



Synthesis and Characterization of Molecular Magnetic Systems

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Introduction:

Clusters of transition metals have attracted much interest from the chemical society and other interdisciplinary research fields. Polynuclear complexes of Fe and Mn have proven interesting due to their magnetic properties. Usually, such clusters exhibit large ground-state magnetic moments and can function as single-molecule magnets due to a high energy barrier to magnetization relaxation. Thus, such molecules can retain magnetic orientation for prolonged periods of time without further addition of energy.^{1,2} These molecular systems have potential application to molecular data storage devices.³

To further increase the functionality of such compounds, redox-active ligands have been introduced in to the cluster core.³ For the scope of this research, ferrocene-1,1'-dicarboxylic acid (Fdch₂, **Figure 1**) was used as a basis for carboxylate ligation within the cluster.^{1,2} The premise of my work was based on previous publication describing Mn and Fe clusters, more specifically an ionic Fe₁₃ cluster, which also utilized Fdch₂ as a redox-active ligand. Redox-active ligation with Fdch₂ is important for data storage devices since the dicarboxylate anion can undergo reversible one-electron reduction/oxidation chemistry. It can also act as a restrictive bridging ligand or chelate with regard to molecular flexibility, however, it can retain rotational properties of its cyclopentadienyl rings to further bridge other units leading to polymers.²

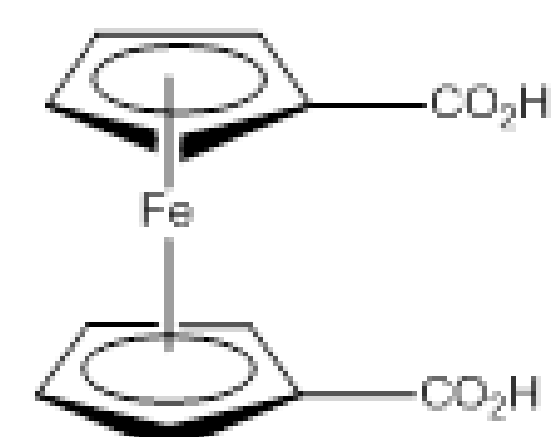


Figure 1: Molecular structure of ferrocene-1,1'-dicarboxylic acid (Fdch₂). The purpose of this research was to find and optimize synthetic conditions for a neutral mixed-valent state cluster via dicarboxylate ligation.

Materials and Methods:

Synthesis: Several experimental conditions were explored:

