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Showcasing research by C. Lichtenberg, H. Grützmacher *et al.*,
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Low-valent iron: an Fe(I) ate compound as a building block for a
linear trinuclear Fe cluster

The trinuclear low-valent iron cluster $[\text{Fe}_3(\text{trop}_2\text{dad})_2]$ was
rationally synthesized using a well-defined Fe^I precursor. The
cluster is based on a redox-active diazadiene-diolefin ligand.
Its electronic structure was evaluated. The modular synthetic
approach opens up possibilities for expansion of this compound
family.

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Low-valent iron: an Fe(I) ate compound as a building block for a linear trinuclear Fe cluster†

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A low-valent trinuclear iron complex with an unusual linear Fe(I)–Fe(II)–Fe(I) unit is presented. It is accessed in a rational approach using a salt metathesis reaction between a new anionic Fe(I) containing heterocycle and FeCl₂. Its electronic structure was studied by single crystal XRD analysis, EPR and Mössbauer spectroscopy, and magnetic susceptibility measurements.

The cluster structure of polynuclear iron compounds can determine the characteristics of (multi-)redox processes,¹ enable cooperative reactivity,² and allow the precise adjustability of magnetic properties.³ While the synthesis of well-defined polynuclear compounds with iron in its more common oxidation states 0, +2, and +3 is rather well-developed, Fe(I) species are scarce and their rational synthesis and detailed characterization remain challenging.⁴ Synthetic difficulties under strongly reducing conditions include ligand dissociation (formation of Fe⁰), ligand decomposition, or disproportionation reactions.

Here we report on a well-established concept for the syntheses of polynuclear sandwich complexes as an approach to low-valent Fe clusters, namely reacting anionic unsaturated building blocks with metals salts.⁵ To this end, we prepared a new mononuclear, anionic Fe(I) diazadiene (dad) diolefin complex, which can be described as a ferradiaza-cyclopentenide, as building block for the preparation of a trinuclear low-valent iron cluster with an unusual linear Fe₃ unit.

Reaction of [FeBr₂(thf)₂] with trop₂dad (trop = 5*H*-dibenzo-*[a,d]*cyclo-hepten-5-yl, dad = diazadiene) gave [FeBr₂(trop₂dad)] (**1**) in quantitative yield (Scheme 1a). The effective magnetic moment of **1** amounts to $\mu_{\text{eff}} = 4.7 \mu_{\text{B}}$ (Evans' method) indicating a d⁶ hs electron configuration at the Fe center. ¹H NMR spectroscopic analysis revealed apparent C_s symmetry in solution. Analysis of the molecular structure, using single crystal X-ray diffraction, shows a distorted tetrahedral coordination geometry around the metal center and the structural parameters indicate a neutral dad ligand coordinated to Fe(II) with free unbound olefin units (ESI†).^{6,7}

Reduction of **1** with excess Na or NaH led to formation of the iron(I) compound **2**, which was isolated in 73% yield as dark brown single crystalline needles (Scheme 1a). X-ray diffraction analysis of a single crystal showed that complex **2** forms a contact ion pair in the solid state (Fig. 1). The trop₂dad acts as tetradentate ligand.

The dad fragment and the Fe atom form an almost planar FeN₂C₂ heterocycle with Fe1 deviating by only 0.12 Å from the N–C–C–N plane. The sodium counter ion interacts asymmetrically with the diazadiene backbone (Na1–N1/2, 2.739(2)/2.982(2) Å). The C31–C32 bond in the dad unit is short (1.368(3) Å) while the two C31/32–N1/2 bonds (1.384(3) Å/1.375(3) Å) correspond to C–N single bonds indicating that the ligand has adopted its fully reduced bis-amido ethene state, (trop₂dad)^{2–}, with two negatively charged amido groups.⁷ The distorted square planar coordination geometry (angle sum around Fe: 367°) is unusual for Fe(I) compounds, but has recently been observed for the complex [NaFe(trop₂dae)(thf)₃] with a non-redox-active, saturated (NC₂H₄N) ligand backbone, which is formally related to **2** by addition/extrusion of H₂.^{9–11} Whereas the average Fe–N distances in **2** are in the same range as observed for [NaFe(trop₂dae)(thf)₃], the Fe–olefin distances are shortened by 0.03 Å suggesting stronger π -back-bonding in compound **2**. This is also reflected in the rather long coordinated C=C^{trop} bonds [C4–C5, 1.449(3); C19–C20, 1.448(3)]. X-band EPR spectroscopy of **2**, in THF/0.1 M [N(*n*Bu)₄][PF₆] at 20 K, revealed a rhombic signal without any (resolved) hyperfine coupling (Fig. 1b). The spectrum is characteristic for an *S* = 1/2 species. The experimental *g*-values (*g*_x = 2.010, *g*_y = 2.095, *g*_z = 2.199) are in reasonable agreement with those predicted by DFT calculations and indicate a higher *g*-anisotropy for **2** than for

