



Accessing iron amides from dimesityliron



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ABSTRACT

A new phase of dimesityliron has been crystallized from diethylether; the crystal structure shows a dinuclear complex with co-crystallized solvent. Crystalline $[\text{Fe}_2(\text{mes})_2(\mu_2\text{-mes})_2] \cdot \text{Et}_2\text{O}$ is a convenient starting material and reacts with di(2-pyridyl)amine to yield rare iron di(2-pyridyl)amido complexes. Crystal structures of air-sensitive $[\text{Fe}_2(\text{mes})_2(\text{dpa})_2]$, $[\text{Fe}_2(\text{dpa})_3\text{Cl}]$ and $[\text{Fe}_4(\text{dpa})_6\text{O}]$ were determined. $[\text{Fe}_4(\text{dpa})_6\text{O}]$ is known, and the dinuclear complexes $[\text{Fe}_2(\text{mes})_2(\text{dpa})_2]$ and $[\text{Fe}_2(\text{dpa})_3\text{Cl}]$ represent only the second and third reports of homometallic iron dpa^- complexes. Long Fe...Fe distances of 3.043(1) and 3.104(2) Å in $[\text{Fe}_2(\text{mes})_2(\text{dpa})_2]$ and $[\text{Fe}_2(\text{dpa})_3\text{Cl}]$, respectively, and very unsymmetrically coordinated amido groups, indicate that the iron atoms are not involved in M–M bonding. This fact, and the relatively low coordination numbers of the high spin Fe(II) atoms are consistent with sensitivity of these compounds towards O_2 . DFT calculations were employed to rationalize the formation of the unusual architectures displayed by the dpa^- complexes of iron.

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Introduction

The ligand di(2-pyridyl)amide (dpa^-), depicted in the prototypical complexes shown in Fig. 1, is the simplest of the poly-2,2'-pyridyl amides. This is a class of ligands that has been used extensively in the groups of Cotton, Berry and Peng, amongst others [1–7], to develop the chemistry of linear polymetallic chains, which can contain up to nine metal ions [1]. The most extensively studied members of this family are the trimetallic 'extended metal atom chains' (EMACs), $\text{M}_3(\text{dpa})_4\text{X}_2$ [2], and bimetallic complexes of the same ligand, $\text{M}_2(\text{dpa})_4$ [3], are also common, Fig. 1 [4–6]. Amongst the first row transition elements, homometallic Cr_3 , Co_3 , Ni_3 and Cu_3 chains are all known. Analogous Fe_2 and Fe_3 compounds are conspicuous by their absence. The only iron-containing trimetallic EMACs are heterotrimetallic $[\text{Cr}_2\text{Fe}(\text{dpa})_4\text{X}_2]$, and $[\text{Mo}_2\text{Fe}(\text{dpa})_4\text{X}_2]$ recently reported by Berry and co-workers [7]. Given the ubiquity of the EMAC architecture, the absence of a homometallic iron complex of this type in the literature is curious, and suggests that a broader range of iron complexes of dpa^- are important synthetic targets. For reference, unsubstituted dpa^- appears in 294 entries of complexes in the CCDC [8]. In no case do any of these involve an

amido-Fe bond, except, and arguably, $[\text{Fe}_4(\text{dpa})_6\text{O}]$, the one known homometallic iron complex of dpa^- , $[\text{Fe}_4(\text{dpa})_6\text{O}]$, reported by Cotton and co-workers in 2000 [9] which adopts an entirely different and unusual, μ_4 -oxo bridged tetrahedral motif.

One explanation for the paucity of iron complexes of dpa^- relates to the typical synthetic conditions employed; reaction of metal halide starting materials with lithiated dpa^- under dry anaerobic conditions. Such conditions will be very challenging for iron(II) which is far more susceptible to oxidation and hydrolysis reactions compared with other late first row divalent transition metal ions. Alternative reaction conditions may increase the chance of isolating reactive Fe(II) complexes of the type in Fig. 1. For this purpose we develop here the use of dimesityliron as a starting material. By avoiding the use of lithium and magnesium amides, it should be possible to minimize the formation of undesired heterometallic complexes and metalates.

Transition metal phenyls are often difficult to prepare and handle, but more inert and soluble metal aryls can be obtained by attaching substituents in the *ortho* and *para* positions of the aryl ligand. The 2,4,6-trimethyl substituted mesityl group ($\text{mes} = 2,4,6$ -trimethylphenyl) is an especially attractive choice, since starting materials like mesityl halides are cheap. Transition metal mesityls are generally available from metathesis reactions between the anhydrous metal halide and mesitylmagnesium bromide in THF.

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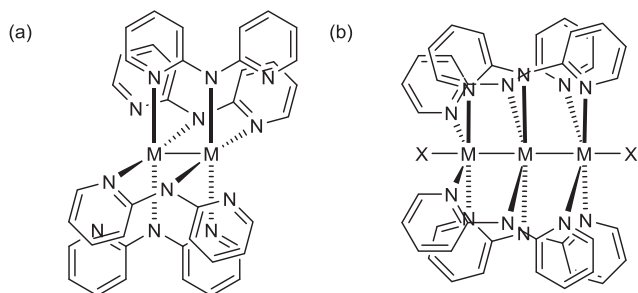


Fig. 1. Common structural types for dpa^- complexes with divalent transition metals.

