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DOI
10.1039/c5cc04908c

Publication date
2015

Document Version
Final published version

Published in
Chemical Communications

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Citation for published version (APA):

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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.
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(0)–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 strongly reducing conditions include ligand dissociation (formal 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.3 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.

† Electronic supplementary information (ESI) available: Experimental and computational details. CCDC 1045323–1045329. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5cc04908c

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Published on 23 July 2015. Downloaded by Universiteit van Amsterdam on 23/03/2016 10:13:00.
the related species [NaFe(trop2dae)(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, \(\mu_{eff}\) 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 \(\mu_B\)) and are consistent with the expected d\(^7\) low-spin electron configuration at the Fe(II) 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\(^{\text{sp2}}\) 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 [FeCl\(_2\)(thf)]\(_{1.5}\) in a 2:1 stoichiometry (Scheme 1b). Indeed, the trinuclear cluster compound [Fe\(_3\)(trop2dad)]\(^{3+}\) 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(trop2dad)(thf)]\(^{3+}\) with Ph\(_3\)CCl (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 Fe\(_3\)\(^{2+}\) units include [Fe\(_3\)(µ\(_2\)-S)\(_2\)Se\(_2\)]\(_{4}^–\) (A),\(^{13a}\) [Fe\(_3\)(µ\(_2\)-S)\(_2\)(Ph)]\(_{3}^–\) (B),\(^{13b}\) [Fe\(_3\)(µ\(_2\)-S(CH\(_2\)CH\(_2\))\(_2\))\(_2\)(C\(_4\)Me\(_2\))\(_2\)]\(_{1}^{2+}\) (C),\(^{13c}\) [Fe\(_3\)(µ\(_2\)-NPPh\(_3\))]\(_2\)(C\(_6\)H\(_6\))\(_2\) (D),\(^{13c}\) [Fe\(_3\)(µ\(_2\)-Me\(_3\)P)(NO\(_3\))]\(_2\)(C\(_6\)H\(_6\))\(_2\) (E),\(^{13d}\) and [Fe\(_3\)(µ\(_2\)-NE\(_3\))]\(_2\)(µ\(_2\)-CH\(_2\)(CH\(_3\)))\(_2\)(CO\(_2\))\(_2\) (F).\(^{13c}\) These 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 Fe\(_2\)N\(_3\) \(_2\) 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\(_{\text{trop}}\) bonds are slightly shortened and C–C\(^{\text{sp2}}\) bonds are slightly elongated and the C–C\(^{\text{sp2}}\) bonds are slightly shortened indicating less efficient Fe → C–C\(^{\text{sp2}}\) backbonding. The central
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 coordinate high-spin Fe$_3$ atoms in
the more intense signal, corresponding to the terminal Fe$_1$ and ligand (trop$_2$dad)$_2^-$Fe$_2$(trop$_2$dad)$_2$.

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

SQUID magnetic susceptibility measurements with microcrystalline 3 reveal $\mu_{\text{eff}} = 5.8 \mu_B$ (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 $\mu_B$ 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-triplet 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 anti-ferromagnetic interactions between all three Fe nuclei. The best fit was obtained with exchange coupling constants $J_{\text{Fe1/Fe3}} = -10.0$ cm$^{-1}, J_{\text{Fe1/Fe2}} = -23.0$ cm$^{-1}$ and local zero field splitting (ZFS) parameters $|D| = 46$ cm$^{-1}$ and $E/D = 0.3$ for the central ferrous ion, Fe2. 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. 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.
The values for $j_B$ 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 $j_B$ values ranging from $-8$ to $-26\, \text{cm}^{-1}$ (see ESF 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, ESF†). 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 $\mu_{\text{eff}} = 5.4(2)\, \mu_B$ 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 (ESF†).

This complex – with a distorted tetragonal structure and an $S = 1$ spin-state, is best described as a hs-Fe(i) center, antiferromagnetically coupled to two mononuclear radical ligands (trop$_3$dad$^{\pm}$) as previously reported for other [Fe$_3$(aad$^{\pm}$)$_2$] 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 $\text{[NaFe(trop}_3\text{dad)(thf)}_2] \,(2)$ was obtained, which contains the redox-active (“innocent”) diazi-diene ligand as (trop$_3$dad$^{\pm}$). The spin density of the unpaired electron is located on the low-spin d$^3$ 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, $[\text{Fe}_3(\text{trop}_3\text{dad})]_3$ (3). Compound 3 has a $\text{lsFe}(\text{lsSeFe})$ 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

The authors thank Dr Inés Rubio Garcia for helpful discussions on EPR spectroscopy. C. L. is grateful for a Feodor Lynen fellowship generously hosted by Prof. François Diederich.