The pentanuclear Fe^{II} cluster [(C$_5$H$_4$)$_6$Fe$_5$]$^{2-}$: bringing together ferrocene sandwiches and homoleptic Fe^{II}-cyclopentadienyl σ-complexes†

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Reaction of [(fc)$_3$(Li)$_6$·(TMEDA)$_2$] with FeCl$_2$ gives the pentanuclear iron complex [(fc)$_3$(Fe)$_2$(Li)$_2$·(TMEDA)$_2$] featuring two ferra[1]ferrocenophane moieties bridged by a 1,1′-ferrocenediyl unit; the non-ferrocene Fe^{II} ions are tetra-coordinate and adopt a high-spin state.

1,1′-Dilithioferrocene,[1] fc(Li)$_2$, is a key starting material for the synthesis of redox-active chelate ligands fc(Do)$_2$ (fc: (C$_5$H$_4$)$_2$Fe; Do: Lewis basic donor site).[2] Such ligands have been receiving increasing attention since a direct Fe → M^{n+} through-space interaction was established for a number of complexes fc(Do)$_2$ML$_m$.[3–5] The degree of this interaction can be influenced by electrochemical manipulation of the ferrocene backbone, thereby offering a tool to modulate the reactivity of M^{n+} under mild conditions and in a reversible manner. Recently, Ephritikhine *et al.* have synthesized the urana[1]ferrocenophane [(fc)$_3$U(Li)$_2$(pyridine)$_3$] and thereby shown that [fc]$^{2-}$ itself may already act as chelating ligand towards transition metal ions.[6] Here, the donor sites are incorporated into the cyclopentadienyl rings, which minimizes the Fe–U distances such that they become equal to the sum of the atomic radii of these elements. The structure of the U^{IV} complex is closely related to those of the Li$^+$-, Mg^{2+}- and Al^{3+}-containing clusters [(fc)$_3$(Li)$_6$·(TMEDA)$_2$],[7] [(fc)$_3$(Mg)$_3$(Li)$_2$(TMP)$_2$·(pyridine)$_2$][8] and [(fc)$_3$(Al)(AlEt)(AlEt$_2$)][9] (TMEDA: tetramethylethylenediamine; TMP: tetramethylpiperidide).[10] The unifying structural motif consists of three 1,1′-ferrocenediyl moieties in a triangular array which create a negatively charged molecular cavity. Depending on the actual compound, this cavity is filled with U^{IV}, Al^{3+}, four Li$^+$ or three Mg^{2+} ions coordinated to the electron lone pairs of the deprotonated carbon atoms. The fact that these rather similar supramolecular aggregates are stable with different numbers and different kinds of metal ions raised the question of whether corresponding complexes with first-row transition metals can be prepared. We chose to attempt the synthesis of an Fe^{II} complex, hoping to obtain an oligonuclear aggregate featuring exclusively η^5-π-coordinated iron centres together with exclusively η^1-σ-coordinated iron centres. Such a compound appeared attractive because it combines ferrocene

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sandwich moieties with the structural motif originally suggested for ferrocene by Kealy and Pauson.[11]

1,1′-Dilithioferrocene, [(fc)$_3$(Li)$_6$·(TMEDA)$_2$] (**1**), reacts with FeCl$_2$ in a stoichiometric ratio of 1 : 2 to give the pentanuclear Fe^{II} complex [(fc)$_3$(Fe)$_2$(Li)$_2$·(TMEDA)$_2$] (**2**) in the form of crimson-purple crystals (λ_{max} = 444 nm).‡

We have observed **2** also as a decomposition product of a sample of 1,1′-dilithioferrocene [(fc)$_3$(Li)$_6$·(TMEDA)$_2$] (**1**), stored in C$_6$D$_6$ over a period of several months (sealed NMR tube, inert atmosphere, r.t.; yield of **2**: 46%; the crystalline sample was characterized by X-ray crystallography and TXRF spectroscopy). The NMR spectra of the mother liquor indicated the concomitant formation of cyclopentadienyl lithium (δ(^{1}H) = 5.58; δ(^{13}C) = 102.5).