The by-product magnesium halides can be precipitated easily, leaving the pure mesityl metal complex in solution. For example, despite being highly oxygen- and moisture-sensitive mesitylcopper prepared in this manner is soluble in many organic solvents and has emerged as a key organometallic synthon for a wide array of copper complexes and clusters, including some that are biorelevant [10]. Thus apart from accessing complexes of dpa^- and related structures, mesityl iron could also be more generally applied as a starting material for the preparation of for example iron amide, alkoxide or thiolate complexes.

Experimental section

General

All operations were carried out under nitrogen using Schlenk techniques. Solvents were distilled from sodium/benzophenone shortly prior to use. Bis(2-pyridyl)amine (Hdpa) was used as supplied (Aldrich) and $[Fe_4Cl_8(THF)_6]$ was prepared according to literature methods [11].

Synthesis

$[Fe_2(mes)_2(\mu_2-mes)_2] \cdot Et_2O$ (**1**)

Mesityl bromide (6.5 mL, 25 mmol) was added dropwise to a suspension of magnesium (0.65 g, 27 mmol) in THF (40 mL). The reaction mixture was stirred overnight yielding mesityl magnesium bromide as a slightly yellow THF solution, which was added dropwise to a suspension of $[Fe_4Cl_8(THF)_6]$ (1.89 g, 11.6 mmol Fe) in THF (20 mL) and 1,4-dioxane (15 mL) at $-40^\circ C$. After 1 h, the reaction mixture was allowed to reach ambient temperature and stirring was continued overnight. The precipitated magnesium bromide and chloride salts were removed by centrifugation and the solution was evaporated to dryness. Diethyl ether (20 mL) was added to the resultant powder at ambient temperature resulting in a dark-red solution (remaining solids, if any, were removed by centrifugation), which was kept at $-35^\circ C$ until a batch of dark red crystals formed. Recrystallization from diethyl ether gave $[Fe_2(mes)_4] \cdot Et_2O$ (**1**) (3.23 g, 9.75 mmol Fe, 84%). The compound was stored at $-40^\circ C$ until use as the crystalline solid under the diethylether mother liquor. The identity and purity of the bulk product was verified from a low temperature powder X-ray diffractogram. Both the single crystal and powder X-ray diffraction analyses were carried out using cryogenic sample handling techniques, *vide infra*.

$[Fe_2(mes)_2(\mu_2-dpa)_2] \cdot CH_3C_6H_5$ (**2**)

Neat bis(2-pyridyl)amine (51 mg, 0.30 mmol) was added to **1** (100 mg, 0.15 mmol Fe) dissolved in toluene (4 mL). A red precipitate formed immediately. The reaction mixture was stirred at room

temperature for 15 min, followed by careful heating to approximately $100^\circ C$ to dissolve the precipitate. The resulting solution was allowed to slowly return to room temperature whereupon small, orange crystals deposited within 30 min in good yield (80 mg, 69%). A crystal of **2** was successfully transferred to the diffractometer using manipulations at low temperature under a nitrogen atmosphere.

$[Fe_2Cl(\mu_2-dpa)_3][Fe_4(\mu_4-O)(\mu_2-dpa)_6] \cdot 3CH_3C_6H_5$ (**3**)

Neat bis(2-pyridyl)amine (51 mg, 0.40 mmol) was added to **1** (100 mg, 0.20 mmol) dissolved in toluene (5 mL). A red precipitate formed immediately. Heating to approximately $100^\circ C$ and subsequent cooling resulted in a few, highly air sensitive, red crystals (estimated 10 mg and less than 10% of the bulk material) that could be hand-picked from an otherwise amorphous material. Adventitious chloride derived from one particular batch of **1** is implicit for the formation of **3**.

Computational details

All calculations of gas-phase electronic structure were performed using the Amsterdam Density Functional package ADF2012 [12] package. A double- ξ Slater-type basis set, extended with a single polarization function, was used to describe the main group atoms, while iron was modelled with a triple- ξ basis set. Electrons in orbitals up to and including 1s {C, N}, 2p {Cl} and 3p {Fe} were considered part of the core and treated in accordance with the frozen core approximation. In all cases configurations corresponding to both ferromagnetic and antiferromagnetic coupling of the Fe centres (the latter through the broken-symmetry approach). Calculations were performed using the gradient corrections to exchange and correlation proposed by Becke and Perdew (BP86) [13] along with the dispersion corrections proposed by Grimme [14]. All structures were optimized using the gradient algorithm of Versluis and Ziegler [15].

X-ray crystallography

All crystals were selected and mounted at low temperature [16] inside a Dewar flask and transferred in liquid nitrogen to a Rigaku R-AXIS IIC image plate system. Diffracted intensities were measured at 100 K using graphite monochromated Mo- $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) from an RU H3R rotating anode operating at 50 kV and 90 mA. Ninety oscillation photos with a rotation angle of 2° were collected and processed using the CRYSTALCLEAR software package. An empirical absorption correction was applied using the REQAB program under CRYSTALCLEAR. Crystal and refinement data are summarized in Table 1. All structures were solved using direct methods and refined using full-matrix least squares calculations on F^2 using SHELX [17] program under the WIN-GX program package [18]. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included in calculated positions and refined using a riding model. Powder diffractograms on **1** were obtained by grinding bulk syntheses products under their mother-liquors and withdrawing a powder sample in a Pasteur pipette at low temperature. The tip of the pipette was broken off under liquid nitrogen and mounted on a goniometer. Diffractograms were collected at 100 K using an R-Axis IIC image plate using graphite monochromated Mo- $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). This procedure results in peak broadening and the calculated diffractograms were adjusted accordingly.

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