

**SUPPORTING INFORMATION**

FOR

**Bis(1,2,3-trimethylindenyl)iron(III) 2,3-Dicyanonaphtho-1,4-quinonide, a  
Non-Metallocene, Charge-Transfer Salt Metamagnet With Complementary  
Donor–Acceptor Geometries**

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Preparation of Potassium 1,2,3-trimethylindenide, K[1,2,3-Me <sub>3</sub> C <sub>9</sub> H <sub>4</sub> ], Fe(1,2,3-Me <sub>3</sub> C <sub>9</sub> H <sub>4</sub> ) <sub>2</sub> , Fe(1,2,3-Me <sub>3</sub> C <sub>9</sub> H <sub>4</sub> ) <sub>2</sub> [DCNQ] .....	S2–S3
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## Experimental

**General Considerations.** Unless mentioned otherwise, all manipulations were performed with the exclusion of air and moisture using Schlenk or glovebox techniques.  $^1\text{H}$ -NMR spectra were obtained on a Bruker DPX-300 at 300 MHz, and were referenced to the residual proton resonances of  $\text{C}_6\text{D}_6$  ( $\delta$  7.15). Elemental analyses were performed by Desert Analytics (Tucson, AZ) and by the Micro-Mass Facility, Department of Chemistry, University of California, Berkeley.

**Materials.** Anhydrous iron(II) chloride and  $\text{K}[\text{N}(\text{SiMe}_3)_2]$  were purchased from Aldrich or Acros and used as received. 2,3-Dicyano-1,4-naphthoquinone<sup>1</sup> and 1,2,3-trimethylindene<sup>2</sup> were synthesized by literature procedures. THF, toluene, and hexanes were distilled under nitrogen from potassium benzophenone ketyl.  $\text{C}_6\text{D}_6$  (Aldrich) was vacuum distilled from Na/K (22/78) alloy and stored over 4A molecular sieves prior to use.

**Synthesis of Potassium 1,2,3-trimethylindenide,  $\text{K}[1,2,3\text{-Me}_3\text{C}_9\text{H}_4]$ .** 1,2,3-trimethylindenene (16.4 g, 0.104 mol) was placed in a 250 mL Erlenmeyer flask containing 200 mL of toluene and a magnetic stirring bar.  $\text{K}[\text{N}(\text{SiMe}_3)_2]$  (20.6 g, 0.103 mol) was added directly to the toluene solution, which immediately formed a dark red solution. The toluene solution was slowly poured into a 500 mL Erlenmeyer flask containing 250 mL of hexanes, which rapidly formed a bright yellow solution. The mixture was stirred overnight. The following day, a large amount of precipitate was observed. The precipitate was isolated by filtration over a medium-porosity glass frit, washed with hexanes (3 x 50 mL), and dried under vacuum to yield 12.8 g (63%) of  $\text{K}[1,2,3\text{-Me}_3\text{C}_9\text{H}_4]$ .

**Synthesis of Bis(1,2,3-trimethylindenyl)iron(II),  $\text{Fe}(1,2,3\text{-Me}_3\text{C}_9\text{H}_4)_2\text{FeCl}_2$ .**  $\text{FeCl}_2$  (0.519 g, 4.09 mmol) and  $\text{K}[1,2,3\text{-Me}_3\text{C}_9\text{H}_4]$  (1.58 g, 8.05 mmol) were placed in a 500 mL Erlenmeyer flask equipped with a magnetic stirring bar. Approximately 125 mL of THF was added, immediately producing a dark purple solution. The mixture was stirred for 6 h, at which time the solvent was removed under vacuum. Hexanes (50 mL) was added to the resultant solid, and insoluble

impurities were removed by filtration over a medium-porosity frit. The filtrate was collected in a 125 mL Schlenk flask. The flask was capped and placed in a –20 °C freezer. Amorphous precipitate was observed after 48 h. The mother liquor was separated from the solid material by cannulation on a Schlenk line, and the solid was dried under vacuum. Fractional sublimation (180–200 °C/300 mTorr) of the material provided  $\text{Fe}(1,2,3\text{-Me}_3\text{C}_9\text{H}_4)_2$  as a purple powder (0.467 g, 31% yield). Anal. Calcd for  $\text{C}_{24}\text{H}_{26}\text{Fe}$ : C, 77.84; H, 7.07. Found: C, 78.35; H, 7.30.  $^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6$ ,  $\delta$ ): 7.14 (m, 4H,  $\text{C}_6$  ring H); 7.00 (m, 4H,  $\text{C}_6$  ring H); 1.77 (s, 12H, 1 & 3-position  $\text{CH}_3$ ); 1.52 (s, 6H, 2-position  $\text{CH}_3$ ).

