Transition metal–saccharide chemistry: D-glucose complexes of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II)

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Metal complexes of D-glucose (D-Glc) from large cation containing dibromo-dichloro salts of dipositive metals [NEt$_4$]$_2$[MBr$_2$Cl$_2$] (M = Mn, Co, Ni, Cu and Zn) and the disodium salt of glucose were synthesized from a MeOH:MeCN mixture. The complexes were characterized by UV-vis absorption, circular dichroism, IR and proton magnetic resonance spectroscopies, and by elemental analysis, and were found to be Na[M(D-Glc)(OMe)Cl]. Cyclic voltammetric studies of these complexes, in the acidic to neutral pH range, indicated no dissociation, even in highly acidic conditions.

Keywords: Co(II), complexes, Cu(II), glucose, Mn(II), Ni(II), saccharide, transition metal, Zn(II).

Introduction

Saccharide molecules possess multihydroxy functionality and this aspect is expected to act as a key in complexation with transition metals to produce saccharide complexes of diverse nature and with a multitude of roles in biology, medicine, catalysis, etc. The relationship between structure and complex formation of neutral carbohydrates with non-transition metal cations was first discussed by Angyal who has also given an extensive account of these interactions in solution (Angyal & Davies 1971, Angyal 1989, 1990). Although there is a volume of information, including the crystal structures, available in the literature regarding the interactions of saccharides with alkali and alkaline earth and other non-transition metal ions (Rendleman 1966a,b, Tajmir-Riahi 1987, 1988, 1990), there is not much information available regarding transition metal–saccharide complexes. This can be mainly attributed to the low reactivity of the hydroxyl groups of the saccharides. The only crystallographically characterized complexes obtained are from the reactions of amines of Co^{3+} and Ni^{2+} with saccharides resulting in the complexation of amino-glycosides in the coordination sphere (Yano 1988). The complex formation by amine derivatives of glucose is known in the literature (Micera *et al.* 1985, Lerivrey *et al.* 1986). Nagy *et al.* (1990) have reported the formation of metal complexes with carbohydrates and nucleotides. This subject has recently been reviewed by Burger & Nagy (1990) and Geraldes & Margarida (1990). In attempts to develop methods to synthesize transition metal saccharide complexes, we have recently reported (Rao *et al.* 1990, 1992, 1994, Rao & Kaiwar 1991, 1993, Kaiwar and Rao 1992) D-glucose (D-Glc) complexes of early first row transition elements, and D-Glc and D-fructose complexes of Fe(III) and Cr(III). In the present paper, we report the results of D-Glc complexes of various divalent first row metal ions such as manganese, cobalt, nickel, copper and zinc starting from [NEt$_4$]$_2$[MCl$_2$Br$_2$] salts.

Materials and methods

Materials

D-Glc was purchased from Allied Chemicals, General Chemical Division, USA (ACS Code 1682), sodium metal was from Merck, tetraethylammonium bromide and metal salts were procured from local commercial sources except MnCl$_2 \cdot$4H$_2$O (Merck, India) and CuCl$_2 \cdot$2H$_2$O (BDH, India). All solvents used were dried and distilled using established procedures.

Methods

UV-vis absorption spectra were measured on a Shimadzu UV-260 spectrophotometer. Circular dichroism (CD) measurements were performed on a JASCO J-600 spectropolarimeter. IR spectra were measured in a KBr matrix on a Perkin Elmer 681 spectrophotometer. Proton Magnetic

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resonance (PMR) spectra in D_2O were recorded on a Varian XL-300 spectrometer. Cyclic voltammetry was performed on a BAS-100B electrochemical analyzer. Metal and sodium contents were determined by inductively coupled plasma atomic emission spectroscopy (IC-PAES).

Sodium salt of D-Glc

All complexes were synthesized from the disodium salt of D-Glc in MeOH as described in an earlier paper (Kaiwar & Rao 1992).

Bis(tetraethylammonium)dibromodichlorometal(II) [NEt₄]₂[MCl₂Br₂] (M = Mn, Co, Ni, Cu and Zn)

These starting metal complexes were prepared by mixing ethanolic solutions of metal(II) dichloride and tetraethylammonium bromide in a 1:2 molar ratio. The crystalline products obtained were recrystallized from a 60:40 MeOH:absolute EtOH mixture. This is similar to the procedure reported in the literature for [NEt₄]₂[MX₄] (Gill & Taylor 1967).