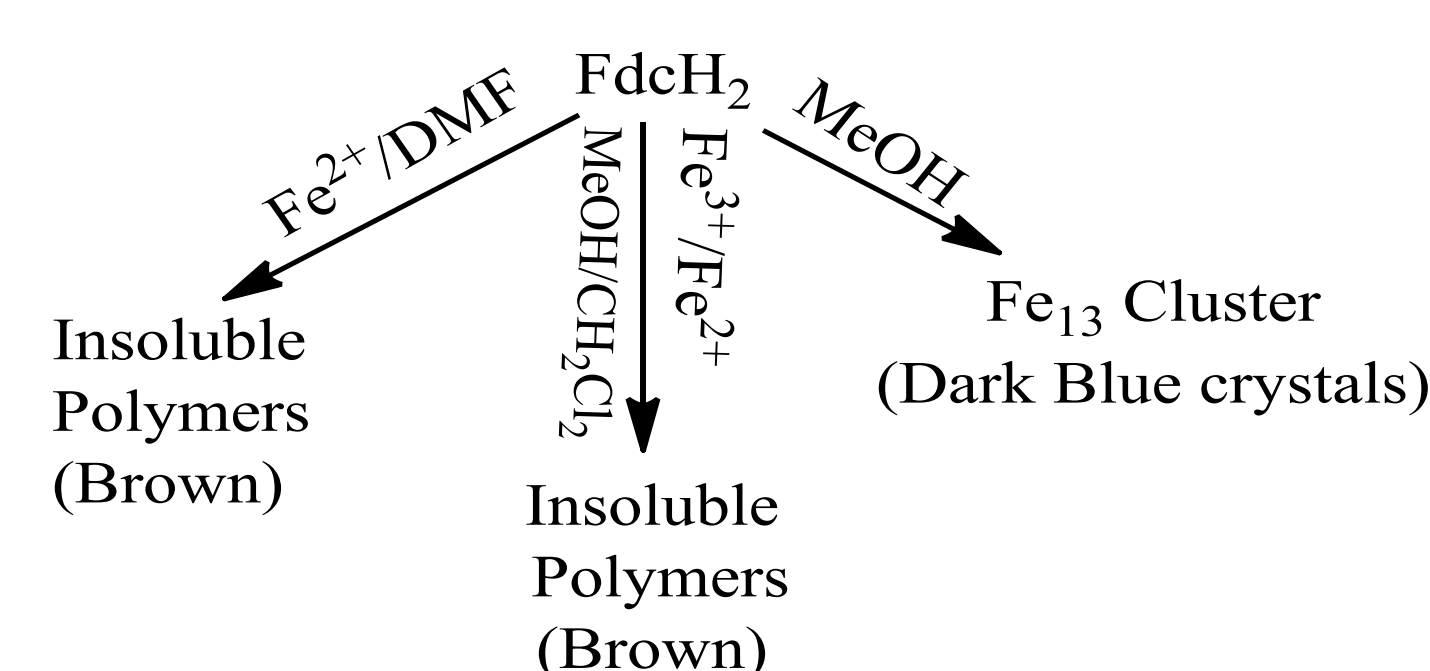


Figure 2: Different reaction schemes

X-ray Crystallography: X-ray diffraction data were collected on a Rigaku RAPID II diffractometer with curved detector using graphite monochromated Mo-K α ($\lambda = 0.71073 \text{ \AA}$) at 123 K. Multi-scan absorption corrections were applied to the data using the Crystal Clear program. The structures were solved by direct method implemented in SHELXS-97 and refined by full-matrix least squares method based on F2 using SHELXL-97 software. PLATON software was used for visualization of the results.

Elemental Analysis: Analysis performed by Altantic Microlab, INC. Analyzed for C, H, and N.

REFERENCES
1. A. Masello, Y. Sanakis, A. K. Boudalis, K.A. Abboud and, G. Christou. "Iron(III) Chemistry with Ferrocene-1,1'-dicarboxylic Acid (fdch₂): An Fe₇ Cluster with an Oxidized fdc- Ligand." *Inorg. Chem.* **2011**, 50 (12), 5646-5654.
2. A. Masello, M. Murugesu, K.A. Abboud, and G. Christou. "A family of ferrocene-rich Mn₇, Mn₈ and Mn₁₃ clusters." *Polyhedron.* **2007**, 26, 2276-2280.
3. J. Lindsey, and D. Bocian. "Molecules for Charge-Based Information Storage." *Accounts of Chem. Research.* **2011**, 44 (8), 638-650.

X-Ray Analysis:

Core Bond Lengths (Å)	
Fe(1)-O(2)	2.171(5)
Fe(1)-O(3)	2.197(4)
Fe(1)-O(4)	2.206(5)
Fe(2)-O(4)	1.977(5)
Fe(2)-O(2)	2.011(4)
Fe(2)-O(1)	2.078(5)
Fe(3)-O(3)	1.957(4)
Fe(3)-O(4)	2.018(5)
Fe(3)-O(1)	2.140(5)
Fe(5)-O(3)	2.014(5)
Fe(5)-O(2)	2.030(5)
Fe(5)-O(1)	2.092(4)
Fe(7)-O(4)	1.922(4)
Fe(8)-O(3)	1.984(5)
Fe(9)-O(2)	1.922(5)

