Outline

- Krekel and Wunderlichich proposed iron gall ink structures
- Iron gall ink model compounds
- Model compound characterization and structural analysis
Krekel’s Structures

- Black-blue insoluble precipitate
- Fe(III) complex
- Tetrahedral – awkward bond angles
- Binding through phenols only

Krekel’s Structures

- Structure of historic ink
- Takes into account impurities such as Fe(III) etc
- Octahedral – but awkward bond lengths
- Decarboxylated

1:1 GA:Fe Structure
Wunderlich’s Structure

- Crystals!!
- Synthesized with Fe(III)Cl₃ not Fe(II)SO₄ as in ink
- Binding through both carboxylic acid and phenols
- Octahedral Fe(III) high spin complex
- Fe(C₇O₅H₂)·H₃O⁺

Crystal had the same structure as Wunderlich’s

Synthesized with Fe(II)Cl₂

Polymeric structure

Fe(C₇O₅H₂)·2H₃O⁺

1:1 GA:Fe Structure

Russell Feller and Anthony Cheetham *Solid State Sciences* 8, 1121-1125, 2006
Model Compound (IGI ppt)

Experimental procedure for a 1:1 GA:IS molar ratio IGI mix

Gallic Acid\(_{(aq)}\) + FeSO\(_4\) \(_{x7H_2O\(_{(s)}\)}\)

\[ \text{Stirred one week in air} \] \[ \rightarrow \] \[ \text{washed/centrifuged 3x} \] \[ \rightarrow \] \[ \text{IGI dark-blue ppt} \]

\[ \text{Insoluble Iron yield 5-8\%} \]

\[ \rightarrow \] \[ \text{Dark supernatant} \]

\[ \text{pH=1.8-2.1} \]

more than 95% iron is present as Fe\(^{2+}\)

Autoxidation of iron(II)

\[ \text{Fe}^{2+} + \text{O}_2 \rightarrow \text{Fe}^{3+} \]

minimal at pH < 4

Barak Morgan, *Chemosphere* 2007, 68, 2080-2084

Autoxidation of catecholates and gallates

A

[Diagram A showing reaction between catecholate and iron(II) in aqueous solution, leading to a complex with water and protons.]  

B

[Diagram B showing formation of a radical from the iron(II) complex, followed by the formation of an iron(III) complex with oxygen.]  

C

[Diagram C showing the reaction of iron(II) complex with oxygen to form an iron(III) complex with a radical, and the production of superoxide ion.]  

**Elemental Analysis:**

<table>
<thead>
<tr>
<th>Sample</th>
<th>IGI ppt This study</th>
<th>Feller’s Iron gallate</th>
<th>Wunderlich’s Iron gallate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron (%)</td>
<td>20.7</td>
<td>----</td>
<td>22.3</td>
</tr>
<tr>
<td>Carbon (%)</td>
<td>30.89</td>
<td>29.95</td>
<td>34.43</td>
</tr>
<tr>
<td>Hydrogen (%)</td>
<td>8.27</td>
<td>2.70</td>
<td>1.24</td>
</tr>
<tr>
<td>Oxygen (by difference) (%)</td>
<td>45.62</td>
<td>----</td>
<td>41.4</td>
</tr>
</tbody>
</table>

a) expected

**Thermogravimetric analysis (TGA):**

68-70 % weight loss (same as Feller), 21% Iron calculated
Atomic ratios:

IGI ppts \( \text{Fe}_1 \text{C}_{6.9} \text{H}_{7.4} \text{O}_{7.7} \)

Wunderlich’s \( \text{Fe}_1 \text{C}_{7.18} \text{H}_{3.07} \text{O}_{6.48} \)

Feller’s \( \text{Fe}_1 \text{C}_7 \)

Krekel’s
What happens if we alter the molar ratios of Gallic acid to FeSO$_4$?

- We prepared IGI ppts from different GA:IS molar ratios: 3:1 2:1 1:1 1:2 1:3 1:4 1:5 1:6 1:7 1:8 1:9

- The IGI ppts extracted have the same elemental composition, Raman, IR, and XPS.

- Same % yield of Fe wrt total iron in the IGI mix.

- ~95% is soluble! In which form is the rest of the iron and gallic acid?
Trying to obtain crystals

- Crystal growth using Wunderlich’s method and other methods, unsuccessful.
- GA+FeSO₄ forms a stable solution in DMF.
- The most crystalline ppt was grown from a IGI mix at a DMF/2-propanol interface.

• X-ray diffraction
• Similar cell size to Wunderlich but different diffraction pattern
• Crystal structure could be different
For benzoates the $\Delta$ value is $\sim 168$

I $\Delta >$ ionic complexes

II $\Delta <$ ionic complexes

III $\Delta$ larger than for II and close to ionic values

Our $\Delta$ value is 149, which implies that we have a type III bridging complex.

Infrared Spectroscopy

- COO stretch bands are both Raman and IR active
- IR spectrum greatly influenced by O-H bands.
There is also no experimental evidence that supports the occurrence in original manuscripts of the iron-gallic acid precipitate structures that are described in literature.


Alana Lee et al Vibrational Spectroscopy 41, 170-175, 2006
Conclusions

- Wunderlich and Feller were able to obtain iron gallate complexes with the same structure starting with iron(II) and iron(III).

- The IGI reaction only forms a 5-8% yield based on the initial amount of iron, independent of the GA:IS molar ratio used.

- The elemental analysis indicates that the Fe:C ratio is 1:7, independent of the GA:IS molar ratio used. This correlates to the iron gallate complexes synthesized by Wunderlich and Feller, but not with the proposed structure by Krekel present in historical documents.
Conclusions

- The elemental analysis, Raman, IR, and XPS of the IGI ppts prepared in this study are identical, independent of the GA:IS molar ratio used.

- Raman and IR spectroscopy shows that the carboxylate group in the gallic acid coordinates to iron in a bridging mode. This also correlates to the iron gallate complexes synthesized by Wunderlich and Feller, but not with the proposed structures by Krekel.
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