



New Insights into the Chemistry and Structure of Iron Gall Ink

Aldo Ponce, Karen Gaskell, and Lynn Brostoff

Library of Congress
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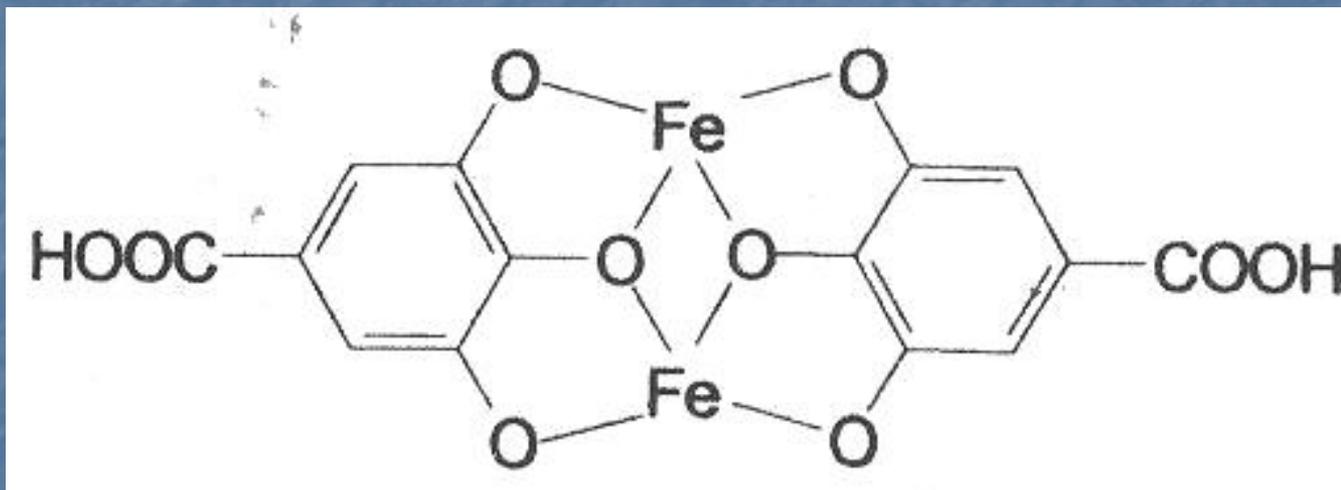
Outline

- Krekel and Wunderlich proposed iron gall ink structures
- Iron gall ink model compounds
- Model compound characterization and structural analysis

Krekel's Structures

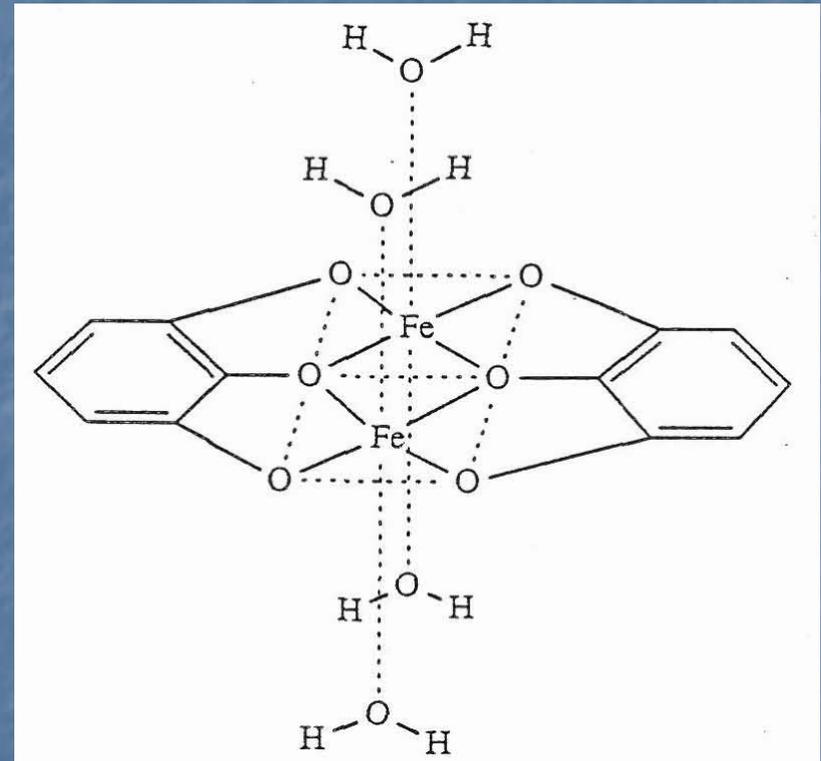
- Black-blue insoluble precipitate
- Fe(III) complex
- Tetrahedral – awkward bond angles
- Binding through phenols only