**Synthesis of  $\text{Fe}(1,2,3\text{-Me}_3\text{C}_9\text{H}_4)_2[\text{DCNQ}]$ .** Under a nitrogen atmosphere, 2,3-dicyano-1,4-naphthoquinone (DCNQ) (68 mg, 0.33 mmol) was dissolved in 5 mL of anhydrous THF in a Schlenk tube. A concentrated solution of  $\text{Fe}(1,2,3\text{-Me}_3\text{C}_9\text{H}_4)_2$  (121 mg, 0.33 mmol) in THF (5 mL) was added to the DCNQ solution, which immediately turned black. The mixture was stirred for 30 min at room temperature, and then was filtered to yield a maroon powder. The solid was washed with diethyl ether (2 x 5 mL) and dried under vacuum. Yield: 162 mg (86%), >300 °C (dec). Anal. Calcd for  $\text{C}_{36}\text{H}_{30}\text{FeN}_2\text{O}_2$ : C, 74.75; H, 5.23; N, 4.84. Found: C (average of two determinations), 70.03; H (average of two determinations), 4.96; N, 4.81. Although the carbon analysis is low, the molar ratio of C:H is 1.19:1 or 35.6:30, which is close to the expected value.

To obtain crystals suitable for X-ray diffraction, the reaction was repeated with the same quantities of reagents. The DCNQ was dissolved in a minimal amount (ca. 2 mL) of anhydrous THF in a Schlenk tube. THF (2 mL) was slowly added on top of the DCNQ solution to form a second layer, after which a solution of  $(1,2,3\text{-Me}_3\text{C}_9\text{H}_4)_2\text{Fe}$  in THF (3 mL) was gently layered on the pure THF. The apparatus was subsequently maintained at –78 °C for 24 h. Filtration yielded air stable black needles.

## References

- (1) Reynolds, G. A.; Van Allan, J. A. *J. Org. Chem.* **1964**, *29*, 3591-3593.
- (2) Ready, T. E.; Chien, J. C. W.; Rausch, M. D. *J. Organomet. Chem.* **1999**, *583*, 11-27.

## X-ray Crystallography of Fe(1,2,3-Me<sub>3</sub>C<sub>9</sub>H<sub>4</sub>)<sub>2</sub>[DCNQI]

### DATA COLLECTION

A crystal (approximate dimensions 0.40 x 0.12 x 0.04 mm<sup>3</sup>) was placed onto the tip of a 0.1 mm diameter glass capillary and mounted on a Bruker SMART Platform CCD diffractometer for a data collection at 173(2) K. A preliminary set of cell constants was calculated from reflections harvested from three sets of 20 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced initial orientation matrices determined from 28 reflections. The data collection was carried out using MoK $\alpha$  radiation (graphite monochromator) with a frame time of 90 seconds and a detector distance of 4.83 cm. A randomly oriented region of reciprocal space was surveyed to the extent of one sphere and to a resolution of 0.84 Å. Three major sections of frames were collected with 0.30° steps in  $\omega$  at three different  $\phi$  settings and a detector position of -28° in 2 $\theta$ . The intensity data were corrected for absorption and decay (SADABS).<sup>1</sup> Final cell constants were calculated from the xyz centroids of 2566 strong reflections from the actual data collection after integration (SAINT).<sup>2</sup> Please refer to Table 1 for additional crystal and refinement information.

### STRUCTURE SOLUTION AND REFINEMENT

The structure was solved using SIR97<sup>3</sup> and refined using SHELXL-97.<sup>4</sup> The space group *Pbca* was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to  $R1 = 0.0580$  and  $wR2 = 0.1664$  ( $F^2$ , all data).

Data collection and structure solution were conducted at the X-Ray Crystallographic Laboratory, S146 Kolthoff Hall, Department of Chemistry, University of Minnesota. All calculations were performed using Pentium computers using the current SHELXTL suite of programs.

<sup>1</sup> An empirical correction for absorption anisotropy, R. Blessing, *Acta Cryst.* **A51**, 33-38 (1995).

