

# Transition-metal saccharide chemistry: synthesis and characterization of D-glucose, D-fructose, D-galactose, D-xylose, D-ribose, and maltose complexes of Co(II)

Rajiv P. Bandwar <sup>a</sup>, Medury D. Sastry <sup>b</sup>, Ramakant M. Kadam <sup>b</sup>,  
Chebrolu P. Rao <sup>a,\*</sup>

<sup>a</sup> *Bioinorganic Laboratory, Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai 400 076, India*

<sup>b</sup> *Radiochemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India*

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## Abstract

Monosaccharide (D-Glc, D-Fru, D-Gal, D-Xyl, and D-Rib) and disaccharide (Mal) complexes of Co(II) were synthesised from nonaqueous solutions using  $[\text{NEt}_4]_2[\text{CoCl}_2\text{Br}_2]$  or  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  and isolated in the solid state. The purified complexes were characterized by diffuse reflectance, aqueous solution absorbance, CD, FTIR, magnetic susceptibility, EPR, and cyclic voltammetric studies. The complexes synthesised from  $[\text{NEt}_4]_2[\text{CoCl}_2\text{Br}_2]$  were found to be primarily dinuclear, whereas those synthesised from  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  were found to be di- or tetra-nuclear. The hydrolytic stability of the complexes followed a trend: D-Rib > Mal > D-Glc > D-Xyl > D-Fru  $\gg$  D-Gal. © 1997 Elsevier Science Ltd. All rights reserved.

**Keywords:** Transition metal; Co(II); Complex; Monosaccharide; Maltose

## 1. Introduction

Interactions of the saccharides with the transition-metal ions is a promising field of bioinorganic chemistry due to the presence of such interactions in biological systems and the manifold applications they offer in areas pertinent to agriculture, industry, and pharmaceutical sciences [1]. Solution studies have clearly demonstrated the complex formation between transition-metal ions and saccharides [2]; however,

the isolated complexes were mostly found to be adducts [3]. Notably, the N-glycosides of Co(III) and Ni(II) [4], the D-lyxose complex of Mo(VI) [5], and Cu(II) complexes of sugar alcohols [6] are the few crystallographically characterized complexes. Optically active mixed ligand complexes with Co(III) and saccharides have been formed, for example  $[\text{Co}(\text{NH}_3)_4(\text{Rib})_2](\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$  [7]. Similar octahedral mixed complexes with D-gluconic acid and Co(III) have been reported [8].

We have previously reported the synthesis, isolation, and characterization of saccharide complexes of Ti(IV) [9],  $\text{VO}^{2+}$  [9,10], Cr(III) [9,11], Mn(II) [12],

\* Corresponding author.

Fe(III) [13], Ni(II) [14], Cu(II) [15], and Zn(II) [16] and some of their bio-interactions. We now report the synthesis and characterization of D-glucose (D-Glc), D-fructose (D-Fru), D-galactose (D-Gal), D-xylose (D-Xyl), D-ribose (D-Rib), and maltose (Mal) complexes of Co(II).

## 2. Materials and methods

All solvents were distilled and dried before use by established procedures. The  $[\text{NEt}_4]_2[\text{CoCl}_2\text{Br}_2]$  salt was prepared by the reported procedure [17].  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (Loba Chemie, India), sodium metal (E. Merck, India), D-Glc (Allied Chemicals, USA), and other saccharides (Aldrich Chemical Company) were used as supplied.

Diffuse reflectance, aqueous solution absorption, circular dichroism (CD), Fourier-transform infrared (FTIR) spectroscopies, room-temperature magnetic susceptibility, and elemental analysis were performed as reported earlier [11–13]. Electron paramagnetic resonance (EPR) spectra at 298 K were recorded on a Varian ESR-112 spectrometer using tetracyanoethylene (TCNE) as field marker ( $g = 2.00277$ ), whereas the EPR of the Co(II)–D-Glc complex (**1**) (diluted in an  $\text{NH}_4\text{Cl}$  matrix) was recorded in the temperature range of 10–100 K using a Bruker ESP-300 spectrometer operating at X-band frequency ( $\nu = 9\text{--}10$  GHz). 1,1-Diphenyl-2'-picrylhydrazyl (DPPH) was used as the field marker ( $g = 2.0036$ ). The temperature was varied from 10–100 K using APD cryosystem equipped with Lake Shore temperature controller. Complex **1** was diluted in an  $\text{NH}_4\text{Cl}$  matrix in two ways: (i) by a dry mixing of complex **1** with  $\text{NH}_4\text{Cl}$  in 2:98 w/w ratio and (ii) by coprecipitating a similar mixture from aqueous solution to obtain a homogenous molecular distribution of complex **1** in an  $\text{NH}_4\text{Cl}$  matrix.

