

X-ray diffraction and Mössbauer spectrometry studies of molecular iron compounds

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Abstract

We have synthesized two new iron complexes that have been structural and magnetically characterized: diphenylguanidinium hexafluoroferrate and hexakisvaline-oxo-triiron(III) chloride. The former crystallizes as monomers with the fluoride ions six-coordinating the Fe(II) ion. Valine iron chloride is comprised of trinuclear complexes, with a well ordered oxo-centered carboxylate core and some disordered organic ligands. The magnetization curves show a paramagnetic behavior. The Mössbauer measurements as a function of temperature show a paramagnetic behavior at 300 K with two Fe sites (one quadrupolar doublet and a broad single line). At 4.2 K, besides the quadrupolar doublet there is a magnetic component which can be attributed to a slow relaxation phenomenon associated to these samples.

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1. Introduction

The advent of organic/molecular based magnets has triggered the research on new classes of molecular magnetic materials.

Magnetochemists have been investigating how the type and coordination mode of the metal ligands change the magnetic behavior of the compounds, and some correlations have been well established [1].

Among the low-dimensional compounds, oxo-bridged trinuclear iron centers have received a lot of attention, especially those with mixed valence triangular iron complexes. Attention has been focused on the interactions among the three iron atoms via the bridging ligands, and the kinetics and mechanisms of electron transfer, which have been studied by several techniques [2]. It is well established that in both mixed-valence (Fe(II)/Fe(III)) and Fe(III) compounds, the metal ions in the tri-iron oxo-

centered units are antiferromagnetically coupled and spin frustration occurs due to the triangular geometry of the Fe₃O core [3].

Other studies have revealed that some bridged iron complexes can show the spin crossover phenomenon, i.e. the transition between a low-spin state to a high-spin state induced by external physical factors like the temperature, pressure or electromagnetic radiation [1]. Such properties make these compounds very interesting for industrial applications as switchable molecular devices [4].

Following our work on the structural and magnetic properties of 3d transition metal compounds with organic ligands [5–7], we have synthesized L-valine iron chloride and diphenylguanidinium hexafluoroferrate (III) [7].

2. Experimental

For synthesizing diphenylguanidinium hexa-fluoroferrate (Guanife sample), the pure metal was dissolved in concentrated fluoric acid. The organic moiety dissolved in ethanol was then added to the solution. After a few months

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the inhomogeneous solid formed was dissolved in water. Crystals could be obtained as reported in Ref. [7], as well as hydrated diphenylguanidium hexafluoroferrate, iron trifluoride trihydrate was formed as identified by powder X-ray studies.

L-valine iron chloride (Valife sample) was synthesized by mixing hydrated iron chloride and L-valine in a water/ethanol solution. After a few months, low quality single crystals could be found in the inhomogeneous precipitate.

^{57}Fe Mössbauer spectra were taken at 300, 77 and 4.2 K in a transmission geometry with a $^{57}\text{Co}/\text{Rh}$ source. The samples were powdered by means of a grinding mortar. The evaluation of the spectra was made using a least-square minimum computer fit to a superposition of Lorentzian shape lines.

The Valife diffractogram was taken with Cu radiation ($\lambda = 0.154056$ nm) at 300 K with reflection geometry. The theoretical diffractogram was calculated using PLATON software.

Magnetization studies, using the DC extraction method and AC susceptibility measurements, were performed using powder in the temperature range 1.6–300 K with a multi-purpose characterization system MAGLAB 2000 (Oxford Instruments).

3. Results

Powder and single crystal diffraction measurements of L-valine iron chloride revealed the great disorder that exists in both of these samples. However the trinuclear iron core is ordered (Fig. 1) and it could be determined that the Fe atoms are bridged by O atoms in an oxo-centered triangular arrangement.

