Inorganica Chimica Acta, 124 (1986) 55–59

Iron(III) Complexes of Sugar-type Ligands

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Received November 15, 1985

Abstract

A series of iron(III) complexes formed with sugar-type ligands (aldoses, ketoses, polyalcohols, sugar acids, di- and trisaccharides) was prepared. The composition of the complexes was determined by standard analytical methods. It was shown that deprotonated alcoholic hydroxy groups participate in the complex formation and polynuclear species are formed. Mössbauer spectra reflected the presence of high spin iron(III) central atoms. EPR spectra showed antiferromagnetic interactions between the iron(III) centres in the complexes indicating dimeric or oligomeric complex structures. The ratio of interacting and isolated iron(III) atoms depend on the nature of the ligand and on the preparation mode of the complexes (metal-to-ligand ratio, pH, diamagnetic dilution, etc.).

Introduction

The absorption and transport of vital metal ions (like iron) *in vivo* is only possible in the form of their complexes. Sugar-type compounds may serve as ligands in these processes [1]. Therefore, study of the complex formation of iron (and other vital metal ions) with sugar-type ligands is needed.

The formation of polynuclear iron(III) complexes of D-fructose [2], of fructose and sorbose [3], of lactobionic acid [4], of glucose, galactose, mannose and lactose [5] was shown by the analysis and structural study of these systems. In the presence of more than one ligand, mixed ligand complexes were also formed [5, 6]. Iron(III) complexes of reducing sugars also contained iron(II) species in some cases [7, 8]. The combination of Mössbauer spectroscopic measurements with EPR [9–11] or magnetic susceptibility [5] studies led to valuable information concerning the electronic structure and intramolecular interactions in the systems.

Contradictory data in the corresponding literature concerning the composition and structure of the complexes reflect the effect of the mode of preparation (concentration of components, pH, solvent, temperature) on the composition of the products. Therefore, one can get reliable information on the effect of the structure of the ligand on the composition of the complexes only by the study of a series of compounds prepared according to a standard procedure. We have prepared accordingly the iron(III) complexes of 18 sugar-type ligands (Table I). The effect of the ligand-to-iron ratio and that of the pH of the solution during the preparation was also studied, in some of the systems (Table II). The analysis of the compounds led to the composition of the complexes. The oxidation state and spin state of the central atoms were characterized by Mössbauer studies. EPR spectroscopy was used for the investigation of magnetic interactions between the paramagnetic iron(III) centres. The results are presented in the following sections.

Experimental

Reagents

Iron salts

Iron(III) perchlorate (Merck), iron(III) chloride (Analar).

Ligands

Lactobionic acid, sodium gluconate and raffinose (Merck), sorbitol (Reachim), dulcitol (Lachema), L-xylose (Fluka), deoxy-D-glucose (Alfa),

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0020-1693/86/$3.50

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TABLE I. Composition and EPR Data of the Complexes

Number	Ligand (L)	L:Fe ratio in the initial solution	pH	Composition	Molecular weight		Negative charge per L	$I_{ia}:I_{is}$
					exp.	calc.		
I	mannitol	8	11.0	$Fe_4L_3(OH)_4(H_2O)_2Na_2$	916	916	3.3	∞
II	sorbitol	3,2	10.0	$Fe_3L_2(OH)_4(H_2O)_8Na$	752	764	3	∞
III	dulcitol	3.0	11.3	$Fe_3L_2(OH)_3Na$	590	602	3.5	∞
IV	1,2-propylene glycol	10.0	14.0	$Fe_2L_2(OH)_2(H_2O)_4$	360	368	2	∞
V	glycerol	10.0	14.0	$Fe_2L_2(OH)_2(H_2O)_4$	388	400	2	∞
VI	deoxy-D-ribose	20	12.5	$Fe_2L(OH)_4Na$	340	334	3	2700
VII	raffinose	4	12.5	$Fe_3L(OH)_6(H_2O)_5Na_2$	992	994	5	900
VIII	deoxy-D-glucose	4.8	12.5	$Fe_3L_2(OH)_4Na_2$	603	606	3.5	850
IX	L-arabinose	8	10.3	$Fe_3L_2(OH)_6(H_2O)_3Na$	642	645	2	700
X	saccharate	2	10.3	$Fe_2L_2(OH)_5(H_2O)_3Na_3$	700	680	2	700
XI	D-mannose	8	10.0	$Fe_2L_2(OH)_2(H_2O)Na$	532	544	2.5	350
XII	fructose	8	10.0	$Fe_2L_2(OH)_2(H_2O)_4Na$	600	599	2.5	330
XIII	L-xylose	5.2	11.5	$Fe_2L_2(OH)_2(H_2O)Na$	486	484	2.5	170
XIV	D-xylose	8	12.0	$Fe_2L_2(OH)_4(H_2O)_6Na$	630	609	1.5	17
XV	gluconate	1.6	10.0	$Fe_2L_2(OH)_4(H_2O)_2Na_2$	640	651	2	105
XVI	lactobionate	1.3	10.3	$Fe_2L_2(OH)_2(H_2O)_{14}Na_2$	1154	1158	3	75
XVII	lactose	2.5	12.5	$Fe_3L_2(OH)_6(H_2O)_6Na_3$	1198	1164	3	22
XVIII	glucose	2	12.0	$Fe_2L_2(OH)_2(H_2O)_4Na$	594	599	2.5	12

