



Synthesis and Characterization of Transition Metal Complexes with Disaccharide–D-Lactose

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Abstract A series of seven different transition metals Nickel(II), Cobalt(II), Manganese(II), Iron(III), Zinc(II), Copper(II) and Cerium(II) complexes with 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 have been the same, but different compounds with different structural formula have been obtained. The infrared spectra spectrums of these complexes have demonstrated the same metal-ion-binding pattern in all these complexes. The electronic spectrums 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 a suitable metal supplements in many biological systems.

Keywords D-Lactose; Coordination modes; Metal disaccharide complexes

1. Introduction

In living organisms, transition metal ions have crucial role where they are found to be coordinated to different biomolecules and participating in many biochemical reactions. Interactions between metal ions and nucleosides, nucleotides polyalcohols and other sugar-type ligands are involved in many biochemical processes in living organisms, including immunological events recognition processes, and pathological conditions [1]. 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 well [4-6]. 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 groups [7]. 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 are difficult [8]. Besides, in solutions of carbohydrates, existence of anomeric and conformational equilibrium for species makes the situation even more difficult [9]. In neutral environment, water molecules bonded to metal ions do not readily substitute by 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 can form. 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 TG, FT- IR, UV-Vis, AA, AES and EA techniques.

Experimental

Materials and Methods

All materials (D-Lactose mono hydrate, Ni(OAc)₂.4H₂O, CoCl₂.2H₂O, MnCl₂.2H₂O, ZnCl₂, (NH₄)₂Ce(NO₃)₆, FeCl₃.6H₂O, CuCl₂.2H₂O, sodium metal and CH₃OH) were analytical reagent grade and were purchased from Merck and used without further purification. Infrared spectra (400–4000 cm⁻¹) were recorded from KBr pellets on a Nicolet Impact 400 D spectrometer. Absorption spectra were recorded using Analyst 300, Perkin Elmer Co. USA spectrophotometer. Elemental analyses were carried out on a CHNS analyzer, CHNS-932, Leco, USA elemental analyzer. Metal contents were determined using atomic emission spectroscopy (AES) Analyst 300, Perkin Elmer Co. USA analyzer. Thermogravimetric analyses were performed on a Model Setaram Labsys TG-DSC instrument with synthetic air in a 50 mL/min flow. All conductivity measurements were performed in water using a Shanghai DDS-11A conductivity apparatus at 25 °C the concentration of the solution was 10⁻³ mol L⁻¹.

Synthesis of the Metal(II)/(III)carbohydrate complexes

All complexes were prepared in an analogous procedure, and a typical procedure for synthesis is given below for one case.

Synthesis 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 a 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 a 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 Na₂[Cu(D-lac)₂]CH₃OH.5H₂O (1), Na₂[Ni(D-lac)₂]2CH₃OH.2H₂O (2), Na₂[Mn(D-lac)₂]3CH₃OH.2H₂O (3), Na₂[Fe(D-lac)₂OH]CH₃OH.3H₂O (4), Na₂[Co(D-lac)₂] CH₃OH.4H₂O (5), Na₂[Zn(D-lac)₂]2CH₃OH.2H₂O (6), Na₂[Ce(D-lac)₂(OH)₂]CH₃OH.3H₂O (7).

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 month. All the complexes reported in this paper are found to yield products in the range 71-80 %. The proposed formula, elemental analysis of metal-D-Lac complexes (1-7) are listed in Table 1. The observed conductivities (Table 1) of the complexes (1-7) suggest that all compounds are electrolytes in water and are consistent with 2:1 electrolytes [10].

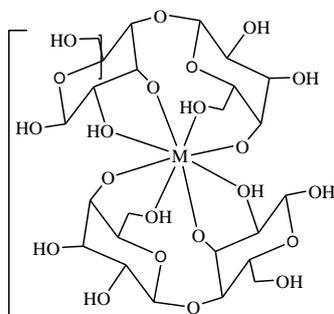


Figure 1: Proposed structures for complexes 1-3



Table 1: Proposed molecular formula and elemental analysis in (%) for metal-D-Lac complexes (1–7)

Compound	Elemental analyses/(%) calculated (found)				Molar conductance
	C	H	Na	metal	$\lambda_m(\Omega^{-1}\text{mol}^{-1}\text{cm}^2)$
(1)	32.99 (33.25)	5.77 (5.89)	5.05 (4.98)	6.98 (6.82)	173
(2)	35.34 (35.11)	5.72 (5.82)	5.21 (5.35)	6.64 (6.58)	121
(3)	35.57 (35.64)	5.98 (5.86)	5.04 (5.14)	6.02 (6.23)	169
(4)	33.98 (33.94)	5.59 (5.68)	5.20 (4.95)	6.32 (6.53)	109.5
(5)	33.83 (33.91)	5.68 (5.62)	5.18 (5.19)	6.64 (6.68)	149.5
(6)	35.08 (35.29)	5.67 (5.67)	5.16 (5.32)	7.34 (7.42)	150.9
(7)	30.49 (30.34)	5.12 (4.99)	4.67 (4.96)	14.23 (14.03)	138.3

FT-IR spectra

The FTIR spectra of all the complexes (1–7) exhibited a broadened bands pattern expected for metal bounded saccharide [11]. 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 complexes [12]. 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 groups [13]. 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 complexes [14]. 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, respectively [15]. 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 $\nu(\text{M-O})$ respectively [16]. 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 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 MeOH [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 MeOH 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 result formation of nickel oxide and copper oxide at 900 °C.

