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Transition metal–saccharide chemistry: synthesis, characterization and solution stability studies of *cis*-dioxomolybdenum saccharide complexes

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Abstract

Six *cis*-dioxomolybdenum(VI) complexes of simple monosaccharides (D-glucose, D-fructose, D-galactose, D-mannose, D-ribose and D-xylose) have been synthesized and characterized by a variety of analytical and spectral methods. Both the solution and solid-state studies have supported the presence of dimeric structures, formed through the *cis*-MoO_2 moieties and the bridging saccharide units. Solution stability of these complexes as a function of time has also been addressed.

Keywords: Transition metal–saccharide chemistry; *cis*-Dioxomolybdenum saccharides; Solution stability; Dimeric structure; Bridging saccharide units

1. Introduction

Molybdenum is the only second-row transition metal ion that is involved in any sort of biological activity. In particular, through its +4, +5 and +6 oxidation states, it plays an important role in various oxidoreductase enzymes [1]. Saccharide units in biological systems and their possible interactions with metal ions has been a promising field in the area of bioinorganic chemistry [2]. Solution studies have clearly demonstrated complex formation between transition metal ions and saccharides [3]; however, the isolated complexes in case of alkali and alkaline earth metal ions were mostly found to be adducts [4]. Notably the N-glycosides of Co(III) and Ni(II) [5], the lyxose complex of Mo(VI) [6] and the Cu (II) complex of sugar alcohols [7] are a few among the crystallographically characterized ones.

During the past decade, in the process of developing the transition metal–saccharide chemistry and biology, we have reported the synthesis, characterization, isolation and solution stability studies of saccharide (D-glucose, D-fructose, D-galactose, D-mannose, D-ribose and D-xylose) complexes of almost all the *3d* transition metal ions, including

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those of divalent (Mn, Co, Ni, Cu and Zn), trivalent (Cr and Fe) and tetravalent (V) species, as well as biointeractions of VO^{2+}, Cr(III) and Fe(III) [2(b)]. We have also reported in vitro reducing abilities of saccharides and related molecules towards Cr(VI) [8], V(V) and Mo(VI) [9] on a comparative scale. In this paper, for the first time, we reported the synthesis, characterization and solution stability studies of saccharide complexes of the *cis*-dioxomolybdenum(VI) moiety.

2. Experimental

Materials and methods.—All solvents were distilled and dried before use by usual procedures. $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ was obtained from LOBA-Chemie (India). All the saccharides were obtained from Aldrich Chemical Co. (USA) or Lancaster Synthesis Ltd. (UK). Sodium metal was obtained from E. Merck (Germany). All reagents were used without further purification. $MoO_2(acac)_2$ was prepared by a reported procedure [10].

Absorption spectra were recorded using a Shimadzu UV-2101 spectrometer. FTIR spectra were recorded in a KBr matrix on an Impact 400 Nicolet FTIR spectrophotometer. Elemental analyses were done on a Carlo–Erba elemental analyzer. Metal content was determined using inductively coupled plasma-atomic emission spectroscopy (ICP-AES) with a Labtam Plasmalab 8440 analyzer. CD experiments were performed on a JASCO J-600 spectropolarimeter. Thermal analysis was performed on a Shimadzu DT-30 thermal analyzer. Cyclic voltammetry was carried out on a BAS-100 electrochemical analyzer.

Syntheses.—All the complexes were synthesized and purified by the same procedure. One typical procedure for synthesis is given below.

