A STUDY OF TRINUCLEAR IRON(III) O-PHTHALATES

Darko HANZEL, D. HANZEL, H. BILINSKI 1, T.A. HIMDAN 1, M. MILJAK 2 and V. VANCINA 3

J. Stefan Institute, E. Kardelj University, Ljubljana, Yugoslavia
1 R. Boskovic Institute, Zagreb, Yugoslavia
2 Institute of Physics, Zagreb, Yugoslavia
3 High School of Printing, Zagreb, Yugoslavia

Mössbauer data as well as infrared and magnetic susceptibility results indicate that Fe(III)-phthalates are high spin ferric complexes with a combination of trinuclear oxo-bridged and monomer structures. Values obtained for the isomer shift and quadrupole splitting parameters suggest that different counter ions, such as OH, NO$_3^-$, and Na, leave the Fe(III) ions in two very distorted octahedral arrangements, although they scarcely affect the electron densities at the iron nuclei.

1. Introduction

Polymeric iron(III) complexes of amino and carboxylic acids are very interesting because they form oxo-bridged trinuclear iron centres (see ref. [1] and references therein). These have been considered as intermediates in the formation of iron polynuclear aggregates found in the iron storage proteins ferritin, haemoglobin and several biological species. These complexes have been studied previously by different magnetic methods, optical spectroscopy, nuclear and spin resonance, as well as by Mössbauer spectroscopy. In order to obtain further information regarding the dependence of their physico-chemical properties on the type of oxygen-containing ligands coordinated to the trimer and the nature of the counter ions, we studied the iron(III)-o-phthalate complexes, prepared under different chemical conditions of precipitation, so that the outer sphere of the phthalate was exchanged by OH$^-$ and/or NO$_3^-$ ligands. The detailed preparation procedure will be published elsewhere [3].

2. Characterization of samples

The hydrolized iron(III) o-phthalate complexes studied were prepared at room temperature by using a solution of iron(III) nitrate, sodium chloride, and a mixture of phthalic acid (C$_8$H$_6$O$_4$) with sodium hydroxide. The molar ratio of
phthalate to iron in solution was varied. Precipitation occurs immediately and the samples were aged, filtered and washed. We studied complexes with the following chemical compositions:

No1  $\text{Fe}_3\text{O}(\text{o-phthal})_3\text{OH}.9\text{H}_2\text{O}$ ($M = 855$)
No2  $\text{Na}(\text{Fe}_3\text{O})(\text{o-phthal})_3(\text{OH})\text{NO}_3.6\text{H}_2\text{O}$ ($M = 886$)
No3  $\text{Na}_2(\text{Fe}_3\text{O})(\text{o-phthal})_3(\text{OH})_3.9\text{H}_2\text{O}$ ($M = 935$)
No4  $\text{Na}_3\text{Fe}_9\text{O}_9(\text{o-phthal})_2(\text{OH})_7\text{NO}_3.8\text{H}_2\text{O}$ ($M = 1369$)
No5  $\text{Na}_2\text{Fe}_{13}\text{O}_{13}(\text{o-phthal})_2(\text{OH})_9(\text{NO}_3)_2.3\text{H}_2\text{O}$ ($M = 1639$).

These complexes show very similar IR spectra, which resemble those of iron(III) dicarboxylic acid complexes containing oxo-bridged tri-iron clusters [2]. Therefore only a typical one is shown in fig. 1. The results of magnetic measurements (fig. 2) are consistent with these observations, which indicate a similar temperature dependence of the molar susceptibility and also of the effective magnetic moment of all these compounds. For a satisfactory description of the temperature dependence of the susceptibility curves, it was necessary to consider the Curie-Weiss term and a temperature independent term of the Van-Vleck type. The magnetic moment of iron at room temperature was found to be less than the spin-only value and it decreases with decreasing temperature, again for all samples. Exceptional behaviour in magnetic, Mössbauer and infra red spectra measurements was found for bulky polymeric precipitates which were prepared in the absence of sodium chloride at rather high values of pH, around 12. These precipitates revealed an unusual magnetic susceptibility behaviour at low temperatures and their Mössbauer spectra are a combination of sextet and doublet patterns [3].

3. Results and discussion

Finely powdered and thin absorbers were used for Mössbauer measurements in order to avoid corrections for saturation and texture effects. The Mössbauer spectra of the different Fe(III)-o-phthalates (No1–No4) are very similar and appear as slightly asymmetric, broadened, quadrupole split doublets in the