

Mössbauer Studies of an Iron(III)-Fulvic Acid Complex

E. H. HANSEN and H. MOSBÆK

Chemistry Department A,
The Technical University of Denmark,
2800 Lyngby, Denmark

Fulvic acid is an amorphous, polymeric fraction of soil organic matter with a number-average molecular weight of approximately 1000.¹ It consists primarily of isolated aromatic rings linked to each other *via* aliphatic chains or saturated cyclic or hydroaromatic structures.² The aromatic rings are heavily substituted with oxygen-containing functional groups, *i.e.*, primarily carboxyls and phenolic hydroxyls, and to a minor extent carbonyls, the presence of which accounts for the ready formation of stable complexes of fulvic acid with metal ions. Products resulting from such interactions are of fundamental significance, but although in recent years a considerable amount of data have been accumulated within this field, very little is actually known as to the nature of the metal-organic matter bonding.

For that reason we recently initiated Mössbauer investigations of an iron(III)-fulvic acid (Fe-FA) complex. Concurrently, a series of experiments were performed with a variety of organic iron chelates, believed through the content of functional groups in the ligands to be structurally related to the Fe-FA complex. Our preliminary experiments clearly demonstrated that the Fe-FA complex was polynuclear. Thus, the Fe-FA Mössbauer spectrum exhibited a large quadrupole splitting, a characteristic which was totally absent in our spectra of the mononuclear iron complexes. Additionally, our experiments with known compounds gave us reason to conclude that the Fe-FA complex was trinuclear. Although it is not customary to use the absorption as a criterion for the nature of the metal-ligand bonding, it should, however, be noted that all the trinuclear complexes and the Fe-FA complex showed a strong absorption in contrast to the mononuclear complexes.

The known trinuclear complexes examined were of the type $[\text{Fe}_3(\text{RCOO})_6(\text{OH})_2] \cdot n\text{H}_2\text{O}$ (where $\text{R}=\text{CH}_3, \text{CH}_2\text{Cl}, \text{CCl}_3, \text{OHCH}_2, \text{OHCH}_2\text{CH}_2, \text{C}_6\text{H}_5, \text{OHC}_6\text{H}_4,$ and

$\text{CH}_3\text{OC}_6\text{H}_4$; and $\text{X}=\text{monovalent anion}$). The magnetic properties of most of these compounds have been studied in detail by Earnshaw *et al.*,³ while Duncan *et al.*⁴ on basis of Mössbauer data have offered structural interpretations of several of the aliphatic acid complexes. Recently, the crystal structure of one of the complexes ($\text{R}=\text{CH}_3$) has been solved.⁵ The purpose of this note is therefore to report our Fe-FA results only, as a more comprehensive analysis will appear later.

Methods of extraction and purification of the fulvic acid as well as a number of analytical characteristics have been reported.^{1,6,7} The Fe-FA complex was prepared according to the procedure outlined by Schnitzer and Hoffman.⁸ The Mössbauer parameters were determined on the solid compounds wafered between aluminium foils at approx. 25°C with an Elron Mössbauer Analyzer. A commercial source of ⁵⁷Co in palladium was used. The spectra were computed from a program using iterations to obtain the best least-squares fit of the experimental data to a set of Lorentzian curves.

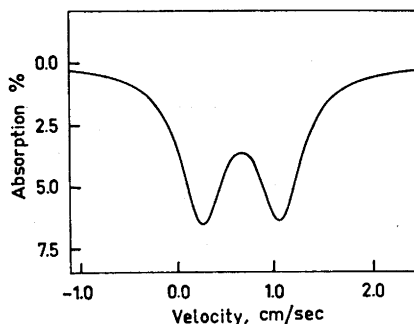


Fig. 1. Mössbauer spectrum of iron(III)-fulvic acid complex.