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Scheme 1 Syntheses of (a): Fe(I) compound **2** and (b): trinuclear **3**⁸ and mononuclear **4**; abbreviations for trop substituent.

Fig. 1 (a) Molecular structure of **2** in the solid state. The asymmetric unit contains two highly similar molecules of **2**, only one of which is shown. Displacement ellipsoids are drawn at the 50% probability level; hydrogen atoms and one set of split positions of disordered thf ligand are omitted for clarity. Selected bond lengths [Å] and angles [°]: Fe1–N1, 1.8776(19); Fe1–N2, 1.8793(19); Fe1–(C4–C5), 1.896(2); Fe1–(C19–C20), 1.899(2); C4–C5, 1.449(3); C19–C20, 1.448(3); C31–C32, 1.368(3); C31–N1, 1.384(3); C32–N2, 1.375(3); N1–Fe1–N2, 82.53(8); (C4–C5)–Fe1–(C19–C20), 99.93(9). (b) Experimental and simulated X-band EPR spectra of **2** in frozen THF/0.1 M [N(nBu)₄][PF₆] at 20 K.

the related species [NaFe(trop₂dae)(thf)₃].⁹ DFT calculations show that **2** is an Fe-centered radical species (spin density at Fe: 1.33) with substantial spin polarization to the coordinating N- and C-atoms (ESI[†]). Magnetic susceptibility data recorded with powder samples of **2** are fully consistent with the EPR spectrum. An effective magnetic moment, μ_{eff} , of 1.80 μ_{B} is obtained, which is field independent (0.01–1 T) and – as expected for $S = 1/2$ – almost invariant in the temperature range of 3–300 K (ESI[†]).

The effective magnetic moment in solution is 1.9(1) μ_{B} at 298 K (Evans' method). Both values are close to the spin only value for one unpaired electron (1.82 μ_{B} for $g_{\text{average}} = 2.10$). The zero field Mössbauer spectrum of solid **2** recorded at 77 K shows a quadrupole doublet with a low isomer shift $\delta = 0.21(1)$ mm s^{−1} and a large quadrupole splitting $|\Delta E_{\text{Q}}| = 2.45(1)$ mm s^{−1} (ESI[†]). The parameters are consistent with the expected d⁷ low-spin electron configuration at the Fe(I) center in **2** with its distorted square planar coordination

geometry. The quadrupole splitting is moderately decreased compared to [NaFe(trop₂dae)(thf)₃], reflecting the more symmetrical coordination geometry in **2**. The isomer shift is within limits of error identical with that observed for [NaFe(trop₂dae)(thf)₃], which is low compared to other Fe(I) species and again indicates significant Fe → (C=C^{trop}) back donation.⁹ Cyclic voltammetry revealed two quasi-reversible redox waves for compound **2** with half potentials $E_{1/2}$ of −1.02 V and −2.40 V vs. Fe/Fe⁺ (ESI[†]).

In order to investigate its ability to serve as building block, **2** was reacted with [FeCl₂(thf)_{1.5}] in a 2:1 stoichiometry (Scheme 1b). Indeed, the trinuclear cluster compound [Fe₃(trop₂dad)₂] (**3**) could be isolated from this metathesis reaction (exchange of two Na(thf)₃⁺ cations for one Fe²⁺) as a deep red-brown single crystalline material in 82% yield. In low yield, **3** was also isolated in an attempt to oxidize [NaFe(trop₂dad)(thf)₃] (**2**) with Ph₃CCl (ESI[†]).¹² This suggests that the mechanism leading to **3** may be more complex than Scheme 1b implies.

