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Transition-metal–saccharide chemistry: synthesis and characterisation of D-galactose, D-fructose, D-glucose, D-xylose, D-ribose, and maltose complexes of Mn(II)

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Abstract

Monosaccharide (D-Gal, D-Fru, D-Glc, D-Xyl, D-Rib) and disaccharide (D-Mal) complexes of Mn(II) were synthesised from non-aqueous solutions using $[NEt_4]_2[MnCl_2Br_2]$ and $MnCl_2 \cdot 4H_2O$. The isolated and purified complexes were characterised by diffuse reflectance, FTIR, EPR, DTA, TGA, magnetic susceptibility, and cyclic voltammetry techniques. Synthesis from $[NEt_4]_2[MnCl_2Br_2]$ yielded dimeric complexes **1–3** and **9**, and from $MnCl_2 \cdot 4H_2O$ it yielded trimeric complexes **4–8**. These water-soluble complexes were found to be anionic with a Mn-to-saccharide ratio of 1:1 for monosaccharide complexes **1–8** and 2:1 for disaccharide complex **9**. The complexes were found to be hydrolytically stable in solution at higher concentrations ($\geq$ 4 mM), as studied by cyclic voltammetry. © 1996 Elsevier Science Ltd.

Keywords: Mn(II) complexes; Monosaccharide–Mn(II) complexes; Maltose–Mn(II) complex

1. Introduction

The interaction of saccharides with transition-metal ions is of biochemical importance partly due to the presence of these complexes in biological systems [1]. Metal–saccharide chemistry plays an important role in the crosslinking of various biomolecules [2] and significantly affects sugar conformations [3,4]. Structural studies have shown that the interaction of saccharides with alkali and alkaline-earth metal ions are non-ionic in nature, although such interactions were presumed to be of simple ionic type [5–7].

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Transition-metal–saccharide interactions have been investigated mostly in solution [8]; however, aminoglycosides of Ni(II) and Co(III) are the only complexes so far that are structurally well characterised [9]. In recent years, our group has reported the synthesis, isolation, characterisation, and biological significance of complexes of simple saccharides with almost all the first-row transition metals, as well as with zinc [10–12]. In our continuing efforts in the field of transition-metal–saccharide chemistry and biology, we report here the synthesis and characterisation of Mn(II)–saccharide complexes of D-galactose (D-Gal), D-fructose (D-Fru), D-glucose (D-Glc), D-xylose (D-Xyl), D-ribose (D-Rib), and D-maltose (D-Mal).

2. Materials and methods

All solvents were distilled and dried before use by established procedures. The $[NEt_4]_2[MnCl_2Br_2]$ salt was prepared by the method of Gill and Taylor [13]. $MnCl_2 \cdot 4H_2O$ and sodium metal (E. Merck, India), D-Glc (Allied Chemicals, USA), and other saccharides (Aldrich Chemical Company) were used as supplied.

Diffuse reflectance spectra (DRS) in the 190–500 nm region were recorded using a Shimadzu UV-260 spectrophotometer. Fourier-transform infrared (FTIR) spectra of the free saccharides and the complexes were recorded in the 4000–400 cm^{-1} region in a KBr matrix on a Nicolet Impact 400 FTIR spectrometer. Electron paramagnetic resonance (EPR) studies of the powder and aqueous solutions, at 298 and 77 K, were carried out on a Varian ESR-112 spectrometer. ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra in D_2O solutions were recorded on a Varian XL-300 spectrometer using 5- and 10-mm probes, respectively. Differential thermal analyses (DTA) and thermogravimetric analyses (TGA) under a N_2 atmosphere were carried out using a DuPont-9900 instrument. DC susceptibility measurements of the complexes at 298 K were carried out on an Oxford Instruments Faraday balance with a magnetic field of 4 kG and a gradient field of 100 Gauss. Variable-temperature magnetic measurements of complex **3** in the region 5–300 K were made on a SQUID magnetometer (Quantum Design). The sample was sealed in a gelatin capsule, and a diamagnetic correction was made for both sample holder and sample. The observed and calculated data were fitted using in-house software [14]. Cyclic voltametric (CV) studies of argon-purged aqueous solutions (made from doubly distilled water) were carried out on a BAS-100B electrochemical analyser, at a potential sweep of 0.1 V/s, using a hanging mercury drop (HMDE) as the working electrode, Pt as the auxiliary electrode, and Ag/AgCl as the reference electrode. C and H analyses were done on a Carlo Erba 1106 elemental analyser, and Mn and Na contents were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on a Plasmalab 8440 instrument.