1:1 GA:Fe Structure



Krekel's Structures

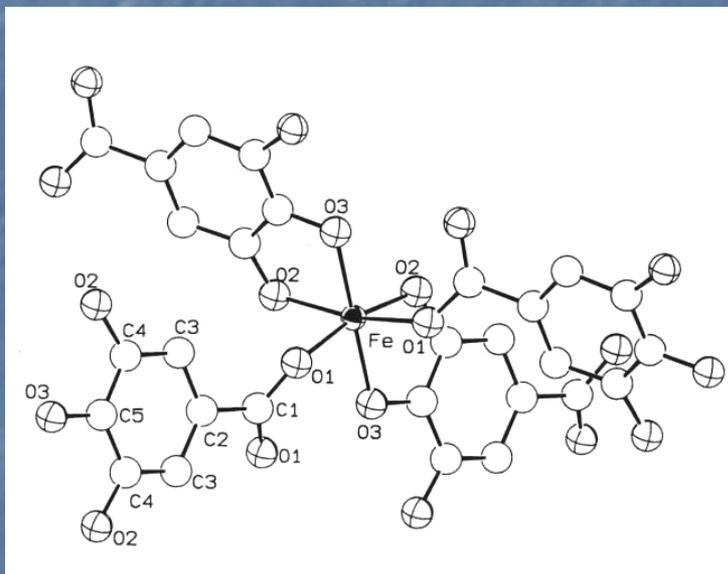
- Structure of historic ink
- Takes into account impurities such as Fe(III) etc
- Octahedral – but awkward bond lengths
- Decarboxylated



1:1 GA:Fe Structure

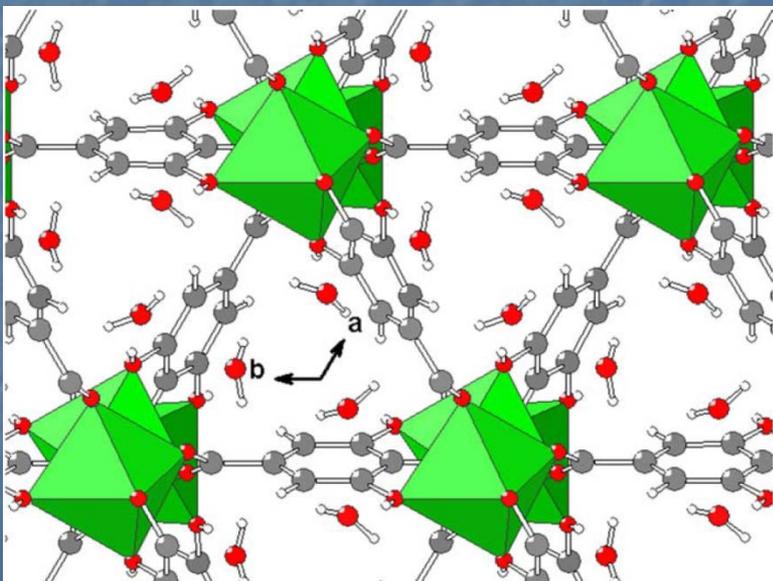
Wunderlich's Structure

- Crystals!!
- Synthesized with Fe(III)Cl_3 not Fe(II)SO_4 as in ink
- Binding through both carboxylic acid and phenols
- Octahedral Fe(III) high spin complex
- $\text{Fe(C}_7\text{O}_5\text{H}_2\text{)} \cdot \text{H}_3\text{O}^+$

