

⁵⁷Fe-MÖSSBAUER STUDY OF A Fe^{II}O₄ CUBANE-LIKE MOIETY

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Abstract

The room temperature ⁵⁷Fe-Mössbauer spectrum of [C(NH₂)₃]₈[Fe(cit)₄].8H₂O, a Fe(II)/citrate complex, containing a cubane-like Fe₄O₄ arrangement, has been recorded and analyzed. The obtained hyperfine parameters, coherent with the structural and electronic features of the compound, reveal that the electronic density of the Fe(II) cations is slightly distorted over the metallic sites.

Keywords: Fe^{II}O₄ cubane; structural peculiarities; ⁵⁷Fe-Mössbauer spectra.

Resumen

Estudio Mössbauer de ⁵⁷Fe de una unidad Fe^{II}O₄ tipo cubano. Se registró y analizó el espectro Mössbauer de ⁵⁷Fe a temperatura ambiente de un complejo de Fe(II)/citrato de composición [C(NH₂)₃]₈[Fe(cit)₄].8H₂O, conteniendo una unidad Fe₄O₄ tipo cubano. Los parámetros hiperfinos obtenidos, coherentes con las características estructurales y electrónicas del compuesto, revelan que la densidad electrónica sobre los cationes Fe(II) no se distribuye uniformemente sobre los sitios metálicos.

Palabras clave: cubano Fe₄O₄; peculiaridades estructurales; espectros Mössbauer de ⁵⁷Fe.

1. Introduction

Metal complexes possessing M₄S₄ or M₄O₄ cubane-like arrangements generated much interest lately due to their biological relevance [1,2]. Recently, a number of citrate complexes of this type, containing M₄O₄ moieties (with M = Mg, Mn, Fe, Co, Ni and Zn), stabilized as salts of the guanidinium cation have been prepared and structurally characterized [3]. From these compounds, those containing Mn(II) and Fe(II) seems to be specially interesting from the biological point of view. To attain a wider insight into their

general physicochemical properties, we have set about systematic studies on both compounds.

In this note, we present the results of the investigation of the ⁵⁷Fe-Mössbauer spectrum of the respective iron complex.

2. Experimental

2.1. Synthesis of the complex

The preparation of the complex, of stoichiometry [C(NH₂)₃]₈[Fe(cit)₄].8H₂O, was performed as described by Hudson *et al.* [3], as follows: To a solution of citric acid (1.0 g, 5.2 mmol) in 40 mL of water, a solution of FeSO₄·7H₂O (1.44 g, 5.2 mmol) in 40 mL of water was added, immediately followed by a solution of guanidinium carbonate (3.78 g, 20.8 mmol) in 40 mL of water. The

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fine crystalline powder, which separated from the solution after a few hours, was collected by filtration, washed with small portions of water and, finally, dried at the pump. Its structure was confirmed by X-ray powder diffractometry, with a Philips PW 1710 diffractometer, using Cu-K α radiation. Because small amounts of Fe(III) impurities –revealed by the spectroscopic studies– were always present in all the samples prepared over several trials, it was impossible to attain a totally pure compound even performing the synthesis under strict anaerobic conditions.

2.2. Mössbauer spectra

Room temperature Mössbauer spectra were taken in transmission geometry using a conventional constant acceleration spectrometer of 512 channels with a 10 mCi nominal activity $^{57}\text{CoRh}$ source, in transmission geometry. The absorber was a powdered sample of about 98 mg.cm $^{-2}$, calculated after the method described by Long *et al.* [4] that yields the optimum absorber thickness. The hyperfine parameters were obtained by fitting the data to lines of Lorentzian shape using a least-squares computer code with constraints. Isomer shifts were calibrated against an α -Fe foil at room temperature.

3. Results and discussion

Citric acid (Figure 1) is a hydroxo polycarboxylic acid which in the present case acts as a quadridentate ligand against the Fe(II) cation, participating in the generation of the cubane-like Fe $_4$ O $_4$ structure. As seen in this figure, the individual citrate units have arms of two sorts. If we identify the two $-\text{CH}_2\text{-COO}^-$ arms as *a* and the single $-\text{COO}^-$ arm as *b* it will be possible to describe the Fe(II) coordination in a more precise way. Around each Fe(II) cation in the [Fe $_4$ (cit) $_4$] $^{8-}$ units, the three O-positions in the cube originated in deprotonated OH-groups of the acid, whereas each Fe(II) cation is additionally associated with *a*-type arms from two separate citrate ligands and a *b*-type arm from a third.

All the six Fe(II)-O distances are very similar and the geometry around Fe(II) is intermediate between octahedral and trigonal-prismatic [3]. Magnetic susceptibility measurements show the presence of high-spin, weakly antiferromagnetically coupled Fe(II) centers, with the μ_{eff} values remaining practically constant at 10.05 μ_B , per Fe $_4$, between 300 and 100 K. The very weak coupling is also evident from the low *J*-value of about -0.43 cm^{-1} [3].

Figure 2 displays the ^{57}Fe -Mössbauer spectrum of one of the investigated samples. The

spectrum exhibits seemingly two quadrupole split signals of very different relative areas. The main one could not be fitted with only one doublet of Lorentzian line-shape; it required two doublets of similar parameters. According to the values of the fitted hyperfine parameters shown in Table I, these data arise from iron cations at three hyperfine sites and in two oxidation states, Fe(II) and Fe(III).