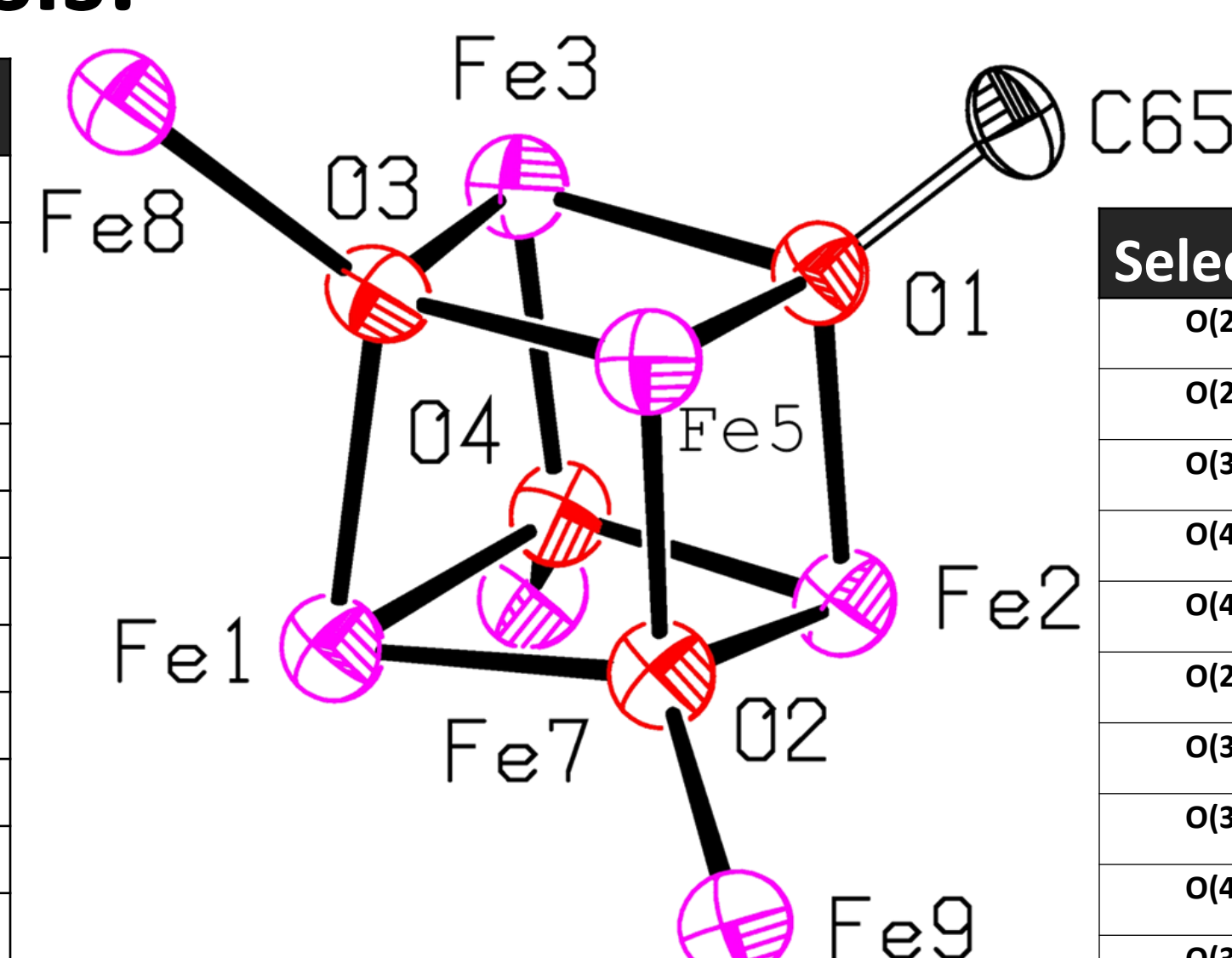


Figure 3: Fe(III)-O core observed in cluster.