## 3. Experimental

The complexes were synthesised using either  $[\text{NEt}_4]_2[\text{CoCl}_2\text{Br}_2]$  or  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ . The saccharides were used as sodium salts generated in situ in MeOH; disodium salts of monosaccharides (D-Glc, D-Fru, D-Gal, D-Xyl, and D-Rib), and the tetrasodium salt of disaccharide (Mal). The syntheses of the complexes were carried out by the procedure described below.

*Synthesis of the Co(II)–D-Glc complex (1) from  $[\text{NEt}_4]_2[\text{CoCl}_2\text{Br}_2]$ .*—D-Glc (2.163 g, 12.0 mmol) was suspended in 140 mL of MeOH by stirring. Freshly cut metallic sodium (0.60 g, 26.1 mmol) was added in pieces to the suspension, which resulted in the dissolution of D-Glc as the sodium salt. After about 30–45 min,  $[\text{NEt}_4]_2[\text{CoCl}_2\text{Br}_2]$  (2.201 g, 4.0 mmol) in 20 mL of MeCN was added slowly with stirring to the methanolic solution of sodium salt of D-Glc (1:3 metal-to-ligand ratio), which resulted in the formation of a reddish-brown precipitate. The reaction mixture was stirred for 1 day, during which time the precipitate changed gradually to brown. The precipitate was isolated by filtration under suction and then stirred in 20-mL portions of (i) MeOH for 1 day, followed by (ii) MeCN for 1 day, and finally (iii) 20 mL of *n*-hexane for about 18 h. However, this procedure was found to be ineffective in removing trace amounts of coprecipitated sodium and/or tetraethylammonium halide salts. Further purification by stirring three times, for about 1 h each time, in a 9:1 MeOH– $\text{H}_2\text{O}$  mixture and twice in absolute MeOH, and filtering gave the pure Co(II)–D-Glc complex (**1**) in 63% yield based on Co content. The Co(II)–D-Fru (**2**) and Co(II)–D-Gal (**3**) complexes were synthesised and purified in an identical manner. The Co(II)–Mal complex (**9**) was synthesised similarly using 2 mmol of  $[\text{NEt}_4]_2[\text{CoCl}_2\text{Br}_2]$  and a metal-to-ligand ratio of 1:2, and the isolated complex was purified in an identical manner. Complexes **2**, **3**, and **9** were obtained in 57%, 61%, and 64% yields, respectively.

*Synthesis of the Co(II)–D-Glc complex (4) from  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ .*—To the sodium salt of D-Glc in 130 mL of MeOH (2.165 g, 12.0 mmol of D-Glc; 0.568 g, 24.7 mmol of Na),  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (0.955 g, 4.0 mmol) in 20 mL of MeOH was added slowly with constant stirring, which resulted in the formation of a violet precipitate that gradually changed to brown in 12–15 h. The stirring was continued for 1 day, after which time the brown precipitate was isolated by filtration under suction. The isolated product, which was soluble in  $\text{H}_2\text{O}$ , was purified by stirring in 30 mL of 9:1 MeOH– $\text{H}_2\text{O}$  mixture for 1–2 h (thrice), and finally with absolute MeOH (twice). The Co(II)–D-Fru (**5**) and Co(II)–D-Gal (**6**) complexes were synthesised and purified similarly. The yields were found to be 68%, 71%, and 65% for complexes **4**, **5**, and **6**, respectively. The Co(II)–D-Xyl (**7**) and Co(II)–D-Rib (**8**) complexes were synthesised similarly using 5 mmol  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ , and were purified in an identical manner to give 78% and 73% yields, respectively.