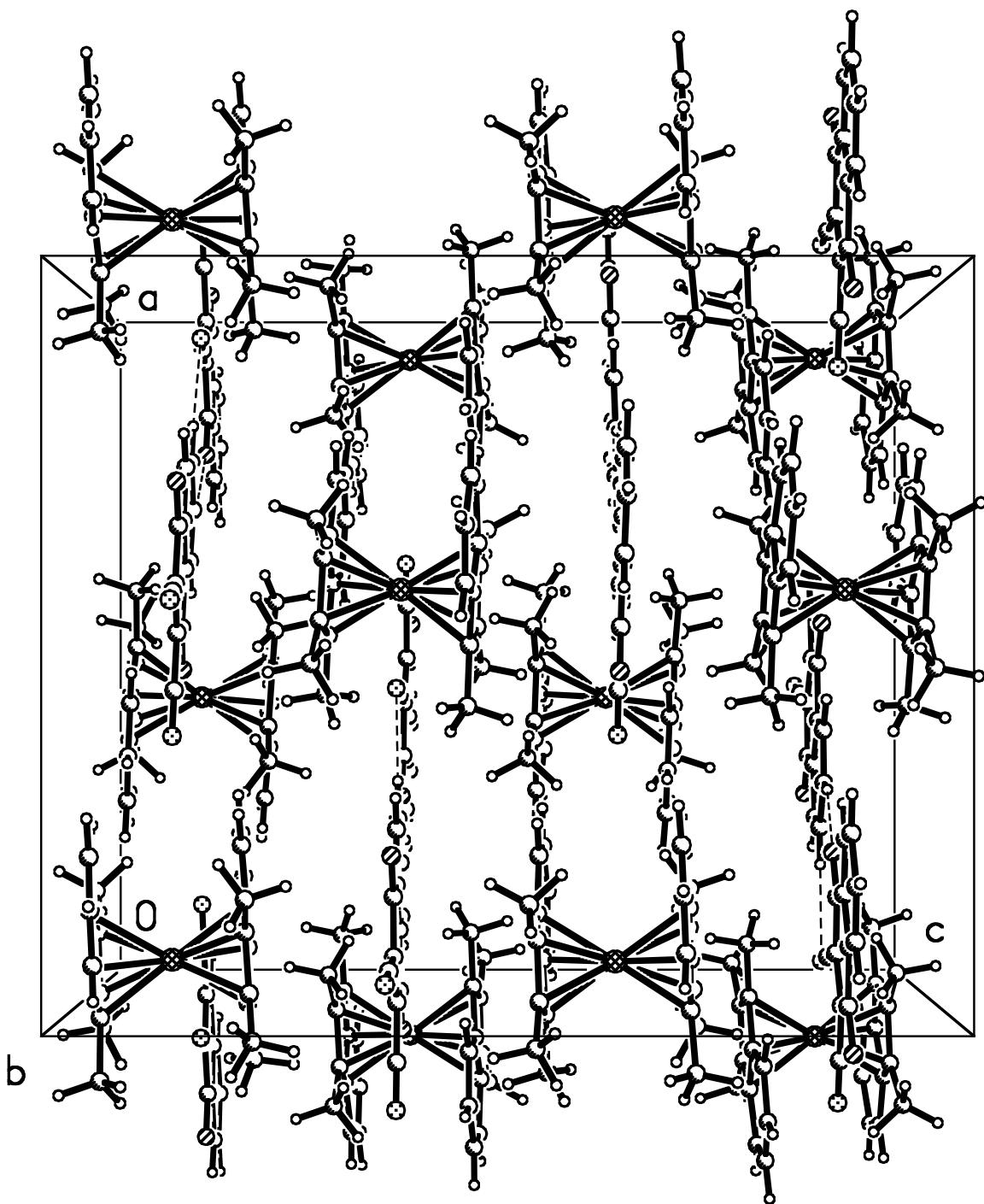
<sup>2</sup> SAINT V6.2, Bruker Analytical X-Ray Systems, Madison, WI (2001).

<sup>3</sup> A. Altomare, M. C. Burla, M. Camalli, G. Casciaro, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna. Sir97: a new tool for crystal structure determination and refinement. *J. Appl. Cryst.* **32**, 115-119 (1998).