The structure of **2** was determined by X-ray crystallography.§ The compound consists of three 1,1′-ferrocenediyl moieties connected by two Fe^{II} and two [Li(TMEDA)]$^+$ ions (Fig. 1). Each molecule of **2** possesses a C_2 axis running through the ferrocene iron ion Fe(2) parallel to the cyclopentadienyl ring Cp(C(31)). The molecular framework of the anionic [(fc)$_3$Fe$_2$]$^{2-}$ subunit consists of two ferra[1]ferrocenophane units linked by one 1,1′-ferrocenediyl bridge (Fig. 2). Moreover, each non-ferrocene iron ion establishes one additional Fe–Cp bond to achieve tetra-coordination (Fe(3)–C(21A); dashed line in Fig. 2). Thus, Fe(3) is coordinated by all three 1,1′-ferrocenediyl ligands *via* the deprotonated carbon atoms C(11), C(21), C(21A), and C(31). The corresponding C–Fe–C bond angles fall in the range between C(21)–Fe(3)–C(21A) = 94.7(1)° and C(21)–Fe(3)–C(31) = 126.8(1)° and thus deviate significantly from the ideal tetrahedral angle of 109°. For a formal classification of the nature of the Fe(3)–Cp bonds, it is helpful to look at the angles defined by Fe(3), the *ipso*-carbon atom and the centre of gravity of each coordinated cyclopentadienyl ring. The corresponding values are 132.1°/127.9° in the case of Cp(C(11))/Cp(C(21)) and 161.9°/163.2° for Cp(C(21A))/Cp(C(31)). These data suggest Fe(3)–C(21A) and Fe(3)–C(31) to be mainly σ-bonds. In contrast, overlap with the π-electron cloud of the respective Cp ring is likely to contribute significantly to Fe(3)–C(11) and Fe(3)–C(21) bonding. There is no obvious correlation between the different Fe–Cp binding modes and the Fe–C bond lengths, however, the shortest contact corresponds to a σ-bond (Fe(3)–C(31) = 2.070(2) Å) and the longest contact to an *ansa*-bond (Fe(3)–C(21) = 2.237(3) Å).

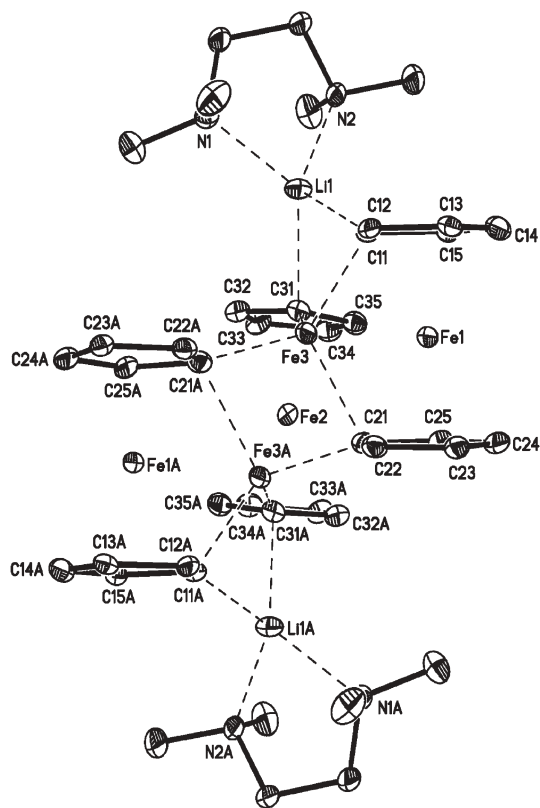Homoleptic organoiron compounds are rare and only one example of a structurally characterized Fe^{II}R$_4$ complex is currently known in the literature (R = alkyl, aryl).[12] In this compound of molecular formula [(C$_{10}$H$_7$)$_4$Fe][LiO(C$_2$H$_5$)$_2$]$_2$,[13] four α-naphthyl