Mo(VI)-D-glucose complex, (**1**). D-glucose (1.62 g, 9 mmol) was suspended in 100 mL of MeOH with stirring. Freshly cut sodium (0.414 g, 18 mmol) was added in pieces to the suspension, which resulted in the dissolution of D-glucose as its sodium salt as reported earlier [11,12]. The solution was stirred for 30–45 min. $MoO_2(acac)_2$ (0.984 g, 3 mmol) was added to the methanolic solution of the sodium salt of D-glucose, which resulted in the formation of a turbid mixture, and the stirring was continued for 24 h. During this time the colour gradually changed to brown with the formation of a precipitate. The precipitate was filtered and washed successively three times with acetone. The product was purified by dissolving the solid in MeOH, followed by reprecipitation with acetone. The isolated solid was dried under vacuum to obtain complex **1** in 44% yield. The Mo(VI)-D-fructose (**2**), Mo(VI)-D-galactose (**3**), Mo(VI)-D-mannose (**4**), Mo(VI)-D-ribose (**5**) and Mo(VI)-D-xylose (**6**), were synthesized adopting a similar procedure, using D-frutcose, D-galactose, D-mannose, D-ribose, and D-xylose, respectively. The product yields of these were 26, 35, 38, 42, and 36%, respectively. The analytical data for all these complexes are summarized in Table 1. All the molybdenum–saccharide complexes reported in this paper were found to be moisture sensitive and highly soluble in water, but sparingly soluble in MeOH.

3. Results and discussion

Thermal analysis.—Thermal degradation studies were carried out in nitrogen atmosphere in the temperature range of 25 to 650 °C. Weight losses

Table 1
Elemental analysis data of complexes **1–6**

Complex	%C	%H	%Na	%Mo
$C_{24}H_{40}O_{28}Na_4Mo_2\cdot 2CH_3OH\cdot 5H_2O\cdot 2CH_3COCH_3$ (**1**)	C 28.87	5.30	6.91	14.42
	O 28.79	5.35	7.30	14.08
$C_{24}H_{40}O_{28}Na_4Mo_2\cdot 2CH_3OH\cdot 5H_2O\cdot 2CH_3COCH_3$ (**2**)	C 28.87	5.30	6.91	14.42
	O 28.52	5.37	7.20	14.57
$C_{24}H_{40}O_{28}Na_4Mo_2\cdot 2CH_3OH\cdot 5H_2O\cdot 2CH_3COCH_3$ (**3**)	C 28.87	5.30	6.91	14.42
	O 28.96	4.88	7.40	14.56
$C_{24}H_{40}O_2Na_4Mo_2\cdot 2CH_3OH\cdot 5H_2O$ (**4**)	C 25.70	4.81	7.57	15.80
	O 25.86	5.12	7.20	15.63
$C_{20}H_{32}O_{24}Na_4Mo_2\cdot CH_3OH\cdot 3H_2O\cdot 4CH_3COCH_3$ (**5**)	C 31.49	5.29	7.31	15.24
	O 30.90	5.33	7.41	15.31
$C_{20}H_{32}O_{24}Na_4Mo_2\cdot 2CH_3OH\cdot 3H_2O\cdot 2CH_3COCH_3$ (**6**)	C 28.63	4.99	7.83	16.34
	O 28.83	4.83	8.02	16.77

were calculated and are summarized, along with the appropriate assignment of the fragments, in Table 2. Within the first 150 °C, all the solvent molecules were found to be lost. The overall weight loss was found to be in the range of 60–80%, indicating the degradation of all the saccharide units in the form of CO, CO_2 and H_2O. Due to the insufficient oxygen being available in the system, mainly non-stoichiometric metal oxides were formed.

FTIR studies.—The FTIR spectra of complexes **1–6** were recorded in a KBr matrix between 4000 and 400 cm^{-1} and compared with those of the corresponding free saccharides. The spectra of all the complexes showed broadening of all the bands, making the assignment of the individual vibrational modes difficult. Generally the transition metal–saccharide complexes show broad FTIR spectra [11,12], though the spectra of the adducts are relatively sharp [4]. The ν_{O-H} bands of the free saccharides are observed in the region 3500–3200 cm^{-1}, which upon complexation, show merging, exhibiting a broad band at ~3400 cm^{-1} with a shoulder at ~3200 cm^{-1}. The ring vibrational frequencies for the bending modes of C–OH, CH_2 and C–CH of the free saccharides (1460–1340 cm^{-1}) showed merging at ~1400 cm^{-1} upon complex formation. The C–O and C–C stretching vibrations in the region 1140–990 cm^{-1} were also merged to give a broad band at ~1050 cm^{-1} upon complexation, in contrast to the sharp bands observed in case of the free saccharides. While the *cis*-MoO_2^{2+} moiety in $MoO_2(acac)_2$ shows two sharp lines, one at 905 and the other at 935 cm^{-1}, these are merged to give a broad and strong line at ~880 cm^{-1} with a high frequency shoulder (~900 cm^{-1}), indicating the presence of the *cis*-MoO_2^{2+} moiety, even in the products (**1–6**). Thus the FTIR spectra of the products are indicative of the complexation of the *cis*-MoO_2 cation with the saccharide units.