Table 1

Proposed molecular formulae and elemental analysis (in %) for Co(II)–saccharide complexes 1–9

Complex/formula		C	H	Co	Na	
1	$C_{12}H_{23}Cl_2Co_2NaO_{13}$	Calcd:	24.54	3.92	20.08	3.92
	$Na[Co_2(Glc)_2(OH)Cl_2]$	Found:	24.46	3.87	20.40	3.64
2	$C_{12}H_{22}Cl_3Co_2Na_{12}O \cdot 2H_2O$	Calcd:	22.45	4.05	18.38	3.59
	$Na[Co_2(Fru)_2Cl_3] \cdot 2H_2O$	Found:	22.62	3.71	18.36	3.16
3	$C_{12}H_{22}Cl_3Co_2NaO_{12}$	Calcd:	23.79	3.63	19.47	3.80
	$Na[Co_2(Gal)_2Cl_3]$	Found:	23.35	3.68	20.01	3.36
4	$C_{18}H_{37}Cl_2Co_4NaO_{22} \cdot 3CH_3OH$	Calcd:	24.45	4.75	22.87	2.23
	$Na[Co_4(Glc)_3(OH)_4Cl_2] \cdot 3CH_3OH$	Found:	24.61	4.40	22.73	2.68
5	$C_{18}H_{37}Cl_2Co_4NaO_{22}$	Calcd:	23.11	3.96	25.22	2.46
	$Na[Co_4(Fru)_3(OH)_4Cl_2]$	Found:	22.86	4.03	25.69	2.68
6	$C_{18}H_{38}ClCo_4NaO_{23}$	Calcd:	23.58	4.15	25.73	2.51
	$Na[Co_4(Gal)_3(OH)_5Cl]$	Found:	23.40	4.13	26.05	2.50
7	$C_{10}H_{19}Cl_2Co_2NaO_{11} \cdot CH_3OH$	Calcd:	23.62	4.12	21.09	4.12
	$Na[Co_2(Xyl)_2(OH)Cl_2] \cdot CH_3OH$	Found:	23.78	3.69	21.09	3.83
8	$C_{10}H_{18}Cl_3Co_2NaO_{10} \cdot 2CH_3OH$	Calcd:	23.63	4.27	19.34	3.77
	$Na[Co_2(Rib)_2Cl_3] \cdot 2CH_3OH$	Found:	23.72	3.64	19.25	4.37
9	$C_{12}H_{19}Cl_2Co_2NaO_{11}$	Calcd:	26.14	3.45	21.40	4.18
	$Na[Co_2(Mal)Cl_2]$	Found:	26.37	3.68	20.89	4.27

The proposed formulae and elemental analysis of Co(II)–saccharide complexes 1–9 are listed in Table 1.

#### 4. Results and discussion

The isolated and purified Co(II)–saccharide complexes from both starting materials were found to be soluble only in water. In the absence of a crystal structure, a definite conclusion regarding the three-dimensional structure could not be obtained; however, an attempt has been made to characterize these complexes by various spectroscopic and analytical techniques as reported in this paper.

**Diffuse reflectance and aqueous solution absorption studies.**—The diffuse reflectance spectra of complexes 1–9 were typical of octahedral Co(II) complexes and were different from those of the precursors,  $[NEt_4]_2[CoCl_2Br_2]$  or  $CoCl_2 \cdot 6H_2O$ , indicating the coordination through oxygens of the hydroxyl groups of saccharides. The presence of a band at  $\sim 690$  nm in the case of complexes 2, 3, and 9 indicated the involvement of  $Cl^-$  in the coordination sphere of these complexes. In other complexes this

transition was masked by a strong peak at  $535 \pm 5$  nm. The aqueous solution absorption spectra of complexes exhibited bands at  $\sim 570$  and  $\sim 520$  nm and were different from those of  $[NEt_4]_2[CoCl_2Br_2]$  or  $CoCl_2 \cdot 6H_2O$  precursors. The latter exhibited bands at  $\sim 511$  and  $\sim 480$  nm, suggesting a weaker coordination of saccharides to Co(II) as compared to  $H_2O$  ligation. This was confirmed by the observation that the saccharide complexes precipitated as hydroxides after a certain period of time as described later under solution stability studies.