General method of reaction

The [NEt₄]₂[MCl₂Br₂] solution in MeCN was added to the *in situ* generated methanolic solution of the disodium salt of D-Glc with stirring. In all the reactions, a 1:3 metal: saccharide molar ratio was employed. After the addition, the reaction mixture was stirred for a further period of about 2 days until no further change in the color was observed. The reaction mixture was filtered, and the residue collected on a frit was washed with diethyl ether and further dried *in vacuo*. Since the bulk of the compound was found to be insoluble in solvents other than water, it was washed by stirring in MeOH for approximately 2 days, followed by MeCN for 2 more days and finally in hexane for about 1 day, in order to remove, by dissolving, any unwanted impurities of varying polarities, which may include unreacted D-Glc, tetraethylammonium and/or sodium salts, likely to get co-precipitated with the complex formed. Finally, after filtering, the product was dried *in vacuo*. Other details of the reactions are provided in individual cases.

Manganese–D-Glc complex

[NEt₄]₂[MnCl₂Br₂] (2.184 g, 4 mmol) in MeCN (15 ml) was added to a D-Glc (2.162 g, 12 mmol) and sodium (0.624 g, 24 mmol) mixture in MeOH (100 ml) which resulted in a brown color and a large amount of precipitate. This changed to a yellowish-brown precipitate after stirring for 12–15 h and remained unchanged even after one more day of stirring. The residue Mn–Glc, after purification, corresponds to a molecular formula of Na[Mn(D-Glc)(OMe)Cl] based on the elemental analysis.

Analysis. Calculated for $C_7H_{14}Mn_1Na_1O_7Cl_1$: C, 25.97; H, 4.33; Mn, 16.99; Na, 7.11; Cl, 10.98. Found: C, 26.38; H, 3.76; Mn, 16.69; Na, 7.31. Satisfactory results were

obtained for the chloride content by Mohr's method. Cathodic reduction potentials, E_p^c, at hanging mercury drop electrode (HMDE) at different pH values: -1.47 V (2.0), -1.55 V (4.0), -1.56 V (6.0), -1.59 V (7.0), -1.62 V (8.0) and -1.63 V (9.0).

Cobalt–D-Glc complex

[NEt₄]₂[CoCl₂Br₂] (2.201 g, 4 mmol) in MeCN (20 ml) was added to a D-Glc (2.163 g, 12 mmol) and sodium (0.6 g, 24 mmol) mixture in MeOH (140 ml). The brownish-red mixture changed to brown after 12–18 h and remained the same for another day. The purified residue, Co–Glc, corresponds to a molecular formula of Na[Co(D-Glc) (OMe)Cl] with 0.4 NaCl and 0.2 NEt₄Br as shown by the elemental analysis.

Analysis. Calculated for $C_{8.6}H_{18}N_{0.2}Co_1Na_{1.4}O_7Cl_{1.4}Br_{0.2}$: C, 26.27; H, 4.58; N, 0.71; Co, 15.00; Na, 8.20; Cl, 12.65; Br, 4.07. Found: C, 25.78; H, 3.98; N, 0.46; Co, 15.40; Na, 8.33. Halide percents found to be satisfactory by Mohr's method. E_p^c values at various pH: -0.80 V, -1.40 V (2.0), -1.11 V, -1.45 V (4.0); -1.12 V, -1.71 V (6.3) and -1.13 V, -1.80 V (8.0).

Nickel–D-Glc complex

[NEt₄]₂[NiCl₂Br₂] (1.099 g, 2 mmol) in MeCN (10 ml) was added to a D-Glc (1.081 g, 6 mmol) and sodium (0.45 g, 19 mmol) mixture in MeOH (75 ml). A pale green residue initially obtained changed to yellow after 1 day of stirring and remained the same for another day. This product, Ni–Glc, was collected and purified as mentioned earlier, and as shown by the elemental analysis, corresponds to molecular mixtures of Na[Ni(D-Glc)(OMe)Cl], 0.1 NEt₄Br and 0.8 NaCl.

Analysis. Calculated for $C_{7.8}H_{16}N_{0.1}O_7Ni_1Na_{1.8}Cl_{1.8}Br_{0.1}$: C, 23.70; H, 4.05; N, 0.35; Ni, 14.86; Na, 10.48; Cl, 16.18; Br, 2.03. Found: C, 23.92; H, 4.35; N, 0.20; Ni, 14.69; Na, 10.51. E_p^c values at various pH: -1.20 V (2.0), -1.25 V (4.0), -1.25 V, -1.47 V (6.0) and -1.26 V, -1.48 V (8.0).

