Carbohydrate Polymers **18** (1992) 221–224

Preparation and characterization of a chitosan–Fe(III) complex

J.M. Nieto, C. Peniche-Covas* & J. Del Bosque

Faculty of Chemistry, University of Havana, Havana 10400, Cuba

(Received 14 June 1991; revised version received and accepted 20 October 1991)

An intramolecular water soluble chitosan–Fe(III) complex was prepared by mixing together chitosan powder with a 1·5 M $FeCl_2$ solution at 30 °C over 24 h in heterogeneous phase followed by extraction with acetone of the excess ferric chloride.

The complex was characterized by IR and far IR spectrometry, differential thermal analysis, differential scanning calorimetry, mass spectrometry and Mössbauer spectroscopy. It was concluded that the ferric ion is coordinated with two chitosan residues, three molecules of water and one chloride ion.

INTRODUCTION

Chitosan, essentially (1,4)-2-amino-2-deoxy-β-D glucan, possesses an elevated chelating capacity, mainly due to the large amount of primary amino groups regularly distributed along the chains it presents (Muzzarelli, 1977).

Complex formation of chitosan with transition metal ions has been widely studied, with reports of the existence of intra- or intermolecular complexes depending on the interaction conditions (nature of the ion, pH, relative chitosan/ion concentration) as shown by Park *et al.* in the case of copper (Park *et al.*, 1984). Ogawa *et al.* (1984) studied the crystalline structure of chitosan complexes with various metal ions by X-ray diffraction, proposing a coordination model in which the metal ion is bound to an amino group of the dimer residue of chitosan. In this study, complexes with Fe(III) were not included due to the solubilization of chitosan films when immersed in ferric sulfate or chloride solutions because of their low pH values (1·68 and 1·56, respectively). At pH 2.56 the films were not destroyed, but no complex formation was observed.

Nevertheless, Fe(III) is adsorbed from its dilute solutions by chitosan (Muzzarelli *et al.*, 1973) and formation of a liquid gel has been reported when interacting chitosan with concentrated solutions of ferric chloride (Muzzarelli, 1977). The present work is devoted to the preparation and characterization of a soluble chitosan–Fe(III) complex.

*To whom correspondence should be addressed.

MATERIALS AND METHODS

Chitosan obtained from shells of lobsters (*Panulirus argus*) according to an established procedure (Garcia *et al.*, 1983) was dissolved in 0·2 M aqueous acetic acid and precipitated in 0·1 M sodium hydroxide. The solid was treated with 0·1 M EDTA solution in ammonia buffer (pH 10), washed with deionized water and dried in air. Ash content was below 0·15%. The percentage of amino groups was 7·12% as determined by potentiometric titration.

Chitosan–Fe(III) complex was prepared by stirring chitosan powder (200 mg) overnight in 1·5 M ferric chloride at 30 °C and pH 1·0. The solid was washed with acetone and dried over phosphorus pentoxide. The amount of Fe(III) in the solid was 8·3% as determined by atomic absorption spectrometry on a UNICAM SP-90A spectrometer.

IR and far IR spectra were recorded in a SPECORD M-80 spectrophotometer using KBr and CsBr pellets, respectively.

Differential thermal analyses were performed on a Labor MOM derivatograph model 1000 TIR (Labor MOM, Hungary); curves were recorded on photosensitive paper using 60 mg of sample and a heating rate of 10 °C min^{-1} in air. Differential scanning calorimetry curves were obtained on a low temperature cell of a TA 4000 METTLER calorimeter at a heating rate of 5 °C min^{-1} in nitrogen.

Pyrolysis mass spectra were recorded on a JEOL HX-110 (Japan) mass spectrometer by direct sample introduction with a heating program from 30 to 400 °C.

Carbohydrate Polymers 0144-8617/92/$05.00

Experimental conditions were: ionization electron energy, 70 eV; accelerating voltage, 10 kV; ionization current 300 μA; post acceleration detector at 20 kV.

Solution viscosities were determined in an Ubbelohde type viscometer immersed in a thermostated bath at 25 ± 0·02 °C using 0·1 M aqueous HCl as solvent.

The Mössbauer spectrum was obtained using a Co^{57} source in Rh matrix and calibrating with hematite, which is equivalent to 0·0865 mm s^{-1} per channel, performing 2 350 000 counts per channel.