**CD studies.**—The CD spectra (Fig. 1) of aqueous solutions of complexes 1–9 were recorded in the visible region of 350–700 nm. The spectra exhibited curves in the visible region with a strong cotton effect indicating the presence of Co(II) ions at the centre of dissymmetry. Electronic transitions in similar molecules should have the same sign of CD and ORD effects when the molecules have the same absolute chirality [18]. However, among the hexose complexes the D-Gal complexes (3 and 6), and among the pentoses the D-Xyl complex (7), were found to exhibit exactly the opposite sign of rotation as compared to their counterparts, D-Glc (1 and 4), D-Fru (2

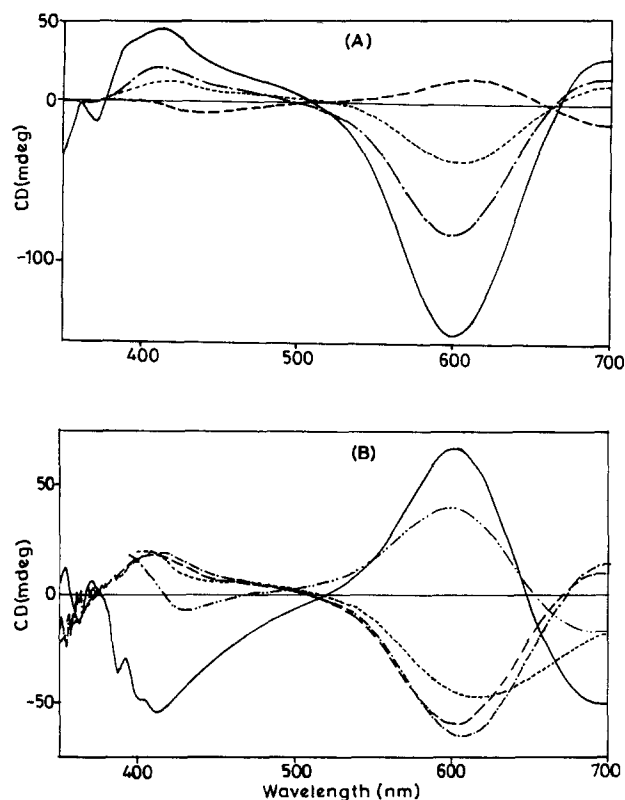


Fig. 1. CD spectra of Co(II)–saccharide complexes: (A) 1 (---), 2 (—), 3 (---), 9 (— · —); and (B) 4 (— · —), 5 (---), 6 (—), 7 (— · —), 8 (---).

and 5), and D-Rib (8), respectively, at the corresponding transition. The disaccharide complex, Co(II)–Mal (9) exhibited a similar sign of rotation to that of the D-Glc complex (1 and 4), which is a monosaccharide unit of maltose.

The difference in the sign of rotation of Co(II)–D-Gal (3 and 6) and Co(II)–D-Xyl (7) complexes from other complexes indicates the inversion of absolute configuration around the metal centre among these complexes. This is attributable to the differences observed in the orientation of hydroxy groups of saccharide molecules. Based on the coordination abilities of the different saccharides [19], a 3,4-*cis*-diol arrangement is proposed for D-Gal complexation as compared to a 3,4-*trans*-diol complexation by D-Glc and D-Fru molecules. Araki and Tajima have reported a similar 3-OH and 4-OH coordination for Cu(II)–saccharide complexes [20]. The D-Rib moiety in the Co(II)–D-Rib complex (8) utilizes a favourable 2,3-*cis*-diol orientation for complexation.

**FTIR studies.**—The FTIR spectra of complexes 1–9, recorded in KBr, were characterized by broadening and merging of bands similar to other transition-metal–saccharide complexes reported by us [9–

16]. All the vibrational modes were affected on sodium salt formation and subsequent complexation of Co(II) to the deprotonated hydroxyl groups, resulting in an extensive rearrangement of the hydrogen-bonding network of the saccharide moiety. This rearrangement in the hydrogen-bonding could also be due to the presence of H<sub>2</sub>O in these hygroscopic compounds. Moreover, the presence of several weak bands in the anomeric region was indicative of the presence of both  $\alpha$  and  $\beta$  forms of the saccharide, wherever the  $\beta$  anomer was used (e.g.,  $\beta$ -D-Fru). In contrast, the  $\alpha$  form was retained after complexation in those cases for which the  $\alpha$  anomer of the saccharide was used (e.g.,  $\alpha$ -D-Glc). The presence of the  $\alpha$  form of the saccharides in the complexes could be explained by the thermodynamic stability of the  $\alpha$  form [21]. Similar results were also observed in case of Zn(II)–saccharide complexes [16].

