

Synthesis and Characterization of Transition Metal Complexes by solid interaction with Disaccharide—D-Lactose and coordination behavior

Pareek Bhawna

Department of Chemistry, Maharishi Markandeshwar (Deemed to be) University, Mullana-133207(Ambala), INDIA
dr.pareekbhawna@gmail.com

Abstract

A series of four different transition metals Nickle(II), Cobalt(II), Manganese(II) and Copper(II) D-Lactose mono hydrate have been synthesized and characterized by elementary analysis, molar conductivity measurements, thermo gravimetric analyses, infrared spectra, atomic emission and electronic spectral data. Even though the method for preparation of these compounds has been the same, but different compounds with different structural formula have been obtained. The infrared spectra of these complexes have demonstrated the same metal-ion-binding pattern in all these complexes.

The electronic spectra can propose the existence of the d-character of the electron transitions in these complexes to some extent. These stable, water soluble metal carbohydrate complexes can be used as suitable metal supplements in many biological systems.

Keywords: D-Lactose; Coordination modes; Metal disaccharide complexes.

Introduction

In living organisms, transition metal ions have crucial role where they are found to be coordinated to different biomolecules participating in many biochemical reactions. Interactions between metal ions and nucleosides, nucleotides polyalcohol's and other sugar-type ligands are involved in many biochemical processes in living organisms including immunological events recognition processes and pathological conditions¹.

Carbohydrates in general including natural and synthetic possess a manifold of donor atoms which enable them the ability to coordinate metal center and providing some additional advantages over other ligands e.g. biocompatibility, non-toxicity, enantiomeric purity, water solubility and well-explored chemistry. In recent years, several examples of carbohydrate compounds have been developed for diverse medicinal applications ranging from compounds with antibiotic, antiviral, or fungicidal activity and anticancer compounds^{2,3}. The applications of metal-carbohydrate complexes are not limited into the biological systems. They can be used not only for stoichiometric or catalytic stereo selective synthesis but also for separation and analysis of chiral compounds as well⁴⁻⁶.

In sugar alcohols, diols, triols, polysaccharides, metal-containing polymers, membranes, gels and fibers, saccharides act as polyolato ligands due to deprotonation of one or more hydroxyl groups⁷. Studying metal saccharides binding sites are not such straight forward task. On one hand, understanding the coordination behavior of sugar molecules is difficult because of their sensitive hygroscopic properties and complicated stereochemistry. On the other hand, due to the low stability of the synthesized metal complexes in neutral or acidic aqueous solutions, determining the binding sites of hydroxyl groups to the metal ions is difficult⁸.

Besides, in solutions of carbohydrates, existence of anomeric and conformational equilibrium for species makes the situation even more difficult⁹. In neutral environment, water molecules bonded to metal ions do not readily substitute donor oxygen atoms due to the low electron density of the oxygen atoms. In alkaline solutions after deprotonation of hydroxy groups, complexes of the metal ions with carbohydrate are formed.

Due to lactose capacity to interact with different metal ions involved in many biochemical reactions, it has a technological as well as a biological, medical, pharmaceutical, food and biomedical applications¹. Herein, metal complexes with D-Lactose mono hydrate have been synthesized and characterized by FT- IR, UV-Vis, AA and EA techniques.

Material and Methods

All materials D-Lactose mono hydrate, Ni(OAc)₂·4H₂O, CoCl₂·2H₂O, MnCl₂·2H₂O, CuCl₂·2H₂O, sodium metal and CH₃OH were of analytical reagent grade and were purchased from Merck and used without further purification. Infrared spectra (400–4000 cm⁻¹) were recorded from sodium hydroxides pellets on a Nicolet Impact 400 D spectrometer. Absorption spectra were recorded using Analyst 300.

Synthesis of the Metal(II)/(III)carbohydrate complexes: All complexes were prepared in an analogous procedure and a typical procedure for synthesis is given for one case.

Synthesis of Na₂[Cu(D-lac)₂]CH₃OH·5H₂O (1): D-Lactose mono hydrate (1.08 g, 3 mmol) was suspended in 10 mL of MeOH at 0 °C and stirred for 30 min. Freshly cut sodium metal (0.138 g, 6 mmol) was added with stirring and the stirring was continued for further 30 min until a white suspension in MeOH was formed. Copper(II)chloride dihydrate (0.1704 g, 1 mmol) was dissolved in 10 mL of methanol and added dropwise to the sodium salt suspension.

