.67 ppm for the protons on the benzylic carbon; the singlet at 1.32 ppm for the *tert*-butyl protons. Due to fast exchange, the hydrogen atoms bonded to the primary nitrogen atom could not be observed in  $\text{CD}_3\text{OD}$  solution. However, these protons are observed in  $\text{DMSO}-d_6$  solution. The  $^1\text{H}$  NMR spectrum of **2** in



**Fig. 1** Structures of  $H_3L'$ ,  $[L'\text{Fe}]$  (**1**),  $HL$ , and proposed structure for the dinuclear  $[L_3\text{M}_2]^{3+}$  cations ( $\text{M} = \text{Fe}$ , (**2**);  $\text{M} = \text{Co}$ , (**3**)).

$\text{CD}_3\text{OD}$  (or  $\text{DMSO}-d_6$ ) solution also displays two singlets for the aromatic and *tert*-butyl protons at 7.50 (7.49) ppm and 1.33 (1.29) ppm, respectively. In contrast to the two sharp benzylic  $\text{CH}_2$  doublets observed for **3**, the respective resonances for **2** appear as broadened features even in  $\text{DMSO}-d_6$  solution. Again, these data clearly demonstrate that complexes **2** and **3** exist as discrete species in  $\text{CD}_3\text{OD}$  or  $\text{DMSO}-d_6$  solution.

### $^{57}\text{Fe}$ Mössbauer Spectroscopy of **1**

Variable-temperature  $^{57}\text{Fe}$  Mössbauer spectra of solid **2** were recorded at 77 K, 180 K and 293 K. At each temperature **2** displays two well resolved quadrupole doublets with similar isomer shifts but different quadrupole splittings (see Figure 2). Furthermore, as the intensity of the inner quadrupole doublet increases (hereafter denoted spectrum II), the intensity of the outer quadrupole doublet (hereafter denoted spectrum I) decreases with increasing temperature. Thus, each spectra were modeled using symmetrically coupled Lorentz functions [19]. The corresponding Mössbauer parameters for both doublets are collected in Table 1.

While the change of isomer shifts with temperature ( $-0.004 \text{ mm s}^{-1} \text{ K}^{-1}$  (spectrum I),  $-0.005 \text{ mm s}^{-1} \text{ K}^{-1}$  (spectrum II)) is typical for  $^{57}\text{Fe}$  [28], the electric quadrupole splitting parameters seem to be nearly independent of temperature. The Mössbauer parameters of spectra I and II fall in a range typical for iron(III) compounds in the low-spin and high-spin state, respectively (see Table 2). Thus, we attribute the two spectra

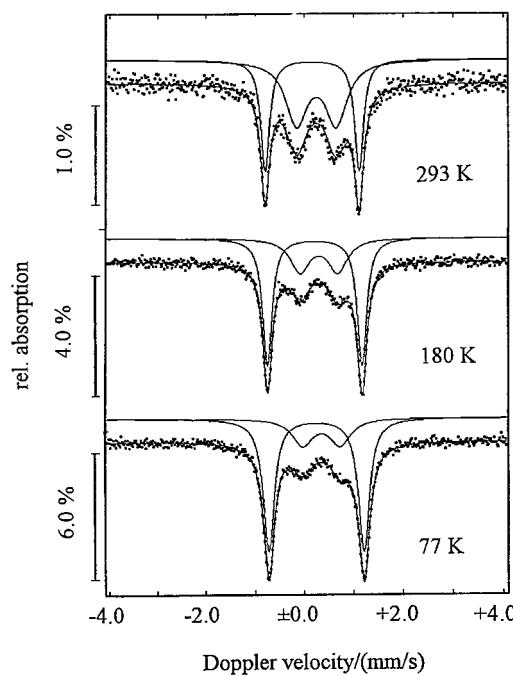


Fig. 2  $^{57}\text{Fe}$  Mössbauer spectra of **2** at 77, 180 and 293 K.

to two different forms of **2**, i.e.  $[\text{L}_3(\text{low-spin Fe})_2]^{3+}$  ((ls,ls)-**2**) and  $[\text{L}_3(\text{high-spin Fe})_2]^{3+}$  ((hs,hs)-**2**), which are in a temperature dependent spin-equilibrium characterized by a spin conversion time that is slow compared to the life-time of the  $I = 3/2$  state of  $^{57}\text{Fe}$ . In accordance with this assignment, the intensity of spectrum I, representing iron(III) in a low-spin state, becomes more intense with decreasing temperature.

