

METAL COMPLEXES OF XANTHAN GUM

Wojciech Ciesielski

*Institute of Chemistry and Environmental Protection, Jan Długosz University,
Armii Krajowej 13/15, 42 201 Częstochowa, Poland; e-mail: wc@wsp.czest.pl*

ABSTRACT

Interactions of selected paramagnetic transition metal salts [Ni (II), Co (II), Cu (II), Fe(III), Mn(II)] with xanthan gum are described. The conductivity, DSC/TG/DTG measurements, and EPR measurements produced evidence for the formation of the Werner-type complexes of metal central atoms with polysaccharide ligand. The polysaccharide hydroxyl groups and the carboxylic groups of xanthan gum were involved in ligation of the central atom.

INTRODUCTION

Although interactions between polysaccharides and metal ions are studied for almost century [1,2], little is known about polysaccharide - metal complexes. Such studies involved mostly glycoproteins and/or anionic saccharides in which the amino group nitrogen atom and oxygen atoms of the ionising groups (for instance, in hyaluronic acid [3]) were the coordination sites for metal atoms [4-10]. In spite of a large number of the hydroxyl groups in polysaccharide molecules, low electron density at the potential oxygen atom donors results in a moderate number of these groups substituting water molecules in the coordination sphere of the central metal atoms [11-13].

Recently, a series of papers was published on complexes of starches [6,14,15] and cellulose [16]. In our former studies [6] anionic potato amylopectin and, in general ligation of metal atoms with potato starch was described. The anionic phosphate and the hydroxyl groups groups which participated in ligation provided formation of clathrates with water molecules trapped in these cages. Thus, it likely, that the formation of the Werner-type complexes with the xanthan gum macro-ligand would additionally increase the water-holding ability of that polysaccharide and additionally stabilized the macroligand and water trapped in it. In order to prove this concept complexes of that gum with Co(II), Cu(II), Fe(III), Mn(II), and Ni(II), metal ions were synthesized and their properties recognized.

Xanthan gum, a branched, is soluble in cold and hot water, stable over a broad range of pH values [17], polysaccharide (I) is a semi-synthetic product of unique properties in stabilisation of hydrocolloids and other water-based systems. Xanthan gum has found applications in food industry and for non-nutritional purposes, for instance, as a biodegradable component of drilling mud [18].

Conductivity measurements

Conductivity measurements were performed at room temperature on aqueous suspension of xanthan gum (0.5 g of dry residue in 10 cm³ of water), salt solutions (0.1 M calculated for anhydrous salt) and aqueous blends of xanthan gum with salts (0.5 g of dry residue in 10 cm³ of 0.1 M aq. salt solution). Results were proven stable within 24 hours. Measurements were run in triplicates. Conductometer (inoLab, Pol-Eko-Aparatura, Poland) working at 1000 Hz provided precision of ± 1 % of recorded value.

RESULTS AND DISCUSSION

Undoubtedly, xanthan gum coordinated to metal ions as documental by increase in differences of conductivity (18 – 49%) caused on admixture of of xanthan gum to aqueous salt solutions (Table 1). The metal ions with the chloride counter ion were the most efficiently coordinated. The effect of the nitrate counter ion upon the formation of complexes was irregular and dependent on counter ion. The most pronounced, 58.1% decrease in the conductivity of the solution was observed for cupric nitrate. Simultaneously, the 37.2% decrease in the conductivity of nickelous nitrate was on the level typical for the majority of salts tested. The decrease in the conductivity in the case of cobaltous nitrate was the lowest among recorded in this study. The acetate counter ion only slightly disturbed efficient coordination of xanthan gum to metal ions. These facts revealed a varying role of counter ions in building the coordination sphere of the complexes.

Table 1. Conductivity of aqueous suspensions of xanthan gum and its metal complexes

	Salt	Complex ^b
	Co(II)	
Chloride	16,58	-40,40
Nitrate(V)	17,69	-18,10
Acetate	20,01	-35,50
	Cu(II)	
Chloride	24,51	-49,00
Nitrate(V)	23,58	-58,10
Acetate	21,54	-22,80
	Fe(III)	
Chloride	22,56	-32,60
	Mn(II)	
Chloride	23,54	-43,40
Acetate	18,95	-41,60
	Ni(II)	
Chloride	14,79	-49,30
Nitrate(V)	18,25	-37,20
Acetate	19,46	-43,60

^aConductivity of xanthan gum is 0.554 mS/cm.