**Magnetic studies.**—The magnetic moments ( $\mu_{\text{eff}}$ ) per ion of the Co(II)–saccharide complexes 1–9 at 298 K were found to be in the range 4.42–4.94  $\mu_{\text{B}}$ , which is larger than the spin-only magnetic moment,  $\mu_{\text{S}} = 3.87\mu_{\text{B}}$ , for high-spin Co(II) complexes. The departure of the observed magnetic moments from the spin-only value suggests a considerable orbital contribution because of the intrinsic orbital angular momentum in the octahedral ground state [18].

**EPR studies.**—High-spin Co(II) has a ground state  $^4T_{2g}$  in an octahedral field. With lowering of the symmetry the three-fold orbital degeneracy is lifted, leaving a ground-state orbital singlet. However, its EPR silence at room temperature shows that it has very short  $T_1$ , due to the proximity of an excited  $^4E$  state. Normally, this is not surprising, as most of the high-spin Co(II) complexes are known to exhibit EPR only at temperatures well below 77 K due to the fact that  $T_1$  increases with a decrease in temperature [22].

From earlier work [23], it is well established that NH<sub>4</sub>Cl, a compound with simple cubic structure, facilitates the stabilization of a high-spin Co(II) complex as a *trans*-octahedral complex. This fact was utilized in the present investigation where the EPR of the Co(II)–D-Glc complex (1) in NH<sub>4</sub>Cl was studied. The NH<sub>4</sub>Cl lattice also has the role of a diamagnetic diluent facilitating the investigation of the isolated Co(II)–D-Glc complex (1). Fig. 2 shows the EPR spectra at 10 K of a Co(II):NH<sub>4</sub>Cl crystal, the complex (1) + NH<sub>4</sub>Cl (system 1, aqueous solution preparation), and the complex (1) + NH<sub>4</sub>Cl (system 2, pure complex). Hence it can be seen that the lines observed in the spectrum of a Co(II):NH<sub>4</sub>Cl crystal

