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Preliminary Communication

A new class of dinuclear compounds: the synthesis and X-ray structural characterization of tris(μ-diphenylformamidinato)diiron

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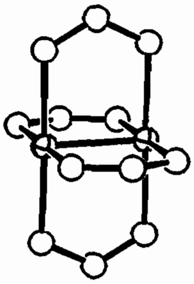
Abstract

A new type of dinuclear metal–metal bonded compound is formed by reacting $FeCl_2(HDPhF)_2$, HDPhF = diphenylformamidine, with butyllithium in THF. The isolated crystalline product, $Fe_2(DPhF)_3$, contains the mixed-valent dinuclear unit bridged by only three formamidinato groups. It has been structurally characterized by X-ray crystallography at −60 °C. Crystal data: monoclinic, space group *C2/c*, $a = 17.154(4)$, $b = 8.255(1)$, $c = 23.400(5)$ Å, $\beta = 93.38(1)°$, $Z = 4$. The Fe–Fe bond distance is 2.2318(8) Å. The EPR spectrum in a toluene glass (10 K) show two signals at g values of 1.99 and 7.94.

Key words: Crystal structures; Iron complexes; Formamidinato complexes; Dinuclear complexes

Introduction

In dinuclear compounds containing metal-to-metal bonds of the heavier transition elements, structures of the lantern type, **1**, are frequently found [1]. In them, the two metal atoms are bridged by four groups such as carboxylato, formamidinato or other stereoelectronically similar species. However, with the exception of chromium [1], cobalt [2], nickel [3] and copper [4], the elements of the first transition series have resisted efforts to synthesize lantern-type compounds. Recently, however, we reported the preparation and characterization of the first divanadium compounds of that type [5], and we have since turned our attention to iron. After a long search for appropriate starting materials, $FeCl_2(HDTolF)_2$ (HDTolF = di-*p*-tolylformamidine) [6] and $FeCl_2(HDPhF)_2$ (HDPhF = diphenylformamidine) were prepared. From the reaction of $FeCl_2(HDPhF)_2$ and methyllithium, $Fe_2(DPhF)_4$ was synthesized and characterized by X-ray crystallography [7]. However, in the course of this work, a remarkable new type of M−M bonded compound was found, in which, the two metal atoms are bridged by three formamidinato ligands.



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In this report, the preparation, X-ray crystal structure and some other properties of $Fe_2(DPhF)_3$ are described.

Experimental

Syntheses

All manipulations were carried out under nitrogen using standard Schlenk techniques. The solvents were dried and deoxygenated by prolonged reflux with Na/K and were freshly distilled under nitrogen prior to use. $FeCl_2(HDPhF)_2$ was prepared in a manner entirely similar to that reported for $FeCl_2(HDTolF)_2$ [6].

$Fe_2(DPhF)_3$

In a typical experiment, $FeCl_2(HDPhF)_2$ (0.40 g, 0.73 mmol) was dissolved in 14 ml of toluene and the solution was cooled to −70 °C. To this was added butyllithium (1.32 mmol). The yellow–brown mixture was stirred in the cold bath for 1 h and then was allowed to reach room temperature. A small amount of solid was present. The mixture was filtered with the aid of Celite. To the solution was added a layer of 20 ml of hexanes and the mixture was cooled to −10 °C. Five days later,

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yellowish crystals were filtered and washed with hexanes (5 ml). After they were dried *in vacuo*, the yield was 0.04 g of $Fe_2(DPhF)_3$ (16% yield).

Results and discussion

Crystalline $Fe_2(DPhF)_3$ is a very air-sensitive product which is formed in small yield from the reaction of $FeCl_2(HDPhF)_2$ with butyllithium in THF. We have more recently been able to increase the yield by using a designed synthesis in which the iron atom in $FeCl_2(HDPhF)_2$ is reduced with $NaHBEt_3$ prior to the reaction with butyllithium, but this method is not yet optimized.

The molecular structure* is shown in Fig. 1. There is a crystallographic two-fold axis, along one of the C–H bonds of a methine group, which bisects the iron–iron bond. The metal-to-metal distance, namely 2.2318(8) Å, is the shortest Fe–Fe bond yet found. The formamidinato ligands are not evenly distributed about the iron–iron line segment. One of the ring–ring dihedral angles is opened (132.6°) while the other two are compressed (116.17 and 111.2°), relative to the ideal of 120°.