3. Experimental

The complexes were synthesised using either $[NEt_4]_2[MnCl_2Br_2]$ or $MnCl_2 \cdot 4H_2O$. The saccharides were used as sodium salts generated in situ in MeOH. Disodium salts of the monosaccharides (D-Gal, D-Fru, D-Glc, D-Xyl, and D-Rib), and tetrasodium salt of disaccharide (Mal) were prepared as reported earlier [11].

A typical method for the preparation of Mn(II)–saccharide complexes **1–3** *and* **9**. *Mn(II)–D-Gal complex* **(1)** *from* $[NEt_4]_2[MnCl_2Br_2]$.—D-Gal (2.165 g, 12.0 mmol) was suspended in 140 mL of MeOH by stirring. Freshly cut metallic sodium (0.582 g, 25.3 mmol) was added in pieces to the suspension, which resulted in the dissolution of D-Gal as a sodium salt. After about 30–45 min, $[NEt_4]_2[MnCl_2Br_2]$ (2.185 g, 4.0 mmol) in 15 mL of MeCN (colourless solution) was added slowly with stirring to the methanolic solution of the sodium salt of D-Gal (1:3 metal-to-ligand ratio), which resulted in the formation of a brown precipitate. The reaction mixture was stirred further for 1 day, and the precipitate was isolated by filtration under suction and then stirred in 30-mL portions of (*i*) MeOH for 1 day, followed by (*ii*) MeCN for 1 day, and finally (*iii*) 30 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 thrice, for about 1 h each time, in MeOH at 40 °C and filtering immediately gave pure Mn(II)–D-Gal complex (**1**) in 71% yield, based on Mn content.

The Mn(II)–D-Fru (**2**) and Mn(II)–D-Glc (**3**) complexes were synthesised and purified in an identical manner. The Mn(II)–D-Mal complex (**9**) was synthesised similarly using 2 mmol of $[NEt_4]_2[MnCl_2Br_2]$ and a metal-to-ligand ratio of 1:2, and the isolated

Table 1
Elemental analysis (%) for Mn(II)–saccharide complexes **1–9**

Complex	Formula		C	H	Mn	Na
1	$C_{12}H_{23}Cl_2Mn_2NaO_{13}\cdot H_2O$	Calcd	24.13	4.19	18.41	3.85
		Found	24.48	3.78	17.94	3.62
2	$C_{12}H_{23}Cl_2Mn_2NaO_{13}$		24.88	3.97	18.98	3.97
			24.53	3.64	18.85	4.28
3	$C_{12}H_{24}ClMn_2NaO_{14}$		25.70	4.28	19.61	4.10
			25.82	3.84	20.01	3.96
4	$C_{18}H_{34}Cl_3Mn_3NaO_{19}\cdot 0.5H_2O$		25.20	4.08	19.23	2.68
			24.95	3.97	19.30	2.24
5	$C_{18}H_{36}ClMn_3NaO_{21}\cdot CH_3OH\cdot H_2O$		26.47	4.88	19.14	2.67
			26.53	4.69	19.06	2.66
6	$C_{18}H_{33}Cl_4Mn_3NaO_{18}\cdot 1.5H_2O$		24.17	4.03	18.44	2.57
			24.23	4.04	18.91	2.24
7	$C_{15}H_{27}Cl_4Mn_3NaO_{15}\cdot 2.5CH_3OH$		24.51	4.32	19.24	2.68
			24.61	4.43	19.19	3.08
8	$C_{15}H_{27}Cl_4Mn_3NaO_{15}\cdot 3.5CH_3OH$		24.98	4.61	18.54	2.59
			25.07	4.53	18.42	3.08
9	$C_{12}H_{20}Br_2Cl_2Mn_2Na_2O_{11}\cdot CH_3OH\cdot H_2O$		20.09	3.35	14.15	5.92
			19.98	3.46	14.78	5.99

complex was purified in an identical manner. Complexes **2**, **3**, and **9** were obtained in 68, 67, and 64% yields, respectively, based on Mn content.