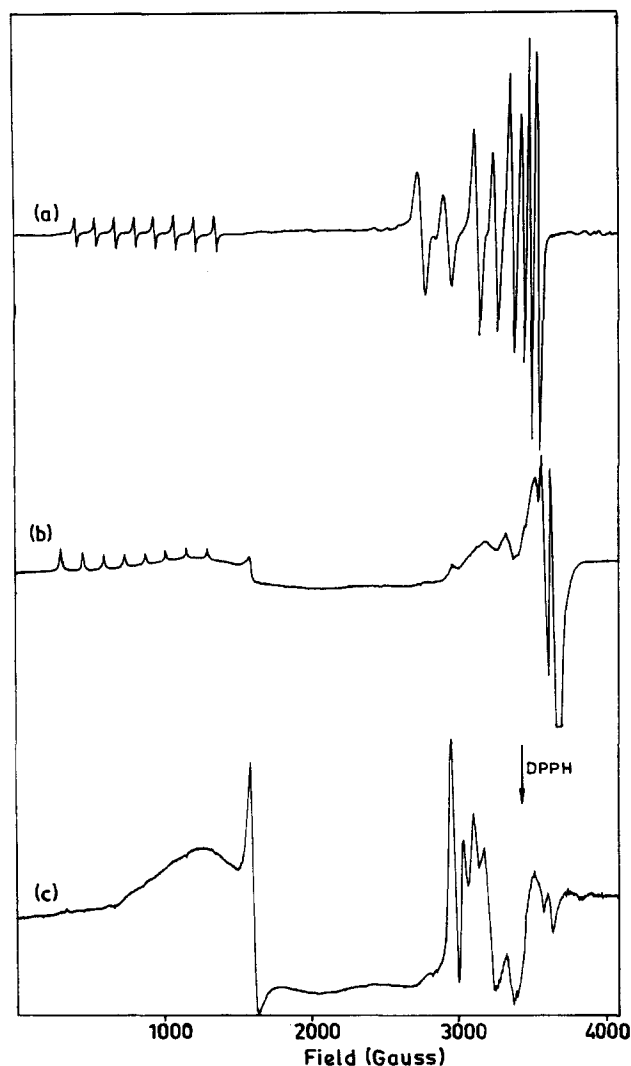


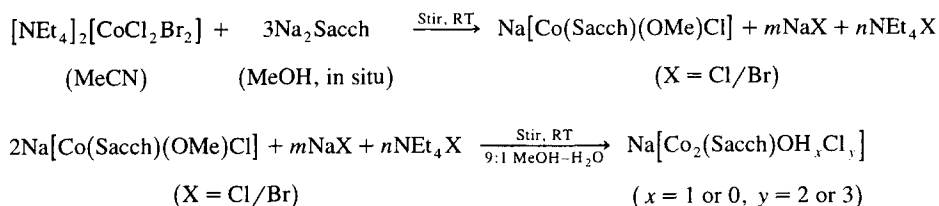
Fig. 2. EPR spectra at 10 K of (a) the Co(II)-doped  $\text{NH}_4\text{Cl}$  crystal, (b) the Co(II)-D-Glc complex **1** (2%) coprecipitated with  $\text{NH}_4\text{Cl}$  from aqueous solution, and (c) a solid mixture of complex **1** (2%) and  $\text{NH}_4\text{Cl}$ .

are also present in system 1, and are absent in the spectrum of the pure complex. On the other hand, the pure complex spectrum consists of an eight-line pattern characteristic of parallel components, and a broad and intense line at  $g = 2.143$ , which is characteristic of a perpendicular component. It may be noted that these features are distinctly different from those expected for high-spin Co(II) in octahedral complexes (Fig. 2a). The spectrum obtained for the pure complex clearly suggests that paramagnetism arises due to an  $S = \frac{1}{2}$  spin state. In addition to this, a sharp line at  $g = 4.298$  is observed corresponding to half the field at which the main resonances were observed. It is well known that dimers of an  $S = \frac{1}{2}$  system do exhibit a half field line [24], suggesting that it point to a similar occurrence here.

EPR studies at 10 K seem to suggest that complex **1** is characterized by an  $S = \frac{1}{2}$  state, and it also forms a dimer. Cobalt can indeed exhibit  $S = \frac{1}{2}$  behaviour if it exists in the low-spin state ( $3d^7: t_{2g}^6 e_g^1$ ) with the unpaired electron being in an  $e_g$  orbital, i.e., either in  $[x^2 - y^2]$  or in  $[dz^2 - r^2]$  orbitals. The relative values of  $g_{\parallel}$  and  $g_{\perp}$  clearly show that the unpaired electron has  $dz^2$  character, implying that the geometry around Co(II) is of an elongated octahedral type. The present work seems to strongly suggest that complex **1** occurs in the low-spin form, also forming a dimer at 10 K. This is not in agreement with the magnetic susceptibility data obtained at 298 K. These two can be reconciled if a possible spin crossover is taken into account with lowering of temperature. It is not unusual to expect such a behaviour, as a large number of first-row transition elements exhibit a *high-spin*  $\rightleftharpoons$  *low-spin* transition when complexed in chelates [18]. However, an independent evidence for spin crossover, such as temperature-dependent magnetic susceptibility measurements, will give greater insight into this phenomenon.

**Cyclic voltammetric studies.**—Electrochemical behaviour of complexes **4–8** was studied in the range of pH 4–10 by cyclic voltammetry at a hanging mercury drop electrode (HMDE) in the potential range  $-0.5$  to  $-1.9$  V, and was compared with that of the precursor,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ . All the complexes **4–8** produced irreversible voltammograms showing only cathodic waves corresponding to the  $\text{Co(II)} \rightarrow \text{Co(I)}$  reduction. The behaviour of the Co(II)-D-Glc complex (**4**) is described here as a typical example. The pH of the freshly prepared aqueous solution of the complex **4** was found to be 8.3, as compared to 5.1 of the  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  salt, suggesting the involvement of deprotonated hydroxyl groups in binding. A cathodic wave at  $-1.30$  V ( $E_p^c$ ) was observed for **4** at this pH, which shifted to  $-1.81$  V with a shoulder at  $-1.68$  V at pH 9.3, indicating the presence of two species having Co(II) coordinated in different environments, probably due to some deprotonation of the free hydroxyl groups of the saccharide moiety. On further increasing the pH to 9.8, only one cathodic wave at  $-1.83$  V was observed, indicating the presence of a uniformly coordinated Co(II) species.