Because the four Fe(II) environments are totally equivalent according to the structural analysis [3], the two Fe(II) doublets should not have very similar parameters; they should be coincident. Therefore, the manifestation of two

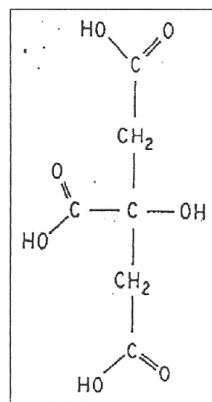


Fig. 1. Schematic structure of citric acid.

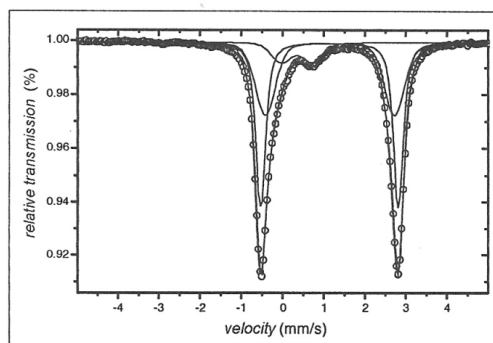


Fig. 2. Room temperature Mössbauer spectrum of [C(NH $_2$) $_3$] $_4$ [Fe(cit) $_4$] $\cdot 8\text{H}_2\text{O}$. Experimental data are shown by circles. The solid line is the result of the least-square fitting described in the text. The thinner lines are the individual quadrupole doublets that make up the calculated spectrum shown in the thicker solid line.

Table I. Hyperfine parameters of the three quadrupole sites that makes up the Mössbauer spectrum of $[\text{C}(\text{NH}_2)_3]_4[\text{Fe}(\text{cit})_4] \cdot 8\text{H}_2\text{O}$. The isomer shifts δ are referred to $\alpha\text{-Fe}$ at room temperature.

The numbers between parentheses are the uncertainties in the least significant figures of the reported value. A is the relative area of the respective quadrupole doublet.

	δ (mm/s)	Δ (mm/s)	A(%)	Γ (mm/s)
Doublet 1	1.15(1)	3.14(1)	39(4)	0.46(3)
Doublet 2	1.14(1)	3.35(1)	50(4)	0.25(2)
Doublet 3	0.35(1)	0.77(1)	11(2)	0.47(4)

Fe(II) Mössbauer signals with the same isomer shift, δ , but with different quadrupole splitting, Δ , indicates that the electronic distribution is not uniform over the metallic sites. These distortions may eventually originate in solid state effects - likely related to the ordering of the guanidinium cations - and in the disordered water molecules existing in the unit cell [3]. The disorder is also reflected by the broader line-width at half maximum, $\Gamma = 0.46$ mm/s, of the less intense doublet.

The value for the isomer shift, $\delta = 1.14 \pm 0.01$ mm/s, for these two sites lies clearly in the range expected for Fe(II) in octahedral or quasi-octahedral oxidic environments, usually found between 1.06 and 1.29 mm/sec [5,6]. The quadrupole splitting values are consistent with the high spin electronic configuration of these cations [7].

In addition to the Fe(II) signals, the current spectrum exhibits as well a third weak doublet. This is likely related to an Fe(III) impurity [5,7], which is probably generated by slow oxidation of the complex during or after its synthesis.

Finally, it is interesting to perform some comparisons of the isomer shift determined for the Fe_4O_4 cluster, with those known for similar

Fe_4S_4 clusters from 4:4 ferredoxins. These values are always lower than in the present case. For example, the oxidized form, $3\text{Fe}^{\text{III}}1\text{Fe}^{\text{II}}$, shows values around 0.30 mm/sec, the intermediate form, $2\text{Fe}^{\text{III}}2\text{Fe}^{\text{II}}$, values of about 0.42 mm/sec, whereas in the reduced form, $1\text{Fe}^{\text{III}}3\text{Fe}^{\text{II}}$, they lie at around 0.57 mm/sec [1,8]. Besides, in the totally reduced form of rubredoxin, containing a $\text{Fe}^{\text{II}}\text{S}_4$ moiety, a δ value of 0.65-0.70 mm/sec have been reported [1,8].

Acknowledgements

The support of the *Consejo Nacional de Investigaciones Científicas y Técnicas de la República Argentina* (CONICET) and of the *Universidad Nacional de La Plata* is gratefully acknowledged. The authors are members of the Research Career from CONICET.

References

- [1] S.J. Lippard & J.M. Berg, *Principles of Bioinorganic Chemistry*, University Science Books, Mill Valley, CA, 1994.
- [2] E.J. Baran, *Química Bioinorgánica*, McGraw-Hill Interamericana de España S. A., Madrid, 1995.
- [3] T.A. Hudson, K.J. Berry, B. Moubaraki, K.S. Murray & R. Robson, *Inorg. Chem.* **45**, 3549 (2006).
- [4] G.J. Long, T.E. Cranshaw & G.M. Longworth, *Mössbauer Effect Refer. Data J.* **6**, 42 (1983).
- [5] F. Menil, *J. Phys. Chem. Solids* **46**, 763 (1985).
- [6] R.C. Mercader, E.J. Baran & M. Weil, *J. Phys. Chem. Solids* **67**, 1781 (2006).
- [7] J.R. Wright, W.A. Hendrickson, S. Osaki & G.T. James, *Physical Methods for Inorganic Biochemistry*, Plenum Press, New York, 1986.
- [8] C.L. Thompson, C.E. Johnson, D.P.E. Dickson, R. Cammack, D.O. Hall, U. Weser & K.K. Rao, *Biochem. J.* **139**, 97 (1974).

Manuscrito recibido el 5 de febrero de 2009.

Aceptado el 27 de marzo de 2009.