



Original article

Spectroscopic Characterization of Cobalt (II) Complexes with Reduced Low-Molar Dextran Derivatives

Žarko Mitić¹, Goran M. Nikolić¹, Milorad Cakić², Sanja Mitić²,
Goran S. Nikolić², Stevo Najman¹

¹University of Niš, Faculty of Medicine, Niš, Serbia

²University of Niš, Faculty of Technology, Leskovac, Serbia

SUMMARY

The formation of Co(II) ion complexes with reduced low-molar dextran (RLMD, Mw 5000 g/mol) was studied at the pH range from 7.0 to 13.5. The cobalt content in synthesized Co(II)-RLMD complexes was ~3–12% (AAS) and it generally increases with pH. Co(II)-RLMD complexes were characterized by UV-Vis spectrophotometry and FTIR spectroscopy. UV-Vis data for synthesized complexes indicate tetragonally distorted Oh coordination of Co(II) ions with O atoms from ligand. The presence of IR bands at 765 cm⁻¹ and 910 cm⁻¹ in Co(II)-RLMD complexes indicates the existence of α-(1→6)O-glycosidic bonds. The similarities in the γ(C-H) range of the IR spectra indicate that there is no difference in the conformation of the glucopyranose units in RLMD and Co(II)-RLMD complexes. The occurrence of water molecules in Co(II)-RLMD complexes was confirmed by FTIR spectroscopy of deuterated samples.

Key words: Co(II)-dextran, AAS, UV-Vis, FTIR

Corresponding author:

Žarko Mitić

Email: zarko.mitic@medfak.ni.ac.rs

INTRODUCTION

Interactions of the metal ions with polysaccharides are very important in the field of medicinal chemistry due to the presence of such interactions in biological system, and various applications of metal ion-polysaccharide complexes which are being offered in the areas related to pharmacy, medicine, agriculture and food industry (1, 2). Detailed characterization of polysaccharide complexes of various metal ions, such as Cu(II) (3, 4), Fe(III) (5, 6), Zn(II) (7, 8), and Ag(I) (9 – 12), has already been described in the literature.

Cobalt is an essential trace element, being an integral part of vitamin B12. Vitamin B12 is a water-soluble vitamin, physiologically active substance with a key role in the normal functioning of the brain and nervous system, and in the formation of blood as well (13). There are literature data about Co(II) complexes with mono - and disaccharides (14) and interactions of polysaccharides with cobalt-based nanoparticles (15). However, only few studies concerning polysaccharide-Co(II) complexes ha-

ve been published in the literature so far (16 – 18), although Co(II) complexes with polysaccharides or their derivatives may have important applications (19).

Microbial polysaccharide dextran is a polymer with α -(1 \rightarrow 6) linked D-glucopyranose units. Dextran is a water-soluble, neutral polysaccharide with numerous applications in the food, cosmetic, chemical and pharmaceutical industries, and medicine (20–24). Cross-linked dextran is known as Sephadex and is widely used for the separation and purification of proteins and carbohydrates (24). Also, dextran may be formed as unwanted deposit in Brazilian sugar cane spirits (25). The dextran produced by *Leuconostocmesenteroides* consists of α -(1 \rightarrow 6)-linked glucan with side chains attached to the 3-positions of the backbone D-glucopyranose units and the degree of branching \sim 5% (Figure 1). Dextrans T-40 and T-70, which are commercially available, are used as drugs, especially as blood plasma volume expanders (22, 23). Dextran may be derivatized easily to control its solubility or provide reactive groups, and its derivatives have numerous potential industrial applications (20, 26).

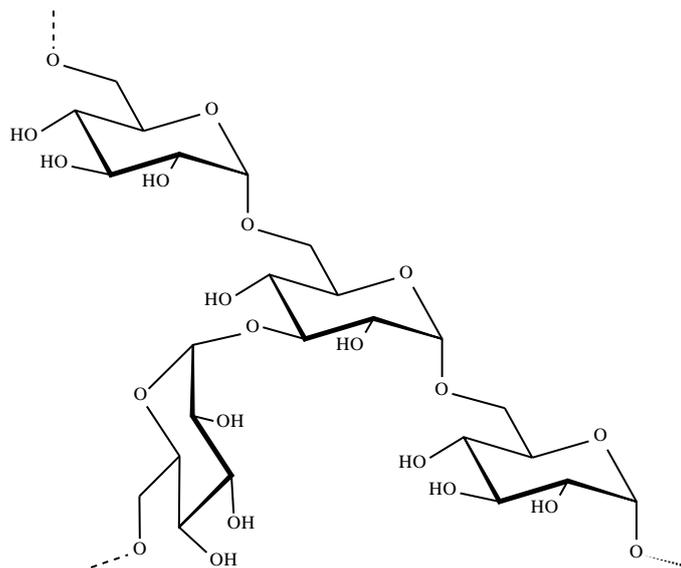


Figure 1. Molecular structure of polysaccharide dextran

Many types of carbohydrate derivatives have been synthesized for biomedical and pharmaceutical applications (24, 27–29). Reduced low-molar dextran (RLMD) was chosen as a complexing material, and its interactions with Co(II) ions were investigated in this study. The complexation process begins in an alkaline solution (pH > 7.5) and involves OH groups in C-2 and

C-3 or C-4 positions of dextran monomer units (α -D-glucopyranose). Co(II)-RLMD complexes were synthesized in aqueous solutions, at the boiling temperature and at different pH values, ranging from 7 to 13.5 (17, 18). The obtained complexes were investigated both in solution and in the solid state.