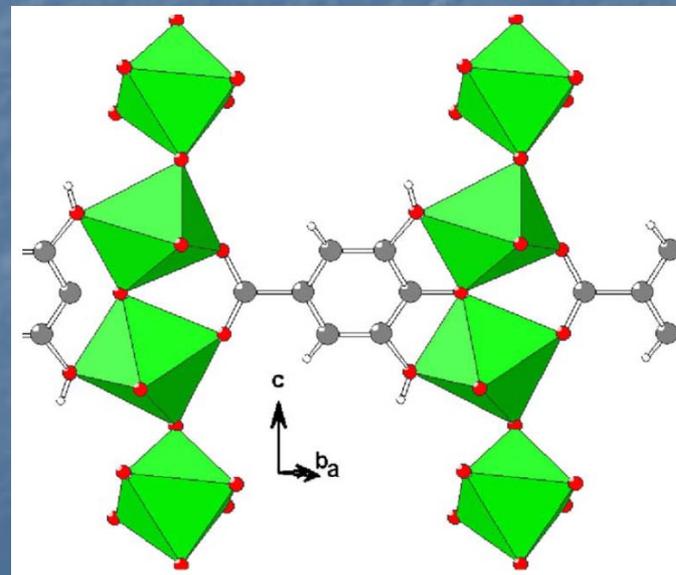


Feller and Cheetham

- Crystal had the same structure as Wunderlich's
- Synthesized with Fe(II)Cl_2
- Polymeric structure
- $\text{Fe}(\text{C}_7\text{O}_5\text{H}_2) \cdot 2\text{H}_3\text{O}^+$

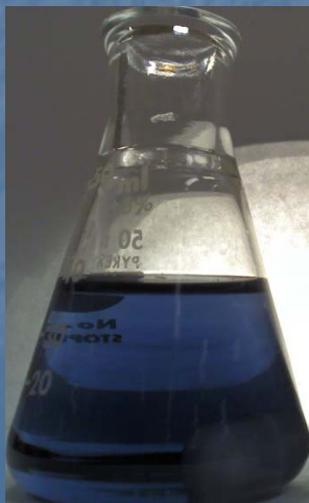
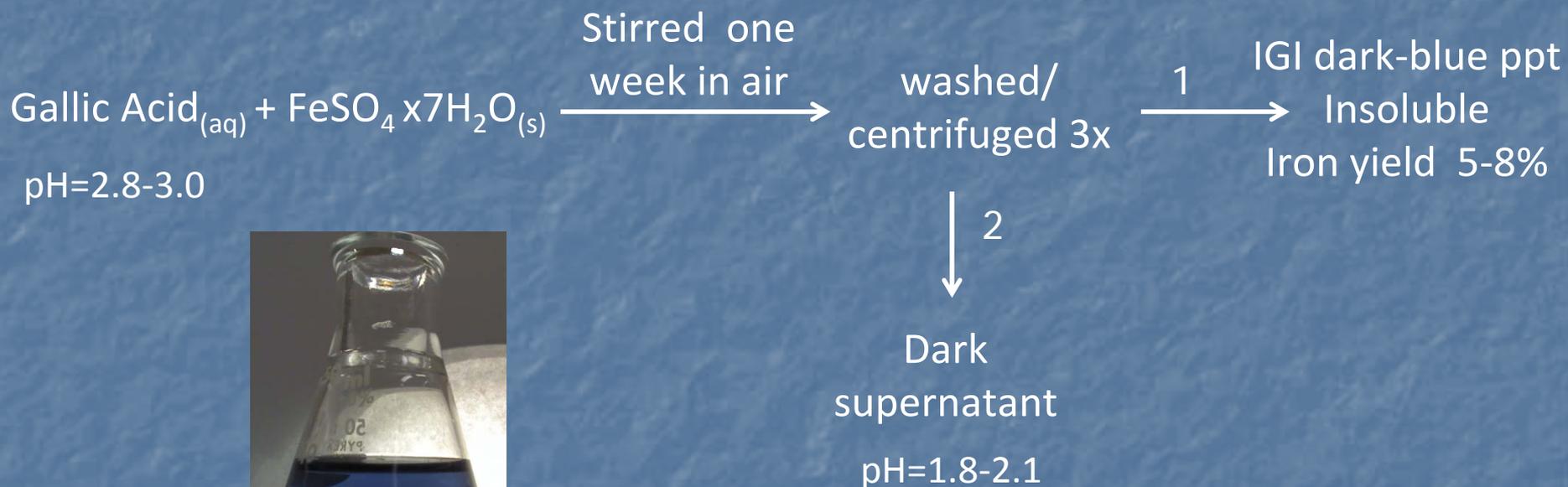