The resulting suspension was allowed to stir for further 12 h to develop a blue color in the reaction mixture. The solid was then filtered, recrystallized in hot methanol (40 °C) and dried under reduced pressure for 9 h to isolate a colored solid. These reactions resulted in products $\text{Na}_2[\text{Cu}(\text{D-lac})_2]\text{CH}_3\text{OH} \cdot 5\text{H}_2\text{O}$.

Results and Discussion

The isolated and purified metal-D-Lac complexes (1-7) are all moderately air stable, soluble in water, but insoluble in any common organic solvents. These complexes slowly capture moisture when exposed to air for several days. However, when the complexes are stored under dry conditions, they do not change colour even for more than several months. All the complexes reported in this study are found to yield products in the range 71-80

From the work done in the past we find that an attempt was made to prepare compounds of transition metals with saccharides. It illustrates that water solubility of the prepared compounds is the main obstacle in isolating them. To avoid this difficulty, de-novo method of solid interaction was selected which does not involve water either as solvent or as the reactant. Sodium salts of saccharides were first prepared which enable them to coordinate with metal ions. Metal salts in which metals were present in their most common oxidation states, were then treated with sodium salts of saccharides.

Formation of coordination compounds was indicated by isolation of crystalline compounds with different colours. These compounds after purification showed solubility in water as expected. M-O bonds were interpreted from I.R. spectra of the obtained compounds. The results are encouraging in explaining the coordination between metal ions and saccharides.

FT-IR spectra: The FTIR spectra of all the complexes (1-7) exhibited a broadened bands pattern expected for metal bounded saccharide¹¹. Usual line broadening was observed in all the saccharide complexes revealing the existence of the coordination of the metal ion through deprotonation of the hydroxyl group of the saccharides and the presence of

the covalency in metal-ligand bond as observed earlier in other cases of transition-metal-saccharide complexes¹².

A broad and intense band observed in the range 3340–3450 cm^{-1} is assigned to $\nu(\text{O-H})$ and indicates the breakage to some extent of the intermolecular hydrogen bonding, which is otherwise present in the solid of the free saccharide. However, these complexes are further indicative of the secondary interactions of saccharides through the free hydroxyl groups¹³.

The $\nu(\text{O-H})$ of H_2O also appears in this region and would overlap with this band. A band observed in the range 2900–2950 cm^{-1} is indicative of the (C-H) stretching vibrations in these complexes¹⁴. Although one-to-one assignments were not possible, the bands that appeared in the regions 1595–1635, 1370–1465 and 1060–1070 cm^{-1} were assignable to the bending vibrations of H_2O , stretching vibration of C-O, C-C and O-C, C-C respectively¹⁵. The IR spectra of the complexes exhibit new bands in the far-IR region at 500–625 cm^{-1} . These absorptions may be assigned to $\nu(\text{M-O})$ respectively¹⁶. Thus, the FT-IR studies have clearly demonstrated the binding of saccharide units to the metal ion and thereby exhibit the complex formation. The FT-IR spectra of ligand and all the complexes are shown in table 2.

Thermal Analysis: The TG and dTG of the complexes were recorded in the range of 25-900°C and showed similar thermal degradation patterns as the other cases of the metal saccharide complexes. An initial weight loss of 7.3% was observed in the range of 50-120 °C indicating the loss of NaOH ¹⁷. The data shows the loss of all the solvent molecules and the ligating saccharide moieties (a weight loss of 40-59%) during the total temperature scan range of 25-600°C, leaving the oxides of metals behind. Typical TG and dTG curves in the case of complexes 1 and 2 are shown in fig. 1 and fig. 2.

From these figures, it can be observed that an endothermic weight loss occurs up to 190 °C, which corresponds to the loss of one molecule of NaOH and H_2O . After this initial weight loss, pyrolysis of the saccharide moiety takes place in the range of 170-500 °C. Finally, the complete thermal degradation of the complexes results in formation of nickel oxide and copper oxide at 900 °C.

