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Preliminary Communication

Divalent iron formamidinato complexes: a highly distorted dinuclear compound

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Abstract

The reaction of $FeCl_2$ with *N,N'*-diphenylformamidine, HDPhF, produces the compound $FeCl_2(HDPhF)_2$ (I) which upon reaction with methyllithium in Et_2O followed by extraction into solvent mixtures containing THF, toluene and hexanes produces crystals of $Fe_2(DPhF)_4$ (II). This dinuclear compound contains four formamidinato bridges but in an arrangement that is highly distorted compared to the previously known structures of $M_2(DPhF)_4$ or $M_2(DTolF)_4$ molecules. The Fe–Fe bond length is 2.462(2) Å. Both I and II have been structurally characterized by X-ray crystallography. Crystal data for I at 21 °C are: triclinic, space group $P\bar{1}$, $a=10.182(1)$, $b=11.233(2)$, $c=13.374(2)$ Å, $\alpha=109.87(1)$, $\beta=96.41(1)$, $\gamma=113.35(1)°$, $Z=2$. For II, the crystal data at -60 °C are: monoclinic, space group $I2/a$, $a=18.001(6)$, $b=10.019(1)$, $c=25.422(9)$ Å, $\beta=105.28(1)$, $Z=4$.

Keywords: Crystal structures; Iron complexes; Formamidinato complexes; Dinuclear complexes

1. Introduction

Compounds containing metal-to-metal bonds of various orders are now known for a large number of the transition series elements [1]. One frequently encountered class of these compounds is the so-called lantern type, in which four ligands bridge two metal centers. However, the frequency with which they are found for elements of the first transition series (FTS) is conspicuously small if chromium(II) is not considered [2]. So far only two forms are known for vanadium [3], two for cobalt [4,5] and one for nickel [6] in which metal-to-metal bonding has been invoked.

A type of ligand which has been instrumental in the formation of the lantern-type compounds for the FTS elements is that of the family of the anions RN–X–NR, X=CR' and N. They are currently found in more metal-to-metal bonded compounds with more different metallic elements than any other ligand type, including the well characterized carboxylato-type ligand.

It has been observed in our laboratories that these ligands (amidinato and triazenato) are quite flexible [7] in their coordination modes. Besides forming bridges between adjacent metal centers, they are also known to form chelates and even to act as monodentate ligands. This flexibility is also manifested within the bridged compounds. The metal-to-metal separations are known to vary from 1.858(1) Å in $Cr_2(DPhTA)_4$ [8] to 2.705(1) Å in $Ag_2(DTolF)_2$ [9][1].

As our studies with vanadium showed, the preparation of an effective starting material is as crucial to the success of the formation of metal-to-metal bonds as is the recognition of an efficient and effective ligand to stabilize such interactions.

The results presented in this paper will show that this is also the case for the iron(II) compounds. An earlier study by Kilner and co-workers [10] using Fe(II) starting materials and $RNXNR^-$ ligands failed to produce any compound of the type $Fe_2(RNXNR)_4$. That study, as well as our own, has shown that the chemistry of Fe(II) with $RNXNR^-$ ligands is very complex. Depending on the choice of starting materials one can isolate and crystallographically characterize a host of compounds such as the tris-chelating $Fe(DTolF)_3$ and $Li(THF)_4[Fe(DPhTA)_3]$ [11], or the dinuclear compound $Fe_2(DPhF)_3$ [12].

We now report the synthesis and X-ray structure of the first-known dinuclear compound of iron(II) of the

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[1] All abbreviations follow the format introduced in Ref. [7].

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lantern type as well as the details for the preparation and structural characterization of the starting material that led to its synthesis, namely $FeCl_2(HDPhF)_2$.

2. Experimental

2.1. Synthesis

All manipulations were carried out under an atmosphere of nitrogen using standard Schlenk techniques. The solvents were purified by conventional methods and were freshly distilled under nitrogen prior to use. $FeCl_2$ was obtained after drying $Fe_4Cl_8(THF)_6$ in vacuo [13]. *N,N'*-Diphenylformamidine was purchased from Aldrich. It was washed extensively with hexanes and recrystallized from toluene/hexanes.