Select Bond Angles in core	
O(2)-Fe(1)-O(3)	79.31(18)
O(2)-Fe(1)-O(4)	79.80(17)
O(3)-Fe(1)-O(4)	79.49(16)
O(4)-Fe(2)-O(2)	89.47(19)
O(4)-Fe(2)-O(1)	82.55(19)
O(2)-Fe(2)-O(1)	81.53(18)
O(3)-Fe(3)-O(4)	90.14(18)
O(3)-Fe(3)-O(1)	80.31(19)
O(4)-Fe(3)-O(1)	80.07(18)
O(3)-Fe(5)-O(1)	80.23(18)
O(2)-Fe(5)-O(1)	80.77(18)
O(3)-Fe(5)-O(2)	87.15(19)

Select Bond Angles

O(3)-Fe(8)-O(14)	95.8(2)
O(16)-Fe(8)-O(26)	169.7(2)
O(2)-Fe(9)-O(30)	95.7(2)

Bond Lengths (Å)

Fe(1)-O(18)	2.039(5)
Fe(5)-O(3)	2.014(5)
Fe(5)-O(8)	2.011(5)
Fe(3)-O(3)	1.957(4)
Fe(3)-O(12)	1.985(5)
Fe(8)-O(3)	1.984(5)
Fe(8)-O(14)	2.018(5)
Fe(8)-O(16)	2.001(5)
Fe(8)-O(26)	2.139(5)
Fe(9)-O(30)	2.034(5)