1:1 GA:Fe Structure



Model Compound (IGI ppt)

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



more than 95% iron is present as Fe²⁺

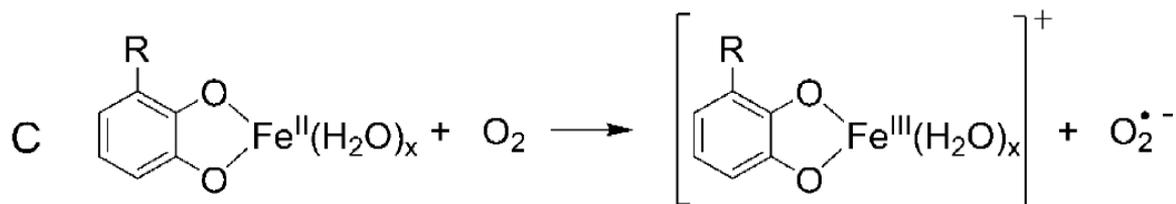
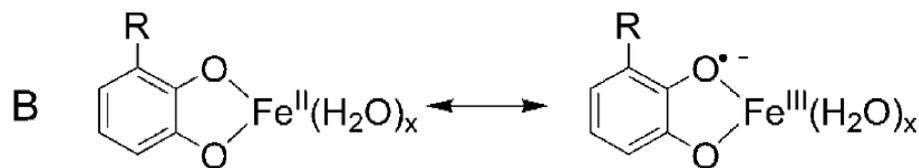
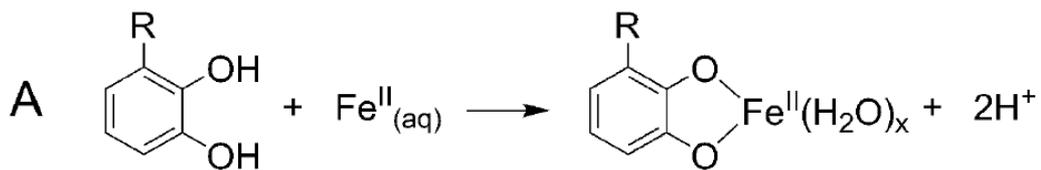
IGI ppt yield

Autoxidation of iron(II)



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

Autoxidation of catecholates and gallates



IGI ppt

- Elemental Analysis:

Sample	IGI ppt This study	Feller's Iron gallate	Wunderlich's Iron gallate
Iron (%)	20.7	----	22.3
Carbon (%)	30.89	29.95 (32.46) ^a	34.43
Hydrogen (%)	8.27	2.70 (2.73) ^a	1.24
Oxygen (by difference) (%)	45.62	----	41.4

a) expected

- Thermogravimetric analysis (TGA) :
68-70 % weight loss (same as Feller), 21% Iron calculated

IGI ppt

Atomic ratios:

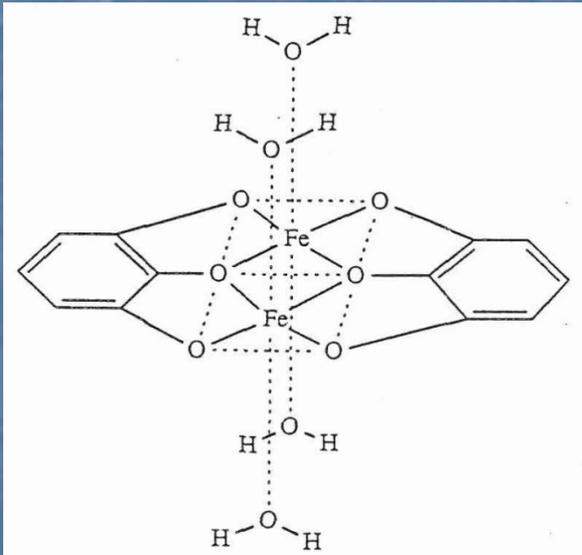
IGI ppts



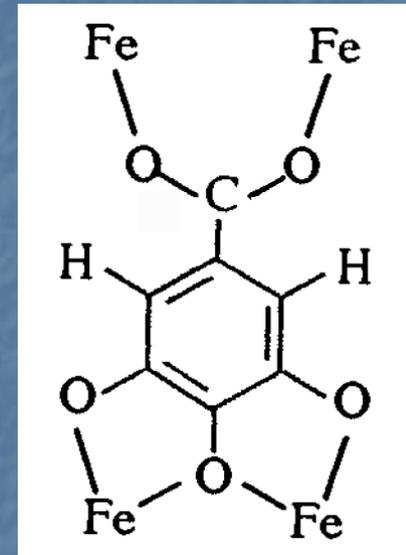
Wunderlich's



Feller's



Krekel's



Wunderlich'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?