2.2. $FeCl_2(HDPhF)_2$ (I)

To a mixture of $FeCl_2$ (0.70 g, 5.5 mmol) and HDPhF (2.00 g, 10.2 mmol) were added 15 ml of toluene. The dark red mixture was then refluxed for 5 h, allowed to return to room temperature, and then filtered. To the light orange solution was added a layer of 20 ml of hexanes. After cooling to 5 °C and then to −5 °C for a day, yellow crystals of **I** were collected by filtration and washed with two 5 ml portions of hexanes. After drying in vacuo the yield was 2.11 g (80%). UV–Vis (toluene): λ_{max} 326 nm (very broad), $\epsilon = 5.0 \times 10^2$ M^{-1} cm^{-1}. X-ray quality crystals were obtained by dissolving 0.15 g of **I** in 5 ml of toluene and adding a layer of 10 ml of hexanes. After one day at room temperature, the crystals were collected.

2.3. $Fe_2(DPhF)_4$ (II)

In a typical experiment, crystalline $FeCl_2(HDPhF)_2$ (0.26 g, 0.50 mmol) was suspended in 15 ml of Et_2O and the mixture was cooled to 0 °C. To this was added a solution of methyllithium in Et_2O (1.0 mmol). The suspension was stirred at room temperature. Methane was liberated. The orange solid was filtered and was immediately dissolved in a mixture of THF:toluene (5 ml + 5 ml). A layer of 20 ml of hexanes was very carefully added to the solution in a round bottom flask. The mixture was kept at room temperature. Very quickly large orange–brown crystals were formed along with a white powder of LiCl. The next day, the crystals were decanted and washed with hexanes. (The LiCl suspended in the hexanes was easily removed by decantation.) After drying, the yield was 0.10 g (45%).

3. Results and discussion

3.1. $FeCl_2(HDPhF)_2$ (I)

The reaction of anhydrous $FeCl_2$ suspended in toluene and HDPhF yields a crystalline material in which the neutral molecules are coordinated to the metal center. The same product can also be isolated from the melt reaction of $FeCl_2$ and HDPhF, in a manner similar to that reported for $FeCl_2(HDTolF)_2$ [7]. However, for reasons that are not clear at the moment, the melt reaction preparation tends to produce slightly oily materials that generally require more purification steps.

The molecular structure[2] of **I**, along with the labeling scheme, is shown in Fig. 1. Some important bond distances and angles are given in Table 1. The iron

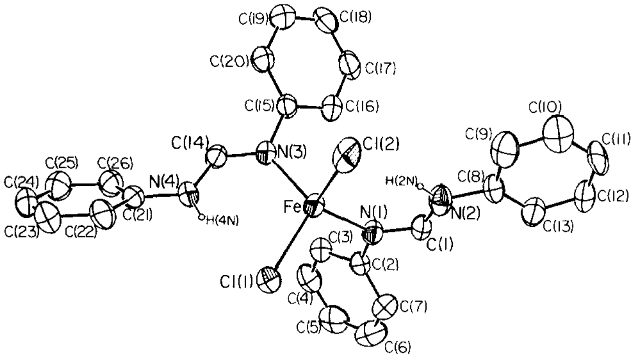

Fig. 1. Thermal ellipsoid plot of the X-ray structure of $FeCl_2(HDPhF)_2$, showing the atom naming scheme. Non-hydrogen atoms are represented by their 50% probability ellipsoids.

Table 1
Selected bond lengths (Å) and angles (°) for $FeCl_2(HDPhF)_2$ (I)[a]

Fe–N(3)	2.081(2)	N(2)–C(1)	1.318(3)
Fe–N(1)	2.083(2)	N(2)–C(8)	1.414(2)
Fe–Cl(1)	2.2855(7)	N(3)–C(14)	1.305(2)
Fe–Cl(2)	2.2968(7)	N(3)–C(15)	1.437(2)
N(1)–C(1)	1.305(2)	N(4)–C(14)	1.322(2)
N(1)–C(2)	1.434(2)	N(4)–C(21)	1.424(2)
N(3)–Fe–N(1)	115.88(6)	C(14)–N(3)–Fe	124.8(1)
N(3)–Fe–Cl(1)	111.61(5)	C(15)–N(3)–Fe	119.5(1)
N(1)–Fe–Cl(1)	105.17(5)	C(1)–N(1)–C(2)	116.6(2)
N(3)–Fe–Cl(2)	101.85(5)	C(1)–N(2)–C(8)	128.1(2)
N(1)–Fe–Cl(2)	109.43(5)	C(14)–N(3)–C(15)	115.1(2)
Cl(1)–Fe–Cl(2)	113.16(3)	C(14)–N(4)–C(21)	124.3(2)
C(1)–N(1)–Fe	125.4(1)	N(1)–C(1)–N(2)	123.0(2)
C(2)–N(1)–Fe	117.6(1)	N(3)–C(14)–N(4)	124.8(2)

[a] Numbers in parentheses are e.s.d.s in the least significant digits.