For the characterization of the carbohydrate com-

plex compounds, different spectroscopic techniques may be applied (3, 28, 30). UV-Vis spectrophotometry and FTIR spectroscopy proved to be very useful combination for the structural characterization of various Co(II) ion complexes with different ligands (19, 31, 32).

UV-Vis spectra can provide relatively reliable information about the ligand arrangement in transitional metal complexes. Co(II) ion can build numerous complex compounds with the different geometric structures, such as tetrahedral (Td), square-planar (D_{4h}), and octahedral (Oh). In octahedral surroundings of the ligands, Co(II) ion builds complexes with the coordination number 6 which can have one from two possible d⁷ configurations: high-spin t_{2g}⁵e_g² with weak-field ligands, or low-spin t_{2g}⁶e_g¹ with strong-field ligands (33). High-spin Co(II) complexes with weak-field ligands (such as O-donors) have electronic configuration t_{2g}⁵e_g², an expected weak Jahn-Teller effect, and according to the Jahn-Teller theorem (34) such complexes are octahedral with tetragonal distortion.

More structure-sensitive instrumental methods, such as Fourier-transform infrared (FTIR) spectroscopy, made it possible to assign the binding of metal ions to OH or other groups, to characterize the metal ion coordination in the complex carbohydrate systems, and monitor the polysaccharide conformation or configuration changes forced by complexation processes (35, 36). The major goal of this work was to use UV-Vis spectrophotometry and FTIR spectroscopy as the main tools to determine the conformation and the structure of this dextran derivative around Co(II) ions. The additional characterization of Co(II)-RLMD complexes was provided by AAS analysis.

Experimental

Materials

RLMD standard with Mw 5000 g/mol and the content of reducing groups of 0.05% (38), was obtained by depolymerization and reduction of dextran with Mw 70000 g/mol(37). NaOH, ethanol, D₂O, and CoCl₂·6H₂O were purchased from Merck (Darmstadt, Germany). Redistilled water was used in the preparation of all solutions.

Complex synthesis

The Co(II)-RLMD complexes were synthesized in aqueous solutions at different pH values (7.5-13.5) at room temperature, using CoCl₂·6H₂O and RLMD, Mw 5000 g/mol. Details of the synthesis have already been described by Mitić et al. (17, 18).

UV-Vis spectrophotometry

The Vis spectra of the aqueous solutions of synthesized complexes were recorded on a Varian Cary-300 Conc. spectrophotometer, in the range of 400–900 nm, in quartz cells (1x1 cm) at room temperature with redistilled water as a reference.

FTIR spectroscopy

The FTIR spectra (an average of 200 scans) were recorded at room temperature on a PerkinElmer Frontier™ FT-IR spectrometer equipped with a standard detector in the range of 4000–400 cm⁻¹ with a resolution of 2 cm⁻¹. The spectrometer was purged with dry nitrogen gas during the measurements. All spectra were baseline-corrected and area-normalized. A Fourier self-deconvolution method was applied to enhance the spectral resolution.

AAS analysis

The cobalt content of the complexes was measured by Atomic Absorption Spectrometry (AAS) on the Perkin Elmer AAnalyst 400 spectrometer (Co-lamp λ = 240.7 nm; the breadth of slot 0.2 nm; the flame: acetylene/air).

RESULTS AND DISCUSSION

The analysis of similar polysaccharide complexes of Fe(III) (5,28) and Cu(II) (3,35) points to the necessity of determining their physicochemical properties in order to obtain the applicable pharmaceutical preparations. Some basic physicochemical properties of Co(II)-RLMD complexes synthesized in this work are shown in Table 1.

The data in Table 1 show that the color of synthesized Co(II)-RLMD complexes can vary from light salmon to dark brown at the pH range 7.5–13.5. The change of reddish color of the initial Co(II) salt solution during the synthesis, at the pH range 13.0-13.5, from light salmon to brown, is the proof of complex formation. Also, the quantity of Co(II) ion bound in Co(II)-RLMD complexes largely increased at pH 12.0 and above, and the solubility of the synthesized Co(II)-RLMD complexes in water varied. The most water-soluble complex was obtained at pH 13.5 and this solution was stable without phase separation for a long period of time. Co(II)-RLMD complexes synthesized at lower pH values were less soluble. Solution pH obviously has an influence on the manner of binding of Co(II) ions into a complex, i.e. on the type and/or number of bonds, because the stability, color, and solubility of the obtained complexes also changed with pH (Table 1).

Table 1. Some basic physicochemical properties of Co(II)-RLMD complexes synthesized at different pH values

pH	Co content (%)	Complex color	Water solubility*	Aqueous solution stability
7.5	3.96	Ochre	Soluble	Stable bright solution, opalescent
8.5	3.61	Dark salmon	Slightly soluble	Layering solution, opalescent
11.0	3.90	Light ochre	Soluble	Bright solution, opalescent
12.0	10.07	Dark ochre	Soluble	Precipitate
13.0	11.89	Light salmon	Soluble	Bright solution, opalescent
13.5	12.89	Dark brown	Very soluble	Stable bright solution

*soluble: 600 mg of complex/20 mLH₂O at room temp. (Eur. Ph.)

In addition, depending on pH, Co(II)-RLMD complexes also have different wave lengths of absorbance maxima in the Vis spectra. The reddish [Co(H₂O)₆]²⁺ ion has an absorbance maximum at 512 nm, while synthesized complexes display absorbance maxima within the range 583–624 nm (Figure 2). With

increase in solution pH, the absorbance maxima shift to longer wavelengths compared with the [Co(H₂O)₆]²⁺ ion and this bathochromic shift of the absorbance maxima of the complexes with increasing pH confirm the formation of different complexes.