Table 2
Thermal analysis data of complexes **1–5**

Complex	Temperature (°C)	% weight loss	Probable species
1	65	8.5	$2CH_3COCH_3$
	155	12.5	$2CH_3OH + 5H_2O$
	225	16	6CO
	260	27	$5.5CO_2$
	640	15.5	$CO_2 + 2CO$
2	90	8.5	$2CH_3COCH_3$
	130	11.5	$2CH_3OH + 4H_2O$
	275	29	$7CO_2$
	335	23	6.3CO
3	95	12	$2CH_3COCH_3 + 2H_2O$
	140	11	$2CH_3OH + 3.5H_2O$
	275	28	$5CO_2 + 2CO + H_2O$
	340	25.5	7CO
4	110	18	$2CH_3OH + 9H_2O$
	220	27	$6CO_2$
	490	27	7CO
5	105	8	$CH_3COCH_3 + 2.5H_2O$
	150	5	CH_3COCH_3
	335	28	$CH_3OH + 6CO_2 + 0.8H_2O$
	360	17	5CO
	400	9	CO_2

Solution absorption studies.—Absorption spectra of freshly prepared aqueous solution of the complexes were recorded in the region of 190 to 800 nm and are shown in Fig. 1. No bands are observed corresponding to the *d–d* transitions, indicating the presence of only Mo(VI) in all the complexes. This observation is also consistent with the fact that the sodium salts of the free saccharides are not good reducing agents, though simple saccharides could reduce the metal ions effectively in acidic conditions. Reducing abilities of sacchrides towards Cr(VI), Mo(VI) and V(V) are well studied in our laboratory [8,9]. In the range from 500 to 190 nm, there are four distinct peaks in all the complexes. With increasing ε values, these peaks appear around 350–375, 288–306, 232 and 207 nm, respectively. The bands observed at 207 and 232 nm are attributed to the possible ligand transitions influenced by the presence of the metal ion; however, in free ligands these transitions appear around 190 nm. A ligand-to-metal charge-transfer band appeared in the range of 288 to 306 nm with a low-energy shoulder at around 350–375 nm. In the aqueous solution of the complexes (**1–6**), the intensity of the 288–306 nm band decreases as a function of time, although the shoulder at 350–375 nm is unaltered. However, the diffused reflectance spectra of these complexes (250–450 nm) in the solid state are comparable with those obtained with the freshly prepared solution of the corresponding complexes. This seems to be consistent with the fact that the dimeric structure formed through weak saccharide bridge, breaks in the solution. The corresponding absorption data are given in Table 3.

Circular dichroism (CD) studies.—CD spectra of **1–6** were taken in aqueous solution in a 0.1 cm quartz cell in the range of 200 to 450 nm. Complex **3** among the hexoses (**1, 3, 4**) and **5** among the pentoses (**5, 6**) showed CD curves of opposite sign

