

On the redox properties of the small pores Fe gallate MOF

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While Metal Organic Frameworks (MOFs) have been primarily designed for sorption purposes, the manipulation of their electronic properties is currently a hot topic. Redox-active MOFs (i.e. solids presenting a redox activity without any collapse of the framework) are indeed of potential interest in various fields, ranging from electrochemical sensing and electrocatalysis to electrochemical energy storage. Whereas the insertion of redox centers (either organic or inorganic) within their framework is rather straightforward, the manipulation of the redox state at a bulk level (and not solely at the surface of the particles) is often more challenging. We will here focus on a specific case, namely a solid built up from a combination of Fe and gallic acid, both being potentially redox active. The amorphous form of this solid, known as historical iron gallate ink (IGI) was the most common writing material from the Middle Ages to the 19th century.[1] The structure of the crystalline Fe(III) form was reported in the early 90's,[2] and further thoroughly studied, notably by neutron diffraction.[3] Although the redox activity of its components was stressed (and the exact oxidation state a matter of controversy in the field of cultural heritage [1]), no definitive structural information was available.

By using carefully controlled synthetic conditions and a complementary set of *in* and *ex situ* experimental tools (infrared, Mössbauer and electron paramagnetic resonance (EPR) spectroscopies together with high resolution X-ray powder diffraction and magnetometry), we will here show that it is possible to deliberately manipulate the oxidation state of this solid, evolving from a fully reduced Fe(II) state to a fully oxidized Fe(III) one through a mixed valence solid solution, without any drastic structural change.[4]

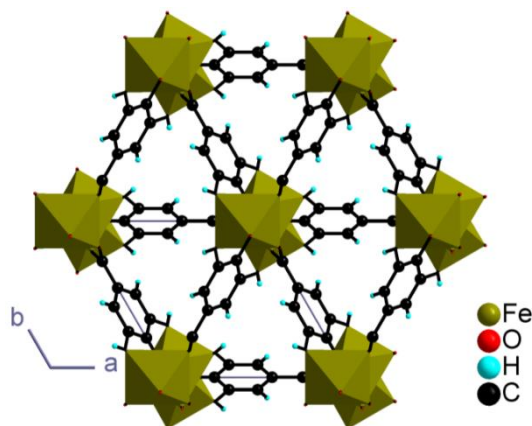


Figure 1. Crystal structure of the Fe(III/II) gallate.

References

- [1] Wagner *et al.*, *Z. Anorg. Allg. Chem.* **2015**, 641, 2384; Ponce *et al.*, *Anal. Chem.* **2016**, 88, 5152.
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- [3] Feller *et al.*, *Solid State Sci.* **2006**, 8, 1121; Saines *et al.*, *Dalton Trans.* **2011**, 40, 6401.
- [4] Guillou *et al.*, *in preparation*.