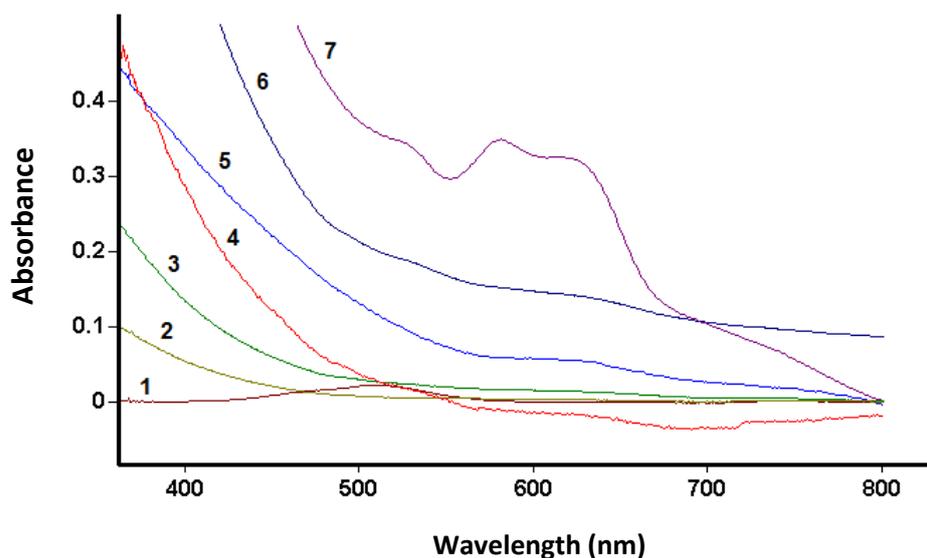


Figure 2. Vis spectra of Co(II)-RLMD complexes synthesized at different pH values: pH=7.5 (1); pH=8.5 (2); pH=11.0 (3); pH=12.0 (4); pH=13.0 (5); pH=13.5 (6), and [Co(OH)₆]⁺ complex at pH 14 (7)

Absorbance maxima in the area of wavelengths around 550 nm were reported for the high-spin Co(II) ion complexes with weak-field ligands (oxygen-donors)

having configuration $t_{2g}^5 e_g^2$ and coordination number six (33). Absorbance maxima, because of the synergic effect, shift to the red region of Vis spectrum (bathochromic

effect). Strengthening of the metal-ligand bond (Co–O) diminishes the splitting energy of d-orbitals and absorbance maxima shift to larger wavelengths (curves 2-6, Figure 2). The appearance of better defined absorbance maxima with higher wavelengths (510, 581, and 628 nm in curve 7, Fig. 2) at pH higher than 13.5 has been connected with the decomposition of Co(II)-RLMD complex into the dark blue cobaltates(II), $[\text{Co}(\text{OH})_4]^{2-}$ and $[\text{Co}(\text{OH})_6]^{4-}$ (40). Thus, these spectrophotometric criteria can be applied for the confirmation of the success of complex synthesis.

From the Vis spectra of Co(II)-RLMD complexes synthesized under different reaction conditions it was possible to see that the wave lengths of the absorbance maxima ranged from 583 to 624nm. The corresponding ligand crystal field splitting energies (Δ) are from 2.13 to 1.99eV. According to the literature data (33, 40), these energy values have been found in the range of energies which are characteristic for the Oh ligand field (Δ_o). Co(II) complexes of organic molecules, such as carbohydrates, have the ability to adopt alternative coordination arrangements, particularly tetragonal (41), and these exhibit distinct spectral properties in the Vis range resulting from Jahn-Teller distortion (34, 43). This points to the possibility that in the structure of the synthesized Co(II)-RLMD complexes, analogous with copper(II)-dextran complexes (44), Co(II) ions are probably in the Ohor tetragonally distorted Oh surroundings (square-bipyramidal) with O atoms which can originate from a ligand or solvent (18).

FTIR spectroscopy was used for further investigation of the structure and properties of polysaccharide ligand and its complexes with Co(II) ion. The FTIR spectra of RLMD and the synthesized Co(II)-RLMD complexes (Figure 3) contain the following characteristic bands: $\nu(\text{O-H}) \sim 3400 \text{ cm}^{-1}$, $\nu(\text{C-H}) \sim 2930 \text{ cm}^{-1}$, $\delta(\text{HOH}) \sim 1645 \text{ cm}^{-1}$, $\delta(\text{C-H}) \sim 1450$ and $\sim 1345 \text{ cm}^{-1}$, $\delta(\text{O-H}) \sim 1420 \text{ cm}^{-1}$, a complex band $\nu(\text{C-O}) 1200\text{--}1000 \text{ cm}^{-1}$, $\gamma(\text{C-H}) 1000\text{--}700 \text{ cm}^{-1}$.

Although the FTIR spectrum of RLMD and FTIR spectra of Co(II)-RLMD complexes synthesized at different pH values are similar, there are some notable differences in the area of vibrations of all types of OH groups and H₂O molecules (Figure 3). This means that in the RLMD FTIR spectrum the wide intensive band at approx. 3400 cm^{-1} , resulting from the stretching vibrations of OH groups and stretching vibrations of constitutional H₂O molecules, and the band at approximately 1645 cm^{-1} which is the result of $\delta(\text{HOH})$, are clearly recognized (35, 39). The positions of these bands changed (wave numbers decreased) as a result of a complex formation i.e. deprotonation of the RLMD ligand OH groups, most likely in the first coordination sphere of the Co(II) ion.