On lowering the pH of the freshly prepared aqueous solution to 7.2, cathodic waves at  $-1.30$  and  $-1.65$  V were observed. At this pH,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  precipitated as hydroxide, whereas the complex persisted in solution, indicating its presence at neutral pH. On further lowering the pH to 4.4 through 5.6, the  $E_p^c$  shifted to cathodic potentials ( $-1.49$  V) due



Scheme 1.

to the formation of an anionic Co–chloro species and hence suggesting a complete breakdown of the Co(II)–D-Glc complex under acidic conditions.

In summary, the cyclic voltammetry studies supported the presence of Co(II)–saccharide complexes at neutral pH. Under alkaline conditions, the complexation was favoured due to the involvement of hydroxyl groups in coordination, whereas under acidic conditions, a dissociation of the complexes was observed. These results are in agreement with those observed for Mn(II)–saccharide [12] and Cu(II)–saccharide complexes [15].

**Solution stability.**—The solution stability of these complexes was studied by observing the precipitate formation from the aqueous solutions. It was observed that the D-Gal complexes **3** and **6** precipitated within a few minutes of the dissolution, whereas D-Fru complexes **2** and **5** precipitated over a period of 1–2 h. The complexes of D-Glc (**1** and **4**), D-Xyl (**7**), and D-Rib (**8**) were found to be stable for several hours and precipitated in an order as follows: D-Xyl > D-Glc > D-Rib over a period of 12–15 h. Thus complexes of D-Rib were found to be most stable as compared to those of other saccharides. Thus the order of hydrolysis among the complexes was found to be D-Gal  $\gg$  D-Fru > D-Xyl > D-Glc > Mal > D-Rib, and, therefore, the hydrolytic stability of these complexes follow a reverse order.

**Nature of the products.**—The formation of complexes from  $[\text{NEt}_4]_2[\text{CoCl}_2\text{Br}_2]$  involves the removal of  $\text{Br}^-$  in nonaqueous reaction media and results in the complexes of the type  $\text{Na}[\text{Co}(\text{Sacch})(\text{OMe})\text{Cl}]$ , along with trace amounts of coprecipitated sodium and/or tetraethylammonium halide salts, which could not be removed by MeOH, MeCN, and *n*-hexane purification. However, after purification in a 9:1 MeOH–H<sub>2</sub>O mixture, these complexes were found to be dinuclear, indicating that the conversion occurred due to the presence of H<sub>2</sub>O, leading to destruction of methoxide and subsequent dimerization, as illustrated in Scheme 1.

The complexes formed from  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  were tetranuclear in the case of **4**, **5**, and **6** and dinuclear in

cases of **7** and **8**. The dinuclear nature of complex **1** was also evident by the presence of a strong peak at  $m/z$  367 in its mass spectrum, indicative of a  $[\text{Co}_2(\text{Glc})\text{Cl}_2]$  species. However, the presence of several weak peaks at  $m/z$  > 600 in the mass spectra of complexes **1**, **3**, **7**, **8**, and **9** may suggest a higher nuclearity for these compounds.

## 5. Conclusions

The synthesis of Co(II)–saccharide complexes has resulted in the formation of di- and tetra-nuclear complexes. The orientation of the hydroxyl groups on the sugar ring is responsible, to a large extent, for the complexation of the Co(II) ion and, hence, governs the absolute chirality of the complexes, as demonstrated by the CD studies. Although high-spin octahedral complexes are formed at room temperature, the EPR studies reveal a high-spin to low-spin crossover at extremely low temperatures and, hence, suggest the chelating mode for saccharide coordination. The Co(II)–saccharide complexes exist at physiological pH, and the complexation is favoured under alkaline conditions.

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