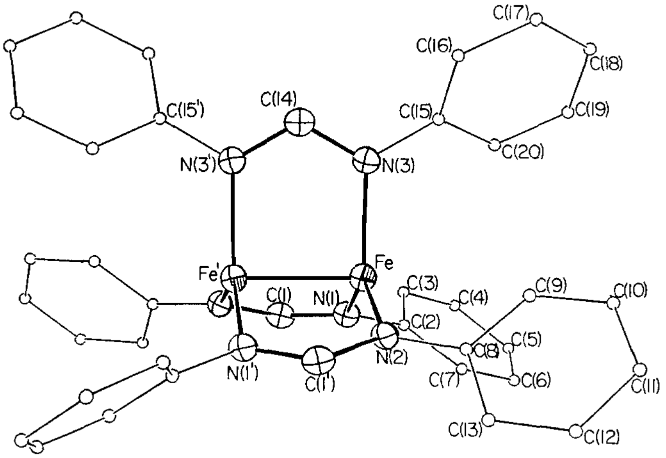

Fig. 1. Thermal ellipsoid plot of the X-ray structure of $Fe_2(DPhF)_3$, showing the atom naming scheme. Atoms C14, H2 (not shown) as well as the mid-point of the Fe–Fe bond sit on a two-fold axis. Atoms are represented by their 30% probability ellipsoids. Phenyl-carbon atoms are shown as arbitrarily-sized spheres. Selected bond lengths (Å) and angles (°): Fe–Fe' 2.2318(8), Fe–N1 2.017(2), Fe–N2 2.025(2), Fe–N3 2.033(2), N1–Fe–N2 132.6(1), N1–Fe–N3 116.18(9), N2–Fe–N3 111.08(9), N1–Fe–Fe' 89.77(7), N2–Fe–Fe' 92.29(6), N3–Fe–Fe' 90.98(6).

Even though other possible reasons for this apparent distortion could not be completely ruled out, the most likely explanation can be found by an analysis of the way in which the compound packs in the crystal. As seen in Fig. 2, the molecules are stacked in the crystal along the two-fold axis with the Fe–Fe bonds all perpendicular to this axis. This packing imposes some short van der Waals contacts.

One of the phenyl groups (C15–C20) points directly to the plane of the phenyl group (C8–C13) of a neighboring molecule. Atom H17 is located 2.85 Å away from the centroid of the C8–C13 ring. Another close contact appears between the group C8–C13 in one molecule and the group C2–C7 of another one. Also, atom H7 is only 2.98 Å away from the centroid defined by the C15–C20 ring.

Further evidence that the distortion of the molecule arises from packing forces is given by looking at the crystal structure of the cobalt analog [8]. It crystallizes in a triclinic space group in which the molecules are not aligned. In this case, namely that of $Co_2(DPhF)_3$·toluene, the three formamidinato groups are distributed in a more regular fashion. Preliminary results of an Xα SW molecular orbital calculation also seem to rule out a distortion based on Jahn–Teller effects. We have also examined the possibility of the presence of a hydride ion in the molecule, but we have found no indication of it. Every ligand hydrogen atom in the molecule was located from the X-ray diffraction studies, and there is no residual electron density that could be attributed to an additional hydrogen atom. We were particularly concerned with the possible presence of a μ-H atom lying in the more open ligand–ligand dihedral angle. As seen in Fig. 3, which is a difference electron density map in the plane Fe, Fe', N3, N3', C14–H2, and in Fig. 4, which is a difference map drawn in the plane that contains C14, H2, the mid-point of the Fe–Fe bond, C1 and C1', the maximum difference density does not exceed 0.22(4) e/Å^3.

Another remarkable characteristic of this compound is its EPR spectrum. A frozen toluene glass at 10 K shows two signals corresponding to g values of 1.99 and 7.94. A further study of the magnetic properties of this compound (including the measurements of the bulk magnetic susceptibility) will be undertaken as soon as our newer synthetic method of preparation is optimized. We are also conducting a further study of the electronic structure using an *ab initio* configuration interaction method.

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*Crystal data for $Fe_2(DPhF)_3$: $M = 697.4$, monoclinic, $C2/c$ (No. 15), $a = 17.154(4)$, $b = 8.255(1)$, $c = 23.400(1)$ Å, $\beta = 93.38(1)$°, $V = 3308(1)$ Å^3, $Z = 4$, $D_{calc} = 1.400$ g cm^{-3}; Mo Kα (0.71073 Å), $T = -60(1)$ °C, Enraf-Nonius CAD-4 diffractometer. An empirical absorption correction, based on ψ scans, was applied. The structure was solved via direct methods (SHELXS-86) and was refined with the SHELXL-93 program. All hydrogen atoms were located in difference Fourier maps, and were included in the least-squares refinement without constraints. For all 2152 data, $R = 0.049$, $R_w^2 = 0.076$. For the 1675 data having $I > 2\sigma(I)$, $R = 0.025$, $R_w^2 = 0.063$.