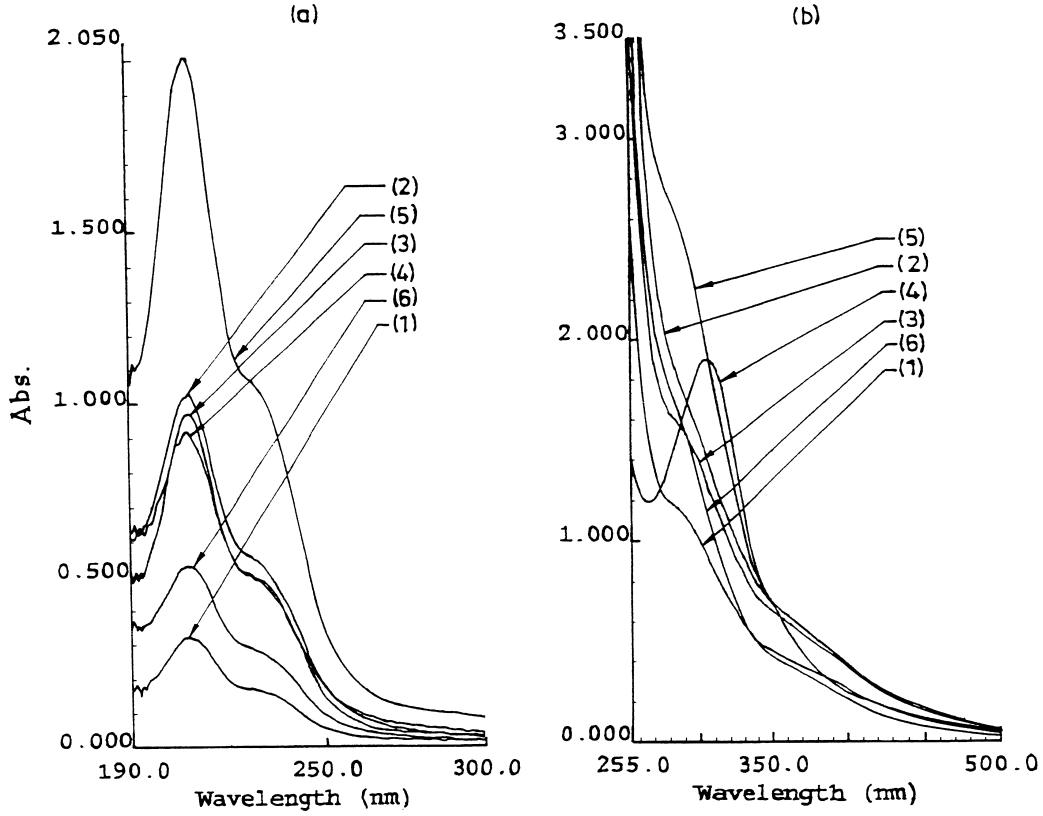

Fig. 1. Absorption spectra of complexes **1–6**: (a) in the region of 190 to 300 nm and (b) in the region of 250 to 500 nm. The spectra shown in (b) are measured with about 100-fold concentrated solution as compared to those given in (a).

compared to those of the complexes **1, 4** and **6**. This is attributable to the difference observed in the orientation of the hydroxyl groups in the saccharides. Based on the coordination abilities of different saccharides [2b,13], a 3,4-*cis*-diol binding is proposed for the D-galactose complex, whereas a 3,4-trans-diol binding is proposed for the D-glucose and D-mannose complexes. Among the pentoses, D-ribose seems to use the favorable 3,4-*cis*-diol orientation for its complexation.

NMR studies.—^{1}H and ^{13}C NMR spectra of the complexes were recorded in D_2O and were compared with those of the corresponding free saccharides. Upon complexation, the individual skeletal proton signals of the saccharide ligands have generally broadened and merged to result in a broad envelope with fine structures in the region of 3.2 to 4.2 ppm as shown in Fig. 2. Further, it is known that the skeletal protons of saccharide moieties exhibit a strongly coupled system in the NMR spectrum. Due to these factors, the assignment of the individual resonances has not been possible for the saccharide complexes of the *cis*-MoO_2^{2+} moiety.

In the ^{13}C NMR spectra of the aqueous solution of the free saccharides, it is seen that the pyranose form is predominantly present in all the cases, with the α-anomer as the major component in D-glucose

Table 3
Absorption and conductivity data for complexes **1–6**

Complex	$\lambda(\varepsilon)$nm($LM^{-1}cm^{-1}$)	Conductivity data($ohm^{-1}M^{-1}cm^2$)	
		Initial	After 48 h
1	373 (250), 290 (760), 232 (5880), 208 (12311)	261	180
2	370 (360), 291 (1300), 231 (9880), 207 (22101)	227	146
3	370 (370), 291 (1000), 232 (7842), 208 (16518)	241	167
4	350 (430), 306 (1200), 231 (3413), 207 (4417)	269	158
5	373 (360), 290 (1500), 232 (9691), 208 (20680)	268	185
6	367 (200), 288 (900), 232 (3976), 208 (8375)	261	199