The structure of **3** was determined by single crystal X-ray diffraction (Fig. 2). It shows an almost linear array of three iron centers [Fe1–Fe2–Fe3, 171.06(3)°], which is rare compared to the frequently observed triangular arrangements in other trinuclear Fe complexes. The few previously isolated examples of compounds with linear Fe₃ units include [Fe₃(μ₂-S)₄(SET)₄]^{3−} (**A**),^{13a} [Fe₃(μ₂-Se)₄(SPh)₄]^{3−} (**B**),^{13b} [Fe₃(μ₂-S(CH₂CH₂S)₂)(C₅Me₅)₂]²⁺ (**C**),^{13g} [Fe₃(μ₂-NPh)₄Cl₄]^{2−} (**D**),^{13c} [Fe₃(μ₂-PMe₂)₃(NO)₃(CO)₄] (**E**),^{13d} and [Fe₃(μ₂-(NET)₂)(μ₂-(CH₃CH)₂-(CO)₂)] (**F**).^{13e,f,14} The Fe–Fe distances of 2.63–2.64 Å in **3** are within the range of values reported for **A–F** (2.47–2.78 Å), which have been considered bonding interactions in case of **E** and **F**. The structure of **3** is best described with two FeN₂C₂ heterocycles, which share the iron atom Fe2 as a spiro-center. Each of the two terminal iron centers Fe1 and Fe3 is coordinated by the N atoms and the olefinic C=C^{trop} groups of one (trop₂dad)^{2−} ligand (angle sum around Fe1/3, 360°). Fe1/3–C^{dad} distances of ca. 2.11 Å suggest the possibility of additional binding interactions with the carbon atoms of the ligand backbone. With respect to compound **2**, the Fe–olefin and Fe–N distances are slightly elongated and the C=C^{trop} bonds are slightly shortened indicating less efficient Fe → C=C^{trop} backbonding. The central

Fig. 2 Molecular structure of $[\text{Fe}_3(\text{trop}_2\text{dad})_2]$ (**3**) in the solid state.⁸ Hydrogen atoms, anellated C_6H_4 groups, and solvent molecules in the lattice are omitted for clarity. Displacement ellipsoids are shown at the 50% probability level; carbon atoms not interacting with Fe centers are drawn as wireframe. Selected bond lengths [Å] and angles [°]: Fe1–Fe2, 2.6410(8); Fe2–Fe3, 2.6340(8); Fe1–N1, 1.976(3); Fe1–N2, 1.984(4); Fe1–C31, 2.104(4); Fe1–C32, 2.111(4); Fe1–(C4=C5), 1.939(4); Fe1–(C19=C20), 1.949(4); Fe2–N1, 2.052(3); Fe2–N2, 2.027(3); N1–C31, 1.393(6); C31–C32, 1.365(6); N2–C32, 1.391(5); C4–C5, 1.437(6); C19–C20, 1.428(7); Fe1–Fe2–Fe3, 171.06(3); dad1–Fe1–Fe3–dad2, 67.8.

iron atom in **3**, Fe2, is coordinated by four nitrogen atoms of the two $(\text{trop}_2\text{dad})^{2-}$ ligands (Fe2–N(1–4), 2.03–2.05 Å) to give a distorted tetrahedral coordination sphere. The two dad backbones are twisted around the Fe_3 axis (dihedral angle dad1–Fe1–Fe3–dad2 $\approx 68^\circ$). The C31=C32^{dad} bonds are again short (C31–C32, 1.365(6) Å) and the C–N bonds long (N1/2–C31/32, 1.39 Å) indicating that both dad units are fully reduced.⁷ This leaves a net charge of +4 for the Fe_3 core indicating low-valent iron centers.