The evolution of spectra observed for **2** corresponds to a gradual spin transition [1] with a change of the relative concentration of the (ls,ls)-**2** form from 73% at 77 K to 42% at 293 K, i.e. more than half of the ferric ions (58%) have occupied the high-spin state. We note that there is no Mössbauer spectroscopic evidence for

Table 1 Parameters of  $^{57}\text{Fe}$  Mössbauer spectra for **2**<sup>a</sup>

T/K [ $^{\circ}\text{C}$ ]	$i_{\text{sub}}^{\text{b}}$	$\delta^{\alpha\text{-Fe}}/\text{mm s}^{-1}$ <sup>c</sup>	$\Gamma/\text{mm s}^{-1}$ <sup>d</sup>	$\Delta E_Q/\text{mm s}^{-1}$ <sup>e</sup>	A/% <sup>f</sup>	$F^{\text{g}}$
77 [-196]	I	+0.35(1)	0.28(1)	1.94(1)	73	1.136
	II	+0.46(1)	0.51(2)	0.76(2)	27	
180 [-93]	I	+0.32(1)	0.23(1)	1.92(1)	65	1.073
	II	+0.41(1)	0.48(1)	0.77(1)	35	
293 [+20]	I	+0.26(1)	0.22(1)	1.91(1)	42	1.19
	II	+0.36(1)	0.53(2)	0.81(1)	58	

<sup>a</sup>) Symmetrical Lorentz functions were used throughout;

<sup>b</sup>) I denotes subspectrum for (ls,ls)-**2**, II denotes subspectrum for (hs,hs)-**2**; <sup>c</sup>) Isomer shift referred to  $\alpha$ -Fe at room temperature ( $\delta^{\alpha\text{-Fe}} = \delta^{\text{Fe(Rh)}} + 0.11 \text{ mm s}^{-1}$ , [25–27]); <sup>d</sup>) Full width at half height. <sup>e</sup>) Quadrupole splitting. <sup>f</sup>) Line area relative to total area. <sup>g</sup>) Normalized value of the  $\chi^2$ -test.

Table 2  $^{57}\text{Fe}$  Mössbauer data for high-spin, low-spin, and spin-crossover iron(III) compounds

compound	T/K [ $^{\circ}\text{C}$ ] <sup>a</sup>	state or S <sup>b</sup>	$\delta^{\alpha\text{-Fe}}/(\text{mm/s})^c$	$\Delta E_Q/(\text{mm/s})^d$	ref.
$\text{FePO}_4 \cdot 4 \text{H}_2\text{O}$	298.2 (25.0)	hs (5/2)	+0.43	0.63	[28]
$\text{Fe}_2(\text{SO}_4)_3 \cdot \text{aq}$	298.2 (25.0)	hs (5/2)	+0.45	0.28	[28]
$\text{Fe}(\text{Ph}_2[16]\text{N}_4)\text{SBz}^e$	300 (27)	hs (5/2)	+0.35	0.71	[29]
$\text{Fe}(\text{Ph}_2[16]\text{N}_4)\text{SPh}^e$	300 (27)	ls (1/2)	+0.04	3.60	[29]
$[(\text{TPP})\text{FeCl}]^f$	300 (27)	hs (5/2)	+0.43	0.46	[30, 31]
$[(\text{TPP})\text{FeIm}_2\text{Cl}]^f$	300 (27)	ls (1/2)	+0.14	2.11	[30, 31]
Phthalocyanine-chloro iron(III)	77 (-196)	(3/2)	+0.38	2.52	[32]
	195 (-78)	(3/2)	+0.33	2.52	
	295 (22)	(3/2)	+0.28	2.51	
$\text{Fe}(\text{amben})\text{Cl}^g$	77 (-196)	ls (1/2)	+0.59	3.65	[33]
		hs (5/2)	+0.73	1.03	
	295 (22)	ls (1/2)	+0.49	3.51	
		hs (5/2)	+0.60	0.60	
$\text{Fe}(\text{amben})\text{Br}^g$	77 (-196)	ls (1/2)	+0.52	3.92	[33]
		hs (5/2)	<sup>h)</sup>	<sup>h)</sup>	
	295 (22)	ls (1/2)	+0.50	3.71	
		hs (5/2)	+0.52	0.93	
$[\text{L}/\text{Fe}] \mathbf{1}$	77 (-196)	ls (1/2)	+0.37(1)	0.97(1)	[14]
	293 (20)	ls (1/2)	+0.29(2)	0.34(1)	