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[2] Crystal data for $FeCl_2(HDPhF)_2$: $M = 519.24$, triclinic, $P\bar{1}$ (No. 2), $a = 10.182(1)$, $b = 11.233(2)$, $c = 13.374(2)$ Å, $\alpha = 109.87(1)$, $\beta = 96.41(1)$, $\gamma = 113.35(1)°$, $V = 1265.9(3)$ Å^3, $Z = 2$, $D_{calc} = 1.362$ g cm^{-3}; Mo Kα (0.71073 Å), $T = 21(1)$ °C, P3/F equiv. diffractometer. An empirical absorption correction, based on ψ-scans, was applied. The structure was solved via direct methods and was refined with the SHELXL-93 program. For all 4465 unique data, $R_1 = 0.061$, $wR^2 = 0.078$. For the 3722 data having $I > 2\sigma(I)$, $R_1 = 0.029$, $wR^2 = 0.075$.

center is surrounded by two chloride ions and two nitrogen atoms in a pseudo-tetrahedral arrangement somewhat similar to that found in $FeCl_2(HDTolF)_2$ [7]. The Fe–ligand distances are essentially the same in both compounds. However, the N–Fe–N bond angles differ by ~20°. The Cl–Fe–Cl bond angle is almost the same in both compounds, namely 113.8°. Consequently, other angles adjust slightly making the coordination about the metal center in **I** closer to that of the ideal tetrahedron.

3.2. $Fe_2(DPhF)_4$ (*II*)

This compound can be obtained in a reproducible way under carefully controlled conditions with the formation of large crystals which are easily isolated. The reaction is quite complex and we do not fully know the identity of some of the intermediate compounds.

$FeCl_2(HDPhF)_2$ reacts with methyllithium in Et_2O to liberate methane and produce an unidentified orange solid, which is highly paramagnetic. The orange material is very soluble in THF. By analogy to another known compound, $Li(THF)_4Fe(DPhTA)_3$, this material could perhaps contain the species $[Fe(DPhF)_2Cl_2]^{2-}$. The orange material also dissolves in mixtures of THF/toluene. Upon addition of a layer of hexanes to those mixtures, the red–orange crystals of $Fe_2(DPhF)_4$ form exclusively along with LiCl. Very different results are obtained if the conditions are modified by using different solvents or even if a different alkyl lithium reagent is used. We have already reported that from the reaction of $FeCl_2(HDPhF)_2$ and butyllithium in toluene a reduced species, namely $Fe_2(DPhF)_3$, is obtained [12]. If the reaction is done using $FeCl_2$ and LiDPhF other products are isolated [11].

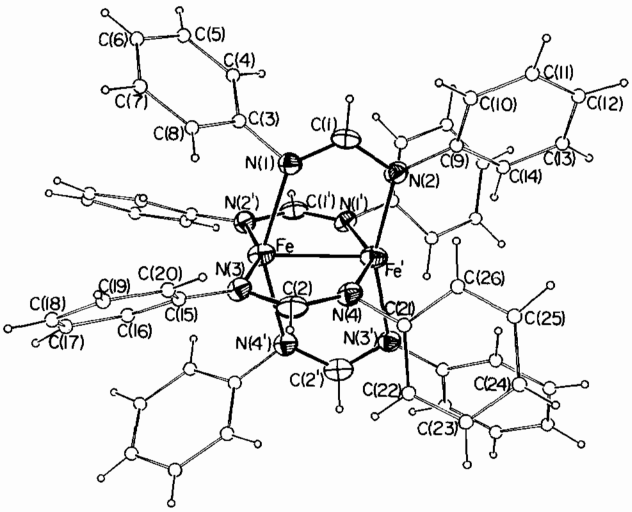

Fig. 2. ORTEP plot of the molecular structure of $Fe_2(DPhF)_4$, showing the atom labeling scheme. The core atoms are represented by their 40% probability ellipsoids. All atoms in phenyl groups as well as the refined methine protons are shown as arbitrarily sized circles.