Fig. 1 Crystal structure of compound **2**; thermal ellipsoids shown at the 50% probability level. Selected bond lengths [Å], atom–atom distances [Å], and angles [°]: Li(1)–C(11) 2.235(5), Li(1)–C(31) 2.344(4), Fe(3)–C(11) 2.113(2), Fe(3)–C(21) 2.237(3), Fe(3)–C(21A) 2.114(3), Fe(3)–C(31) 2.070(2), Fe(1)···Fe(3) 2.686(1), Fe(3)···Fe(3A) 2.465(1); C(11)–Fe(3)–C(21) 99.2(1), C(11)–Fe(3)–C(21A) 117.4(1), C(11)–Fe(3)–C(31) 108.2(1), C(21)–Fe(3)–C(21A) 94.7(1), C(21)–Fe(3)–C(31) 126.8(1), C(21A)–Fe(3)–C(31) 110.6(1), Fe(3)–C(21)–Fe(3A) 69.0(1). Symmetry transformation used to generate equivalent atoms: $-x + 1$, y, $-z + 3/2$ (A).
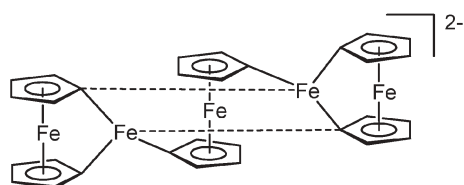
Fig. 2 Schematic representation of the $[(fc)_3Fe_2]^{2-}$ core of complex **2**.

substituents are coordinated to the central Fe^{II} ion *via* σ-bonds in a distorted tetrahedral geometry (mean Fe^{II}–C bond length: 2.126 Å). Another interesting complex for comparison is $[Fe_2(Mes)_2(\mu\text{-}Mes)_2]^{14}$ in which terminal as well as bridging mesityl ligands are present. Here, the terminal Fe^{II}–C bonds tend to be somewhat shorter (average value: 2.024 Å) than the bridging Fe^{II}–C bonds (average value: 2.130 Å; two crystallographically independent molecules in the unit cell). The $[Li(TMEDA)]^+$ counterion in **2** is coordinated by C(11) and C(31) such that Cp(C(11)) and Cp(C(31)) are shared between Fe(3) and Li(1) whereas Cp(C(21)) bridges the two iron ions Fe(3) and Fe(3A). Fe(3) and the ferrocene iron centre Fe(1) are located at a distance of 2.686(1) Å. This value may be compared with the Fe···M distances

in *trans*-$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ (Fe^I···Fe^I = 2.539(1) Å),[15] $[(\pi\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)(\mu_3\text{-}S)W(CO)_5]^{16}$ (Fe^{II}···Fe^{II} = 2.592(4) Å), and $[(fcS_2)Ni(PMe_2Ph)]$ (Fe^{II}···Ni^{II} = 2.886(1) Å)[3] in which direct bonds between the two metal centres have been postulated. The distance between the non-ferrocene iron atoms in **2** amounts to Fe(3)···Fe(3A) = 2.465(1) Å. It is thus significantly shorter not only than the Fe···Fe contacts mentioned above but also than the average Fe···Fe distance of 2.615 Å in the two crystallographically independent molecules of $[Fe_2(Mes)_2(\mu\text{-}Mes)_2]$.

2 possesses a paramagnetic nature; meaningful NMR spectra were therefore not obtained. The molar susceptibility of a sample of **2** was determined by SQUID measurements at a temperature of 300 K.¶ We assume that the three ferrocene Fe^{II} ions of **2** still adopt the usual low-spin state ($S = 0$) such that the two σ-bonded iron centres are the only spin carriers. Based on this model, an effective magnetic moment of 5.3 μB can be deduced for each of the two bridging Fe^{II} ions in accord with an $S = 2$ spin state (note: the typical magnetic moments for high-spin Fe^{II} centres are in the range between 5.1–5.7 μB[17]).