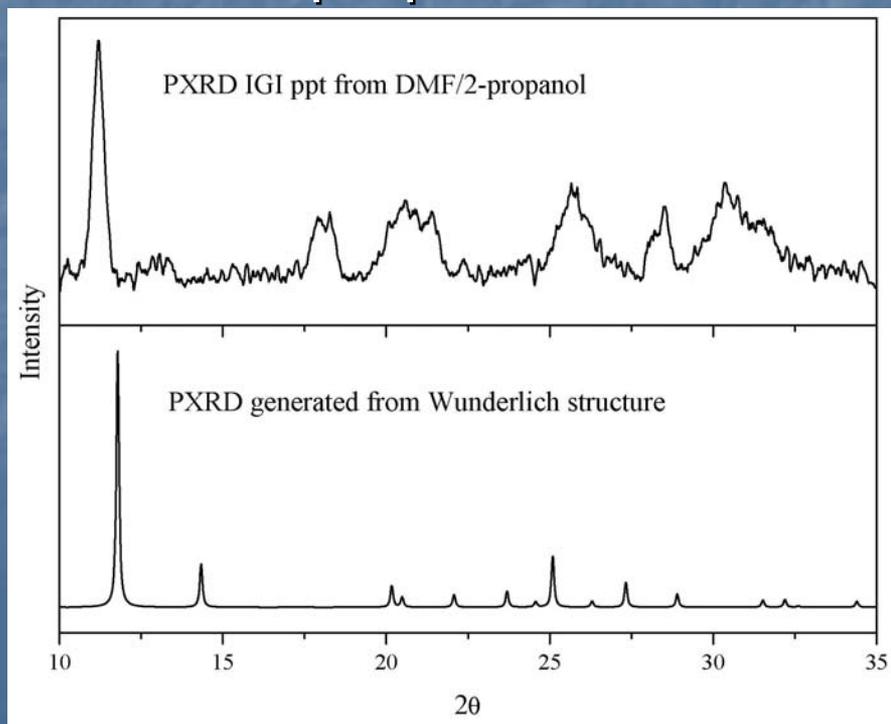


+3-week-old,
excess IS

+3-week-old,
excess GA

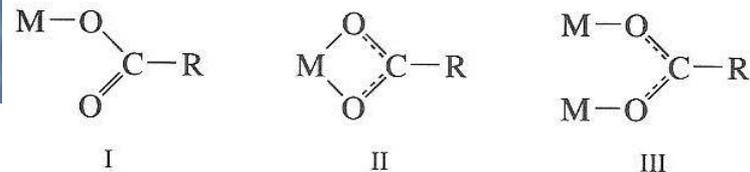
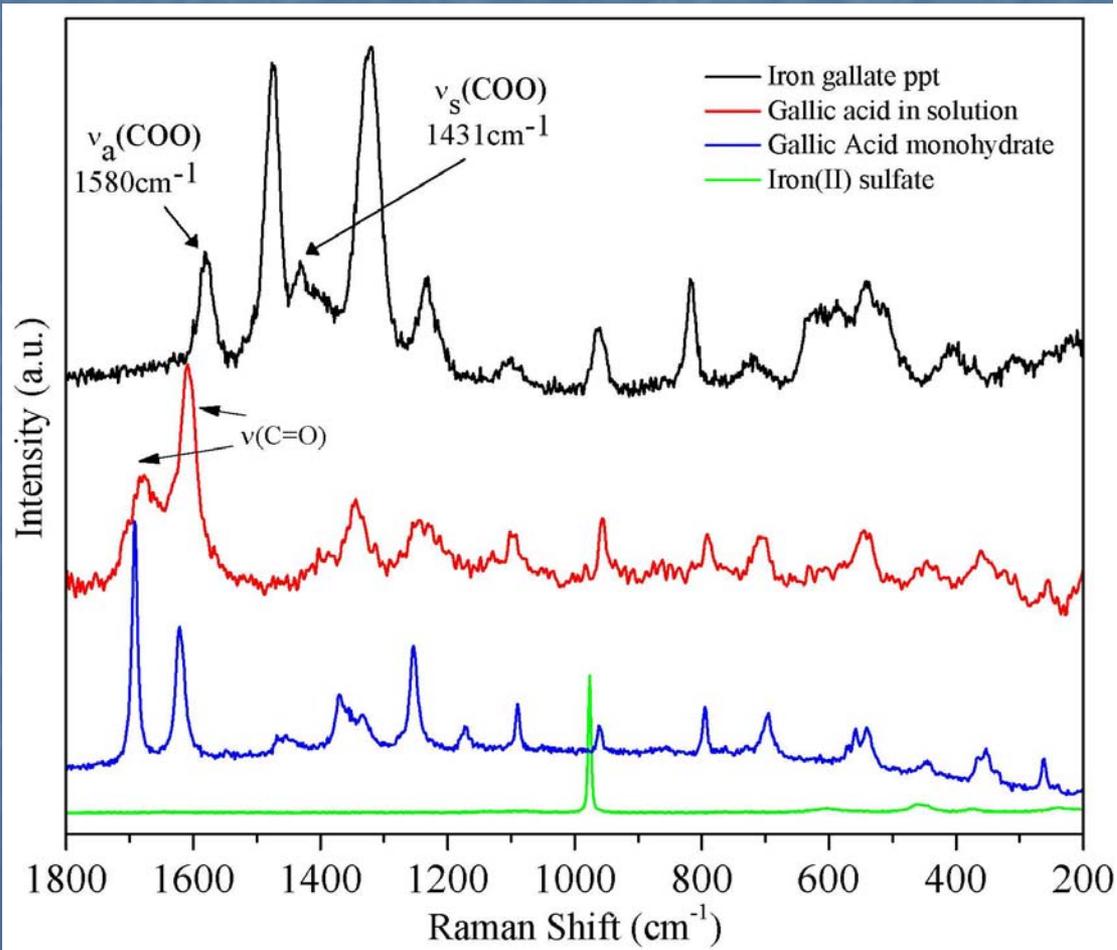
Trying to obtain crystals