Copper–D-Glc complex

[NEt₄]₂[CuCl₂Br₂] (1.087 g, 2 mmol) in MeCN (20 ml) was added to a D-Glc (1.084 g, 6 mmol) and sodium (0.29 g, 12.6 mmol) mixture in McOH (75 ml). A green residue obtained initially persisted even after 2 days. On filtering through a G-3 frit, a grey colored residue was obtained and the filtrate showed some bluish turbidity. On filtering this filtrate through a G-4 frit, a hygroscopic blue residue was obtained which turned to a syrupy black mass which could not be dried by the general method. On dissolving this syrupy mass in H_2O, a dark green solution resulted and only its aqueous solution absorption spectrum was measured. However, the residue (from G-3 frit), Cu–Glc, after purification gave some insoluble fraction in H_2O, but was totally soluble in acidic conditions. Therefore it can be

a mixture of Na[Cu(D-Glc)(D-Glc)], 2[Cu(D-Glc)₂], 0.5 Et₄NBr·H₂O and 5.5 NaCl as shown by the elemental analysis.

Analysis. Calculated for $C_{40}H_{76}N_{0.5}Cu_3Na_{6.5}O_{36.5}Cl_{5.5}$ $Br_{0.5}$: C, 27.87; H, 4.41; N, 0.41; Cu, 11.07; Na, 8.68; Cl, 11.34; Br, 2.32. Found: C, 27.48; H, 4.82; N, 0.40; Cu, 11.32; Na, 8.73. Halides (Cl and Br) were estimated by Mohr's method and found to be in agreement with the calculated values.

Zinc–D-Glc complex

[NEt₄]₂[ZnCl₂Br₂] (1.15 g, 2.1 mmol) in MeCN (20 ml) was added to a D-Glc (1.12 g, 6.22 mmol) and sodium (0.298 g, 13 mmol) mixture in MeOH (70 ml) resulting in a white turbidity and this remained unchanged for 1 day. The white residue, Zn–Glc, corresponds to a formula Na[Zn(D-Glc)(OMe)Cl]·H₂O plus 0.3 NaCl and 0.1 NEt₄Br salts based on the elemental analysis.

Analysis. Calculated for $C_{7.8}H_{18}N_{0.1}O_8Zn_1Na_{1.3}Cl_{1.3}Br_{0.1}$: C, 23.97; H, 4.61; N, 0.36; Zn, 16.75; Na, 7.66; Cl, 11.82; Br, 2.05. Found: C, 23.48; H, 4.15; N, 0.22; Zn, 16.91; Na, 7.27. E_p^c values at various pH: −1.05 V, −1.38 V (4.0), −1.14 V, −1.39 V (6.5), −1.13 V and −1.28 V (from −1.14 V of previous pH), −1.5 V broad (7.5).

Results and discussions

The complexes prepared by the described method utilize the dibromo-dichloro salts of divalent transition metal ions, i.e. manganese, cobalt, nickel, copper and zinc. This gives a starting material with a preformed metal center having four easy leaving groups and thus facilitating the formation of metal–D-Glc complexes in non-aqueous solvents. All the D-Glc complexes are highly soluble in

water. These are characterized using UV-vis absorption, CD, IR, PMR, elemental analysis and CV techniques.

The aqueous solution absorption spectra of Ni–Glc and Co–Glc complexes (Fig. 1A) are characteristically tetrahedral and are different from their precursor molecules (Fig. 1B), indicating the formation of the complex through oxygen atoms. The diffuse reflectance spectra agree well with the solution ones, indicating that there is no change in the nature of the complex even in the solution. Complex formation and the tetrahedral geometry of the metal center are confirmed in all the cases (except those of manganese and zinc) after comparing with spectra of precursor molecules in the visible region. D-Glc complexes of Mn²⁺ (d⁵) and Zn²⁺ (d¹⁰) do not give absorption spectra in the visible region, as expected.