Table 4
^{13}C NMR shift values ($\Delta\delta$ ppm) for **1** and **3**–**6**, based on the signal from the most abundant anomeric forms

Complex	C-1	C-2	C-3	C-4	C-5	C-6
1	4.39	2.78	3.69	5.04	1.32	3.24
3	0.66	1.52	6.41	5.70	1.43	2.54
4	4.70	3.68	6.44	9.61	1.54	2.59
5	0.50	1.54	4.96	5.88	1.18	—
6	4.34	2.40	2.10	4.20	2.60	—

and D-mannose, and the β anomer as the major component in D-fructose, D-galactose, D-ribose and D-xylose. The interpretation of the ^{13}C NMR spectra of the complexes was made based on the shift of signals arising from the most abundant form. The coordination induced shifts (CIS) in each carbon, $\Delta\delta$ ($\delta_{complex} - \delta_{ligand}$, ppm) are given in Table 4. All the carbon signals are shifted to different extents due to the influence of metal-ion binding. The maximum shifts have been generally observed with C-3 and C-4 in the complexes, indicating the favorable interactions of C-3 and C-4 hydroxyls with the metal ion. However, the considerable shifts observed in C-6 (hexoses) or C-5 (pentoses) can be attributed to the electric and magnetic through-space effect of the metal ion [14]. The magnitude of the shift observed in case of C-1 is not the same in all the complexes: it is large in complex **1, 4**, and **6**, but not so significant in **3** and **5**. Araki and Tajima [15] showed that when the monosaccharides have the arabinopyranose conformation, the interaction with the metal ion is site specific, involving the C-3 and C-4 hydroxyls. It is also worth noting that the affinity of lectins towards monosaccharides is sensitive to the orientation of the OH groups at C-3 and C-4 centers [16]. Considering all these aspects, chelation of the monosaccharide units in all the complexes has been predicted to be through C-3 and C-4 hydroxyls. The shift of C-1 in some cases (**1, 4** and **6**) may be due to the involvement of this OH in a weak bridging between the two metal centers in the formation of dimeric complexes.

Cyclic voltammetry.—The cyclic voltammetry studies were conducted in 0.07 M aqueous KCl with 0.001 M concentration of the complexes, using Pt working and Ag–AgCl reference electrodes, in the potential range +0.5 to −0.5 V (Fig. 3). A cathodic reduction peak assignable for the Mo(VI)→Mo(V) appeared at −137, −112, −135, −155, −107 and −134 mV for complexes **1**–**6**, respectively. In case of **1, 2, 3**, and **6** the voltammogrammes are irreversible, while in **4** and **5**, these are quasireversible. Weak anodic oxidation peaks are observed at −50 and −20 mV for **4** and **5** with ΔE_p values of 105 and 87 mV, respectively. The quasi and/or irreversible behaviour observed with these complexes may indicate a fast chemical complication including decomposition, coupled with the primary electron-transfer step. Thus the studies

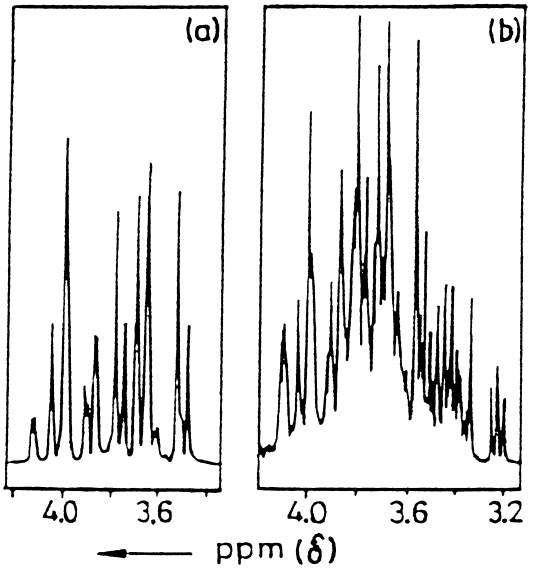

Fig. 2. ^1H NMR spectra of (a) D-glucose and (b) complex **1** in D_2O.