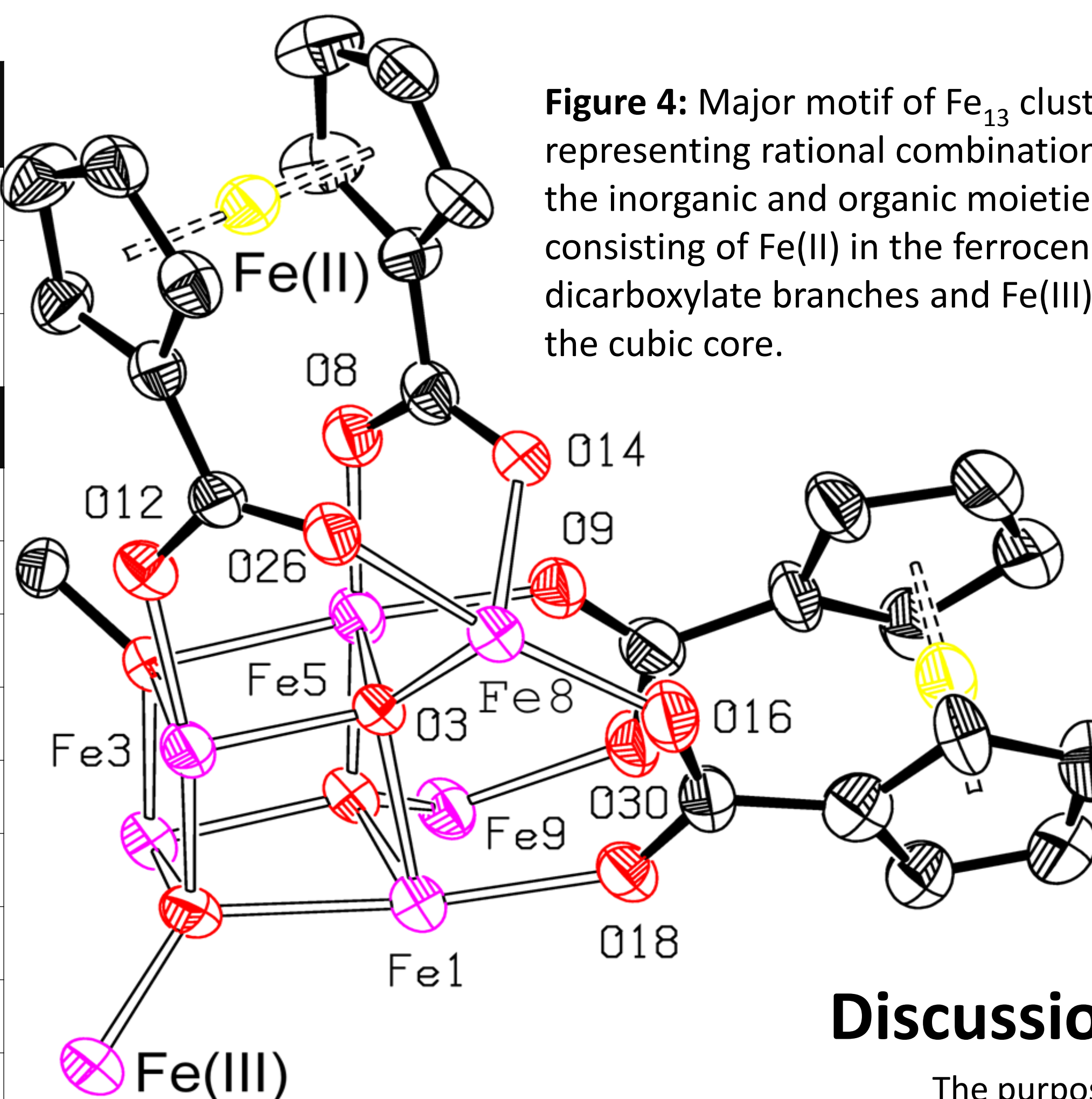


Figure 4: Major motif of Fe₁₃ cluster representing rational combination of the inorganic and organic moieties, consisting of Fe(II) in the ferrocene dicarboxylate branches and Fe(III) in the cubic core.