A typical method for the preparation of Mn(II) complexes **4–6**. *Mn(II)–D-Gal complex* (**4**) *from $MnCl_2 \cdot 4H_2O$.*—To the sodium salt of D-Gal in 150 mL of MeOH (2.162 g, 12.0 mmol of D-Gal, 0.576 g, 25.0 mmol of Na) $MnCl_2 \cdot 4H_2O$ (0.792 g, 4.0 mmol) in 20 mL of MeOH was added slowly with constant stirring, which resulted in the formation of the complex as a brown precipitate. Stirring was continued for 1 day under ambient conditions, after which the complex was isolated by filtration under suction. The isolated product, which is soluble in H_2O, was purified by stirring in 30 mL of 90–10 v/v MeOH–H_2O mixture for 1–2 h (thrice), and finally with absolute MeOH (twice).

The complexes Mn(II)–D-Fru (**5**) and Mn(II)–D-Glc (**6**) were synthesised and purified similarly. The yields were found to be 64, 71, and 67%, respectively, for complexes **4**, **5**, and **6**, based on the Mn content. Mn(II)–D-Xyl (**7**) and Mn(II)–D-Rib (**8**) complexes were synthesised similarly using 5 mmol of $MnCl_2 \cdot 4H_2O$ and purified in an identical manner to give 72 and 68% yields, respectively, based on the Mn content.

For elemental analysis data see Table 1.

4. Results and discussion

Complexes **1–3** and **9** were synthesised from $[NEt_4]_2[MnCl_2Br_2]$ in MeCN, whereas complexes **4–8** were synthesised from $MnCl_2 \cdot 4H_2O$ in MeOH. The isolated and purified Mn(II)–saccharide complexes prepared by either procedure are soluble only in water and were characterised by various spectroscopic and analytical techniques as described below.

Diffuse reflectance spectroscopy.—The diffuse reflectance spectra of the complexes **1–9** exhibited remarkably identical behaviour, even though these complexes were synthesised from different precursors. All the complexes showed similar broad bands at 445, 340, and 270 nm arising from spin-forbidden transitions [15]. The band shapes were similar to that of the typical tetrahedral precursor compound $[NEt_4]_2[MnCl_2Br_2]$, which shows broad bands at ~ 450 and ~ 350 nm and a sharp band at 280 nm. The spectral broadening in tetrahedral complexes is expected due to the proximity of individual transitions arising in a relatively weaker tetrahedral ligand field. Thus the complexes were found to be tetrahedral in solid state.

FTIR spectroscopy.—The FTIR spectra of these complexes exhibited merged and broadened bands compared to the spectra of free and uncomplexed saccharides and hence were indicative of complex formation. These bands were centered around 3400 $[\nu_{OH}]$, 1400 $[\delta_{(OCH,CH_2,CCH)}]$, 1080 $[\nu_{(CO,CC)}]$, and 800 cm^{-1} $[\delta_{(CCH,CH)}, \nu_{(CC,CO)}]$. The occurrence of broad bands for all the vibrational modes rendered the individual assignments difficult. This excessive broadening of saccharide vibrations seems to originate from the coordination of the Mn(II) ion to the saccharide through its deprotonated hydroxyl groups and the presence of covalency in metal–ligand bonds to some extent. However, such broadening was not observed in metal–saccharide adducts of alkali and alkaline-earth metal ions as reported in the literature [6,7]. Even the

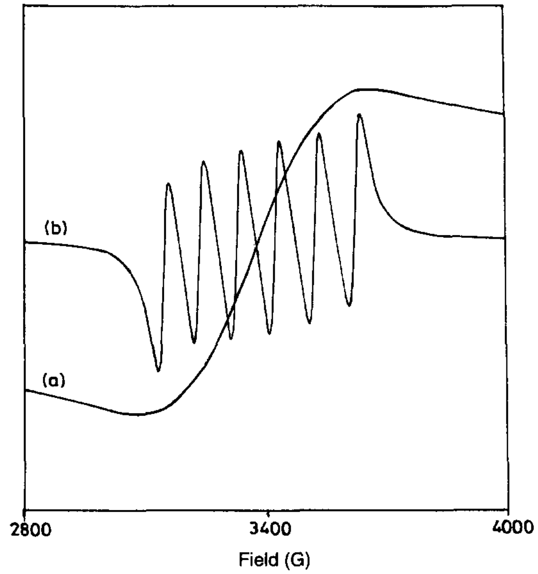

Fig. 1. EPR spectra of complex **1** at 298 K. (a) Powder; (b) aqueous solution. Field marker TCNE; $g = 2.00277$ (3380 G).