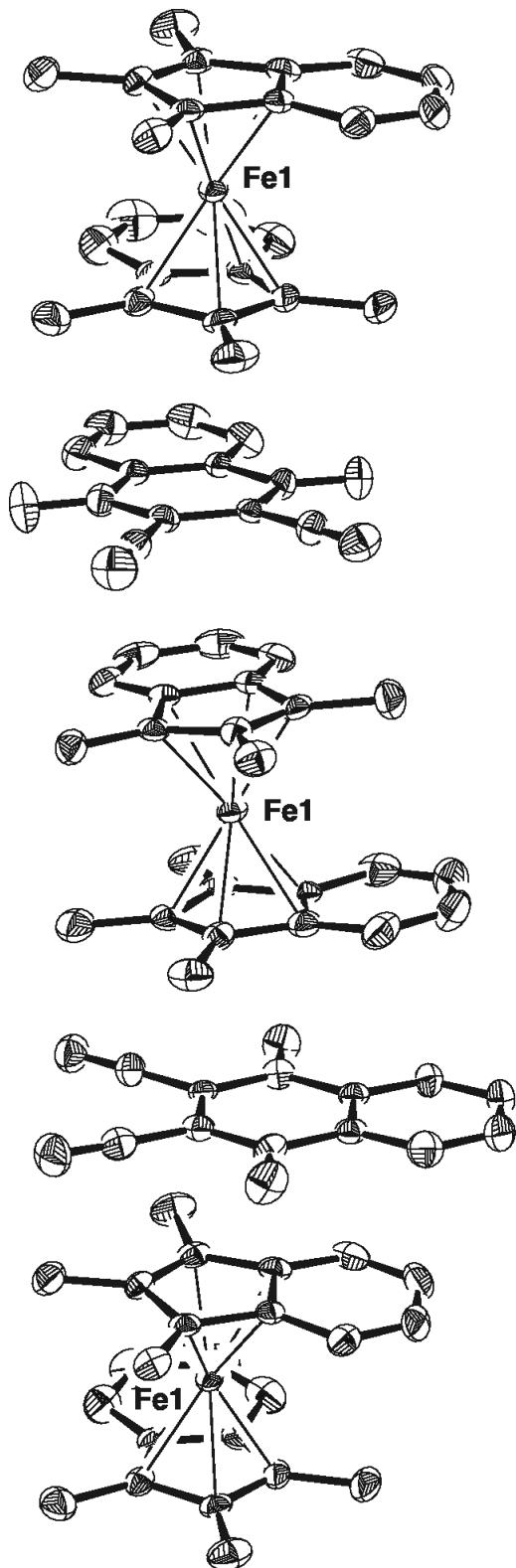
<sup>4</sup> SHELXTL V6.10, Bruker Analytical X-Ray Systems, Madison, WI (2000).

**Table 1. Crystal data and structure refinement for Fe(1,2,3-Me<sub>3</sub>C<sub>9</sub>H<sub>4</sub>)<sub>2</sub>[DCNQ]**

Empirical formula	C <sub>36</sub> H <sub>30</sub> FeN <sub>2</sub> O <sub>2</sub>		
Formula weight	578.47		
Temperature	173(2) K		
Wavelength	0.71073 Å		
Crystal system	Orthorhombic		
Space group	<i>Pbca</i>		
Unit cell dimensions	<i>a</i> = 17.020(1) Å	<i>α</i> = 90°	
	<i>b</i> = 15.989(1) Å	<i>β</i> = 90°	
	<i>c</i> = 20.364(2) Å	<i>γ</i> = 90°	
Volume	5541.8(7) Å <sup>3</sup>		
<i>Z</i>	8		
Density (calculated)	1.387 Mg/m <sup>3</sup>		
Absorption coefficient	0.581 mm <sup>-1</sup>		
<i>F</i> (000)	2416		
Crystal color, morphology	black, needle		
Crystal size	0.40 x 0.12 x 0.04 mm <sup>3</sup>		
Theta range for data collection	2.00 to 25.05°		
Index ranges	-18 ≤ <i>h</i> ≤ 20, -19 ≤ <i>k</i> ≤ 19, -24 ≤ <i>l</i> ≤ 24		
Reflections collected	34191		
Independent reflections	4896 [ <i>R</i> (int) = 0.1217]		
Observed reflections	2606		
Completeness to theta = 25.05°	99.8%		
Absorption correction	Multi-scan		
Max. and min. transmission	0.9771 and 0.8008		
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>		
Data / restraints / parameters	4896 / 0 / 376		
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.055		
Final <i>R</i> indices [ <i>I</i> >2sigma( <i>I</i> )]	<i>R</i> 1 = 0.0580, <i>wR</i> 2 = 0.1174		
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1472, <i>wR</i> 2 = 0.1664		
Largest diff. peak and hole	0.465 and -0.544 e.Å <sup>-3</sup>		



Packing diagram of  $\text{Fe}(1,2,3\text{-Me}_3\text{C}_9\text{H}_4)_2[\text{DCNQ}]$ , projected down the crystallographic *b* axis.



Extended stack of donors and acceptors in  $\text{Fe}(1,2,3\text{-Me}_3\text{C}_9\text{H}_4)_2[\text{DCNQ}]$ .