

Oxygenation of neutral P-S compounds by a trinuclear iron carboxylate: Synthesis and structures of a mixed and a univalent iron cluster

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Mössbauer spectra of **1**:

The Mössbauer spectra of sample **1** in the temperature range 15K- 220K contain three
10 distinguishable quadrupolar split resonances with no electronic delocalization on the Mössbauer time
scale. A superposition of quadrupole doublets with Lorentzian line shapes was used to fit spectra.
Since the structure contains three crystallographically different iron sites, a three site fit was done.
Spectral subcomponents I and III have Mössbauer spectral parameters characteristic of high-spin
iron(II), with close values of isomer shifts, 0.94 and 0.79 mm/s and of quadrupole splitting
15 parameters, 1.79 and 1.57 mm/s, respectively. The isomer shift and quadrupole splitting of component
II is consistent with high spin iron(III) (IS = 0.25 mm/s, QS = 0.56 mm/s). The room temperature
spectrum represents a superposition of two iron sites. The right doublet might be attributed to Fe(II)
high-spin, while the central doublet – to the high spin Fe with intermediate oxidation state +2.5 due to
the possible fast electron delocalisation between the central iron atoms.

20 The compound exhibits intermediate spin relaxation phenomena in its Mössbauer spectrum,
appearing at ≈ 10 K with magnetic hyperfine lines developing at 3K, superimposed on a broad
absorption envelope at the centre of the spectrum. The large unresolved central absorption area in the
3K spectrum makes the satisfactory fit a difficult task. The main interactions responsible for the slow
spin relaxation in **1** in the absence of an applied field are difficult to establish properly from powder
25 samples. Very low temperature studies or under applied field would therefore be necessary. Studies
along these lines are the objective of future work.

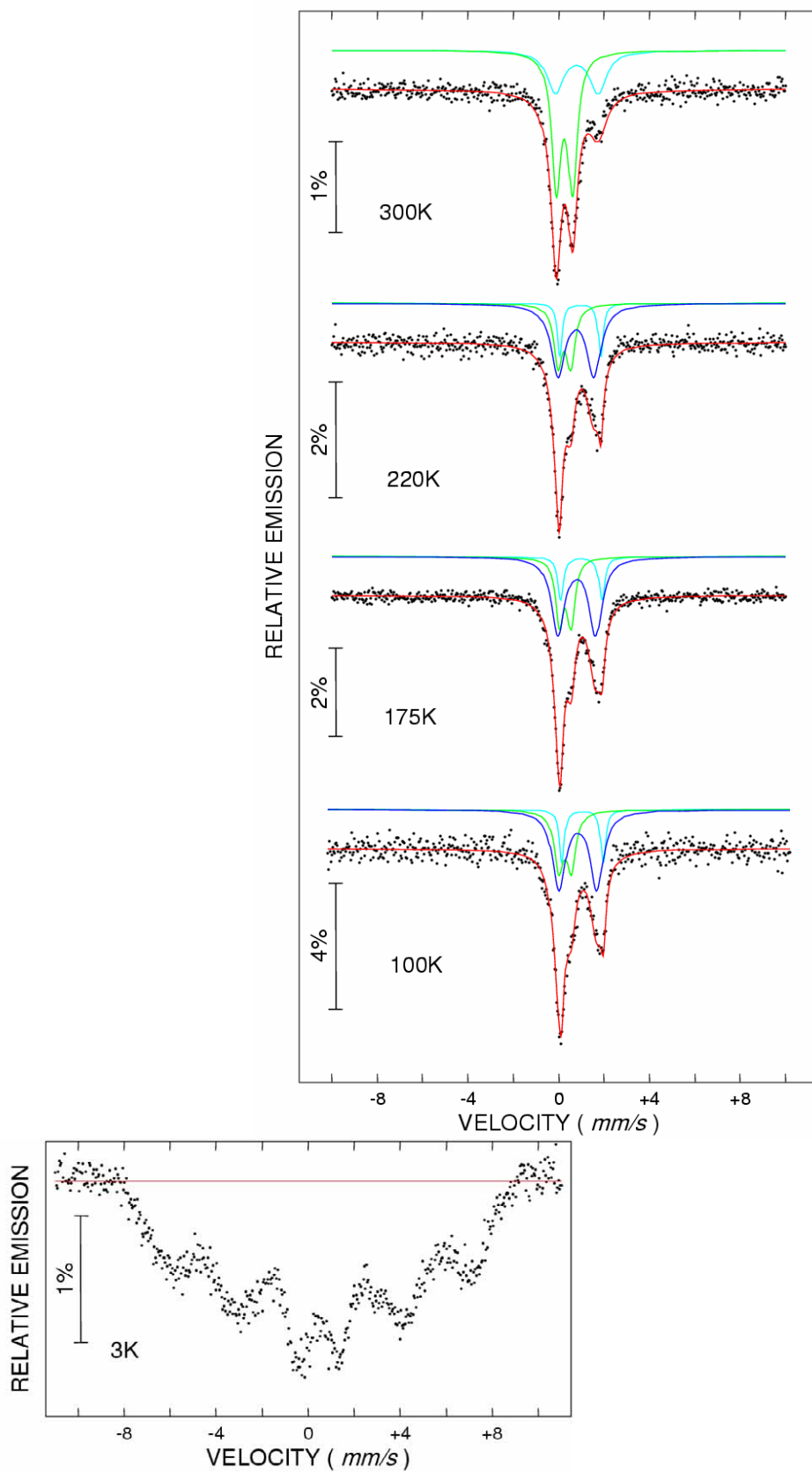
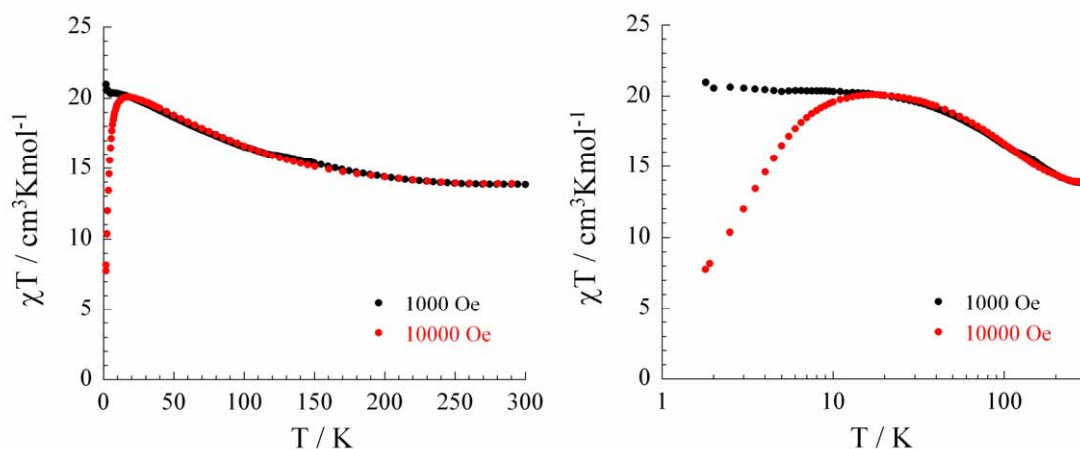