We already know that the complexation of copper(II) ions with reduced low-molar pullulan (RLMP)(3) and RLMD (43) produced different types of the complexes depending on the pH value, and the spectral picture

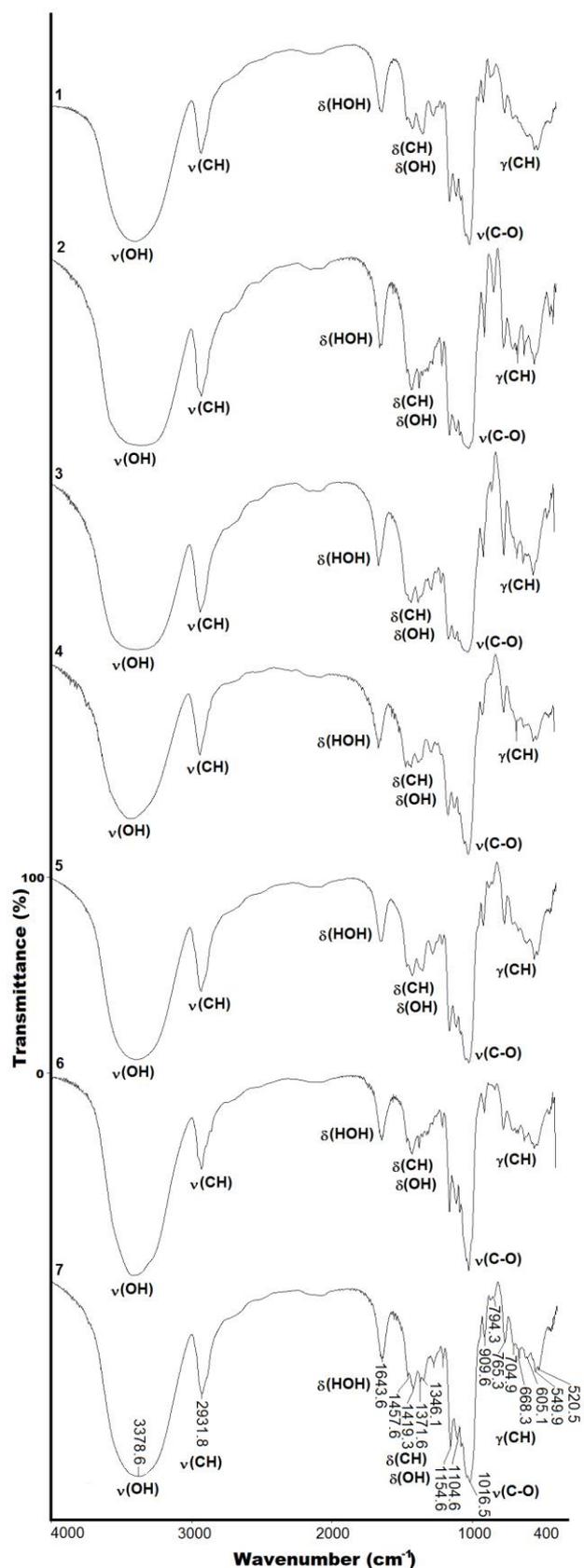


Figure 3. FTIR spectra of RLMD (Mw=5000 g/mol)(1) and Co(II)-RLMD complexes synthesized at different pH values: pH=7.5 (2); pH=8.5 (3); pH=11.0 (4); pH=12.0 (5); pH=13.0 (6), and pH=13.5 (7)

in this region is very similar. If similar complexes are formed in the case Co(II) ions, bands in this region should be compared with the stretching vibrations of OH ligand groups and coordinated H₂O molecules in the complex which is synthesized at pH 7.5 with regard to the OH ligand groups and the OH-groups in the first coordination sphere of the Co(II) ions in the complexes synthesized at pH>10. FTIR study in a particular region of OH (3400 and 1420 cm⁻¹) and CH (2930, 1450, and 1345 cm⁻¹) vibrations indicates different binding between the central metal ion and ligand, depending on pH and metal content. In the case of the Co(II)-RLMD complexes, OH groups participate in the formation of the Co(II)-ligand linkages. As a result, the band at 3400 cm⁻¹ for $\nu(\text{O-H})$ vibrations in RLMD (Figure 3, curve 1) shifted to approximately 3380 cm⁻¹ in Co(II)-RLMD complexes (Figure 3, curves 2-7). This finding suggests that this band can be considered as characteristic for the type of Co(II)-ligand links. In the 1200–1000 cm⁻¹ region, the spectra of RLMD and the Co(II)-RLMD complexes comprise a number of highly overlapping bands. IR range from 1000 to 700 cm⁻¹ is of special interest for structural investigation of this type of complexes (39). Both the number and frequencies of the bands in this IR range depend on the conformation of the D-glucopyranose units (35). The similarities of FTIR spectra in the $\gamma(\text{C-H})$ range indicate that there is no difference in the confor-

mation of the glucopyranose units in the RLMD and synthesized complexes, and they probably exhibit C1 chair conformation (910 and 840 cm⁻¹). IR bands from ring deformations and scaffold vibrations were observed at 705, 668, 605, 550, and 520 cm⁻¹. The IR bands at 765 and 910 cm⁻¹ indicate the existence of $\alpha(1\rightarrow6)$ O-glycosidic bond. The $\alpha(1\rightarrow6)$ O-glycosidic bond content is greater than 95%, which points to the high linearity of polysaccharide dextran. In the IR spectra of dextrans synthesized by different microorganisms, the different band intensity from $\gamma(\text{C-H})$ vibrations at 794 cm⁻¹, which indicates the presence of $\alpha(1\rightarrow3)$ -bond in dextran macromolecules, was noticed.