Chloride determinations were performed by potentiometric titration with discontinuous addition of $AgNO_3$ solution as described by Alpizar *et al.* (1990).

RESULTS AND DISCUSSION

The IR spectrum of chitosan shown in Fig. 1 exhibits the characteristic absorption bands at 1650, 1555 and 1320 cm^{-1} corresponding to amide I, II and III bands and the absorption band at 1600 cm^{-1} due to the amino groups bending vibration (Peniche *et al.*, 1984). In contrast with chitosan, chitosan-Fe(III) complex exhibits only two strong absorption bands at 1620 and 1520 cm^{-1} in the region between 1700 and 1500 cm^{-1}, which is indicative of coordination through the amino groups (Hirano *et al.*, 1982) together with interaction with the metal ion of the N-acetyl-amino groups remaining in the chitosan macromolecules (Muzzarelli, 1977).

The far IR spectrum of the chitosan-Fe(III) complex exhibits an intense broad band at 400 cm^{-1} which is absent in the spectrum of chitosan and can be attributed to Fe—O valence vibrations. Fe—N valence vibrations would also appear in this spectral region but they are to be expected at lower frequencies (Nakamoto, 1970).

The thermal behavior of the chitosan-Fe(III) complex

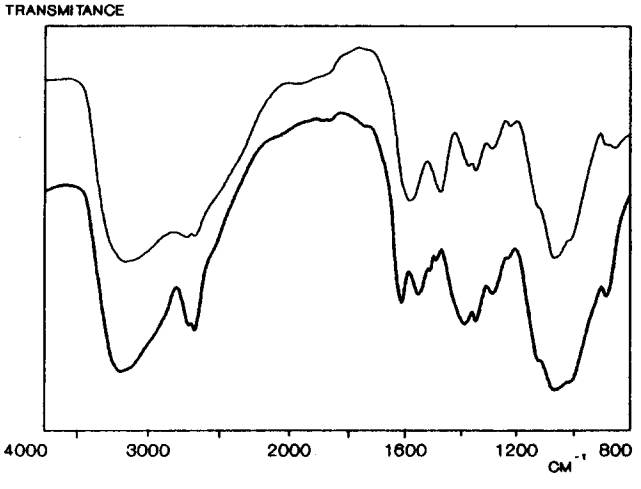

Fig. 1. Infrared spectra of chitosan (——) and the chitosan-Fe(III) complex (——).

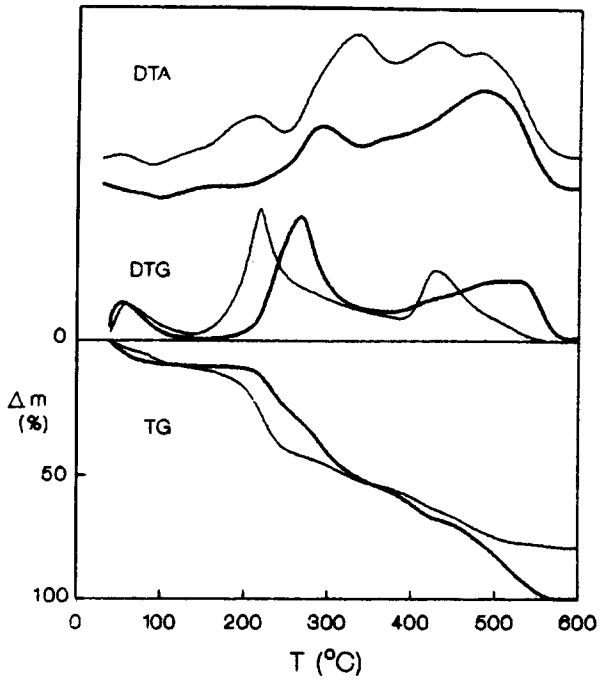

Fig. 2. DTA, TG and DTG curves of chitosan (——) and the chitosan-Fe(III) complex (——).

also differs significantly from that of chitosan as can be observed in Fig. 2, where differential thermal analysis (DTA), thermogravimetric (TG) and differential thermogravimetric (DTG) curves evidence the lower thermal stability of the complex: while chitosan has two main decomposition stages with maximum decomposition rates at 270 °C (associated with a weight loss of 45·5%) and 500 °C (40.7% weight loss), the complex exhibits three decomposition stages at 190, 300 and 420 °C, respectively. The maximum decomposition rate appears for the first two at 217 °C (47·3% weight loss) and for the third one at 480 °C (18·5% weight loss).