The spin state of the all-ferric compounds, **A** and **B**, with their linear Fe^{3+} – Fe^{3+} – Fe^{3+} array has been investigated in detail, but the coupling patterns and spin states of comparable compounds, like **E**, **F**, containing low-valent iron are presently unknown. Zero-field Mössbauer spectroscopy at 77 K gave a spectrum of **3** with two quadrupole doublets with an intensity ratio of 2 : 1 (ESI[†]). Both, the high isomer shift ($\delta = 0.92(1) \text{ mm s}^{-1}$) and the moderately large quadrupole splitting ($|\Delta E_Q| = 1.88(1) \text{ mm s}^{-1}$) of the less intense signal assigned to the central Fe2 ion are characteristic of a high-spin $\text{Fe}(\text{II})$ electron configuration.¹⁵ The Mössbauer parameters of the more intense signal, corresponding to the terminal Fe1 and Fe3 atoms in **3**, amount to $\delta = 0.37(1) \text{ mm s}^{-1}$ and $|\Delta E_Q| = 1.09(1) \text{ mm s}^{-1}$. These values are within the broad range of isomer shifts (0.20–1.09 mm s^{-1}) and quadrupole splittings ($|\Delta E_Q| = 0.89$ –3.48 mm s^{-1}) reported for $\text{Fe}(\text{I})$ species.^{9,16} The low isomer shift, however, being below the value reported for a three coordinate high-spin β -diketiminato $\text{Fe}(\text{I})$ compound with an alkyne ligand ($\delta = 0.44 \text{ mm s}^{-1}$),¹⁷ hints at a low-spin electron configuration of the terminal $\text{Fe}(\text{I})$ ions in **3** (local spin states $S_{\text{Fe1}} = S_{\text{Fe3}} = 1/2$). Compared to compound **2**, the terminal Fe atoms in **3** show a higher isomer shift, indicating a lower s-electron density at the Fe nucleus due to less significant $\text{Fe}^{\text{terminal}} \rightarrow \text{ligand}$ back donation in **3**, which

is in agreement with the observed elongated $\text{Fe}^{\text{terminal}}$ –ligand bonds in **3** (*vide supra*).

SQUID magnetic susceptibility measurements with microcrystalline **3** reveal $\mu_{\text{eff}} = 5.8 \mu_{\text{B}}$ (300 K, 1 T) (Fig. 3 top and ESI[†]). Above *ca.* 200 K, μ_{eff} is almost constant, whereas below it gradually decreases reaching $2.01 \mu_{\text{B}}$ at 2 K. This reveals rather weak total exchange splitting of the spin system in the energy interval kT for temperatures up to *ca.* 200 K. Data analysis with a spin coupling model for a spin triad of isosceles topology with $S_{\text{Fe1}} = S_{\text{Fe3}} = 1/2$, $S_{\text{Fe2}} = 2$, according to local $1s\text{-Fe}(\text{I})\text{-}hs\text{-Fe}(\text{II})\text{-}1s\text{-Fe}(\text{I})$ electron configurations reveals anti-ferromagnetic interactions between all three Fe nuclei.¹⁸ The best fit was obtained with exchange coupling constants $J_{\text{Fe1/3Fe2}} = -10.0 \text{ cm}^{-1}$, $J_{\text{Fe1Fe3}} = -23.0 \text{ cm}^{-1}$ and local zero field splitting (ZFS) parameters $|D| = 46 \text{ cm}^{-1}$ and $E/D = 0.3$ for the central ferrous ion, Fe2.¹⁹ The absolute values of the coupling constants are approximately one order of magnitude smaller than those observed in the sulfur bridged all-ferric trinuclear compound **A**.^{13a} The competition of moderately strong all-antiferromagnetic spin coupling and the local ZFS of $S_{\text{Fe2}} = 2$ leads to a large number of close-lying magnetic sublevels, in accord with the gradual slope of $\mu_{\text{eff}}(T)$. The twenty eigenstates $|m_{s,\text{Fe1}}, m_{s,\text{Fe2}}, m_{s,\text{Fe3}}\rangle$ of the coupled spin system are spread out in an extremely narrow energy range of $<300 \text{ cm}^{-1}$ ($<0.86 \text{ kcal mol}^{-1}$) without showing any structure of isolated total spin manifolds. As can be seen from the energy level plots in Fig. 3

Fig. 3 Top: Plots of molar magnetic susceptibility (circles) and effective magnetic moment (triangles) of solid $[\text{Fe}_3(\text{trop}_2\text{dad})_2]$ (**3**) vs. temperature (red lines indicate fits (see text)). Bottom: Energy plot of the magnetic eigenstates for **3** vs. fields applied in x, y, z-directions with respect to the magnetic axes defined by the zero field splitting tensor of Fe2.