FTIR spectroscopy coupled with D₂O isotopic exchange proved to be a very sensitive method for determining the OH group coordination and is related to the bonding strength of hydrogen atoms (44, 45). We also applied FTIR spectroscopy to determine spectral manifestation of the changes in the complex structure caused by recrystallization from D₂O. The deconvoluted FTIR spectra of RLMD and Co(II)-RLMD complexes were compared with the deconvoluted spectra of their analogs recrystallized from D₂O in order to find the specific spectral peculiarities that allow one to obtain the information about the structure and the conformation of these macromolecules in solvents that exhibit different influences on their intra- and intermolecular interactions.

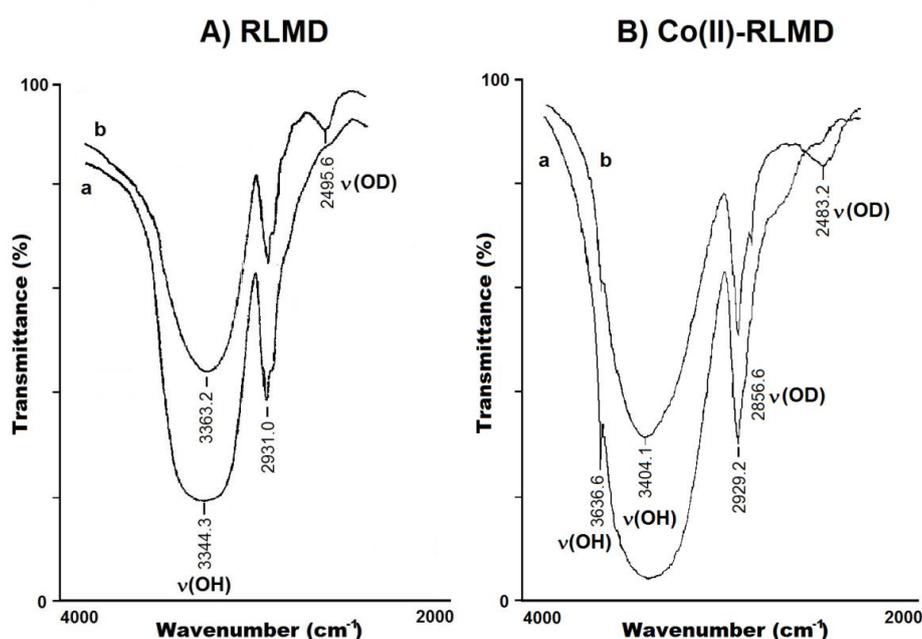


Figure 4. Deconvoluted FTIR spectra of A) RLMD and B) Co(II)-RLMD complex synthesized at pH 13.5 (a), and their deuterated analogues (b) in the range of $\nu(\text{OH})$ vibrations

In the range of $\nu(\text{O-D})$ vibrations, one new band appears at about 2495 cm^{-1} in the FTIR spectrum of deuterated RLMD (Figure 4 A) and this is obviously the consequence of isotopic exchange in some OH groups whose $\nu(\text{OH})$ vibrations are manifested by the presence of a broad intensive band at about 3350 cm^{-1} . As for the Co(II)-RLMD complex, a new band appears in the FTIR spectrum of deuterated complex synthesized at pH 13.5 at about 2483 cm^{-1} in the range of $\nu(\text{O-D})$ vibrations (Figure 4B). Partners of these vibrations are expected to be $\nu(\text{O-H})$ vibrations manifested by the broad intensive band at about 3400 cm^{-1} . Sharp band at 3636 cm^{-1} in the deconvoluted FTIR spectrum of Co(II)-RLMD complex may be attributed to $\nu(\text{O-H})$ vibrations of the free OH groups which are not included in the formation of hydrogen bonds. Complete deuteration of these OH groups results in the disappearance of this band and appearance of new sharp band at 2856 cm^{-1} in the FTIR spectrum of deuterated Co(II)-RLMD complex.

On the basis of IR spectrum in the stretching OD region of HDO molecules and Falk criteria (46), it can be

concluded that both RLMD and Co(II)-RLMD complex have one crystallographic type of H_2O molecule. According to the correlation of Berglund et al. (44, 45), estimated Ow. O distances are 283.1 pm for RLMD and 281.8 pm for Co(II)-RLMD complex, and H_2O protons take part in the formation of relatively weak hydrogen bonds. Probably, Co(II)-RLMD complexes are formed by the displacement of H_2O molecules from the first coordination sphere of Co(II) ion by the OH groups of ligand. No effect on the conformation change of α -D-glucopyranose units with C1 chair conformations was observed for the deuterated Co(II)-RLMD complexes evidenced by the appearance of FTIR spectra in the range of $1000\text{--}700\text{ cm}^{-1}$.

Based on the correlation of data obtained by the spectroscopic techniques used in this study for the characterization of synthesized Co(II)-RLMD complexes, we propose the structure with tetragonal distorted Oh coordination for the complexes synthesized at pH > 11. The proposed structure is given in Figure 5.