Figure 1. Mössbauer spectra of compound 1 at 300, 220, 175, 100 and 3K.

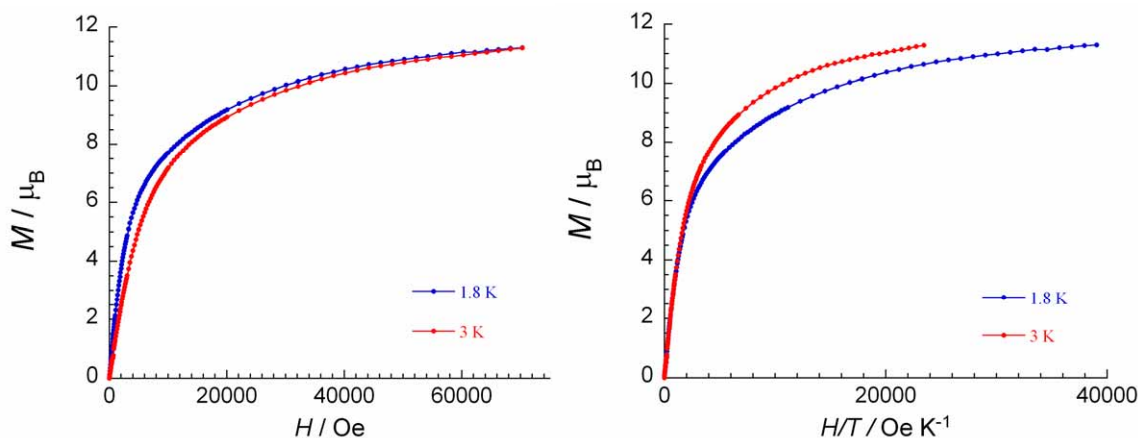
Magnetic susceptibility of 1:



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At room temperature, the χT product is $13.85 \text{ cm}^3 \text{ K mol}^{-1}$. This value is quite low in comparison to the expected value ($23.75 \text{ cm}^3 \text{ K mol}^{-1}$) for the presence of two spin-only HS Fe(III) ions ($S = 5/2$, $g = 2$, $C = 4.375 \text{ cm}^3 \text{ K mol}^{-1}$) and five spin-only HS Fe(II) ions ($S = 2$, $g = 2$, $C = 3.0 \text{ cm}^3 \text{ K mol}^{-1}$) and to the expected value ($25.125 \text{ cm}^3 \text{ K mol}^{-1}$) for three HS Fe(III) and four HS Fe(II) ions. Decreasing the temperature, the χT product continuously increases to reach $20.82 \text{ cm}^3 \text{ K mol}^{-1}$ at 1.8 K. These types of behavior suggest the presence of dominant ferromagnetic interactions between spin carriers leading to a ground state configuration where the spins are not compensated. The final decrease of the χT product at 10000 Oe below 15 K is probably the result of magnetic anisotropy and / or intermolecular interactions.

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The M vs H measurements at 1.8 and 3.0 K done as a function of the field reveal (i) a slow increase of the magnetization and (ii) the absence of a true saturation of the magnetization that reaches at $11.3 \mu_B$ at 7 T. This behavior suggests the presence of magnetic anisotropy and probably the field induced population of low lying excited states in the system. Moreover, the presentation of the data as an M vs H/T plot confirms the presence of anisotropy and/or low lying excited states.

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