<sup>a</sup>) Temperature; <sup>b</sup>) Spin quantum number; <sup>c</sup>) Isomer shift related to  $\alpha$ -Fe at room temperature and normal pressure; data from literature converted herein according to ref. [26];

<sup>d</sup>) Quadrupole splitting; <sup>e</sup>)  $\text{H}_2(\text{Ph}_2[16]\text{N}_4) = 7,15\text{-Diphenyl-1,5,9,13-tetraazahexadeca-5,7,13,15-tetraene};$  <sup>f</sup>)  $\text{TPPH}_2 = \text{meso-Tetr phenylporphine}$ , Im = Imidazole; <sup>g</sup>)  $\text{H}_2\text{amben} = 1,2\text{-bis(o-iminobenzylideneamino)ethane}$ ; <sup>h</sup>) Without statement.

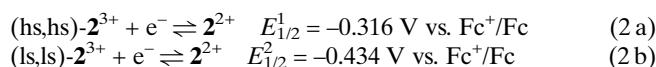
the existence of the  $[L_3(\text{ls-Fe}^{\text{III}})(\text{hs-Fe}^{\text{III}})]^{3+}$  form containing the two ferric ions in two different spin multiplicity states within the dinuclear compound. It is conspicuous that the spin transition in **2** leads to sharply resolved resonances in the Mössbauer spectra. In general, only iron(II) low-/high-spin transitions demand slow relaxation times with respect to the Mössbauer time scale (at least below room temperature) so that their spin states are recognized in well resolved resonances and characteristic parameters [1, 23]. In contrast, the fluctuation rates in the spin transitions observed in octahedral iron(III) complexes are faster and often exceed the Mössbauer time scale so that large line broadening or time averaged spectra are observed.

The isomer shifts and quadrupole splittings observed for **2** might be compared with those determined for **1** [14]. However, in this case fast relaxation renders the two expected quadrupole doublets to collapse into a single doublet at all temperatures in the range 4.2 K to 300 K (for example  $\delta = +0.37 \text{ mm s}^{-1}$ ,  $\Delta E_Q = 0.97(1) \text{ mm s}^{-1}$  at 77 K). If fast relaxation would occur in **2** at 77 K, one estimates a value of  $\Delta E_Q = 1.35 \text{ mm s}^{-1}$  for a hypothetical, time averaged superposition of the two  $\Delta E_Q$  ( $77 \text{ K} = 1.94$  and  $\Delta E_Q (77 \text{ K}) = 0.76 \text{ mm s}^{-1}$  quadrupole doublets.

### Cyclovoltammetry of **2**

The electrochemical behaviour of **2** has been examined by cyclic voltammetry and square wave voltammetry. Figure 3 a shows the cyclic voltammogram of **2** in acetonitrile solution containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate at a scan rate of 100 mV s<sup>-1</sup>. In the potential range +1.30 to -1.00 V vs. Ag/AgCl two sets of two overlapping quasi-reversible one-electron reduction waves are observed. The corresponding  $E_{1/2}$  values were derived from the square wave voltammogram displayed in Fig. 3 b.