The CD spectra of the aqueous solutions of the complexes (Fig. 2) exhibit curves at almost the same positions as in the absorption spectra, thus indicating these transitions to be CD active. Moreover, the similar signs of
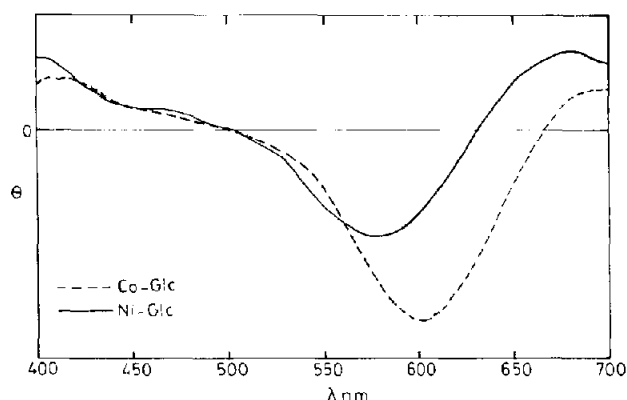
Figure 2. CD curves of Co–Glc (θ_{601} = −33.4 mdeg) and Ni–Glc (θ_{582} = −1.2 mdeg) in H₂O using a 3.0 cm cell.
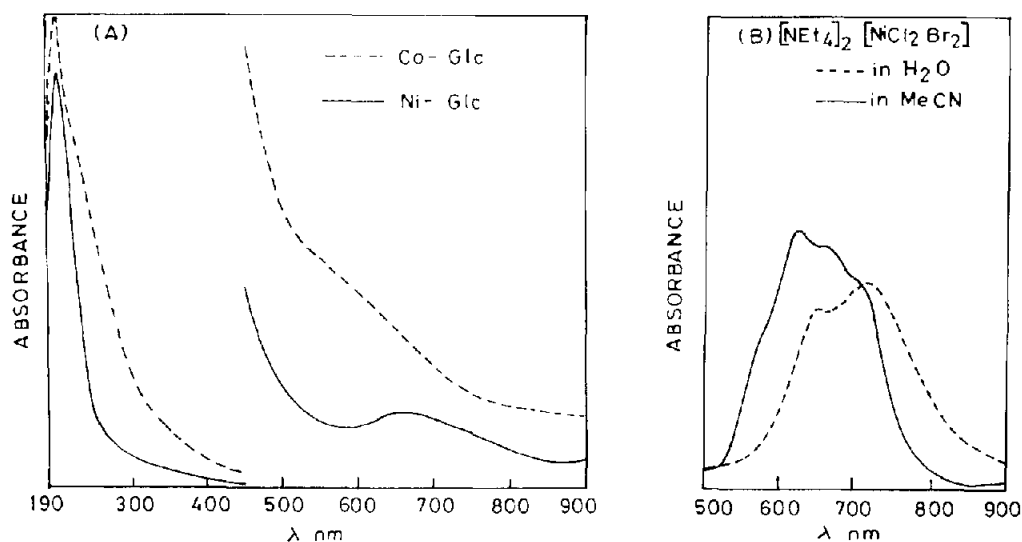
Figure 1. UV-vis absorption spectra of (**A**) Co–Glc and Ni–Glc in H₂O. Pathlengths: 900–450 nm (5.0 cm); 450–190 nm (0.5 cm). (**B**) [NEt₄]₂[NiCl₂Br₂] in H₂O and in MeCN.

rotation of these curves suggests that the coordination geometries in these complexes are similar and the overall configurations are identical.