TABLE II. The Effect of the Composition of the Reaction Mixture on the Complexes

Number	Ligand (L)	L:Fe ratio in the initial solution	pH	Composition	Molecular weight		Negative charge per L	$I_{ia}:I_{is}$
					exp.	calc.		
XIX	mannitol	1	12.0	$Fe_2L_2(OH)_2(H_2O)_4Na$	620	602	2.5	∞
XX	mannitol	2	12.0	$Fe_2L_2(OH)_2Na$	528	531	2.5	2000
XXI	mannitol	2	14.0	$FeL(OH)_3(H_2O)Na_2$	358	350	2	11
X	saccharate	2	10.3	$Fe_2L_2(OH)_5(H_2O)_3Na_3$	698	680	2	700
XXII	saccharate	2	12.5	$Fe_2L_2(OH)_6Na_4$	683	666	2	300
XXIII	lactose	1	12.5	$Fe_4L_3(OH)_9(H_2O)_5Na_5$	1598	1660	2.6	45
XVII	lactose	2.5	12.5	$Fe_3L_2(OH)_6(H_2O)_6Na_3$	1198	1164	3	22
XXIV	lactose	1	14.0	$FeL(OH)_5(H_2O)_5Na_4$	663	681	2	2
XXV	glucose	1	12.0	$Fe_2L_2(OH)_2Na$	522	526	2.5	45
XVIII	glucose	2	12.0	$Fe_2L_2(OH)_2(H_2O)_4Na$	594	598	2.5	12

1,2-propylene glycol (Fluka), all other reagents (Reanal).

The iron(III) complexes were prepared according to the basic procedure presented in ref. 3. Suitable portions of the aqueous solutions of the iron(III) salt and the ligand were mixed to get the required ligand-to-metal ratio in the mixture given for each complex in Tables I and II. On addition of sodium hydroxide to the solution, the hydrolysis products of iron(III) precipitated first; these dissolved, however, with increasing pH of the solution. The pH change of the mixture was controlled potentiometrically using a Radiometer G 202B electrode during this procedure. The pH of the alkaline solution is presented for each product in Tables I and II.

For the study of the effect of sodium hydroxide concentration in the solution on the composition of the complexes formed, the preparation was repeated in some of the systems (saccharate, lactose, mannitol) using different amounts of sodium hydroxide (Table II).

The iron(III) complexes were precipitated from the aqueous solutions by adding ethanol. After separating the solid substances from the alkaline solutions by centrifugation, they were dissolved in a small portion of distilled water and reprecipitated by ethanol. The solid complexes were washed with acetone and subsequently with diethyl ether, and dried and stored *in vacuo*.

TABLE III. The Effect of Diamagnetic Dilution on the Fe(III) → Fe(III) Interaction in Mannitol Complexes

Number	Fe:Al ratio mol (%)	Metal:L ratio	pH	$I_{ia}:I_{is}$
XIX	1.00:0.0	2	12.0	2000
XXVI	0.33:0.66	2	12.0	0.7
XXVII	0.15:0.85	2	12.0	0.6
XXVIII	0.05:0.95	2	12.0	0.1

Diamagnetically diluted iron(III) mannitol complexes were prepared in an analogous way using aluminium ion containing iron(III) solutions (Table III). Paper electrophoretic measurements showed that the complexes (except those of 1,2-propylene glycol and glycerol) are anions containing sodium as cation.