In both DTA curves there is a small endothermic peak with maximum weight loss velocity around 53 °C due to water release by the samples.

The differential scanning calorimetry (DSC) curves of chitosan and chitosan-Fe(III) complex (Fig. 3) show an important qualitative difference as to the nature of the water contained in these compounds. While water content is similar in chitosan (9.7%) and in the complex (10·2%) the amount of heat absorbed due to liberation of water in chitosan (111 J g^{-1}) is much smaller than in the complex (680 J g^{-1}), indicating that whereas in the former it is of reticular nature, at least part of it is coordinated to the metal ion in the latter.

The fragmentation pattern of the mass spectrum of the complex (Fig. 4) resembles more that reported for chitosan hydrochloride (Hayes & Davies, 1978) than that of chitosan itself (Mattai & Hayes, 1982), which is another manifestation of the lower stability of the complex. In fact, the presence of fragments at *m/z* 36

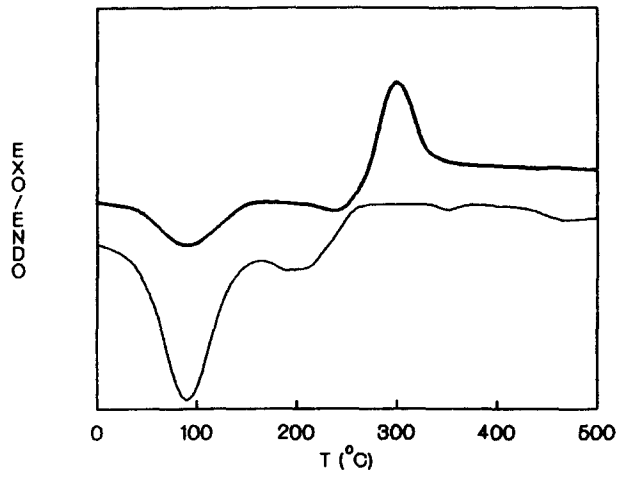

Fig. 3. Differential scanning calorimetry (DSC) curves of chitosan (——) and the chitosan-Fe(III) complex (——).

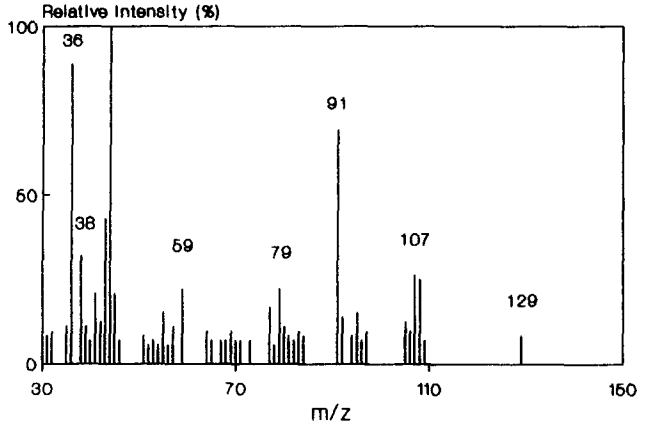

Fig. 4. Mass spectrum of the chitosan-Fe(III) complex.

and 38 (in a 3 : 1 ratio) in the mass spectrum of the complex is indicative of HCl liberation (Terentiev & Sankiavichus, 1987) during complex degradation.

The Mössbauer spectrum of the chitosan-Fe(III) complex (Fig. 5) exhibits an isomeric shift δ = +0·324 mm s^{-1} typical of high spin Fe(III) complexes with σ-donor ligands. Furthermore, the doublet with quadrupolar splitting ε = 0·540 mm s^{-1} indicates the existence of a distorted octahedric complex produced by the presence of ligands of different nature.

The intramolecular nature of the complex is evidenced from the viscosity of its solutions. The viscosity number of a 0·05 g dliter^{-1} solution of the complex was 0·19 dliter g^{-1}, much smaller than that of a chitosan solution of the same concentration in 0·1 M aqueous HCl which was 5·91 dliter g^{-1}.