Compound **2** is sensitive towards air and moisture. In order to identify the decomposition product(s), we dissolved a sample of **2** in THF and exposed it to air for a short period of time. The reaction mixture was then investigated by MALDI-TOF mass spectrometry in the positive ion mode using a 2,5-dihydroxybenzoic acid (DHB) matrix. In contrast to *a priori* expectations, we did not find any indication that parent ferrocene was liberated. In fact, the spectrum is characterized by a series of equidistant peaks ($\Delta(m/z) = 184$) in the range between $m/z = 368$ and $m/z = 1840$. The first peak can be assigned to a $[\text{-}fc_2\text{-}]^+$ fragment, the last to the $[\text{-}fc_{10}\text{-}]^+$ ion and the mass difference between adjacent peaks corresponds to a 1,1′-ferrocenediyl repeat unit. Thus, oxidative C–C coupling reactions obviously take place under the measurement conditions applied. The non-ferrocene Fe^{II} ions are most likely involved in oligo(ferrocenylene) formation because a comparable peak pattern is absent in the MALDI-TOF-MS of **1**.

In summary, we have prepared the pentanuclear homoleptic Fe^{II} cluster $[(fc)_3Fe_2]^{2-}$ which contains the structural motif of a ferra[1]ferrocenophane and proves the suitability of $[fc]^{2-}$ as ligand towards d-block metal ions. A detailed investigation of electronic and magnetic interactions between the five iron centres of **2** is currently under way in our laboratory.

Notes and references

‡ *Synthesis of 2*: All manipulations were carried out in an argon-filled glove box. A mixture of $[(fc)_3(Li)_6\cdot(TMEDA)_2]$ **1** (0.194 g, 0.235 mmol) and $FeCl_2$ (0.063 g, 0.497 mmol) in benzene (10 mL) was stirred for 2 d at r.t. All the insolubles were removed by filtration. Single crystals suitable for X-ray crystallography were grown from the filtrate at r.t. upon slow evaporation of the solvent. Yield of single-crystalline material *ca.* 50%. UV-vis: $\lambda_{max}(C_6H_6)$/nm 298 (ε/dm^3 mol^{-1} cm^{-1} 4046), 444 (453).
§ *Crystal data of 2*: $C_{42}H_{56}Fe_5Li_2N_4$, $M = 910.04$ g mol^{-1}, monoclinic, $a = $ 21.5484(17) Å, $b = 10.5554(10)$ Å, $c = 17.5984(14)$ Å, $\beta = 98.862(6)°$, $U = $

3955.0(6) Å^3, $T = 100(2)$ K, space group $C2/c$, $Z = 4$, $\mu(\text{Mo-K}\alpha) = 1.826$ mm^{-1}, 19130 reflections measured, 3575 unique ($R_{int} = 0.0598$) which were used in all calculations. The final $wR(F^2)$ was 0.0416 (all data). **2** is isostructural to the Li$^+$ complex [(fc)$_3$(Li)$_6$·(TMEDA)$_2$] (**1**), and the unit cell parameters of both compounds are almost identical. We have therefore re-determined the crystal structure of **1** at a temperature of 173 K ($C_{42}H_{56}Fe_3Li_6N_4$, $M = 826.10$ g mol^{-1}, monoclinic, $a = 21.420(5)$ Å, $b = 10.730(3)$ Å, $c = 17.830(4)$ Å, $\beta = 99.533(17)°$, $U = 4041.4(17)$ Å^3, $T = 173(2)$ K, space group $C2/c$, $Z = 4$, $\mu(\text{Mo-K}\alpha) = 1.097$ mm^{-1}, 9280 reflections measured, 3787 unique ($R_{int} = 0.1753$), final $wR(F^2) = 0.1055$ (all data); for an ORTEP plot see the Supplementary Material). **1** has previously been characterized by X-ray crystallography at a measurement temperature of 295 K.[7] The differing atoms in **1** and **2** could be unequivocally determined. They showed up in a difference map with clearly distinguishable heights and could be successfully refined as Li in **1** and Fe in **2**. It is impossible to refine Li(2) and Li(3) as Fe in **1** and Fe(3) as Li in **2**. CCDC reference numbers: 296319 (**1**), 296318 (**2**). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b602359b

¶ *Magnetic characterization of* **2**: Measurements on **2** (6.5 mg) were carried out under inert conditions in a sealed glass ampoule with a Quantum-Design SQUID magnetometer in the temperature range from 300 K to 2 K and a field of 0.1 T.

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