Table 2: FT-IR data for D-Lac-complexes (1-7)

Compound	$\nu(\text{M-O})/\text{cm}^{-1}$	$\nu(\text{C-O})/\text{cm}^{-1}$	$\nu(\text{O-H})/\text{cm}^{-1}$
$\text{Na}_2[\text{Cu}(\text{D-lac})_2]\text{CH}_3\text{OH}.5\text{H}_2\text{O}$ (1)	624 m	1068 s	3385 b,s
$\text{Na}_2[\text{Ni}(\text{D-lac})_2]2\text{CH}_3\text{OH}.2\text{H}_2\text{O}$ (2)	468 w	1066 s	3384 b,s
$\text{Na}_2[\text{Mn}(\text{D-lac})_2]3\text{CH}_3\text{OH}.2\text{H}_2\text{O}$ (3)	535 m	1067 s	3386 b,s
$\text{Na}_2[\text{Fe}(\text{D-lac})_2\text{OH}]\text{CH}_3\text{OH}.3\text{H}_2\text{O}$ (4)	530 w	1067 s	3385 b,s
$\text{Na}_2[\text{Co}(\text{D-lac})_2]\text{CH}_3\text{OH}.4\text{H}_2\text{O}$ (5)	600 m	1070 s	3453 b,s
$\text{Na}_2[\text{Zn}(\text{D-lac})_2]2\text{CH}_3\text{OH}.2\text{H}_2\text{O}$ (6)	625 m	1068 s	3385 b,s
$\text{Na}_2[\text{Ce}(\text{Dlac})_2(\text{OH})_2]\text{CH}_3\text{OH}.3\text{H}_2\text{O}$ (7)	562m	1065 s	3386 b,s

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



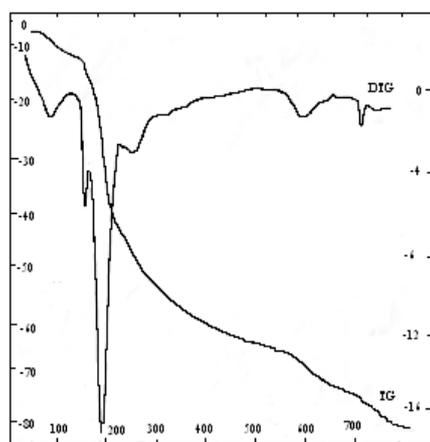


Figure 1: Thermogravimetric analysis for complex 1

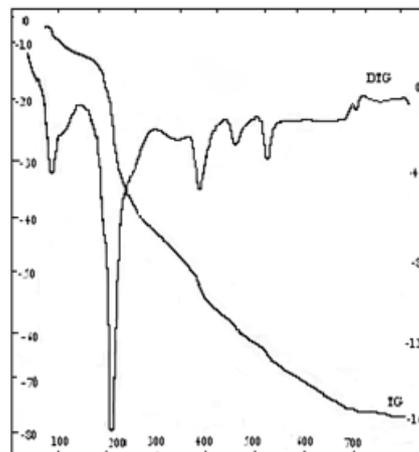


Figure 2: Thermogravimetric analysis for complex 2

Electronic Spectroscopy

The aqueous solution absorption spectra were recorded in the range 190–800 nm, and the corresponding data are reported in Table 3, Fig. 3. The solution absorption bands observed in the regions of 195–205 nm are attributed to the internal ligand transfers ($n \rightarrow \sigma^*$)⁹. The bands observed in the regions of 270–370 nm may correspond to oxo \rightarrow metal charge transfer transitions indicating the formation of a metal-saccharide complex as the formation of such complex was considered in the reaction between metal ions and D-Lactose monohydrate. The other bands observed around 520–680 nm are characteristic of the $d-d$ transitions for octahedral. The Zn(II) (d^{10}), Ce(IV) (P^6), complexes do not exhibit any characteristic $d-d$ transitions [18]. The band observed in the visible region, 682 for Cu(II) complex was assignable to the ${}^2E_g \rightarrow {}^2T_{2g}$ [19] and band observed in the visible region 520 nm in the Ni(II) complex was assignable to the ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ transition arising from a distorted octahedral d^8 system. However, the ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transition was masked by a strong LMCT band at ~ 370 nm which was otherwise present in the spectra of the precursors [20].

Table 3: UV-Vis data of aqueous solution absorption for 1–7

Compound	λ (nm)
1	245,682
2	195,520
3	235,250,280
4	235,300,530
5	195,275,525
6	205,270
7	195,275

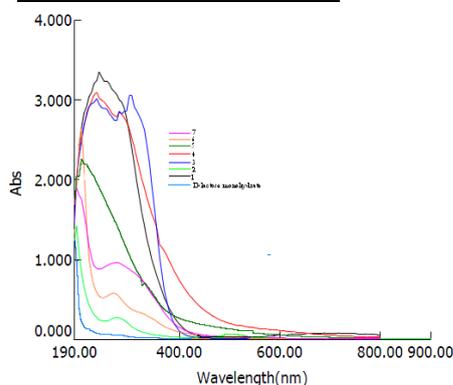


Figure 3: Aqueous absorption spectra of the ligand D-lactose monohydrate and metals-disaccharide complexes, 1-7



Conclusion

The associated significance of transition-metal saccharide interactions in biological systems accounts for the importance of studying these interactions [21]. The first row metal ions-D-Lactose mono hydrate complexes mentioned in this paper are the first of this kind of compound reported in the solid state, and well extend into our on-going research in the field of transition-metal saccharide chemistry. While the FT-IR and absorption spectra have demonstrated the direct binding of the saccharide moieties with the metal ions, the procedures reported here has led to the formation of mono-nuclear complexes.

Acknowledgements

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