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


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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 $[\text{Fe}_3(\text{trop2dad})_2]$ 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.
A low-valent trinuclear iron complex with an unusual linear Fe(−Fe(−Fe(− unit is presented. It is accessed in a rational approach using a salt metathesis reaction between a new anionic Fe(− 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, enable cooperative reactivity, and allow the precise adjustability of magnetic properties. 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(− species are scarce and their rational synthesis and detailed characterization remain challenging. Synthetic difficulties under strongly reducing conditions include ligand dissociation (formation of Fe(0)), 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. To this end, we prepared a new mononuclear, anionic Fe(− 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)] with trop2dad (trop = 5H-dibenzo-[a,d]cyclo-hepten-5-yl, dad = diazadiene) gave [FeBr2(trop2dad)] in quantitative yield (Scheme 1a). The effective magnetic moment of 1 amounts to μeff = 4.7 μB (Evans’ method) indicating a d6 hs electron configuration at the Fe center. 1H NMR spectroscopic analysis revealed apparent C2 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(− with free unbound olefin units (ESI†).

Reduction of 1 with excess Na or NaH led to formation of the iron(−) 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 Fecenter and the structural parameters indicate a neutral dad ligand coordinated to Fe(−) with free unbound olefin units (ESI†).

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

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the related species [NaFe(trop$_2$dae)(thf)$_3$]. 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, $\mu_{\text{eff}}$ of 1.80 $\mu_B$ 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) $\mu_B$ at 298 K (Evans’ method). Both values are close to the spin only value for one unpaired electron (1.82 $\mu_B$ (Evans’ method)). Both values are close to the spin only value for one unpaired electron (1.82 $\mu_B$ (Evans’ method)). Both values are close to the spin only value for one unpaired electron (1.82 $\mu_B$ (Evans’ method)). Both values are close to the spin only value for one unpaired electron (1.82 $\mu_B$ (Evans’ method)). Both values are close to the spin only value for one unpaired electron (1.82 $\mu_B$ (Evans’ method)). Both values are close to the spin only value for one unpaired electron (1.82 $\mu_B$ (Evans’ method)). Both values are close to the spin only value for one unpaired electron (1.82 $\mu_B$ (Evans’ method)). Both values are close to the spin only value for one unpaired electron (1.82 $\mu_B$ (Evans’ method)). Both values are close to the spin only value for one unpaired electron (1.82 $\mu_B$ (Evans’ method)). Both values are close to the spin only value for one unpaired electron (1.82 $\mu_B$ (Evans’ method)).

In order to investigate its ability to serve as building block, 2 was reacted with [FeCl$_2$(thf)$_3$] in a 2:1 stoichiometry (Scheme 1b). Indeed, the trinuclear cluster compound [Fe$_3$(trop$_2$dad)$_2$] (3) could be isolated from this metathesis reaction (exchange of two Na(thf)$_3$ cations for one Fe$^{2+}$) as a deep red-brown single crystalline material in 82% yield. In low yield, 3 was also isolated in an attempt to oxidize [NaFe(trop$_2$dad)(thf)$_3$] (2) with Ph$_3$Cl (ESI†). 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)$^\circ$] with PPh$_3$Cl (ESI†). This suggests that the mechanism leading to 3 may be more complex than Scheme 1b implies.

The structure of 3 is best described with two FeN$_2$C$_2$ 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 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 (C–C5), 1.8962(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)$_4$][PF$_6$] at 20 K.

**Scheme 1** Syntheses of (a): Fe(I) compound 2 and (b): trinuclear 3$^{2+}$ and mononuclear 4, abbreviations for trop substituent.
linear Fe$^{3+}$–Fe$^{3+}$–Fe$^{3+}$ array has been investigated in detail, but the due to less significant Feterminal isomer shift, indicating a lower s-electron density at the Fe nucleus isomer shifts (0.20–1.09 mm s$^{-1}$) of the terminal Fe I ion in the solid state. 7 This leaves a net charge of +4 for the Fe 3 core which is in agreement with the observed elongated Fe$_{\text{terminal}}$–ligand bonds in 3 (vide supra).