^bGiven as increase in conductivity resulting from complexation (in%).

Inspection of the results of the electron paramagnetic resonance studies (Table 2) confirmed the formation of complexes of metal ions with the xanthan gum ligand. The coordination sphere around the cation always changed because of degeneration of orbitals. In several spectra, the interaction of unpaired spin localised on the metal cation with other atoms generated a splitting of signals.

Table 2. *g*-Factor in EPR spectra of salts and complexes with xanthan gum

	Salt	Complex
	Co(II)	
Chloride	2,2448	2,0219 II; 2,2641 ⊥
Nitrate(V)	2,2423	1,992; 2,0311
Acetate	2,0011	2,0026; 2,0505; 2,1994
	Cu(II)	
Chloride	2,1073	2,0016; 2,2106
Nitrate(V)	2,3148 II; 2,0946 ⊥	2,1310
Acetate	2,0231 II; 2,1652 ⊥	2,0012; 2,1672
	Fe(III)	
Chloride	2,2109	1,9926; 2,1261
	Mn(II)	
Chloride	1,9884	2,3126
Acetate	2,0125	2,1726; A = 102G; A ₁ = 121G
	Ni(II)	
Chloride	1,9876	1,9926; A = 162G
Nitrate(V)	2,2201	2,1792; 2,0021
Acetate	2,2452	1,8002

In its complexes, the Co (II) central atom had the d^9 configuration. In all spectra, the delocalisation of unpaired electron from the Co (II) ion towards the ligand could be seen. The cobalt cation had the high spin density. It was likely that the magnetic induction caused a coupling of the $d_{x^2-y^2}$ and d_{xy} orbitals. However, in the spectrum of the complex with $\text{Co}(\text{OCOCH}_3)_2$ the shift of *g*-factor was low. It might suggest a weak delocalisation of unpaired electron suggesting a square planar arrangement of ligands around the central atom.

In the spectra of Ni(II) complexes with gelatinised xanthan gum splitting of *g*-factor was observed. It might suggest asymmetry in arrangement of equatorial ligands. A low shift of *g*-factor in the spectrum of the complex with NiCl_2 suggested that the complex might be square planar in contrast to other complexes of that metal showing a remarkable shift of that factor and, therefore, considered as octahedral species.

The spectral parameters pointed to the high-spin character of the Fe(III) and Mn(II) central atoms in complexes with xanthan gum. The unpaired electron of the central atoms was shifted to the ligand. A large shift of *g*-factor in complexes resulted from the cancellation of degeneration of the d_{xz} and d_{yz} orbitals.

g-Factor for the Cu(II) cation with the nitrate and chloride counter ions informed that the complexes were monomeric and that the unpaired electron

was localised in the $d_{x^2-y^2}$ orbital. There was an octahedral symmetry around central atom with a small Jahn-Teller distortion. In the case of acetate, the g -factor ($g = 4.3$) pointed to dimeric species were detected in the corresponding complex. The acetate anion, probably, was included into the inner coordination sphere and the complex might be square planar. The effects of the metal atoms on the degeneration of orbitals could be arranged in the following orders:

chlorides: Ni > Fe > Cu > Co > Mn

nitrate: Co > Cu > Ni

acetates: Ni > Co > Cu > Mn

They showed the lack of any regularity in the arrangement of these orders. Different structure of the inner coordination sphere could be charged for it.

The thermogravimetric (TG), differential thermogravimetric, and differential scanning calorimetric studies essentially contributed to the knowledge of the structure of metal complexes of xanthan gum. Figures presents shortened thermal characteristic of xanthan gum and its metal complexes ranging from room temperature to the point of decomposition of the complex, respectively.

Xanthan gum processed in the manner necessary for a preparation of metal complexes decomposed as follows (Fig. 1). The TG-line declined immediately after heating was applied. This step of $tg \alpha = 0.33$ lasted up to 124 °C and only a flat shoulder on the DTG line additionally characterized this step. A fast weight loss ($tg \alpha = 3.64$) followed from 124 °C. It was slightly exothermic. Corresponding DTG peak had its minimum at 127.2 °C and the DSC maximum was located at 129 °C. Although the temperature region of this process suggested that it might be associated with the loss of water included on precipitation of the gum from its solution, the exothermic character of this step suggested that the water desorption might be accompanied by another process. It was likely that on precipitation, the gum formed cages with trapped water. It prevented the gum from taking a typical five-fold helical structure. After water desorption the gum turned into this favoured conformation.