The sodium content of each sample was determined by flame photometry. The iron content was measured by EDTA titration in acidic solution using sulfosalycilic acid as indicator. The thermoanalytical (TG and DTG) study of the complexes was performed by a MOM-Q derivatograph using a heating rate of 10 ℃/min from 25 to 1000 ℃. From the weight loss below 150 ℃, the coordinated water content could be calculated, and from the weight loss between 150 and 1000 ℃, the organic ligand content was determined. With the knowledge of the sodium, iron, organic ligand and water content of the solid samples, we established, on the basis of the mass balance and charge balance equations, the number of coordinated OH^- ions per iron(III) and the number of deprotonated alcoholic OH groups per organic ligand.

The ligand-to-iron ratios reflected the formation of species containing two, three or four central iron(III) atoms per complex ion. The composition of the complexes established from the analytical data are presented in Tables I and II, together with the molecular weight values derived from experimental analytical data (exp) and calculated on the basis of the stated compositions (calc). The good agreement between the corresponding two values for each complex seems to prove the correctness of the stated composition.

The Mössbauer spectra were recorded as presented previously [12] at room and liquid nitrogen temperatures. ^{57}Co in palladium served as Mössbauer source. The Mössbauer parameters were derived by the computer evaluation of the spectra. The isomer shift values refer to that of metallic iron at room temperature. The Mössbauer spectra were used to control the uniform composition (equivalency of iron(III) atoms) of the samples.

The EPR spectra were recorded on an ERS 220 apparatus at room temperature in the X-band (9.5 GHz) with 100 kHz modulation. The microwave power was 10 mW; the amplitude of modulation was 0.1 mT.

The EPR spectra reflected the presence of interacting (ia) and isolated (is) paramagnetic centres in the samples. The concentration ratio of these two types of iron(III) central atoms in the complexes was calculated from the integral intensity ratio ($I_{ia}:I_{is}$) of the corresponding two types of EPR patterns. Typical examples are shown in Fig. 1 presenting the EPR spectra of the mannitol, raffinose and D-xylose complexes, respectively. The $I_{ia}:I_{is}$ ratio decreases in the above order of the complexes. The $I_{ia}:I_{is}$ values for each complex are presented in the Tables.

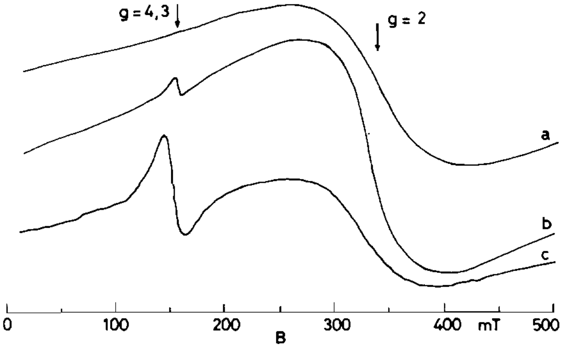


Fig. 1. The EPR spectra of the iron(III) complexes of: (a) mannitol, (b) raffinose and (c) D-xylose.

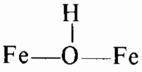
Results and Discussion

The data in Table I show that for the different ligand-containing systems, a different ligand-to-iron ratio and/or a different pH in the initial solution of the preparation process are needed to get uniform compounds that can be well-characterized analytically.

The sugar-type ligands contain deprotonated alcoholic oxygens in the complexes. In contrast to literature data [5], at least two such oxygens per ligand are needed for the coordination of polyalcohols and sugars. In the case of sugar acids (except lactobionic acid), besides the carboxylate oxygens one deprotonated hydroxy oxygen is sufficient for the complex-forming process. In complexes of ligands containing more than four alcoholic OH groups and in those of the deoxy sugars, more than two deprotonated hydroxy oxygens per ligand are coordinated to iron. For example raffinose (a trisaccharide) is bound by five such oxygens to the iron(III) central atoms.

In the complexes shown in Table I (except those of deoxyribose and raffinose), more than one (usually two) of the corresponding ligands are bound to iron.