Table 2
Selected bond lengths (Å) and angles (°) for $Fe_2(DPhF)_2$ (**II**)^{a,b}

Fe–Fe′	2.462(2)	N(1)–C(3)	1.422(5)
Fe–N(2)′	2.002(4)	N(2)–C(1)	1.321(6)
Fe–N(3)	2.009(4)	N(2)–C(9)	1.416(6)
Fe–N(1)	2.164(4)	N(3)–C(2)	1.316(6)
Fe–N(4)′	2.171(4)	N(3)–C(15)	1.406(6)
N(1)–C(1)	1.311(6)	N(4)–C(2)	1.320(6)
		N(4)–C(21)	1.427(6)
N(2)′–Fe–N(3)	155.5(2)	Fe′–N(2)–C(1)	110.0(4)
N(2)′–Fe–N(1)	91.6(1)	Fe′–N(2)–C(9)	129.7(3)
N(3)–Fe–N(1)	95.4(1)	Fe–N(3)–C(2)	108.6(3)
N(2)′–Fe–N(4)′	94.3(1)	Fe–N(2)–C(15)	131.9(3)
N(3)–Fe–N(4)′	91.6(1)	Fe′–N(4)–C(2)	130.9(4)
N(1)–Fe–N(4)′	149.2(2)	Fe′–N(4)–C(21)	110.2(3)
Fe′–Fe–N(2)′	101.6(1)	C(1)–N(1)–C(3)	117.0(4)
Fe′–Fe–N(3)	102.9(1)	C(1)–N(2)–C(9)	120.3(4)
Fe′–Fe–N(1)	75.1(1)	C(2)–N(3)–C(15)	119.5(4)
Fe′–Fe–N(4)′	74.1(1)	C(2)–N(4)–C(21)	117.0(4)
Fe–N(1)–C(1)	130.3(3)	N(2)–C(1)–N(1)	122.9(5)
Fe–N(1)–C(3)	111.8(3)	N(3)–C(2)–N(4)	123.2(5)

[a] Numbers in parentheses are e.s.d.s in the least significant digits.
[b] Symmetry transformations used to generate equivalent atoms: $-x+\frac{1}{2}$, y, $-z$.

The molecular structure[3] of **II**, shown in Fig. 2, is significantly different from those found in other $M_2(RNXNR)_4$ compounds [3]. A two-fold axis bisects the Fe–Fe vector and lies between the planes formed by the Fe–Fe–N–C–N rings. In contrast to the other compounds known with this stoichiometry (but different metal centers), there are significant distortions. Two of the bridges are pulled towards one end of the molecule while the other two are pulled in the opposite direction, giving the core a significant deviation from the frequently encountered D_{4h} symmetry. As seen in Table 2, there are two short (~2.00 Å) and two long (~2.17 Å) Fe–N distances. The short distances are 0.02 Å shorter than those found in $Fe_2(DPhF)_3$ and the longer ones are the same as those found in $[Li(THF)_4][Fe(DPhTA)_3$ [11]. The average of all Fe–N distances in **II** (2.086 Å) is almost identical to the average for those found in **I** (2.082 Å). The difference between the obtuse angles and the acute angles defined by the Fe–Fe–N entity

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[3] Crystal data for $Fe_2(DPhF)_4$: $M=892.65$, monoclinic, $I2/a$ (No. 15), $a=18.001(6)$, $b=10.019(1)$, $c=25.422(9)$ Å, $\beta=105.28(1)°$, $V=4423(2)$ Å^3, $Z=4$, $D_{calc}=1.341$ g cm^{-3}, Mo Kα (0.71073 Å), $T=-60(1)$ °C, Enraf-Nonius CAD-4. An empirical absorption correction, based on ψ-scans, was applied. The structure was solved via direct methods and was refined with the SHELXL-93 program. All hydrogen atoms were located in difference Fourier maps. The two independent methine hydrogen atoms were allowed to refine without constraints, while each group of five phenyl hydrogen atoms was refined with a common isotropic displacement parameter. The position of each hydrogen atom was allowed to refine freely. For all 2888 data, $R_1=0.127$, $wR^2=0.109$. For the 1696 data having $I>2\sigma(I)$, $R_1=0.040$, $wR^2=0.086$.