Zn(II)–saccharide complexes, synthesised similarly, exhibited broad bands due to coordination through deprotonated hydroxyl groups of saccharides; otherwise, the broadening and merging of bands was found to be ubiquitous in case of all other similarly prepared transition-metal–saccharide complexes reported by our group [10–12].

EPR spectroscopy.—EPR spectra were measured both in the powder and in aqueous solution states for both starting materials and the complexes **1**–**9** at 298 and 77 K. The EPR results were determined via simple first-order spectral analysis. Powder and aqueous solution EPR spectra of complex **1** at 298 K are shown in Fig. 1. Powder EPR spectra of both the starting materials and the complexes exhibited a broad signal at $g \sim 2$ with band widths (ΔH) of ≥ 500 G. Although the signal for dimer due to the forbidden $\Delta m_s \pm 2$ transition was not observed even at 77 K, the broad band at $g \sim 2$ was also not resolved into a hyperfine structure of six lines, thus indicating a strong dipolar interaction between the Mn(II) ions. However, the band width was reduced (~ 420 G) on diluting the solid sample (2%) in a ZnO matrix, due to reduced dipolar interactions. On the other hand, the aqueous solution EPR spectra of the precursors and all the complexes exhibited six lines with $g_{av} = 2.003 \pm 0.001$ as expected due to $S = 5/2$ and $I = 5/2$ for the high-spin Mn(II) ion. The hyperfine coupling constants $(A_{iso} = 95$ G) for these complexes were typical of Mn(II) in a distorted octahedral environment [16].

Magnetic susceptibility.—Magnetic susceptibility measurements were carried out at 298 K, and the calculated magnetic moments per ion for complexes **1**–**9** are given in Table 2. The μ_{eff}/ion for the complexes lie in the range 5.40–5.90 Bohr magnetons (BM), which are marginally lower than the μ_S value of 5.92 BM. The departure of the

Table 2
Proposed molecular formulae for the complexes **1–9** with observed magnetic moments at 298 K

Complex	Molecular formula	μ_{eff} /ion (BM)
1	$\mathrm{Na[Mn_2(D\text{-}Gal)_2(OH)Cl_2]\cdot H_2O}$	5.71
2	$\mathrm{Na[Mn_2(D\text{-}Fru)_2(OH)Cl_2]}$	5.69
3	$\mathrm{Na[Mn_2(D\text{-}Glc)_2(OH)_2Cl]}$	5.68
4	$\mathrm{Na[Mn_3(D\text{-}Gal)_3(OH)Cl_3]\cdot 0.5H_2O}$	5.82
5	$\mathrm{Na[Mn_3(D\text{-}Fru)_3(OH)_3Cl]\cdot CH_3OH\cdot H_2O}$	5.72
6	$\mathrm{Na[Mn_3(D\text{-}Glc)_3Cl_4]\cdot 1.5H_2O}$	5.90
7	$\mathrm{Na[Mn_3(D\text{-}Xyl)_3Cl_4]\cdot 2.5CH_3OH}$	5.50
8	$\mathrm{Na[Mn_3(D\text{-}Rib)_3Cl_4]\cdot 3.5CH_3OH}$	5.40
9	$\mathrm{Na_2[Mn_2(D\text{-}Mal)Cl_2Br_2]\cdot CH_3OH\cdot H_2O}$	5.66

observed magnetic moments from the spin-only moment could be attributed to some covalence in metal–ligand bonds [15], which is expected for the coordination of deprotonated hydroxyl groups of saccharides due to the formation of sodium salts to enhance their reactivity. The variable-temperature magnetic susceptibility of complex **3** in the range 5–300 K exhibited an antiferromagnetic behaviour as shown in Fig. 2. As can be seen from the plot of $\chi \cdot T$ vs. T, a best fit is obtained up to about 30 K for the complex as a dimer with $J = -1.7\ \mathrm{cm^{-1}}$; however, below 30 K, a marginal difference in the calculated and observed values suggests the presence of a trace amount of isolated low-molecular-weight impurity in the complex. On taking into account a presence of about 5% monomer impurity, a reasonably good fit between the observed and theoretical values was obtained.