The iron complexes crystallize in a cubic system, possibly with P2, 3 space group, and with a three-fold axis passing through the central O atom. There are two symmetry independent tri-nuclear iron cores. Fig. 1 shows one of these iron complexes, where the disordered tails of the

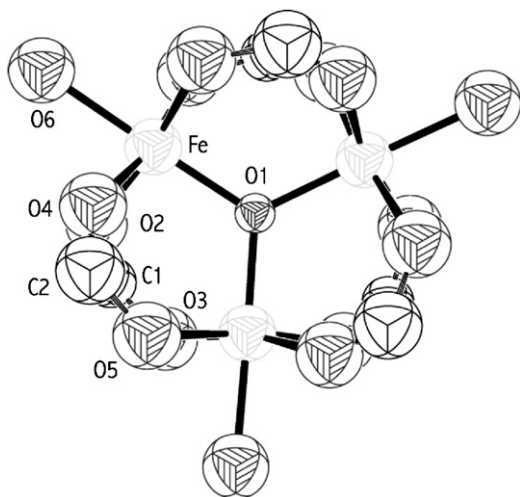


Fig. 1. Diagram showing the oxo-centered trinuclear core of L-valine iron chloride.

amino acid were omitted leaving only the carboxylic group of each L-valine moiety.

A powder diffractogram calculated from a model that includes all the atoms that could be refined from the single crystal data, compares well with the experimental diffraction pattern (up to 20°) as shown in Fig. 2. Diphenylguanidium hexafluoroferrate crystallizes in space group $R\bar{3}c$. In this compound each iron is octahedrally coordinated by six fluoride ions at a distance of $1.933(1)$ Å, such that the hexa-fluoroferrate iron has an exact 32 symmetry. Fig. 3 shows a FeF_6 ion hydrogen bonded to the organic cation. F–Fe–F angles are very close to 90.0° or 180.0° .

Fig. 4 shows the curves of magnetic field dependence of the magnetization, $M(B)$, up to 8 T, taken at several temperatures. Above 20 K the linearity of the $M(B)$ curves was obtained, as expected for paramagnetic states, although, at temperatures below, a small non-linearity was noticed. No hysteresis loop was found, even at the lowest temperature, 1.7 K.

Fig. 5 shows Mössbauer spectra recorded at different temperatures for the Valife sample: the fitted parameters for the two samples are listed in Table 1. Isomer shift values of Valife are consistent with Fe^{3+} ions located in

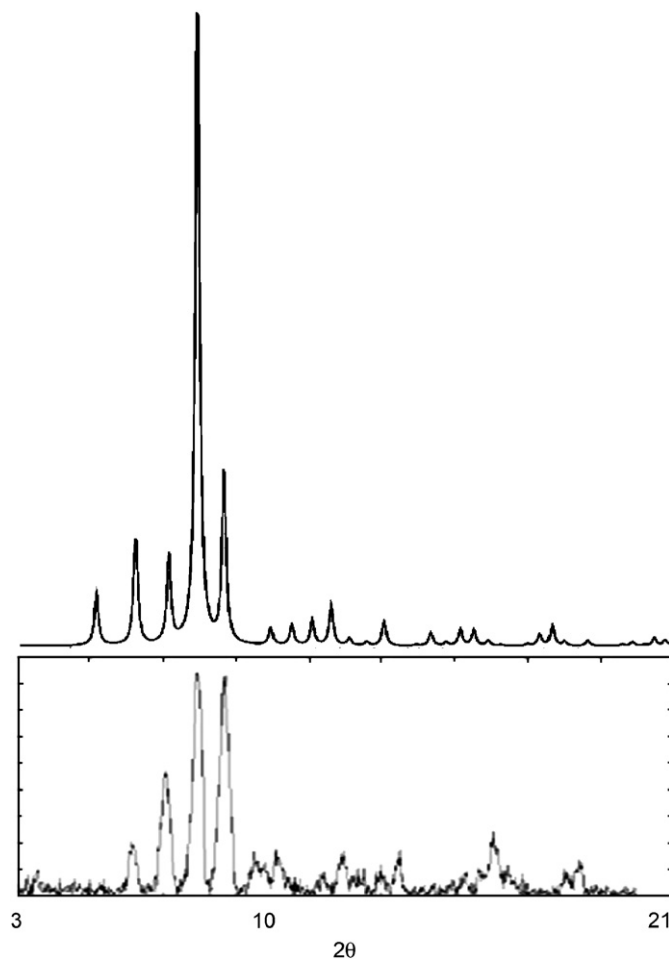


Fig. 2. Experimental (down) compared to calculated diffractogram (up) using the single crystal data.