IR spectra of the complexes (Fig. 3) indicate an overall breakage of extensive intermolecular hydrogen bonding, on complex formation, exhibiting an almost symmetric band around $3400 \, cm^{-1}$ accompanied by a small low frequency component as a shoulder at $3250 \pm 10 \, cm^{-1}$. The intermolecular hydrogen bonded species is otherwise present in the free D-Glc (Gritsan *et al.* 1983, Tajmir-Riahi 1987) as shown by characteristic ν_{O-H} bands around $3240-3460 \, cm^{-1}$. Probable interactions through sodium ions are observed as a low OH stretching frequency at $3400 \, cm^{-1}$. The $3250 \, cm^{-1}$ shoulder can be assigned to some intermolecular hydrogen bonded species. This region is further overlapped with ν_{OH} of water molecules. The bands observed around $1600 \pm 10 \, cm^{-1}$ can be assigned to the bending vibrations of H_2O present in the compounds. However, this can be also due to some $>C=O$ groups, which possibly can arise from the epimerized product of the bound saccharide, resulting in an open form. In fact, an open aldehyde group ($< 5\%$) has been observed in the PMR spectra at 8.46 p.p.m. The sharp bands observed in free D-Glc in the regions of
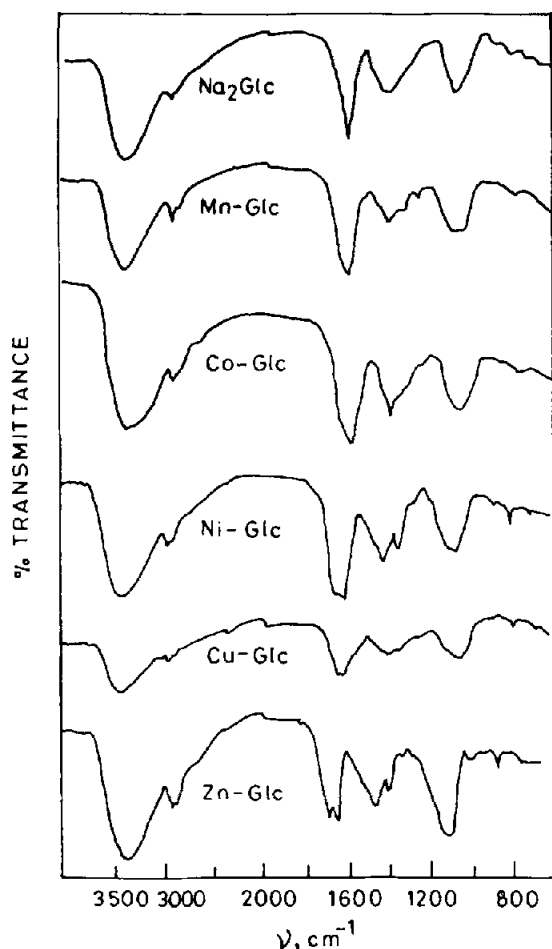

Figure 3. IR spectra of D-Glc complexes in KBr.

$1340-1460 \, cm^{-1}$ $[\delta_{(OCH.CH_2.CCH)}]$, $990-1140 \, cm^{-1}$ $[\nu_{(CO.CC)}]$ and $770-840 \, cm^{-1}$ $[\delta_{(CCH.CH)}, \nu_{(CC.CO)}]$ are merged and broadened into three groups around 1400, 1080 (with shoulders at 1100 and $1040 \, cm^{-1}$) and $800 \, cm^{-1}$, respectively, indicating the presence of metal–saccharide interactions. Whereas Tajmir-Riahi had reported sharp bands for the non-transition metal–saccharide adducts (Tajmir-Riahi 1987, 1989), the interactions with the transition metals seems to influence the skeletal vibrations. Consequently, the information obtained in the $600-900 \, cm^{-1}$ region is not sufficient to derive any definite conclusion regarding the anomeric nature of the complexes. As a matter of fact, broad bands are observed in almost all the transition metal–saccharides complexes reported so far by us (Rao *et al.* 1984, 1990, 1992, Rao and Kaiwar 1991, 1992, 1993, Kaiwar and Rao 1992).

In the PMR spectra, taken in D_2O, the peaks corresponding to the saccharide in the range 3.5–4.5 p.p.m. are merged and broadened upon complexation as compared with that of free saccharide and hence are difficult to assign to individual protons. The broadening is extensive in the case of highly paramagnetic metals like manganese and to some extent in cobalt. The presence of ethyl groups of the NEt_4^+ ion is indicated by CH_3 (1.25 p.p.m.) and CH_2 (3.26 p.p.m.) peaks. The methoxy proton resonance occur at 3.38 p.p.m., indicating its involvement in the complexation. There is also formation of some open aldehydic product ($< 5\%$) as shown by the ratio of 8.46 to 3.5–4.5 p.p.m. resonances, which can be attributed to the epimerization of the saccharide used due to the interaction with the metal.

The formulae of the complexes were proposed on the basis of elemental percentages and keeping in view some other aspects derived from the above mentioned studies. As a matter of fact, the nitrogen percent and the sodium content served as useful guidelines for the quantitative presence of trace amounts of NEt_4Br and NaCl. As the compounds are hygroscopic and are not handled in anaerobic conditions, the hydrogen percentages are generally hampered.