The isomer shift, δ (relative to sodium nitroprusside) of the Fe-FA complex was 0.64 mm/sec, and the quadrupole splitting, ΔE_Q , was 0.80 mm/sec (Fig. 1), while the δ and ΔE_Q values for the other compounds varied from 0.64–0.67 mm/sec and 0.44–0.72 mm/sec, respectively. These results show that all the complexes are very similar in so far as the environments of the iron atoms are concerned, indicating that the Fe-FA complex just as the known compounds is high spin. Stereochemically,

the trinuclear complexes are formulated with a trimeric cation in which two carboxylate groups bridge each of the sides of the equilateral triangle, whose vertices are the metal atoms and whose centre is an oxygen atom.²⁻⁵

While the OH-groups of the aliphatic ligands do not participate directly in the complex formation, it is most likely that the phenolic OH-groups as found in the salicylic acid and the fulvic acid play an active role in this respect. Thus, methylation of the OH-groups of salicylic acid caused ΔE_{c} to decrease to a value similar to that of benzoic acid. Also, for a fulvic acid preparation Schnitzer and Skinner⁹ found that blocking of either carboxyls or phenolic hydroxyls caused significant reductions in metal retention; and both groups appeared to react simultaneously.

Furthermore, the Mössbauer spectrum of the polynuclear Fe—FA complex indicates that the complex formation is associated with specific structures which form part of a well organized molecular system. This is in accordance with recent ESR measurements of a series of fulvic acid fractions which gave a linear relationship between \bar{M}_n and free radical content per \bar{M}_n .¹⁰

Schnitzer and Hansen¹¹ previously found that in aqueous solutions at low pH-values, the Fe—FA complexes formed were mononuclear. For a series of metal ions it was, however, similarly demonstrated that except at high ionic strengths metal/FA ratios generally increased above 1.0 with increase in pH, indicating the formation of polynuclear complexes.

1. Hansen, E. H. and Schnitzer, M. *Anal. Chim. Acta* **46** (1969) 247.
2. Hansen, E. H. *Dansk Kemi* **50** (1969) 9.
3. Earnshaw, A., Figgis, B. N. and Lewis, J. *J. Chem. Soc. A* **1966** 1656.
4. Duncan, J. F., Golding, R. M. and Mok, K. F. *J. Inorg. Nucl. Chem.* **28** (1966) 1114.
5. Anzenhofer, K. and De Boer, J. J. *Rec. Trav. Chim.* **88** (1969) 286.
6. Schnitzer, M. and Skinner, S. I. M. *Soil Sci.* **96** (1963) 86.
7. Kodama, H. and Schnitzer, M. *Fuel (London)* **46** (1967) 87.
8. Schnitzer, M. and Hoffman, I. *Geochim. Cosmochim. Acta* **31** (1967) 7.
9. Schnitzer, M. and Skinner, S. I. M. *Soil Sci.* **99** (1965) 278.
10. Schnitzer, M. and Skinner, S. I. M. *Soil Sci.* **108** (1969) 383.
11. Schnitzer, M. and Hansen, E. H. *Soil Sci.* **109** (1970) 333.

Received September 25, 1970.

Circular Dichroism of 2-O-Acetyl-3,6-dideoxy-D-xylo-hexopyranosides and of *Salmonella typhimurium* Lipopolysaccharides

HANS B. BOREN, PER J. GAREGG and SIGFRID SVENSSON

Institutionen för organisk kemi, Stockholms Universitet, S-104 05 Stockholm 50, Sweden

The repeating unit of the O-specific sidechains of the *Salmonella typhimurium* (serogroup B) lipopolysaccharide may be formulated as shown on top of p. 3085.¹⁻³

The position of the O-acetyl group has been established^{2,3} by methylation of a modified lipopolysaccharide in which all free hydroxyl groups had been protected by acetal formation with methyl vinyl ether.⁴ After replacement of acetyl by methyl followed by acid hydrolysis the only methylated sugar present was 3,6-dideoxy-2-O-methyl-D-xylo-hexose (2-O-methylabequose) showing that the acetyl groups are exclusively attached to the position 2 of the dideoxy sugar. The degree of acetylation at the 2-position varies from 50% (*S. typhimurium* LT 2) to nearly 100% (*S. typhimurium* 395 MS). The anomeric configuration of the terminal abequose residues has been allocated on the basis of the rapid initial decrease in optical rotation of the polysaccharide in acid solution. Since 3,6-dideoxyhexosides are known to undergo fast hydrolysis in acid, the configuration at C-1 of the abequose units was thus designated as $\alpha,^2,3$