Table 1
FT-IR data for D-Lac-complexes (1-7)

Compound	$\nu(\text{M-O})/\text{cm}^{-1}$	$\nu(\text{C-O})/\text{cm}^{-1}$	$\nu(\text{O-H})/\text{cm}^{-1}$
$[\text{Cu}(\text{D-lac})_2]\text{CH}_3\text{OH} \cdot 5\text{H}_2\text{O}$ (1)	624 m	1068 s	3385 b,s
$[\text{Ni}(\text{D-lac})_2] 2\text{CH}_3\text{OH} \cdot 2\text{H}_2\text{O}$ (2)	468 w	1066 s	3384 b,s
$[\text{Mn}(\text{D-lac})_2] 3\text{CH}_3\text{OH} \cdot 2\text{H}_2\text{O}$ (3)	535 m	1067 s	3386 b,s
$\text{Na}_2[\text{Co}(\text{D-lac})_2] \text{CH}_3\text{OH} \cdot 4\text{H}_2\text{O}$ (5)	600 m	1070 s	3453 b,s

b = broad, s = strong, m = medium, w = weak

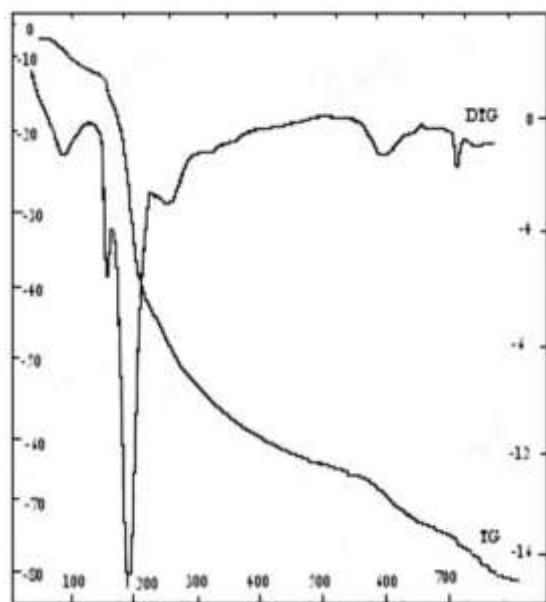


Figure 1: Thermogravimetric analysis for complex 1

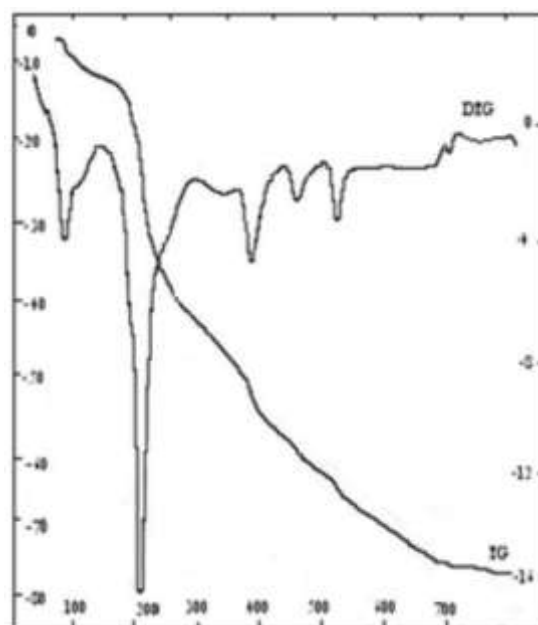


Figure 2: Thermogravimetric analysis for complex 2

Conclusion

The associated significance of transition-metal saccharide interactions in biological systems accounts for the importance of studying these interactions¹⁵. This kind of compound was reported in the solid state and well extended into our on-going research in the field of transition-metal saccharide chemistry. FT-IR and absorption spectra have demonstrated the direct binding of the saccharide moieties with the metal ions and the procedures reported here have led to the formation of mono-nuclear complexes.

Acknowledgement

I appreciate the moral support given to me by the Head of Department of Chemistry, Govt. College, Ajmer to complete the research work. I am also thankful to the laboratory staff who helped me in every stage of my work. I am indebted to the R.S.E.I section of C.D.R.I. Lucknow for analyzing my samples for I.R. studies.

References

- Verissimo L.M., Ribeiro V.C., Ribeiro A.C., Melia Rodrigo M. and Esteso M.A., Influence of lactose on the diffusion of calcium ions at physiological, Temperature, *Food Chemistry*, **163**(15), 284–288 (2014)
- Shivankar V.S. and Thakkar N.V., Chiral mixed ligand Co(II) and Ni(II) complexes: synthesis and biological activity, *Acta Poloniae Pharmaceutica*, **61**(2), 127-133 (2004)
- Burkhardt A., Buchholz A., Görls H. and Plass W., Synthesis, Structure and Magnetic Properties of a Tetranuclear Copper(II) Complex on the Basis of a 2-Substituted Glucopyranoside Schiff Base Ligand, *European Journal of Inorganic Chemistry*, **206**(17), 3400-3406 (2006)
- Lippold J., Becher J., Klemm D. and Plass W., Chiral oxovanadium(V) complexes with a 6-amino-6-deoxyglucopyranoside-based Schiff-base ligand: Catalytic

asymmetric sulfoxidation and structural characterization, *Journal of Molecular Catalysis A: Chemical*, **299**, 12-17 (2009)