Thermal analysis.—The TGA and DTA of the complexes recorded in the range of 25–900 °C showed an initial loss of MeOH and free H_2O in the range of 50–120 °C. Typical DTA and TGA curves in the case of complex **5** are shown in Fig. 3. From this

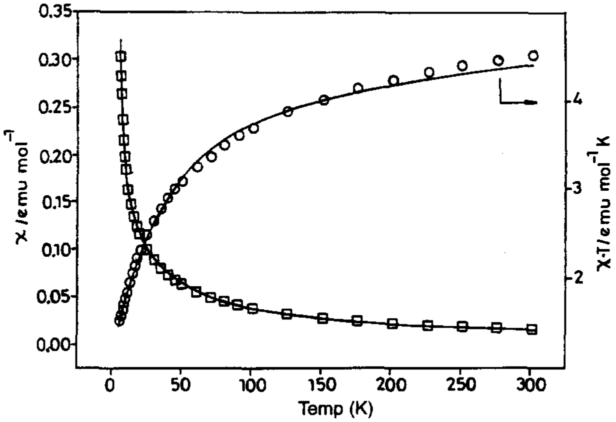

Fig. 2. Variable-temperature magnetic susceptibility of complex **3**: □ (χ) and ○ ($\chi \cdot T$) are experimental points; solid lines are the theoretical fit.

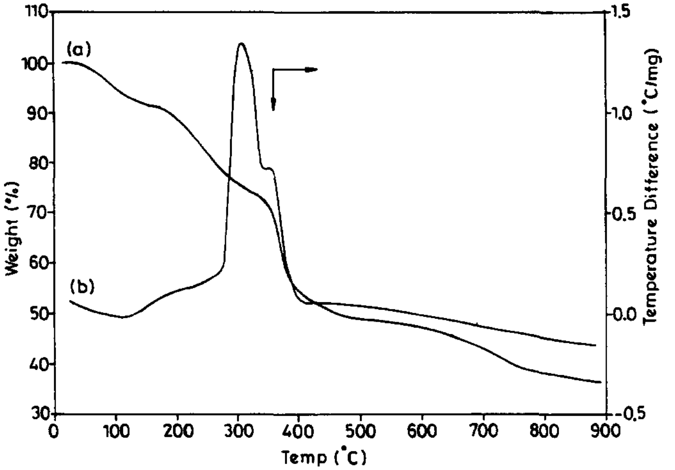

Fig. 3. (a) Thermogravimetric analysis and (b) differential thermal analysis curves for complex 5.

figure it can be observed that an endothermic weight loss occurs up to 110 °C, which corresponds to the loss of one molecule each of MeOH and H_2O. The observed weight loss (5.5%) is in good agreement with the calculated loss (5.8%) based on its proposed formula. After this initial weight loss, pyrolysis of the saccharide moiety takes place in the range of 200–400 °C as three exothermic processes [7]. Finally, the complete thermal degradation of the complex results in the formation of manganese oxide, MnO_2 at 900 °C, which was confirmed from its X-ray powder diffraction pattern [17].

Cyclic voltammetry.—Cyclic voltametric studies of the complexes were carried out in the pH range of 4.5–9.5. All the complexes exhibited similar irreversible voltammograms, and the voltametric behaviour was found to be reproducible in the pH range studied. Fig. 4 shows the voltammograms of complex **2** at various pH values. The corresponding voltametric data for the complexes **1**–**9** are listed in Table 3. All the complexes exhibited a pH ≥ 8 on dissolution in water, as compared to pH ≤ 7 for their precursors ($[NEt_4]_2[MnCl_2Br_2]$ or $MnCl_2 \cdot 4H_2O$), indicating an involvement of deprotonated hydroxyl groups in binding Mn(II) in the complex.

As can be seen from Fig. 4, the voltammogram of complex **2** exhibited two cathodic peaks (E_p^c) at -1.62 and -1.76 V, at pH 8.0 with a peak–current ratio of 2:1. The occurrence of two cathodic peaks was assignable to the differences in reduction of $Mn^{2+} \rightarrow Mn^0$ from differently bound Mn(II) ions. On comparison with the voltammogram of $[NEt_4]_2[MnCl_2Br_2]$ at similar pH, E_p^c at -1.62 V was attributable to the reduction of unbound Mn(II) species, while that at -1.76 V could be due to the reduction of complexed Mn(II) to the deprotonated saccharide. On increasing the pH to 9.2, three cathodic peaks at $E_p^c = -1.72$, -1.76, and -1.85 V were obtained in equal peak–current ratios, suggesting the conversion of half of the unbound species to weakly bound form ($E_p^c = -1.76$ V). The shift of -1.76 to -1.85 V could be assigned to the hindrance in reduction of a strongly complexed Mn(II) species due to an increased negative charge on the complex. On decreasing the pH from 8.0 to 7.1, E_p^c at -1.59 V