The temperature-variable <sup>57</sup>Fe Mössbauer spectroscopy already indicated a temperature dependent electronic spin equilibrium between (hs,hs)-**2** and (ls,ls)-**2**, which are approximately equally populated at room temperature. Accordingly, we assign the first two electron transfer processes as is indicated in eqs. (2 a, 2 b), assuming metal-centered reduction waves for (hs,hs)-**2** and (ls,ls)-**2**. These processes both afford the mixed-valent species **2**<sup>2+</sup>.



The splitting of the first cathodic process ( $\Delta E_{1/2} = 0.118 \text{ V}$ ) together with approximately equal current peak areas for both reduction waves are in good agreement with the existence of a 58% / 42% equilibrium mixture of the (hs,hs)-**2**<sup>3+</sup> and (ls,ls)-**2**<sup>3+</sup>-species previously established by <sup>57</sup>Fe Mössbauer spectro-

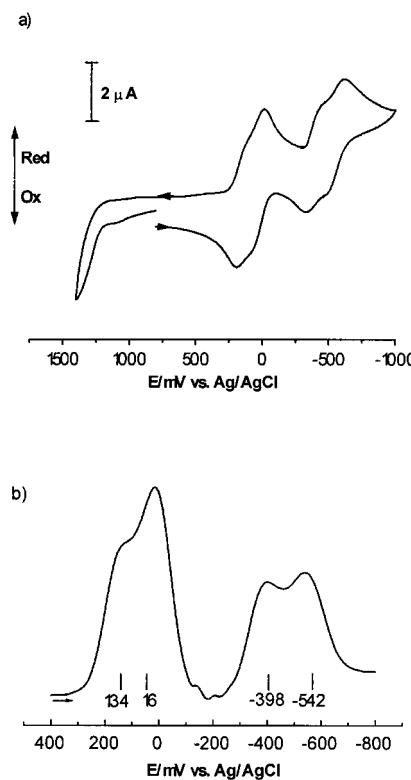


Fig. 3 a) Cyclic voltammogram of **2** in  $\text{CH}_3\text{CN}$  (0.1 M  $[\text{Bu}_4\text{N}]^+\text{[PF}_6^-]$  supporting electrolyte, Pt-disk working electrode, ferrocene internal standard, scan rate  $100 \text{ mV s}^{-1}$ ) and b) the corresponding square wave voltammogram.

scopy. Furthermore, the well defined reduction waves observed for (hs,hs)-**2**<sup>3+</sup> and (ls,ls)-**2**<sup>3+</sup> demonstrate that the spin conversion time of both species is also slow compared to the time scale of the CV experiment. Compared to (hs,hs)-**2** the species (ls,ls)-**2** is reduced at a more negative potential ( $\Delta E_{1/2} = 0.118 \text{ V}$ ) which amounts to a  $10.6 \text{ kJ/mol}$  relative stabilisation of the (ls,ls)-**2** form. At more negative potentials a similar electrochemical behaviour is seen for the mixed-valent species **2**<sup>2+</sup> ( $E_{1/2}^3 = -0.848 \text{ V}$  vs.  $\text{Fc}^+/\text{Fc}$ ,  $E_{1/2}^4 = -0.992 \text{ V}$  vs.  $\text{Fc}^+/\text{Fc}$ ;  $\Delta E_{1/2}^{3/4} = 0.144 \text{ V}$ ). Here the observed electron transfer processes were assigned to the metal-centered reduction of **2**<sup>2+</sup> to form the dinuclear iron(II) species **2**<sup>1+</sup> [20].

### Conclusions

It has been shown by cyclovoltammetric and <sup>57</sup>Fe Mössbauer spectroscopic studies that the dinuclear complex cation  $[\text{L}_3\text{Fe}_2]^{3+}$  (**2**) exhibits spin-crossover behaviour. The characteristics of the spin equilibrium in  $[\text{L}_3\text{Fe}_2]^{3+}$  differ markedly from those observed in mononuclear iron(III) complexes exhibiting a similar coordination environment. In particular, spin conversion between (ls,ls)-**2** and (hs,hs)-**2** in **2** is slower than in  $[\text{L}'\text{Fe}]$  (**1**). Obviously is the increase in the spin con-

version time a result of two adjacent Fe-*fac*-N<sub>3</sub>S<sub>3</sub> spin-crossover fragments, which are bridged by the thiolate sulfur atoms and which are strongly antiferromagnetically coupled. Thus, the properties of other spin-cross-over compounds may also be affected by incorporation of such fragments into di- or polynuclear compounds. Such investigations are currently underway.