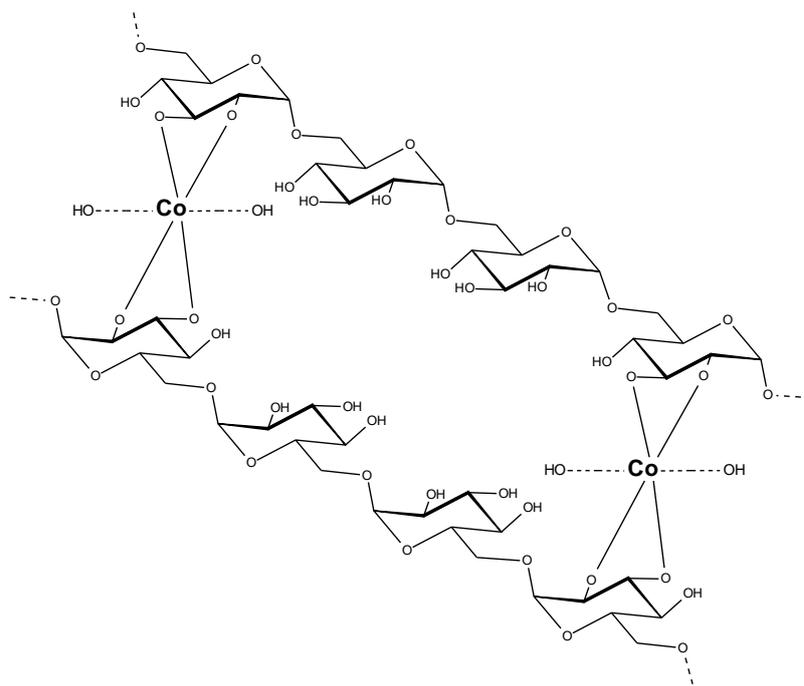


Figure 5. Proposed structure of Co(II)-RLMD complex and positions of Co(II) ions into the polysaccharide dextran molecule for complexes synthesized at pH>11

CONCLUSIONS

The formation of Co(II) ion complexes with reduced low-molar dextran in aqueous solutions was obser-

ved at pH 7.5–13.5. The cobalt content in synthesized Co(II)-RLMD complexes was ~3–12% (AAS) and generally increased with pH. With the increase in pH, the light absorbance maxima of complex solutions showed

red shift compared to $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ ion. The spectrophotometric parameters of the investigated complexes are characteristic for Co(II) ion in octahedral or tetragonally distorted octahedral coordination with O ligand atoms. A part of FTIR spectra, in the range on $1000\text{--}700\text{cm}^{-1}$ of Co(II)-RLMD complexes, indicated no influence of complexing process on the conformation change of C1 glucopyranose units. The results of FTIR investigations showed that RLMD and synthesized Co(II)-RLMD

complexes are crystal hydrate molecules with one crystallographic type of H_2O .

Acknowledgement:

This study was partially supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (grant No. 172044) and internal project financed by the Faculty of Medicine, University of Niš, Republic of Serbia (grant No. 11-14629-4/16).

References

- Sibikina OV, Iozep AA, Moskvina AV. Polysaccharide complexes with metal cations: Structure and application (A review). *Pharm Chem J* 2009; 43: 341–5. <https://doi.org/10.1007/s11094-009-0292-1>
- Gyurcsik B, Nagy L. Carbohydrates as ligands: Coordination equilibria and structure of the metal complexes. *Coord Chem Rev* 2000; 203(1):81–149. [https://doi.org/10.1016/S0010-8545\(99\)00183-6](https://doi.org/10.1016/S0010-8545(99)00183-6)
- Mitić Ž, Cakić M, Nikolić GM, et al. Synthesis, physicochemical and spectroscopic characterization of copper(II)-polysaccharide pullulan complexes by UV-Vis, ATR-FTIR, and EPR. *Carbohydr Res* 2011; 346: 434–41. <https://doi.org/10.1016/j.carres.2010.12.011>
- Rudd TR, Skidmore MA, Guimond SE, et al. Site-specific interactions of copper(II) ions with heparin revealed with complementary (SRCD, NMR, FTIR and EPR) spectroscopic techniques. *Carbohydr Res* 2008; 343: 2184–93. <https://doi.org/10.1016/j.carres.2007.12.019>
- Ilić Lj, Ristić S, Cakić M, et al. Polynuclear complex Fe(III) with pullulan oligomers, process of its obtaining, and pharmaceutical preparations on the basis of the complex. EP 1363951 (A2); WO 0246241 (A2) 2003.
- Somsook E, Hinsin D, Buakhrong P, et al. Interactions between iron(III) and sucrose, dextran, or starch in complexes. *Carbohydr Polym* 2005; 61: 281–7. <https://doi.org/10.1016/j.carbpol.2005.04.019>
- Bandwar RP, Flora SJS, Rao CP. Influence of zinc-saccharide complexes on some haematological parameters in rats. *BioMetals* 1997; 10: 337–41. <https://doi.org/10.1023/A:1018336819420>
- Luo Z, Zou J, Chen H, et al. Synthesis and characterization of amylose–zinc inclusion complexes. *Carbohydr Polym* 2016; 137: 314–20. <https://doi.org/10.1016/j.carbpol.2015.10.100>
- Bankura KP, Maity D, Mollick MMR, et al. Synthesis, characterization and antimicrobial activity of dextran stabilized silver nanoparticles in aqueous medium. *Carbohydr Polym* 2012; 89: 1159–65. <https://doi.org/10.1016/j.carbpol.2012.03.089>
- Kanmani P, Lim ST. Synthesis and characterization of pullulan-mediated silver nanoparticles and its antimicrobial activities. *Carbohydr Polym* 2013; 97: 421–8. <https://doi.org/10.1016/j.carbpol.2013.04.048>
- Glišić S, Cakić M, Nikolić G, et al. Synthesis, characterization and antimicrobial activity of carboxymethyl dextran stabilized silver nanoparticles. *J Mol Struct* 2015; 1084: 345–51. <https://doi.org/10.1016/j.molstruc.2014.12.048>
- Cakić M, Glišić S, Nikolić G, et al. Synthesis, characterization and antimicrobial activity of dextran sulphate stabilized silver nanoparticles. *J Mol Struct* 2016; 1110: 156–61. <https://doi.org/10.1016/j.molstruc.2016.01.040>
- Okamoto S, Eltis LD. The biological occurrence and trafficking of cobalt. *Metallomics* 2011; 3: 963–70. <https://doi.org/10.1039/c1mt00056j>
- Bandwar RP, Sastry MD, Kadam RM et al. Transition-metal saccharide chemistry: Synthesis and characterization of D-glucose, D-fructose, D-galactose, D-xylose, D-ribose, and maltose complexes of Co(II). *Carbohydr Res* 1997; 297: 333–9. [https://doi.org/10.1016/S0008-6215\(96\)00285-6](https://doi.org/10.1016/S0008-6215(96)00285-6)
- Bondarenko OM, Ivask A, Kahru A, et al. Bacterial polysaccharide levan as stabilizing, non-toxic and functional coating material for microelement-nanoparticles. *Carbohydr Polym* 2016; 136: 710–20. <https://doi.org/10.1016/j.carbpol.2015.09.093>
- Tratar Pirc E, Arčon I, Kodre A, et al. Metal-ion environment in solid Mn(II), Co(II) and Ni(II) hyaluronates. *Carbohydr Res* 2004; 339: 2549–54. <https://doi.org/10.1016/j.carres.2004.07.025>