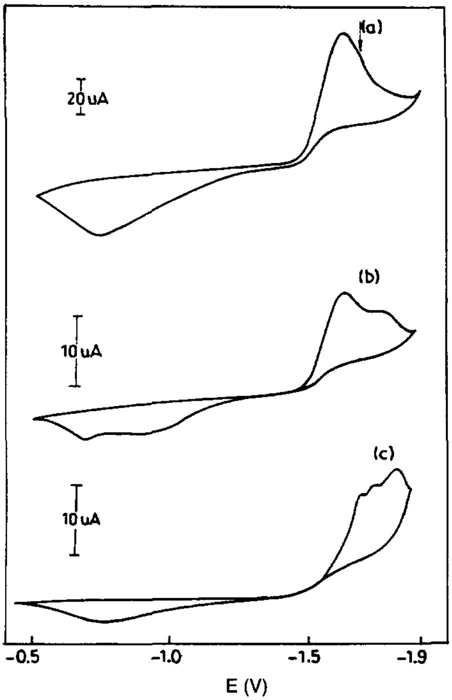

Fig. 4. Cyclic voltammograms of complex **2** at a hanging mercury drop electrode at various pH: (a) 7.1; (b) 8.0; (c) 9.2.

was observed with a shoulder at − 1.66 V. These were assignable to the anodic shifts of two peaks (− 1.62 and − 1.76 V) observed at pH 8.0 and as expected due to the weakening of the metal coordination upon protonation of several hydroxyl groups of saccharides resulting in easier reduction of Mn(II) (− 1.66 V). Further lowering the pH to 5.7 resulted in only one cathodic peak at − 1.56 V, which is assignable to the reduction of uncomplexed Mn(II) and is comparable to that of the $[NEt_4]_2[MnCl_2Br_2]$ salt at similar pH. Similar voltametric behaviour (as discussed above) was obtained for all the complexes, **1–9**, reported here.

In summary, comparison of the cyclic voltametric studies demonstrated the complexation of Mn(II) to the saccharides in aqueous solution depending upon the pH of the solution. Although the complexation was well favoured at pH ≥ 8, some percent of complexation persisted even near neutral pH, and no interaction was observed below pH 6.

Solution stability.—Generally, metal–saccharide complexes are expected to be of low stability [18]. Dilute solutions of these complexes with concentrations ≤ 1.5 mM resulted in their precipitation as hydroxides in 15–30 min, whereas concentrations ≥ 4 mM were found to be stable even over a week, with no precipitation, as confirmed from the cyclic voltametric measurements taken during this time period. No precipitation was observed in the entire pH range studied, whereas the starting materials

Table 3
Cyclic voltametric data for complexes **1–9** at HMDE

Complex	pH	E_p ^{c} (V)	E_p ^{a} (V) [a]
1	6.2	−1.56	−0.89
	8.0	−1.65, −1.81	−0.79, −0.95 (br)
	9.5	−1.73	—
2	5.7	−1.56	−0.72
	7.1	−1.59, −1.66 (sh)	−0.73
	8.0	−1.62, −1.76	−0.68, −0.9 (br)
	9.2	−1.72, −1.76, −1.84	−0.81
3	5.4	−1.55,	−0.75
	7.2	−1.59, −1.66 (sh)	−0.76
	8.0	−1.64, −1.78	−0.70
	9.4	−1.72, −1.74, −1.82	−0.77
4	4.6	−1.41, −1.55	−0.9 (br)
	5.9	−1.53	−0.9 (br)
	7.3	−1.61, −1.65	−0.9 (br)
	8.3	−1.64	−0.9 (br)
5	4.1	−1.45, −1.54,	—
	5.1	−1.52	−0.92
	7.4	−1.55, −1.59	−0.80
	8.4	−1.60, −1.64	−0.82
6	4.1	−1.56	−0.70 (br)
	6.3	−1.57	−0.68
	7.3	−1.58	−0.73
	8.4	−1.60 (sh), −1.64	—
7	5.4	−1.54	−0.85
	7.1	−1.59, −1.64	−0.86
	8.1	−1.68, −1.74 (sh)	−0.9 (br)
	9.4	−1.72, −1.76	—
8	5.6	−1.54	−0.74
	7.2	−1.59, −1.67 (sh)	−0.75
	8.2	−1.65, −1.74	−0.74, −0.96
	9.4	−1.72, −1.78, −1.84	−0.92 (br)
9	5.3	−1.53	−0.89
	7.1	−1.54, −1.63	−0.75
	8.1	−1.62, −1.80	−0.67
	9.5	−1.71	—

[a] br = broad, sh = shoulder.