The chemically identical ligands in the complex may differ, however, in their state of protonation. In complexes **XI**, **XII**, **XIII**, and **XVIII** one of the ligands is bound by two deprotonated alcoholic oxygens to iron and the other with three such oxygens. Ligands containing one and two (compound **XIV**) or three and four (complexes **I** and **III**) deprotonated alcoholic OH groups are coordinated by iron(III). This results in a small decrease in the symmetry of the coordination sphere of iron(III), which is reflected by larger Mössbauer quadrupole splitting (*QS*) values (0.82–0.86 mm/s, whereas *QS* values of the complexes with ligands in identical protonation state are between 0.72–0.79 mm/s). The *QS* values also reflect the distortion caused by the coordination of deprotonated carboxylate and alcoholic OH groups in the complexes of sugar acids ($QS = 0.82$–0.92). Naturally, other structural features may also influence the symmetry around the iron(III) central atom and also the *QS* values. The Mössbauer isomer shift (*IS*) values of all complexes were found to be equal within experimental error (0.47 ± 0.02 mm/s), indicating that the electron density at the place of the iron nucleus is less dependent on the nature of the donor oxygens than the electric field gradient round this nucleus. For all of the complexes, the sum of deprotonated organic ligand oxygens and coordinated hydroxide ions per iron is smaller than the coordination number of iron. The free coordination sites are occupied either by bridging OH^- ions (forming



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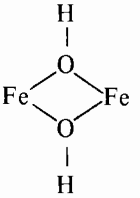
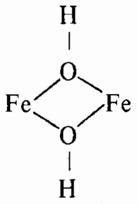


bridges) or by non-deprotonated alcoholic oxygens, or in some cases by water oxygens. With increasing water content of the samples, the iron–iron interaction decreases (as shown by the EPR measurements); thus, in samples showing strong Fe(III)–Fe(III) interactions, the water molecules present in stoichiometric amount are supposed to be bound by hydrogen bridges either to the free alcoholic hydroxy groups of the organic ligand or to the coordinated OH^- ions.

The EPR spectra of most of the complexes consist of two components: (i) a broad pattern of $g \sim 2$ value with peak-to-peak widths between 35 and 250 mT (in most of the studied systems 100–150 mT); (ii) a narrow component of $g' \sim 4.3$ value with peak-to-peak widths between 5 and 30 mT (in most of the studied systems 15–20 mT).

The broad component of the EPR pattern indicates strong interaction between the paramagnetic high spin iron(III) centres in the polynuclear species. Its shape and peak-to-peak width depend on dipole–dipole and exchange interactions. The dominance of the former results in Gauss curves, that of the latter in Lorentzian curves. The spectra of our complexes showed a mixture of both with some asymmetry. The amplitude of the low field peak is smaller than that of the other. The asymmetry increases with increasing width of the EPR line. A similar EPR pattern was recorded [13] due to antiferromagnetic interactions between the iron(III) centres in iron(III) complexes containing



moieties.

The narrow component of $g' \sim 4.3$ in the EPR pattern reflects the presence of isolated high spin iron(III) centres in the compounds. Complexes of polyalcohols (except some specially prepared samples) did not contain this narrow spectral component; consequently, they do not contain isolated iron(III) centres.

The low peak-to-peak width indicates that the local surroundings of the isolated iron(III) centres do not have axial symmetry.

The intensity ratio (I_{ia}:I_{is}) of the spectral components characterizing the interacting (ia) and isolated (is) iron(III) centres was determined for each spectrum. The results are presented in the Tables. At first approximation the I_{ia}:I_{is} ratio can be considered proportional to the concentration ratio of the two types of iron(III) centres in the samples.

It can be seen that in all of the complexes the interacting iron(III) centres dominate. The lowest value of I_{ia}:I_{is} ratio recorded in the systems investigated was ~2, but in most systems we found values between 75 and ∞. Only the high sensitivity of EPR spectroscopy made the detection of isolated iron(III) centres possible in compounds **VI–XVIII** and **XX–XXVIII**.

From the data presented in the Tables one can conclude that the concentration ratio of the two types of species depends:

(i) on the nature (structure) of the organic ligand; the presence of carbonyl or carboxylate oxygen is needed for the appearance of isolated iron(III) centres in the polynuclear species; latter oxygens are stronger electron pair donors than those of alcoholic OH groups;

(ii) on the preparation mode; increasing ligand-to-iron ratio in the initial solution and increase of the pH of this solution caused the decrease of I_{ia}:I_{is}.

It can be seen that interactions increasing the separation of the iron(III) centres result in the increase of I_{is}. To get independent proof for this suggestion, the mannitol complex of iron(III) was precipitated from solutions containing the aluminium(III) ion. In this way mixed iron–aluminium mannitol complexes were formed with different iron-to-aluminium ratios, but compositions otherwise identical to compound I. With increasing aluminium content the I_{ia}:I_{is} ratio decreased dramatically, indicating that the paramagnetic iron(III) atoms are separated by the diamagnetic aluminium(III) centres.

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