These two steps of the weight loss were followed by a plateau ranging up to 231.8 °C after which further decomposition took place with a moderate rate ($tg \alpha = 0.33$). It was over at 290 °C with a total 91% weight loss. The temperature region of this step was slightly higher than that of the main decomposition step of the commercial sample of the polysaccharide.

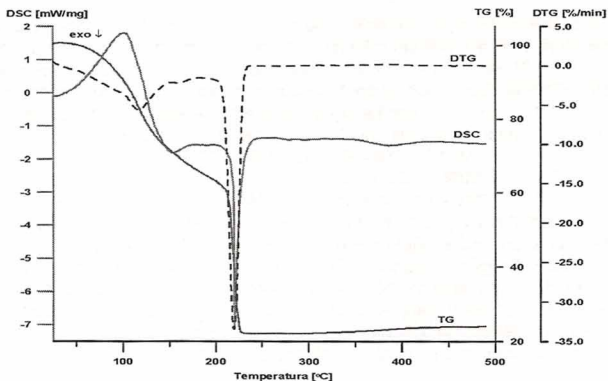


Figure 1. The TG/DTG/DSC diagram for xanthan gum.

A majority of investigated complexes showed a spectacular ability of holding water in its structure and this ability was assigned to the formation of clathrates. It should be noted that this is also a property of xanthan gum itself. However, inspection of Table 3 showed that complexes with $\text{Co}(\text{NO}_3)_2$, NiCl_2 , and MnCl_2 clathrated over 40% of water whereas precipitated xanthan gum held only 30% of water. Complexes with CuCl_2 , $\text{Cu}(\text{OCOCH}_3)_2$, FeCl_3 , $\text{Mn}(\text{OCOCH}_3)_2$ and $\text{Ni}(\text{NO}_3)_2$ included less water than precipitated xanthan gum. The pattern of evolution of water from the complexes with $\text{Cu}(\text{NO}_3)_2$ and $\text{Ni}(\text{OCOCH}_3)_2$ (Fig. 2) suggested that these complexes contained only surface sorbed water.

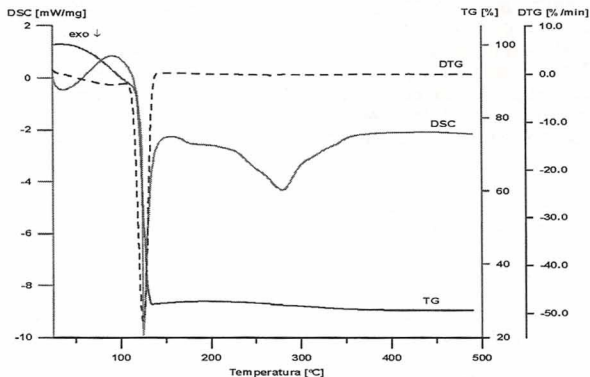


Figure 2. The TG/DTG/DSC diagram for the xanthan gum - $\text{Cu}(\text{NO}_3)_2$ complex.

Complexes with CoCl_2 and $\text{Co}(\text{OCOCH}_3)_2$ were anhydrous (Fig. 3) and pathing of thermogram for complex of $\text{Co}(\text{NO}_3)_2$ (Fig. 4) with several peaks related to water loss was typical for complex clathrates.

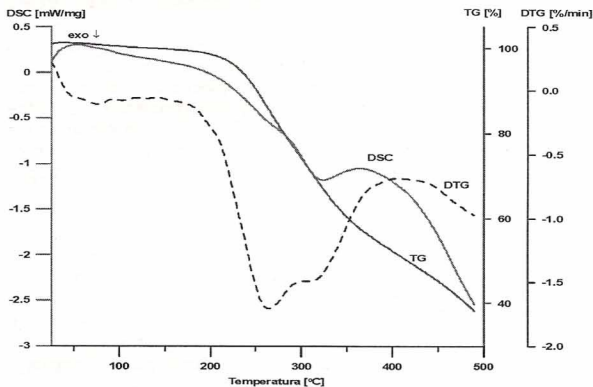


Figure 3. The TG/DTG/DSC diagram for the xanthan gum - $\text{Co}(\text{OCOCH}_3)_2$ complex.