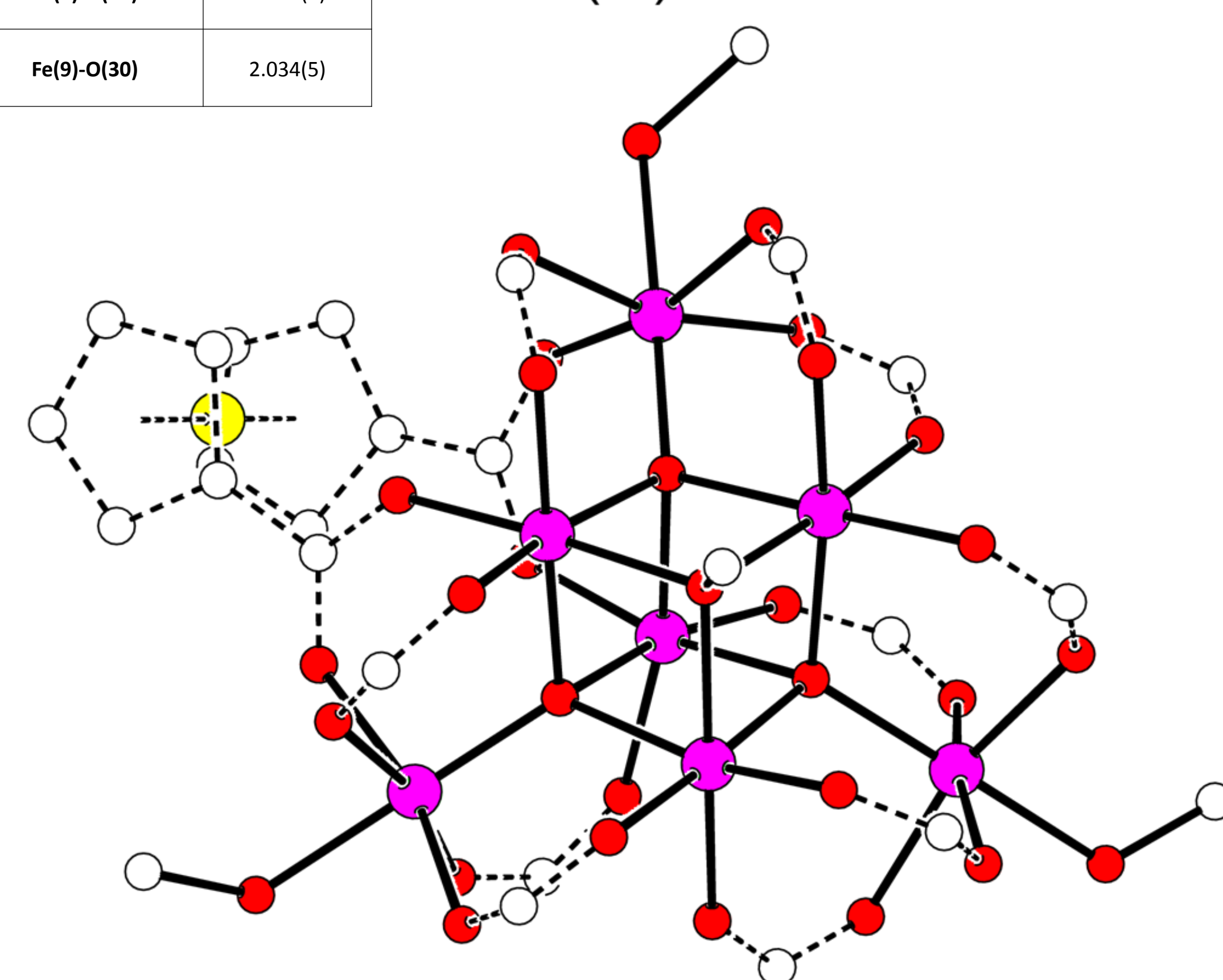


Figure 5: Structure highlighting ferrocene dicarboxylate moieties (represented by dotted lines).