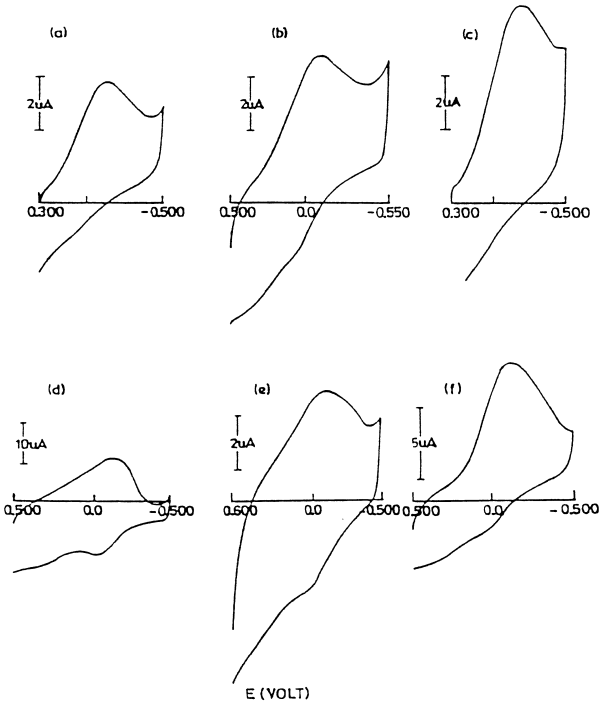

Fig. 3. Cyclic voltamogrammes of the complexes: (a) **1**, (b) **2**, (c) **3**, (d) **4**, (e) **5**, (f) **6**.

indicated that the saccharide ligands can provide environment suitable for stabilizing higher oxidation state of metal ions, such as Mo(VI), probably due to the availability of several oxo-donor groups.

Solution stability studies.—Stability studies have been performed in aqueous media, mainly through UV-vis absorption studies, but also through the change in pH of the aqueous solution of the complexes. The changes occurring in the pH of the aqueous solution of the complexes were measured as a function of time as shown in Fig. 4. All the complexes showed a decrease in the pH value by 0.5–2.5 units over a period of 48 h. As the hydrolysis of the complexes is expected to go through the changes in the H^+ ion concentration, a change in pH is very well expected. The decrease in pH follows an order; **3** (2.5) > **1**∼**5** (2.2) > **2** (1.8) > **4** (1.7) > **6** (0.5), indicating that the relative rate of hydrolysis of the complexes in solution is different. However, no precipitation was observed during this period.

The absorption spectra were monitored as a function of time for **1, 3, 4** and **5**. Practically no change was observed in the band positions and intensities of the two higher energy ligand transition bands, but a noticeable decrease was observed in the intensity of the lower energy LMCT band at ∼300 nm in all the cases. The decrease is rapid with **4**, moderate with **1** and **5**, and slow with **3**. But there are no changes observed in the other LMCT band (∼350 nm). Typical spectra as a function of time were observed in the case of complex **4** (Fig. 5).

CD spectra are measured as a function of time in case of **4** (up to 30 min) and **5** (up to 73 min). While **4** showed marginal changes in the spectra, **5** showed appreciable changes in the band observed around 260 to 270 nm, in its position and ellipticity, indicating the breakage of the complex in the solution over a period of time. A quantitation has not been possible from the CD spectra.

The conductivity data of freshly prepared solutions of **1** to **6** are consistent with a 4:1 electrolyte, however, shows a decrease in values when left in solution for ∼48 h (Table 3). The decrease in conductivity indicates dissociation of the complexes in solution over a period of time, leaving various neutral species including those of saccharides in solution. Due to such breakage, the solution will have a number of species present and hence cannot be easily characterized.