- Yang L., Su Y., Wu J., Liu W. and Jin X., Sugar interaction with metal ions. The coordination behavior of neutral galactitol to Ca(II) and lanthanide ions, *Carbohydrate Research*, **337**(16), 148-1493 (2002)
- Bazito R.C. and Seoud O.A. El, Sugar-based anionic surfactants: synthesis and micelle formation of sodium methyl 2-acylamido-2-deoxy-6-O-sulfo-d-glucopyranosides, *Carbohydrate Research*, **332**(1), 95-102 (2001)
- Geibelmann A., Klufers P., Kropfgans C., Mayer P. and Piotrowski H., Carbohydrate-Metal Interactions Shaped by Supramolecular Assembling, *Angewandte Chemie International Edition*, **44**(6), 924-927 (2005)
- Saladini M., Ferrari E. and Menabue L., Co-ordination of transition metal ions by galactaric acid: a potentiometric and spectroscopic study, *Journal of Inorganic Biochemistry*, **92**(2), 121-127 (2002)
- Cerchiaro G., Carlos A. and Costa Ferreira A., Investigations of different carbohydrate anomers in copper(II) complexes with d-glucose, d-fructose and d-galactose by Raman and EPR spectroscopy, *Carbohydrate Research*, **340**(15), 2352-2359 (2005)
- Geetha K., Raghavan M.S.S., Kulshreshtha S.K., Sasikala R. and Rao C.P., Transition-metal saccharide chemistry: synthesis, spectroscopy, electrochemistry and magnetic susceptibility studies of iron(III) complexes of mono- and disaccharides, *Carbohydrate Research*, **27**(2), 163-175 (1995)
- Caki M.D., Nikolić G.S. and Ilić Lj. A., FTIR spectra of iron(III) complexes with dextran, pullulan and inulin oligomers, *Bull. Chem. Technol. Macedon*, **21**(2), 135-146 (2002)
- Yang L., Tian W., Xu Y., Su Y., Gao S., Wang Z., Weng S., Yan C. and Wu J., Interactions between metal ions and carbohydrates: the coordination behavior of neutral erythritol to

transition metal ions, *Journal of Inorganic Biochemistry*, **98**(8), 1284-1292 (2004)

13. Mukhopadhyay A., Kolehmainen E. and Rao C.P., Lanthanide-saccharide chemistry: synthesis and characterisation of Ce(III)-saccharide complexes, *Carbohydrate Research*, **324**(1), 3-37 (2000)

14. Etcheverry S.B., Barrio D.A., Williams P.A.M. and Baran E., On the interaction of the vanadyl(IV) cation with lactose, *Biological Trace Element Research*, **84**(1), 227-238 (2001)

15. Bandwar R.P. and Rao C.P., *Carbohydrate Research*, **297**, 341-346 (1997)

16. Swamy S.J., Reddy E.R., Raju D.N. and Jyothi V., Synthesis and Spectral Investigations of Manganese(II), Cobalt(II), Nickel(II), Copper(II) and Zinc(II) Complexes of New Polydentate Ligands Containing a 1,8-Naphthyridine Moiety, *Molecules*, **11**(12), 1000-1008 (2006)

17. Bandwar R.P., Rao C.P., Giralt M., Hidalgo J. and Kulkarni G.U., Transition-Metal Saccharide Chemistry and Biology-Saccharide Complexes of Cu(II) and their effect on in Vivo Metallothionein Synthesis in Mice, *Journal of Inorganic Biochemistry*, **23**(1), 37-44 (1997)

18. Bandwar R.P. and Rao C.P., Transition-metal saccharide chemistry: synthesis and characterization of d-glucose, d-fructose, d-galactose, d-xylose, d-ribose and maltose complexes of Ni(II), *Carbohydrate Research*, **297**(4), 341-346 (1997)

19. Zhang W., Jiang T., Ren S., Zhang Z., Guan H. and Yu J., Metal-N-saccharide chemistry: synthesis and structure determination of two Cu(II) complexes containing glycosylamines, *Carbohydrate Research*, **339**(12), 2139-2143 (2004).

(Received 22nd August 2019, accepted 24th October 2019)