- 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

Raman Spectroscopy



Deacon and Phillips

$$\Delta = [\nu_a(\text{CO}_2^-) - \nu_s(\text{CO}_2^-)]$$

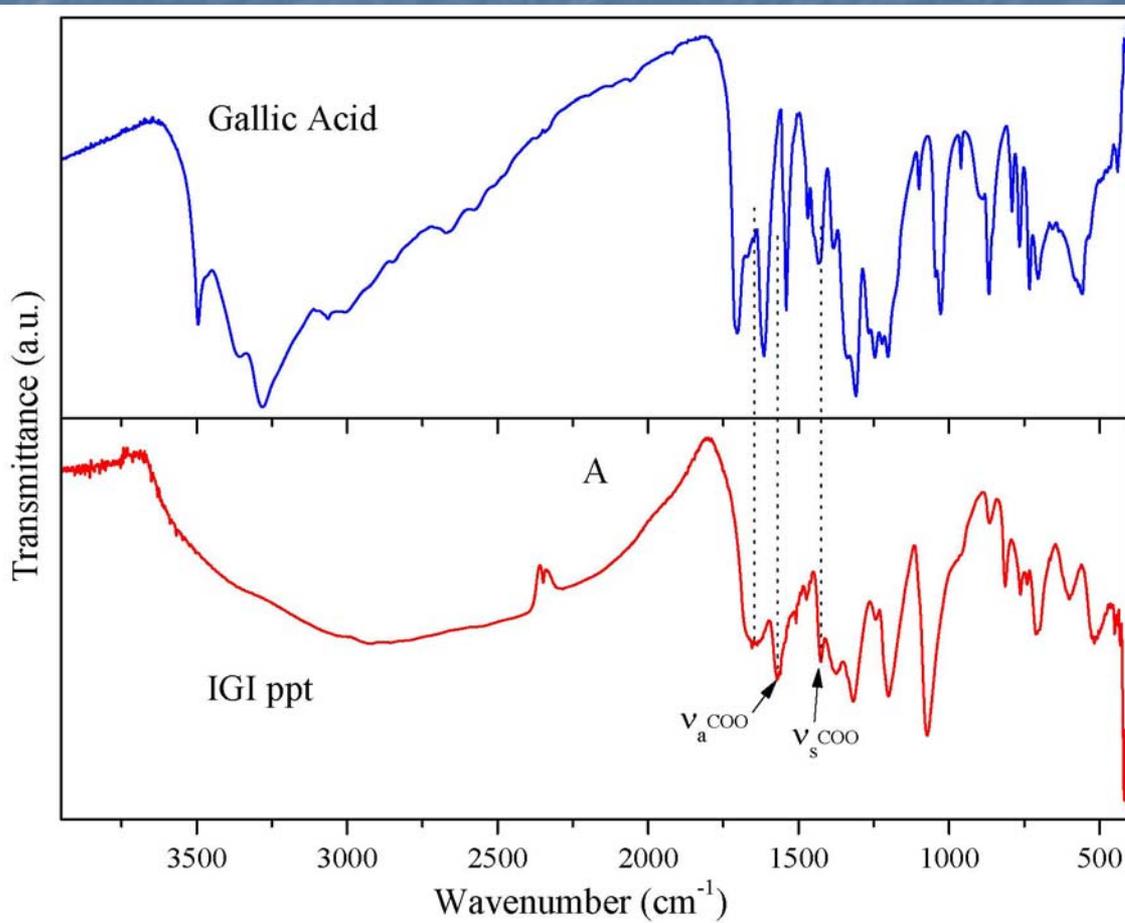
For benzoates the Δ value is ~ 168

- I $\Delta >$ ionic complexes
- II $\Delta <$ ionic complexes
- III Δ larger than for II and close to ionic values

Our Δ value is 149, which implies that **we have a type III bridging complex.**

Kazuo Nakamoto "Infrared and Raman spectra of inorganic and coordination compounds, Part B: applications in coordination, organometallic, and bioinorganic chemistry". 5th edition, Wiley, 1997