Nature of the products.—All the saccharide complexes reported here (**1–6**) possesses the *cis*-dioxo molybdenum function with Mo in its +6

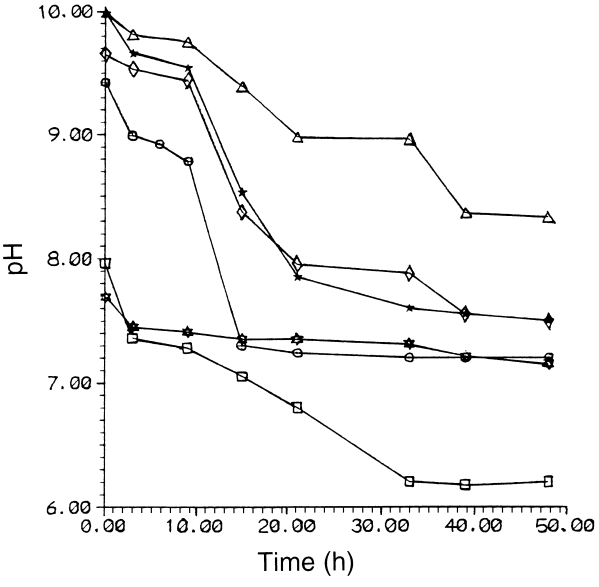

Fig. 4. Changes in the pH as a function of time for the complexes in their aqueous solution: 1⊕, 2□, 3★, 4△, 5◇, 6☆.

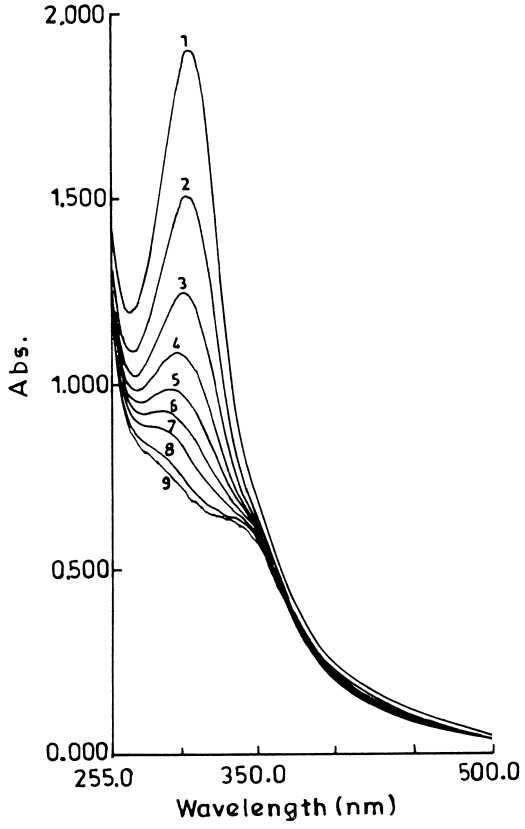

Fig. 5. Absorption spectra as a function of time for complex **4** in aqueous solution: 1, 0 min; 2, 2 min; 3, 4 min; 4, 6 min; 5, 8 min; 6, 10 min; 7, 12 min; 8, 15 min; 9, 18 min.

oxidation state, which is confirmed by the absence of any EPR signal and also by the absence of any *d–d* transition in the absorption spectra. All the complexes are anionic in nature with sodium as the counter cation. EXAFS studies in case of iron–saccharide complexes suggested that the saccharide ligands act as bidentate chelate ones [17]. While Tajmir-Riahi reported [18] non-transition metal–saccharide adducts, the interaction with the transition metal seems to influence the skeletal vibrations perhaps due to the uneven vibronic coupling in the solid state of these complexes. Based on the analytical and spectral data as measured both in the solid and solution states, the complexes exhibited a formula, $Na_4[Mo_2O_4(\mu\text{-sacch})_2(sacch)_2]$, with varying number of solvent molecules associated with each of these (as given in Table 1). It is known that the mutarotation of monosaccharides takes place in the presence of the transition metal ions as reported in the literature. It is also known that in presence of molybdate, C-2 epimerisation is expected in mildly acidic solutions [19]. However, in the present case, the aqueous solutions of the complexes have not shown any acidic pH as can be noted from the time variable pH monitoring experiments The solution studies provided strong support for the dimeric nature of the complexes and at the same time reveal that the nature of bridging is not identical in all the cases, as understood based on the ^{13}C NMR studies. However,