The cyclic voltammetric studies of the metal complexes of D-Glc were carried out in N_2 purged aqueous solutions, at HMDE, using Me_4NCl as the supporting electrolyte, Ag/AgCl as the reference electrode and at a scan speed of $100 \, mV \, s^{-1}$. These studies were conducted at different pH values from acidic to neutral and compared with those of starting materials. At higher pH values (pH $\geqslant$ 9.0), it was difficult to study the electrochemical behavior due to the formation of metal hydroxides. All the complexes exhibit irreversible cathodic reduction peaks depending on the pH of the solution. The cyclic voltammograms are shown in Fig. 4(a–d). As evident from the data, the cathodic peak potential, E_p^c, for the reduction of $M^{2+} \rightarrow M^+$ shifts to more negative values. This can be attributed to the stronger binding of the metal with the saccharide moiety as the pH is increased, due to deprotonation of several free hydroxyl groups. However, at pH ~ 8, the cathodic wave seems to be splitting (-1.14 V wave of pH 6.5 splitting into -1.13 V and -1.28 V in the case of Zn–Glc)
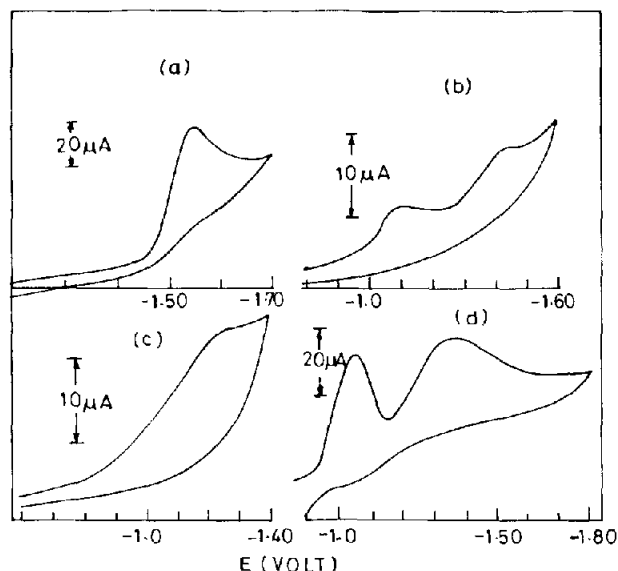
Figure 4. Cyclic voltammograms of D-Glc complexes in H_2O at pH 4.0, at HMDE. Scan speed 100 mV s^{-1}. (a) Mn–Glc, (b) Co–Glc, (c) Ni–Glc and (d) Zn–Glc.

probably due to formation of some different species having a weaker binding to the metal ion thus allowing the reduction $M^{2+} \rightarrow M^+$ to take place at lower cathodic potentials. Moreover, the absence of reversible voltammograms ($M^{2+} \rightleftharpoons M^+$) even at low pH suggests that the complexes are not hydrolyzed and the free metal ion is not liberated, indicating the stability of the complexes in acidic solutions. We have reported a similar behavior for iron–saccharide complexes in the pH range 2–12 (Rao *et al.* 1992, 1994). However, the copper complex shows a completely reversible peak at pH ~ 2 characteristic of Cu(II)-aquo species.

Conclusions

The complexes possess a D-Glc moiety, a methoxy and a chloride as ligands. The methoxy group participation (which is confirmed from the PMR spectra) is due to the formation of methoxide during preparation of the disodium salts of saccharides in MeOH, which, because of its basicity, is a good ligating group in non-aqueous solvents. Thus, one can expect the formation of the complexes of the type $Na[M(D-Glc)(OMe)Cl]$ from $[NEt_4Br]_2$ $[MCl_2Br_2]$, from an MeOH:MeCN mixture, where both the bromides are easily removed along with one of the chlorides. The copper complex, however, exhibited a slightly different behavior, as mentioned in the experimental section, and therefore it is proposed to be a mixture of a neutral and an ionic product. Thus, the present work convincingly provides simple and reproducible experimental methods to synthesize water soluble

saccharide complexes of first row transition metals in a non-aqueous solvent mixture (MeOH:MeCN) from easy to prepare starting materials $[NEt_4]_2[MCl_2Br_2]$ (with a preformed metal center) and the disodium salt of D-Glc. Our recent biological studies on intestinal absorption of D-Glc and D-fructose complexes with labeled Fe(III) have shown them to be remarkably absorbed as compared with simple ferric salts. In addition, due to their stability over a wide pH range, they are suitable nutritional supplements. The saccharide complexes of Cr(III) have been found to alter the structure of *neo* plasmid DNA, *in vitro*, thus providing some insights into chromium toxicity in biological systems. Since transition metal–saccharide complexes find many applications ranging from those in biotechnology, agriculture, pharmacology to synthetic chemistry and catalysis (Whitfield *et al.* 1993), these complexes might prove to be important molecules. Also, metal complexation by saccharides may be useful in environmental detoxification of certain toxic metals.

Acknowledgments

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