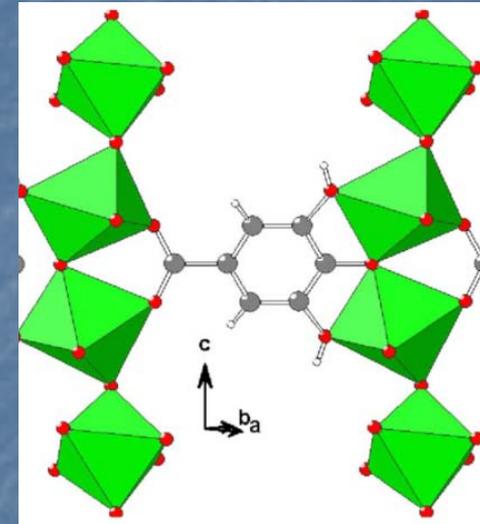
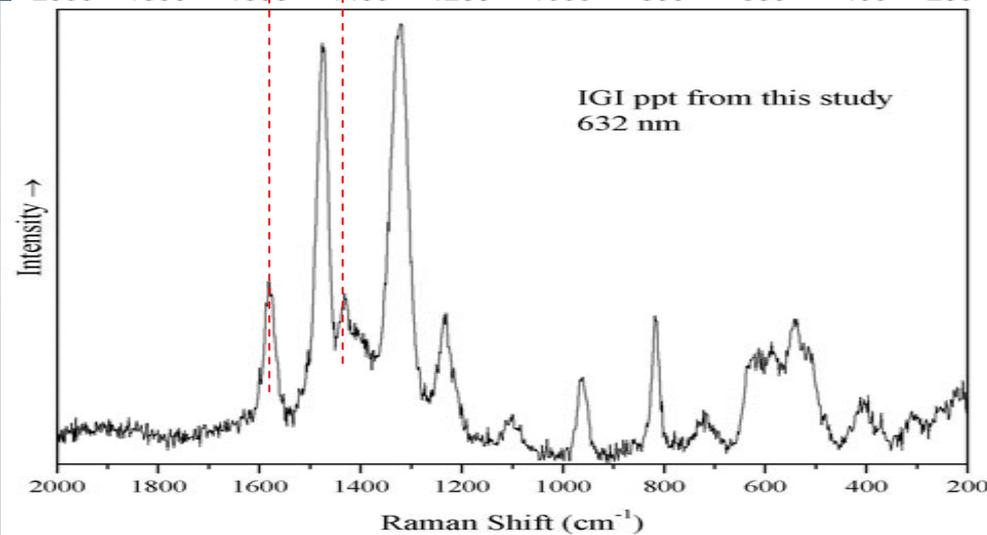
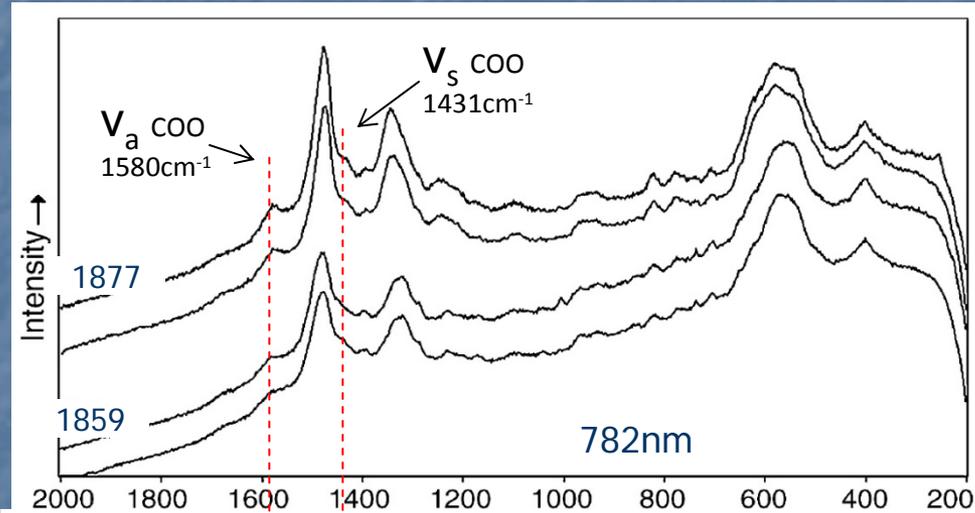
Infrared Spectroscopy



- 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."

Véronique Rouchon *et al. Anal. Chem.* **2011**, 83, 2589-2597



Wunderlich's

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.



Acknowledgement

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