$[NEt_4]_2[MnCl_2Br_2]$ and $MnCl_2 \cdot 4H_2O$ gave insoluble hydroxides. A similar robust hydrolytic behaviour over a wide pH range was observed in our previous studies with the saccharide complexes of VO^{2+}, Cr(III) and Fe(III) [10–12].

Nature of the products.—The Mn(II)–saccharide complexes synthesised from both the starting materials are brown in colour and dissolve only in water to give brown solutions. Complexes **1** and **2** are dinuclear and correspond to a formula $Na[Mn_2(Sacch)_2(OH)Cl_2] \cdot nH_2O$, where Sacch = D-Gal (**1**) or D-Fru (**2**) and $n = 1$ and 0 for **1** and **2**, respectively, whereas complex **3** is also dimeric corresponding to a formula $Na[Mn_2(D\text{-}Glc)_2(OH)_2Cl]$. Complex **4** corresponds to a trinuclear formula $Na[Mn_3(D\text{-}Gal)_3(OH)Cl_3] \cdot 0.5H_2O$, whereas complex **5** corresponds to $Na[Mn_3(D\text{-}Fru)_3(OH)_3Cl] \cdot CH_3OH \cdot H_2O$. Complexes **6**–**8** have a formula $Na[Mn_3(Sacch)_3Cl_4] \cdot xCH_3OH \cdot yH_2O$, where Sacch = D-Glc (**6**, $x = 0$, $y = 1.5$), D-Xyl (**7**, $x = 2.5$, $y = 0$), or D-Rib (**8**, $x = 3.5$, $y = 0$). The Mal complex **9** corresponds to $Na_2[Mn_2(D\text{-}Mal)Cl_2Br_2] \cdot CH_3OH \cdot H_2O$. Thus it can be seen that the complexes obtained from $[NEt_4]_2[MnCl_2Br_2]$ (**1**–**3**, **9**) are predominantly dimeric and those from $MnCl_2 \cdot 4H_2O$ (**4**–**8**) are trimeric. This may be attributable to the variations in the reaction medium and in the polarities of the purifying solvents/mixtures, as well as in the experimental conditions (see Experimental section). FAB mass spectral analysis of the complexes **2** and **3** revealed the dimeric nature of these complexes by the presence of moderate peaks at *m/z* 306 [assignable as $Mn_2O(Sacch)$] and 290 [assignable as $Mn_2(Sacch)$] in both the cases. However, it is interesting to note that all the monosaccharide complexes **1**–**8** have a 1:1 Mn-to-saccharide ratio, while the disaccharide complex **9** apparently has a ratio of 2:1. The complexes were found to be tetrahedral in the solid state and octahedral in aqueous solutions. These Mn(II)–saccharide complexes are highly paramagnetic in nature as observed from the calculated magnetic moments (Table 2). The effect of a paramagnetic ion on skeletal ^1H and ^{13}C nuclear resonances of saccharide was clearly evident from the excessive broadening of ^1H NMR peaks in the region of 3.5–4.5 ppm and ^{13}C NMR peaks in the 60–80 ppm region.

5. Conclusions

As mentioned earlier, transition-metal–saccharide interactions have been explored mostly in solution studies [8]; however, no attempts were made to isolate these complexes in the solid state. The synthetic procedures reported by us are thus unprecedented in this direction and provide simple and reproducible experimental methods to synthesise isolable, water-soluble transition-metal–saccharide complexes. The use of the sodium salts of the saccharides enhances their reactivity towards metal-ion coordination and results in complexation through deprotonated hydroxyl groups compared to non-ionic interactions in case of adducts formed from simple saccharides. The natural occurrence of such complexes in biological systems [1] makes the transition-metal–saccharide chemistry even more challenging to bioinorganic chemists. Moreover, these Mn(II)–saccharide complexes are expected to be of paramount importance due to the use of such complexes for pharmaceutical, agricultural, and catalytic applications [4].

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