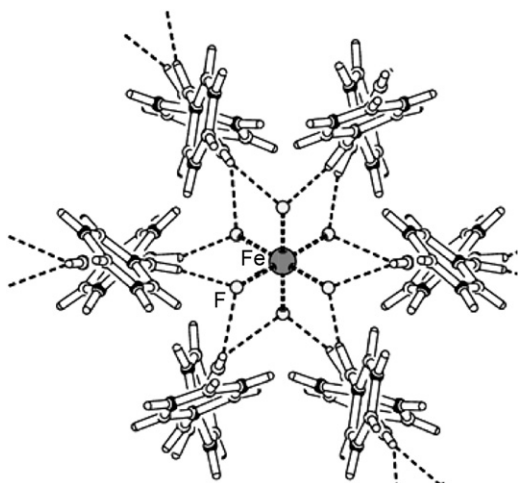


Fig. 3. Diagram showing the FeF_6^{3+} hydrogen bonded to the organic moiety of the Guanife sample.

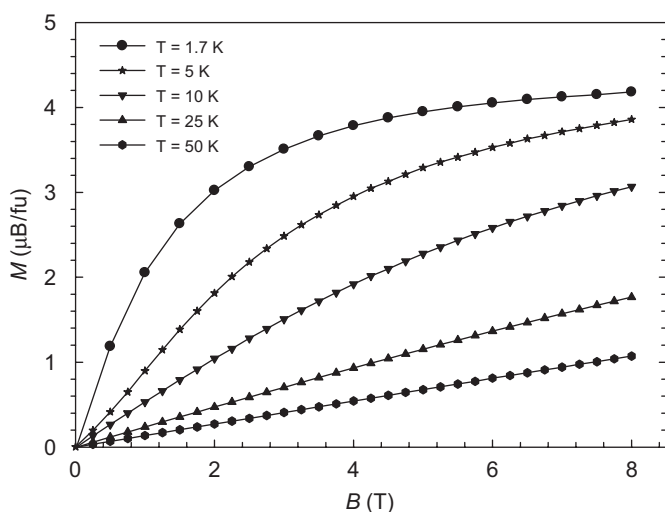


Fig. 4. Magnetic field dependence of magnetization of Valife sample at different temperatures.

octahedral coordination. The 300 K spectrum shows an asymmetrical quadrupolar doublet: the isomer shift is typical of a high spin state (HS) Fe^{3+} ion located in octahedral unit but remains slightly lower than the values of usual ferric fluorides [8]. The asymmetry is due to some preferential texture originated from platelet-shape powdered sample. When decreasing the temperature down to 77 K, the quadrupolar doublet splits into a magnetic sextet and a quadrupolar doublet with narrow lines, the hyperfine parameters are consistent with those obtained at 300 K. At lower temperatures, one distinguishes a magnetic sextet, a quadrupolar doublet superimposed to a broadened single line at the center of the spectrum. The model consists therefore in three components where the linewidth of the quadrupolar doublet was fixed during the refinement, allowing thus a more accurate estimation of the Fe atom proportion associated to the single line.