SQUID magnetic susceptibility measurements with microcrystalline 3 reveal $\mu_{\text{eff}} = 5.8 \mu_0$ (300 K, 1 T) (Fig. 3 top and ESI†). Above ca. 200 K, $\mu_{\text{eff}}$ is almost constant, whereas below it gradually decreases reaching 2.01 $\mu_0$ 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 Is-Fe(i)–hs-Fe(ii)–Is-Fe(i) electron configurations reveals antiferromagnetic interactions between all three Fe nuclei. 18 The best fit was obtained with exchange coupling constants $J_{\text{Fe1}/3\text{Fe2}} = -10.0$ cm$^{-1}$, $J_{\text{Fe1Fe3}} = -23.0$ cm$^{-1}$ and local zero field splitting (ZFS) parameters $|D| = 46$ 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-ferrous trinuclear compound A. 15 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 $|m_{\text{Fe1}}, m_{\text{Fe2}}, m_{\text{Fe3}}\rangle$ of the coupled spin system are spread out in an extremely narrow energy range of $<300$ cm$^{-1}$ (<0.86 kcal mol$^{-1}$) without showing any structure of isolated total spin manifolds. As can be seen from the energy level plots in Fig. 3.

Iron atom in 3, Fe2, is coordinated by four nitrogen atoms of the two (trop$^{2}$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 Fe3 axis (dihedral angle dad1–Fe1–Fe3–dad2 $\approx 68^\circ$). The C31–C32$^{\text{dad}}$ bonds are again short (C31–C32, 1.365(6) Å) and the C–N bonds long (N12–C31/32, 1.391(5) Å) indicating that both dad units are fully reduced. 2 These leave a net charge of +4 for the Fe3 core indicating low-valent iron centers.

The spin state of the all-ferrous 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 ($\delta = 0.92(1)$ mm s$^{-1}$) and the moderately large quadrupole splitting ($|\Delta E_Q| = 1.88(1)$ mm s$^{-1}$) of the less intense signal assigned to the central Fe2 ion are characteristic of a high-spin Fe(ii) electron configuration. 15 The Mössbauer parameters of the more intense signal, corresponding to the terminal Fe1 and Fe3 atoms in 3, amount to $\delta = 0.37(1)$ mm s$^{-1}$ and $|\Delta E_Q| = 1.09(1)$ 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 Fe(ii) species. 9,16 The low isomer shift, however, being below the value reported for a three coordinate high-spin $\beta$-diketiminato Fe(i) compound with an alkyne ligand ($\delta = 0.44$ mm s$^{-1}$), 17 hints at a low-spin electron configuration of the terminal Fe(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 Fe$_{\text{terminal}}$ → ligand back donation in 3, which

![Fig. 2 Molecular structure of $[\text{Fe}_3(trop^{2}\text{dad})_2]$ (3) in the solid state.](image-url)

![Fig. 3 Top: Plots of molar magnetic susceptibility (circles) and effective magnetic moment (triangle) of solid $[\text{Fe}_3(trop^{2}\text{dad})_2]$ (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.](image-url)
Notes and references


8. Dashed lines between Fe atoms in 3 are guides to the eye.


11. Chemical transformation from the saturated to the unsaturated ligand backbone was observed in a Ru complex under catalytic conditions in the conversion of MeOH/water mixtures to CO2 and H2R. E. Rodríguez-Lugo, M. Trincado, M. Vogt, F. Twes, G. Santiso-Quinones and H. Grützmacher, *Nat. Chem.*, 2013, 5, 342.

12. In a competing reaction pathway, addition of the radical [CPh3]− affords compound 1 with the experimental data (ESI†).


14. There are a neutral central part of C and two coordination isoferns of F.


18. Theoretical models for spin coupled trihalogen compounds with local spin states 1 = 1/2, 2 = 1/2, 3 = 1/2, 4 = 1/2 were not in agreement with the experimental data (ESI†).

19. The sign of D does not have much physical meaning here, because the rhombicity parameter is at its maximum.

20. Possible reasons are (i) a slight field dependency of the effective magnetic moment of 3 (qESI†), (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.

21. 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†).