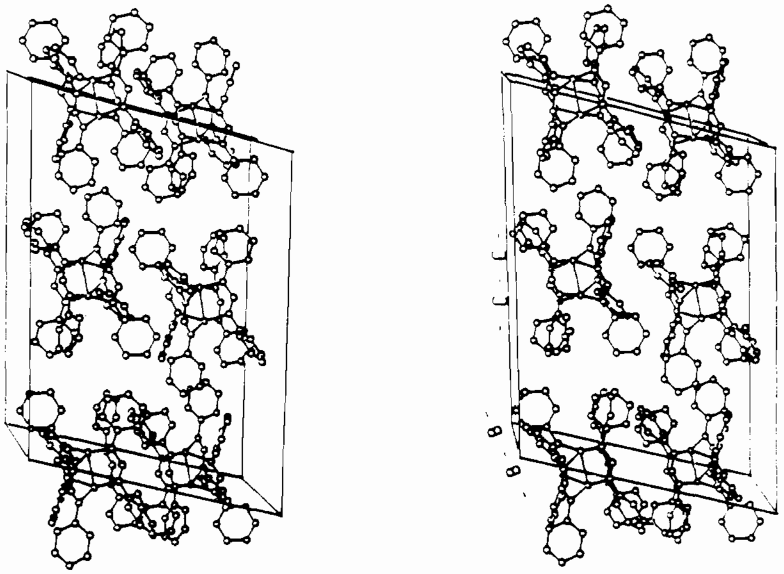

Fig. 3. Stereo view of the extended structure of $Fe_2(DPhF)_4$, viewed along the *b* axis.

is a remarkable value of 27.6°. It seems almost as if the two iron atoms are trying to display tetrahedral coordination. The correctness of the structure is attested by the fact that, despite the highly distorted coordination of the central unit, there is high geometric regularity for all four crystallographically independent phenyl rings. The molecular packing, indicated in Fig. 3, reveals no unusual intermolecular interactions that might contribute to the distortion around the metal centers. The phenomenon appears to be due to intrinsic electronic effects within the molecule, but these are not yet understood.

Another important feature of this molecule is the relatively long Fe–Fe separation of 2.462(2) Å. This is comparable to that found in similar compounds of the heavier congener, ruthenium, for which metal-to-metal distances are known to vary from 2.3994(6) to 2.474(1) Å [14–16] and is almost as long as that found in $Ni_2(DTolF)_4$ (2.485(2) Å) [6]. It is considerably longer than those found in $Co_2(DTolTA)_4$ (2.265(2) Å) [4] and $Co_2(DPhBz)_4$ (2.302(1) Å) [5]. It should be noted, however, that even though the Fe–Fe separation might seem long, it is very short when compared to that found in other dinuclear compounds of the type $[Fe_2X_2]^{2+}$, X = F or Cl [17, 18], for which the metal atom separations are greater than 3.0 Å.

The Fe–Fe bond distance in **II** is, however, a lot longer than that reported for the reduced species $Fe_2(DPhF)_3$ in which it is 2.2318(8) Å [12]. It is also longer than that recently reported for $[Fe_2\{(\eta^2\text{-}C(Mes)NBu^t)_2(\mu\text{-}C(Mes){=}NBu^t)_2]$ (Mes = 2,4,6-$Me_3C_6H_2$) [19] in which the Fe–Fe bond length was found to be 2.366(2) Å. However, the iron-to-iron bond distance in **II** is considerably shorter than those found in $[\{(PhCN)(Mes)Fe\}_2\{\mu\text{-}N{=}CPhMes\}_2]$ (2.860(2) Å) or $[Fe_2(Mes)_2(\mu\text{-}Mes)_2]$ (2.617(1) and 2.612(6) Å) [19,20].

We are currently in the process of doing molecular orbital calculations and magnetic studies with the hope that they will give us some insight into the nature of the iron–iron bond and the reason for the unusual, distorted structure of $Fe_2(DPhF)_4$.

4. Supplementary material

The following tables are available from the authors on request prior to the publication of a full paper for compounds **I** and **II**: an expanded description of the crystallographic procedures; tables of data collection and structure refinement parameters; atomic parameters; bond distances; bond angles; anisotropic displacement parameters and a list of observed and calculated structure factors (40 pages).

Acknowledgements

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