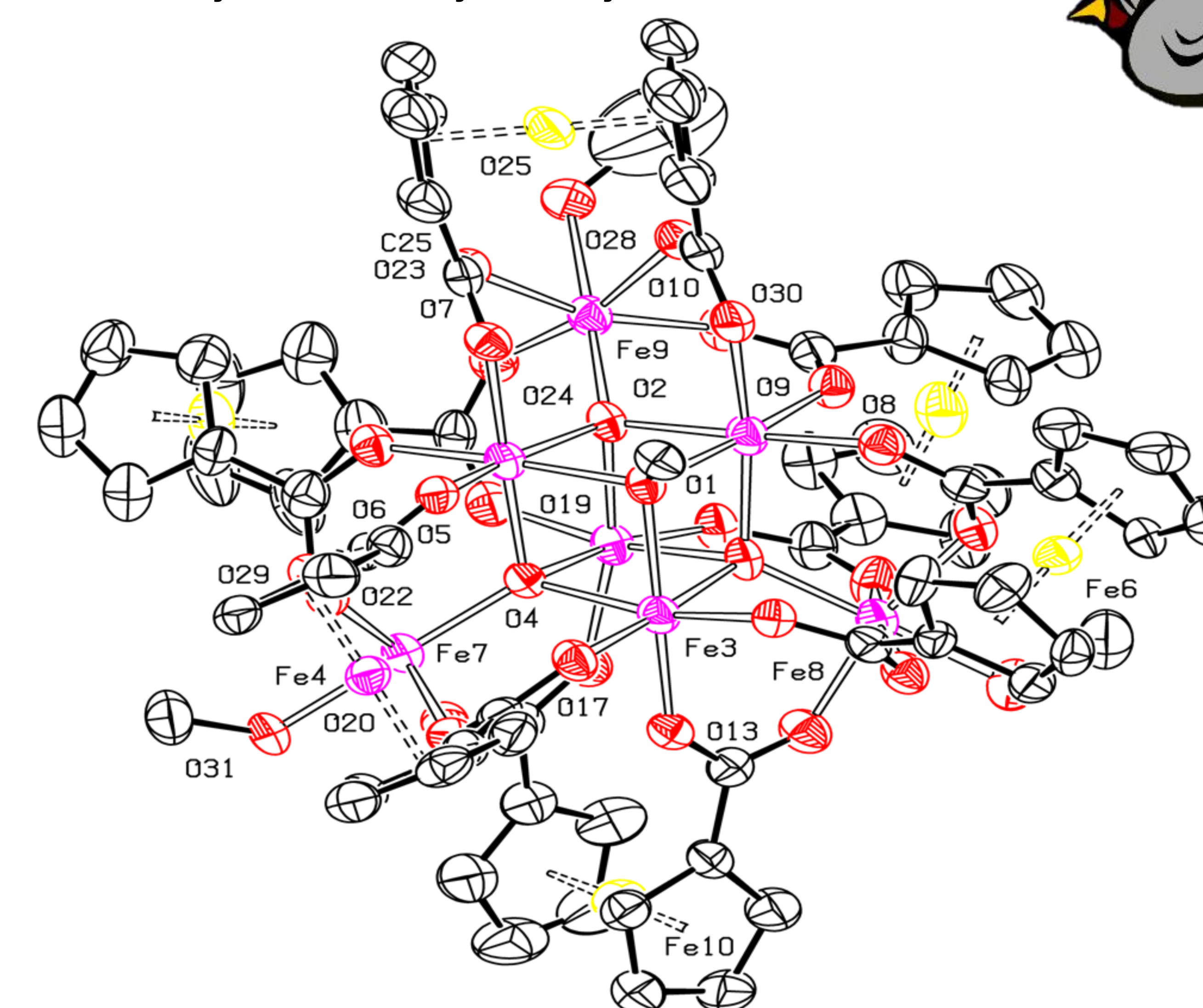


Figure 6: Complete representation of neutral Fe₁₃ cluster structure based on crystallographic analysis (X-ray diffraction). Hydrogen atoms omitted for clarity.

Elemental Analysis:

Results from duplicate-elemental analysis (observed) and the theoretical percent mass of C, H, and N. Differences can be attributed to solvents being presented in structure.

Element	Theory	Observed	Average Observed
C	41.52	44.3	44.25
H	2.89	3.96	4.015
N	0	0	0

Discussion:

The purpose of this experiment was to optimize synthetic condition of a neutral Fe₁₃ cluster based on previous reported results. Crystallographic analysis supported the presence of an Fe₁₃ cluster, revealed Fe(II) and Fe(III) atoms within the cluster. Furthermore, it was deduced that the presence of Fe(II) and Fe(III) in the cluster is attributed only to a decomposition, via solvolysis, of Fdch₂. The color change from orange (initial solution of Fdch₂ in MeOH) to dark-blue (final product) can be attributed to the one electron oxidation of Fe(III) to Fe(II).

The crystal structure of the Fe₁₃ cluster is better described as a combination of the inorganic and organic moieties. Thus, the inorganic core consists of cubane Fe₄O₄ formed from four hexacoordinated Fe(III) ionic nature, more specifically, when analyzing magnetic properties of cations, three μ_4 -oxo, and one μ_3 -methoxo bridges. The surroundings of the octacoordinated irons consists of only oxygen atoms originated from oxo-, methoxo- and carboxyl ligands. Corresponding distances for Fe(III)-O within the inorganic core lie within the range of 1.99 to 2.20 Å, the dicarboxylate ligand with regard to the driving force of this while angles vary from 79 to 105°, with angles around 90° in the cubic core. Organic functionality is introduced through Fdch₂ bridges which build up a coordination environment for all iron cations within the inorganic cluster. The unique role of the Fdch₂ bridges exists in the binding of each carboxyl group to two irons in the inorganic core; therefore, six Fdch₂ ligands are involved in coordination with Fe(III) centers. Coordination environment of the hexacoordinated iron(III) ions consist of four oxygen atoms from fdcH₂ ligands located in equatorial positions and two oxygen atoms from μ_4 -oxo ligand and

OMe- oxygen. Elemental Analysis confirmed the identity of the compound with some differences in composition; these differences can be attributed to solvent coordination within the cluster.

Overall, this experiment was successful in that it yielded a neutral cluster with the same topology as previously reported cationic species; the only difference exists in the coordination: neutral cluster was coordinated with MeO- and cationic cluster was coordinated with MeOH. The importance of a neutral paramagnetic cluster for data storage lies strictly in its ease of application. For example, published work by Masello *et al* on their synthesis of a cationic species expressed problems regarding the characterization of the compound due to its ionic nature, more specifically, when analyzing magnetic properties of their compound, the paramagnetic effects of the counter ion, [FeCl₄]⁻, on the cluster became evident.² However, one similarity between our synthesis and the synthesis of the cationic species is the importance of the dicarboxylate ligand with regard to the driving force of this reaction. The relevance of such compound to data storage lies within its five ferrocene substituents which can be separately oxidized resulting in six different oxidation potentials.

In the future, I hope to perform Powder diffraction, Mössbauer Spectroscopy and Electron Paramagnetic Resonance (EPR) to further characterize the compound. Further research could also include experimentation with other alcohols.