From the amino groups content of chitosan (7·12%) and the amount of water and Fe present in the complex (10·2 and 8·3%, respectively) it can be readily shown that for each of Fe(III) ion there are 2 moles of amino groups and 4 moles of water. On this basis the following composition can be proposed for the complex

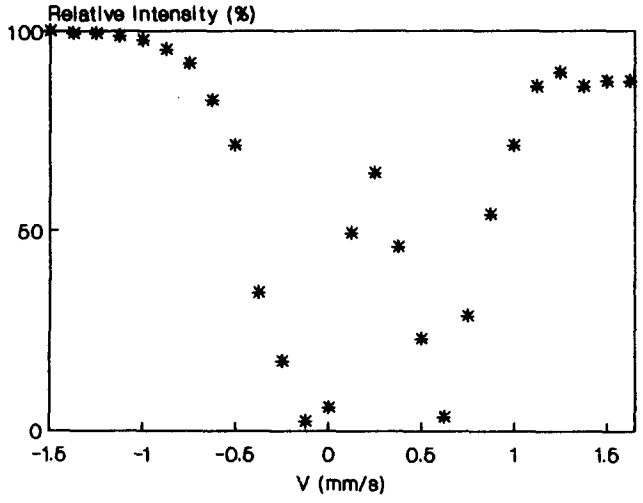

Fig. 5. Mössbauer spectrum of the chitosan-Fe(III) complex: isomeric shift δ = +0·324 mm s^{-1}, quadrupolar splitting = 0·540 mm s^{-1}.

$$[Fe(H_2O)_{4-x}(Glu)_2Cl_x]\ Cl_{3-x} \cdot xH_2O$$

where Glu represents a glucosamine residue. The amount x of chloride ions inside the coordination shell of the complex was determined potentiometrically to be one, so that the general formula of the complex is

$$[Fe(H_2O)_3(Glu)_2Cl]\ Cl_2 \cdot H_2O$$

The coordination mode found for the ferric chloride complex differs from that of cadmium and zinc chloride complexes, since in these cases it was shown that four bonds of the metal ion are coordinated with one amino group of chitosan, two chloride ions and one water molecule (Ogawa *et al.*, 1984). In cadmium and zinc chloride complexes the metal ion is bound to an amino group of the chitosan chain in a pendant fashion, whereas in the ferric chloride complex the metal ion is coordinated with two amino groups of the same chitosan chain.

REFERENCES

Alpízar, J., López, R., Albertús, F., Ramírez, E. & Esteva, A.M. (1980). *Revista Cubana de Química*, Vol. IV, No. 2. In press.

García, I., Oviedo, D., Nieto, J.M., Peniche, C. & Henríquez, R.D. (1983). Cuban Patent No. 35844, ONITEEM, La Habana.

Hayes, E.R. & Davies, D.H. (1978). In *Proc. First Int. Conf. on Chitin/Chitosan*, ed. R.A.A. Muzzarelli & E.R. Pariser. MIT Sea Grant Program, Cambridge, MA, 406–20.

Hirano, S., Kondo, Y. & Nakazawa, Y. (1982). *Carbohydrate Research*, **100**, 131–4.

Mattai, J. & Hayes, E.R. (1982). *J. Anal. Appl. Pyrol.*, **3**, 327–35.

Muzzarelli, R.A.A. (1977). *Chitin*, Pergamon Press, Oxford.

Muzzarelli, R.A.A. & Rochetti, R. (1973). *Anal. Chim. Acta*, **64**, 371–9.

Nakamoto, K. (1970). *Infrared Spectra of Inorganic and Coordination Compounds*, 2nd edn, Wiley-Interscience, New York.

Ogawa, K., Oka, K., Miyanishi, T. & Hirano, S. (1984). In *Chitin, Chitosan and Related Enzymes*, ed. J.P. Zikakis. Academic Press, Orlando, FL, pp. 327–45.

Park, J.W., Park, M. & Park, K.K. (1984). *Bull. Kor. Chem. Soc.*, **5** (3), 108–12.

Peniche, C., Nieto, J.M., García, I. & Fernández-Bertrán, J.R. (1984). *Bioorg. Khim.*, **10**(9), 1248–52.

Terentiev, P.B. & Sankiavichus, A.P. (1987). *Mass Spectrometry Analysis of Biologically Active Nitrogen Bases*. Ed. Mokslas, URSS.