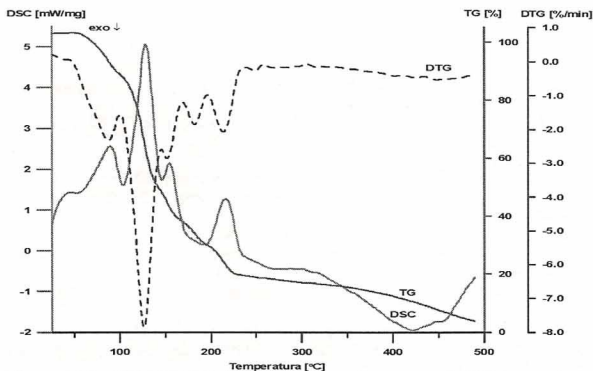


Figure 4. The TG/DTG/DSC diagram for the xanthan gum - $\text{Co}(\text{NO}_3)_2$ complex .

In terms of the thermal stability expressed as a point of thermal decomposition of anhydrous complexes (TG line), only complexes of cobaltous and nickelous chlorides and acetates were more stable than free ligand. The coordination of

the ligand to cupric nitrate and acetate decreased the rate of decomposition of the ligand expressed as the slope of the TG line in the corresponding region (tg α). Coordination to $\text{Co}(\text{OCOCH}_3)_2$ and MnCl_2 , CuCl_2 and $\text{Ni}(\text{NO}_3)_2$ only slightly influenced the decomposition rate whereas in the other cases a strong acceleration of decomposition was observed. The decomposition of complexes with cobaltous and nickelous chlorides, and cobaltous nitrate proceeded exothermically as free ligand did but the other complexes decomposed endothermically showing that products of decomposition did not form any complexes and/or compounds with salts and/or products of their thermal decomposition. These differences could not be explained as the result of the octahedral and square planar structures of the inner coordination sphere of the complex but certainly the coordination of the ligand had an impact to the ability of the formation of clathrates with involvement of the intermolecular hydrogen bonds.

CONCLUSIONS

1. Xanthan gum coordinated to Co (II), Cr (III), Cu (II), Fe (II), and Mn (II) to form the Werner-type complexes.
2. Ligation of the central atom involved lone electron pairs of the polysaccharide hydroxyl group and COO^- groups of xanthan gum.
3. The complexes were mainly octahedral but square planar complexes were also formed.
4. The coordination contributed to the formation of clathrates in which water molecules were trapped.

REFERENCES

1. Gyurcsik B, Nagay L, *Coord Chem Rev* 2000; 203: 81.
2. Bandwar R, Rao C, *Carbohydr Res* 1996; 287: 157.
3. Merce A, Carrera L, Romanholi L, Recio M, *J Inorg Biochem* 2002; 89: 212.
4. Burger K, Nagay L, Gyurcsik B, *J Mol Liq* 1995; 65/66: 213.
5. Nagay L, Szorcsik A, *J Inorg Biochem* 2002; 89: 1.
6. Ciesielski W, Tomasik P, Lii CY, Yen MT, *Carbohydr Polym* 2003; 51: 47.
7. Matsui Y, Kurita T, Yagi M, Okayama T, Mochida K, Data Y, *Bull Chem Soc Jpn* 1975; 48: 2187.
8. Solpan D, Sahan M, *J Appl Polym Sci* 1995; 55: 383.
9. Burger K, Nagay L, *Metal complexes of carbohydrates and sugar type ligands, Biocoordination Chemistry*, Ellis Horwood, London, 1990, 236.
10. Norkus E, Vaiciuniene J, Vuorinen T, Heikkilä M, *Carbohydr Polym* 2002; 50: 159.
11. Saladini M, Menabue L, Ferrari E, *Carbohydr Res* 2001; 336: 55.
12. Gajda T, Gyurcsik B, Jakusch T, Burger K, Henry B, Delpuech J, *Inorg Chim Acta* 1998; 275-276: 130.
13. Yang L, Su Y, Liu W, Jin X, Wu J, *Carbohydr Res* 2002; 337: 1485.
14. Lii CY, Tomasik P, Yen MT, Lai VMF, *Int J Food Sci Technol* 2001; 36: 321.
15. Ciesielski W, Tomasik P, *Termochim. Acta* in press.
16. Alekseev YuE, Gamovskii AD, Zhdanov YuA, *Usp Khim* 1998; 67: 723.
17. Katzbauer B, *Polym. Degr. Stab* 1998; 59: 81.
18. Wang F, Sun Z, Wang Y, *Food Hydrocoll* 2001; 15: 575.