(bottom), at most a group of four 'ground state' levels can be regarded as somewhat isolated from more excited levels. But according to spin Hamiltonian theory, these N states would translate into a corresponding effective spin $S' = 3/2$ (since then $N = 2S' + 1$), which would not be a meaningful concept for a trimer with an even number of electrons. Moreover, the energy separation is also not sufficient to prevent field-dependent mixing of the manifold with excited states. Thus, total spins S with values ranging from $S_1 + S_2 + S_3 = 3$ to $S_2 - S_1 - S_3 = 1$ are not good quantum numbers for **3** and a physically meaningful assignment of a ground state spin is therefore not possible.

The values for J_{ij} and $|D|$ obtained from parameter optimization are not unique. Other solutions with similar goodness can be obtained with D values in the range $|D| = 40 \pm 20 \text{ cm}^{-1}$ in conjunction with negative J_{ij} values ranging from -8 to -26 cm^{-1} (see ESI† for error plots).

Variable-field magnetic measurements could not solve the ambiguities because at base temperatures, where the field effects are significant, the measurements are obscured by additional intermolecular interactions (Fig. S9, ESI†). In any case, however, competition between different antiferromagnetic exchange pathways in the spin trimer and the local ZFS at Fe2 leads to strong spin mixing such that a well-separated ground state with a physically meaningful total spin does not exist for **3**.

The effective magnetic moment of **3** in solution was determined with the Evans' method and gives $\mu_{\text{eff}} = 5.4(2) \mu_{\text{B}}$ at 298 K, which is slightly lower than that determined in the solid state.²⁰ Compound **3**, dissolved in toluene, is EPR silent at 20 K and at 298 K.²¹

Solutions of the tri-iron cluster **3** are not particularly stable. After 4 d, workup of a solution of *in situ* generated **3** afforded compound **4** in 22% isolated yield (Scheme 1b). Formally, **3** is transformed into **4** by extrusion of two Fe(0) atoms. Compound **4** was independently and rationally synthesized (Scheme 1b) and fully characterized (ESI†). This complex – with a distorted tetragonal structure and an $S = 1$ spin-state, is best described as a hs-Fe(II) center, antiferromagnetically coupled to two monoanionic radical ligands ($\text{trop}_2\text{dad}^\bullet$)^{•–} as previously reported for other $[\text{Fe}(\text{II})(\text{dad}^\bullet)_2]$ complexes.²² Compound **4** is a potential precursor for trinuclear clusters as it contains four olefinic trop units that can act as strong field ligands towards electron rich transition metal centers.

A new heterobimetallic complex $[\text{NaFe}(\text{trop}_2\text{dad})(\text{thf})_3]$ (**2**) was obtained, which contains the redox-active ("non-innocent") diazadiene ligand as $(\text{trop}_2\text{dad})^{2-}$. The spin density of the unpaired electron is located on the low-spin d^7 -valence electron configured iron center. As a building block, **2** can be utilized for the synthesis of the first thoroughly investigated paramagnetic low-valent trinuclear iron cluster with an unusual linear Fe_3 unit, $[\text{Fe}_3(\text{trop}_2\text{dad})_2]$ (**3**). Compound **3** has a ls-Fe(I)–hs-Fe(II)–ls-Fe(I) electronic structure with a large number of magnetic sublevels close to the ground state. Eventually, the detailed spectroscopic features obtained here with well-defined molecular Fe(I) complexes will help to better characterize supposedly low-valent iron centers in metallo-enzymes and heterogeneous catalysts.²³

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- Theoretical models for spin coupled trinuclear compounds with local spin states $S_{\text{Fe1}} = S_{\text{Fe3}} = 3/2$, $S_{\text{Fe2}} = 2$ were not in agreement with the experimental data (ESI†).
- The sign of D does not have much physical meaning here, because the rhombicity parameter is at its maximum.
- Possible reasons are (i) a slight field dependency of the effective magnetic moment of **3** (*cf.*, ESI†), (ii) the relatively poor solubility of **3** (albeit filtration of samples used for the Evans' method did not leave visible amounts of solid residue) and (iii) slightly different J , D , and E/D values for **3** in solution.
- Samples of **3** gave an X-band EPR signal, which is characteristic for small magnetic particles, which are present as minor impurities or form during decomposition of **3** (ESI†).
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