## Experimental

**General Information.** The ligand HL · (HCl)<sub>2</sub> was prepared by reduction of benzyl-[2,6-di(hydroximinoformyl)-4-*tert*-butyl-phenyl]sulfide with sodium in liquid ammonia [21]. Unless otherwise noted all other chemicals were of reagent grade and used without further purification. All solvents were pre-dried over molecular sieves and freshly distilled from appropriate drying agents. The syntheses of metal complexes were performed under an atmosphere of dry nitrogen except where mentioned explicitly. CHN-Analyses were determined with a Perkin Elmer Elemental Analyzer 240. IR spectra were recorded on a Bruker IFS25 spectrophotometer as KBr pellets. NMR spectra were recorded on a Bruker model ARX200 spectrometer. Absorption spectra were recorded on a Jasco V-750 UV/VIS/NIR spectrometer. Room temperature magnetic susceptibility measurements were determined with a Johnson Matthey model Mark II magnetic susceptibility balance. Cyclic voltammetry measurements were carried out at 25 °C with an EG & G Princeton Applied Research Potentiostat/Galvanostat Model 263 A. All potentials were scaled to ferrocenium (Fc<sup>+</sup>)/ferrocene (Fc) as internal standard [22]. Melting points were determined in capillaries and are uncorrected.

**Mössbauer spectroscopy.** <sup>57</sup>Fe Mössbauer spectra were collected in constant acceleration modus with a <sup>57</sup>Co(Rh) source (Amersham) [23]. The specimen (131 mg of ground **2** in an acryl holder) was placed in a continuously controlled variable temperature cryostat at low pressure, the source was at room temperature and normal pressure. The transmission of the  $\gamma$ -radiation was detected by means of a NaI(Tl) scintillation counter. The actual velocity of the system was calibrated using  $\alpha$ -iron foil as an external standard. The intensities were digitalized and stored in a multichannel analyzer with 1024 data channels. The  $\delta$  scale is related to the shift of  $\alpha$ -iron as origin of the ordinate. The iron contamination in the beam was neglected. The experimental curve fit was carried out iteratively with the Mössbauer spectra fit routine “SITE” from the “NORMOS” program package [24], using the least-squares method in a thin absorber approximation with symmetrical (or asymmetrical) Lorentz functions. The spectral parameters ( $\delta^{\alpha\text{-Fe}}$ ,  $\Gamma$ ,  $\Delta E_Q$ ,  $A$ ) could each be fixed or correlated in groups in the case of a multi-line fit. Fits were aimed for with largely open parameters.

**Synthesis of [L<sub>3</sub>Fe<sub>2</sub>]/[ClO<sub>4</sub>]<sub>3</sub> (2).** To a solution of HL · (HCl)<sub>2</sub> (892 mg, 3.00 mmol) in methanol (20 ml) was added solid FeCl<sub>2</sub> (254 mg, 2.00 mmol) and the resulting pale yellow solution stirred for 5 min. A 0.50 M solution of NaOMe in methanol (18 ml, 9.00 mmol) was added, producing a yellowish-green precipitate. The suspension was allowed to stir in air until a dark red solution was obtained. Addition of a saturated solution of LiClO<sub>4</sub> (1.50 g) in methanol (2 ml) afforded a brown-red microcrystalline solid, which was fil-

tered, washed with cold methanol (1 ml) and ether (3 ml), and dried in vacuo. A second crop of crystals was obtained by concentrating the mother liquor. Yield: 925 mg (85%), m.p. 120–122 °C (decomp.). *Caution!* Transition-metal perchlorates are hazardous and may explode. Only small quantities should be prepared and great care taken.