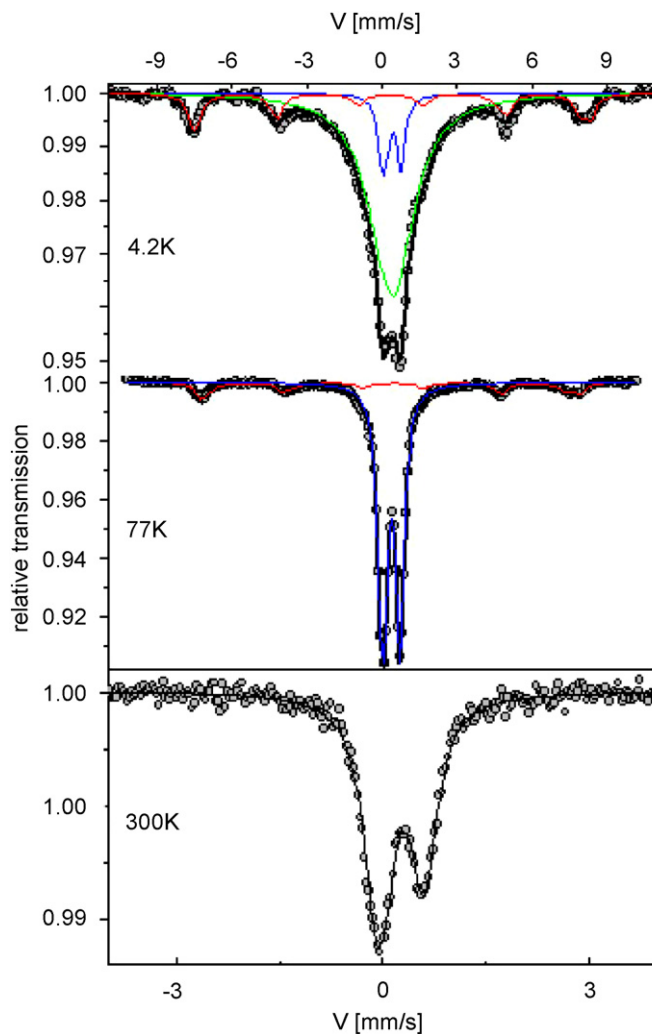


Fig. 5. ^{57}Fe Mössbauer spectra of the Valife sample taken at the indicated temperatures.

Table 1
Best-fit values of spectral parameters obtained from ^{57}Fe Mössbauer spectra. The values of IS are relative to $\alpha\text{-Fe}$ at 300 K

	IS (mm/s) \pm	Γ (mm/s) \pm	QS or 2ϵ (mm/s) \pm	B_{hf} (T) ± 0.5	% ± 2
Valife 300 K	0.02	0.02	0.64	–	54
Valife 77 K	0.49 0.51	0.70 0.40	–0.04 0.67	45.5 –	13 81
Valife 4.2 K	0.54 0.51	0.40 0.50	0.67 –0.0	– 48.3	11 73 15

These different components result probably from both the structure of this molecular compound and the presence of defects. Indeed, the single line suggest the presence of slow relaxation phenomena at low temperature coming from non-interacting isolated clusters while the magnetic

ordered contribution does originate from interacting clusters, because of the presence of defects as evidenced from X-ray diffraction (XRD).

The evolution of Mössbauer spectra differs from that of Valife (not shown here). In a previous study [7], the sites of the Guanife spectrum at RT has been ascribed to FeF_6 and $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$. One observes in Guanife only a quadrupolar doublet at 77 with broad lines and the combination of a broad single line superimposed to a magnetic sextet. Such hyperfine structure suggests also slow magnetic relaxation phenomena.

Further experiments as in-field Mössbauer spectra and FC and ZFC magnetic measurements have to be performed to model the magnetic behaviour and its dependence as a function of temperature on both Guanife and Valife molecular compounds.

References

- [1] O. Khan, *Molecular Magnetism*, Wiley-VCH, New York, 1993.
- [2] R.D. Cannon, U.A. Jayasooriya, S.K. Koske, R.P. White, J.H. Williams, *J. Am. Chem. Soc.* 113 (1991) 4158.
- [3] R.D. Cannon, R.P. White, *Prog. Inorg. Chem.* 36 (1988) 195.
- [4] A.B. Gaspar, V. Ksenofontov, J.A. Real, P. Gutlich, *Chem. Phys. Lett.* 373 (2003) 385.
- [5] M. Ramos Silva, A. Matos Beja, J.A. Paixão, L. Alte da Veiga, J. Martín-Gil, F. Javier Martín Gil, *Acta Crystallogr. C* 52 (1996) 2892.
- [6] M. Ramos Silva, A. Matos Beja, J.A. Paixão, L. Alte da Veiga, J. Martín-Gil, *Z. Kristallogr.* 214 (1999) 477.
- [7] M. Ramos Silva, A. Matos Beja, B.F.O. Costa, J.A. Paixão, L. Alte da Veiga, *J. Fluorine Chem.* 106 (2000) 77.
- [8] J.M. Greneche, F. Varret, in: G. Long, F. Grandjean (Eds.), *Mössbauer Spectroscopy Applied to Magnetism and Materials Science*, Plenum Press, New York, 1993, pp. 161–203 (and references therein).