17. Mitić ŽJ, Nikolić GS, Cakić MD, et al. The investigation of Co(II)-dextran complexes. *Hem Ind* 2007; 61: 257–62.
<https://doi.org/10.2298/HEMIND0704257M>
18. Mitić Ž, Cakić M, Nikolić G. Fourier-Transform IR spectroscopic investigations of Cobalt(II)-dextran complexes by using D2O isotopic exchange. *Spectroscopy* 2010; 24: 269–75.
<https://doi.org/10.1155/2010/712460>
19. Tawfik SM, Hefni HH. Synthesis and antimicrobial activity of polysaccharide alginate derived cationic surfactant-metal(II) complexes. *Int J BiolMacromol* 2016; 82: 562–72.
<https://doi.org/10.1016/j.ijbiomac.2015.09.043>
20. Jeanes A. Dextrans and Pullulans: Industrially Significant α -D-Glucans, in: P.A. Sandford, A. Laskin, (Eds.), *Extracellular Microbial Polysaccharides*, ACS Symposium Series, No. 45, 1977: 284–96.
21. Stanković RI, Jovanović S, Ilić Lj et al. Study of aqueous dextran solutions under high pressures and different temperatures by dynamic light scattering. *Polymer* 1991; 32: 235–40.
[https://doi.org/10.1016/0032-3861\(91\)90008-7](https://doi.org/10.1016/0032-3861(91)90008-7)
22. Bowman HW. Clinical evaluation of dextran as a plasma volume expander. *J Am Med Assoc* 1953; 153: 24–6.
<https://doi.org/10.1001/jama.1953.02940180026009>
23. De Belder AN. *Dextran*, Amersham Biosciences AB (Chapter 5), Uppsala, Sweden, 2003.
24. Naessens M, Cerdobbel A, Soetaert W, et al. Leucostocodextranase and dextran: Production, properties and applications. *J Chem Tech Biotechnol* 2005; 80: 845–60.
<https://doi.org/10.1002/jctb.1322>
25. De Aquino FWB, Franco DW. Formation of dextran deposits in Brazilian sugar cane spirits. *J Agric Food Chem* 2011; 59: 8249–8255.
<https://doi.org/10.1021/jf201041z>
26. Mitić Ž, Ph.D. Thesis, Synthesis and the spectra-structure correlation of some biometal complexes with dextran and pullulan, University of Niš, Serbia, 2009.
27. Donot F, Fontana A, Baccou JC, et al. Microbial exopolysaccharides: Main examples of synthesis, excretion, genetics and extraction. *Carbohydr Polym* 2012; 87: 951–62.
<https://doi.org/10.1016/j.carbpol.2011.08.083>
28. Oshtrakh MI, Semionkin VA, Prokopenko PG et al. Hyperfine interactions in the iron cores from various pharmaceutically important iron-dextran complexes and human ferritin: A comparative study by Mössbauer spectroscopy. *Int J BiolMacromol* 2001; 29: 303–14.
[https://doi.org/10.1016/S0141-8130\(01\)00181-7](https://doi.org/10.1016/S0141-8130(01)00181-7)
29. Cakić M, Mitić Ž, Nikolić G, et al. Design and optimization of drugs used to treat copper deficiency. *Expert Opin Drug Discov* 2013; 8: 1253–63.
<https://doi.org/10.1517/17460441.2013.825245>
30. Yang L, Tian W, Xu Y, et al. Interactions between metal ions and carbohydrates: The coordination behavior of neutral erythritol to transition metal ions. *J Inorg Biochem* 2004; 98: 1284–92.
<https://doi.org/10.1016/j.jinorgbio.2004.04.012>
31. Bera M, Patra A. Study of potential binding of biologically important sugars with a dinuclear cobalt(II) complex. *Carbohydr Res* 2011; 346: 733–38.
<https://doi.org/10.1016/j.carres.2011.02.010>
32. Nikolić RS, Nikolić GM, Krstić NS. Spectroscopic study of paracetamol-biometal (M²⁺) ion complexes. *Eur J Pharm Sci* 2011; 44: 187–8.
33. Lever ABP. *Inorganic Electronic Spectroscopy*. 2nd ed., Elsevier, New York, 1984.
34. Jahn HA, Teller E. *Proc. R. Soc. London, Ser. A* 1937; 161: 220–5.
<https://doi.org/10.1098/rspa.1937.0142>
35. Mitić Ž, Nikolić G, Cakić M, et al. FTIR spectroscopic characterization of Cu(II) coordination compounds with exopolysaccharide pullulan and its derivatives. *J Mol Struct* 2009; 924-6: 264–73.
<https://doi.org/10.1016/j.molstruc.2009.01.019>
36. Jeremić K, Ilić Lj, Jovanović S. Kinetics of dextran depolymerization in aqueous HCl. *Eur Polym J* 1985; 21: 537–40.