C<sub>36</sub>H<sub>57</sub>Fe<sub>2</sub>N<sub>6</sub>O<sub>12</sub>S<sub>3</sub>Cl<sub>3</sub> Calcd. C 40.03; H 5.32; N 7.78% (1080.11) Found C 39.39; H 5.31; N 7.46%

UV/vis (CH<sub>3</sub>CN, 295 K):  $\lambda_{\max}$  ( $\epsilon[M^{-1} \text{ cm}^{-1}]$ ) = 313 (19583), 361 (9264), 414 (4022), 511 (1824).

IR (KBr, cm<sup>-1</sup>):  $\tilde{\nu}$  = 3419 s br, 3082 s, 2954 s, 2868 m, 1596 m, 1461 m, 1405 w, 1388 w, 1364 m, 1312 m, 1236 w, 1204 w, 1141 m, 1119 s, 1108 s, 1087 vs, 994 m, 963 m, 941 m, 881 m, 805 m, 750 m, 626 m.

<sup>1</sup>H NMR (CD<sub>3</sub>OD, ppm):  $\delta$  = 7.50 (s, 6 H, ArH), 3.75 (s br, 12 H, PhCH<sub>2</sub>), 1.33 (s, 27 H, CH<sub>3</sub>).

<sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, ppm):  $\delta$  = 7.60 (s br, 6 H, NH<sub>2</sub>), 7.49 (s, 6 H, ArH), 5.60 (s br, 6 H, NH<sub>2</sub>), 3.95 (s br, 6 H, PhCH<sub>2</sub>), 3.69 (s br, 6 H, PhCH<sub>2</sub>), 1.29 (s, 27 H, CH<sub>3</sub>).

**Synthesis of [L<sub>3</sub>Co<sub>2</sub>]/[ClO<sub>4</sub>]<sub>3</sub> (3).** This compound was prepared by the procedure detailed above for **2** except that CoCl<sub>2</sub> · 6 H<sub>2</sub>O (476 mg, 2.00 mmol) was used instead of FeCl<sub>2</sub>. Yield: 740 mg (68%) of brown needles, m.p. 125–127 °C (decomp.). *Caution!* Transition-metal perchlorates are hazardous and may explode. Only small quantities should be prepared and great care taken.

C<sub>36</sub>H<sub>57</sub>Co<sub>2</sub>N<sub>6</sub>O<sub>12</sub>S<sub>3</sub>Cl<sub>3</sub> Calcd.: C 39.80; H 5.29; N 7.74% (1086.29) Found: C 39.62; H 5.22; N 7.52%

UV/vis (CH<sub>3</sub>CN, 295 K):  $\lambda_{\max}$  ( $\epsilon[M^{-1} \text{ cm}^{-1}]$ ) = 364 (11218), 416 (6429), 476 (3085), 576 (842).

IR (KBr, cm<sup>-1</sup>):  $\tilde{\nu}$  = 3419 s br, 3082 s, 2954 s, 2868 m, 1596 m, 1460 m, 1407 w, 1388 w, 1364 m, 1315 m, 1236 w, 1203 w, 1141 m, 1119 s, 1108 s, 1087 vs, 997 m, 964 m, 942 m, 882 m, 806 m, 761 m, 626 m.

<sup>1</sup>H NMR (CD<sub>3</sub>OD, ppm):  $\delta$  = 7.48 (s, 6 H, ArH), 3.97 (d,  $J$  = 13 Hz, 6 H, PhCH<sub>2</sub>), 3.66 (d,  $J$  = 13 Hz, 6 H, PhCH<sub>2</sub>), 1.32 (s, 27 H, CH<sub>3</sub>).

<sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, ppm):  $\delta$  = 7.44 (s, 6 H, ArH), 5.50 (m, 12 H, NH<sub>2</sub>), 3.83 (m, 6 H, PhCH<sub>2</sub>), 3.70 (m, 6 H, PhCH<sub>2</sub>), 1.29 (s, 27 H, CH<sub>3</sub>).

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