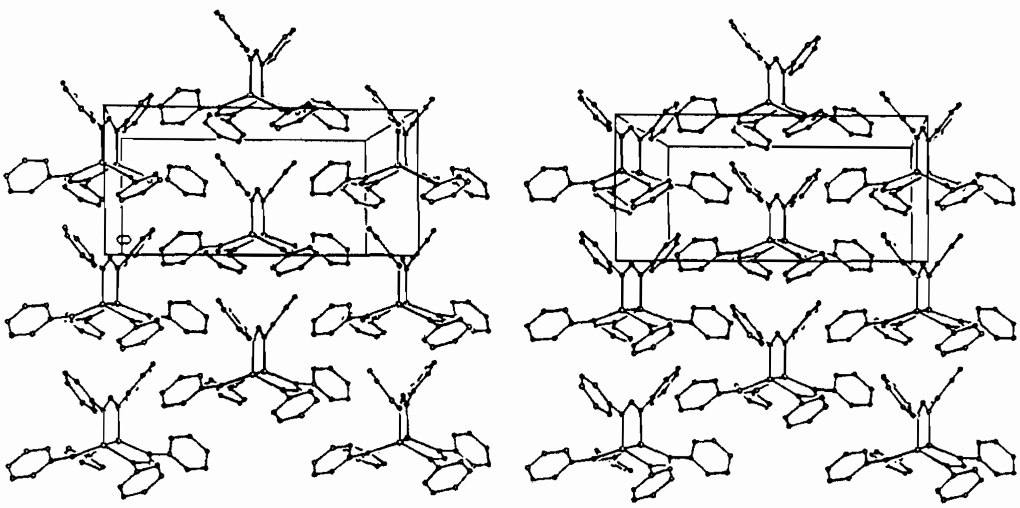

Fig. 2. Extended structure of $Fe_2(DPhF)_3$, viewed along the *c* axis. The crystallographic two-fold axis (*b*) is vertical in the drawing. In a given molecule, the two DPhF ligands, related to each other by the two-fold axis, are splayed apart by van der Waals contacts with the middle ligand of a molecule displaced from the original by [010].

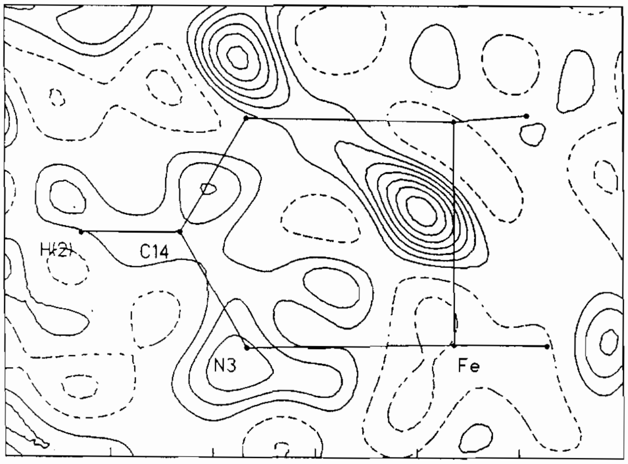

Fig. 3. Difference Fourier map calculated at the end of the crystal structure determination of $Fe_2(DPhF)_3$. A contoured section in a plane containing the Fe–Fe bond and the crystallographic diad axis is shown. The minimum electron density is -0.19 e/Å^3 and the maximum is 0.38 e/Å^3. The average density is 0.01 e/Å^3. Contours are drawn at densities of -0.15 and -0.05 e/Å^3, as broken lines. The positive contours (solid lines) are drawn from 0.05 to 0.35, in 0.05 e/Å^3 increments.

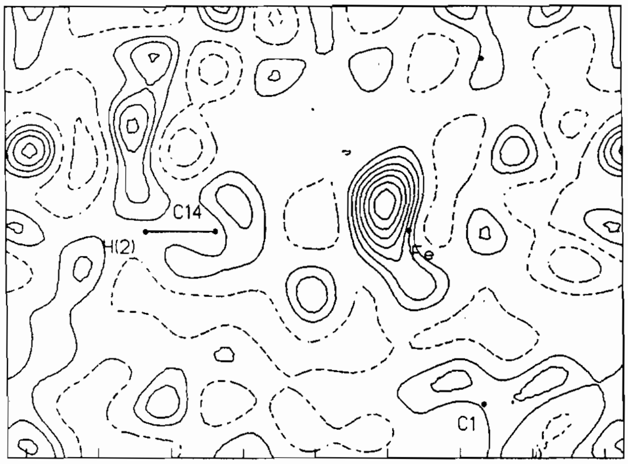

Fig. 4. Section of the difference Fourier map calculated at the end of the structure determination of $Fe_2(DPhF)_3$. The Fe–Fe vector is perpendicular to the plane of the drawing, and the diad runs horizontally in the drawing. The minimum electron difference is -0.23 e/Å^3 and the maximum is 0.39 e/Å^3. The average electron density is 0.00. Broken lines represent electron densities of -0.15 and -0.05 e/Å^3. Solid lines, electron densities between 0.05 and 0.35 e/Å^3, are drawn at 0.05 e/Å^3 increments.

Supplementary material

The following tables are available from the authors on request prior to the publication of a full paper: data collection and structure refinement parameters; atomic parameters; bond distances; bond angles; anisotropic displacement parameters and a list of observed and calculated structure factors (22 pages).

Acknowledgements

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