37. Somogyi M. A new reagent for the determination of sugars. *J Biol Chem* 1945; 160: 61–68.
38. Shingel KI. Determination of structural peculiarities of dextran, pullulan and γ -irradiated pullulan by Fourier-transform IR spectroscopy. *Carbohydr Res* 2002; 337: 1445–51.
[https://doi.org/10.1016/S0008-6215\(02\)00209-4](https://doi.org/10.1016/S0008-6215(02)00209-4)
39. Wiberg E, Holleman AF, Wiberg N. *Inorganic Chemistry*, Academic Press, New York, 2001: 1478–9.
40. Cotton FA, Wilkinson G. *Advanced Inorganic Chemistry*. 4th ed. Wiley-Interscience, New York, 1980.
41. Bernhardt PV, Lawrance GA. Transition metal groups 9-12 Vol. 6, in: Fenton DE. (Eds.), *Comprehensive Coordination Chemistry II*, 2nd ed., Elsevier-Perigamon, USA, 2003: 2–122.
42. Bernhardt PV, Brik MG, Avram NM, Avram CN. Part III. Jahn-Teller Effect for the 3d Ions (Orbital Triplets in a Cubic Crystal Field), in: Köppel H, Yarkony DR, Barentzen H. (Eds.), *The Jahn-Teller Effect Fundamentals and Implications for Physics and Chemistry*, Berlin Heidelberg, Springer-Verlag, 2009: 347–70.
43. Cakić M, Mitić Ž, Nikolić GS, et al. The investigations of bioactive copper(II) complexes with reduced low-molecular dextran. *Spectroscopy* 2008; 22: 177–85.
<https://doi.org/10.1155/2008/754741>
44. Berglund B, Lindgren J, Tegenfeldt J. O-H and O-D stretching vibrations in isotopically dilute HDO molecules in some solid hydrates. *J Mol Struct* 1978; 43: 169–77.
[https://doi.org/10.1016/0022-2860\(78\)80004-0](https://doi.org/10.1016/0022-2860(78)80004-0)
45. Berglund B, Lindgren J, Tegenfeldt J. On the correlation between deuterium quadrupole coupling constants, O-H and O-D stretching frequencies and hydrogen-bond distances in solid hydrates. *J Mol Struct* 1978; 43: 179–91.
[https://doi.org/10.1016/0022-2860\(78\)80005-2](https://doi.org/10.1016/0022-2860(78)80005-2)
46. Brink G, Falk M. Infrared studies of water in crystalline hydrates: Ba (NO₂)₂•H₂O. *Spectrochim-Acta A* 1971; 27: 1811–15.

Spektroskopska karakterizacija kobalt(II) kompleksa sa redukovanim niskomolarnim derivatima dekstrana

Žarko Mitić¹, Goran M. Nikolić¹, Milorad Cakić², Sanja Mitić²,
Goran S. Nikolić², Stevo Najman¹

¹Univerzitet u Nišu, Medicinski fakultet, Niš, Srbija

²Univerzitet u Nišu, Tehnološki fakultet, Leskovac, Srbija

SAŽETAK

U radu je ispitivano formiranje kompleksa Co(II)-jona sa redukovanim niskomolarnim dekstranom (RNMD, Mw 5000 g/mol) u oblasti pH od 7,0 do 13,5. Sadržaj kobalta u sintetisanim Co(II)-RNMD kompleksima iznosi 3-12% (AAS) i generalno se povećava sa porastom pH. Co(II)-RNMD kompleksi okarakterisani su primenom metoda UV-Vis spektrofotometrije i FTIR spektroskopije. UV-Vis spektrofotometrijski podaci za sintetisane komplekse ukazuju na tetragonalno izobličenu Oh koordinaciju Co(II)-jona sa O atomima iz liganda. Prisustvo IR traka na 765 cm⁻¹ i 910 cm⁻¹ u Co(II)-RNMD kompleksima ukazuje na postojanje α -(1→6) O-glikozidnih veza. Sličnosti u oblasti γ (C-H) vibracija IR spektara ukazuju da nema razlika u konformaciji glukopiranoznih jedinica kod RNMD i u sintetisanim kompleksima Co(II)-RNMD. Prisustvo molekula vode u Co(II)-RNMD kompleksima potvrđeno je FTIR spektroskopijom deuterisanih uzoraka.

Ključne reči: Co(II)-dekstran, AAS, UV-Vis, FTIR