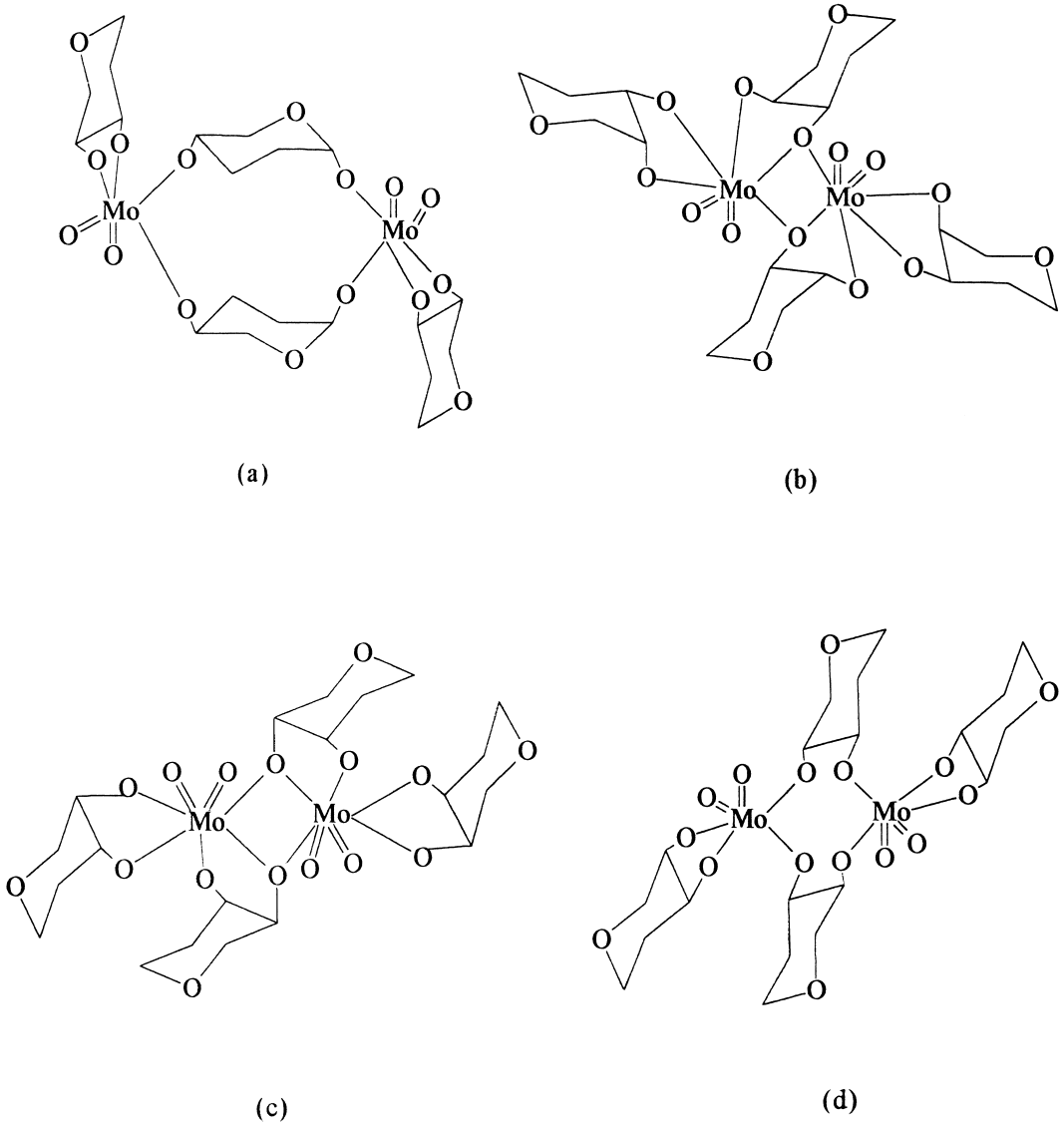

Fig. 6. Four different structural types possible for the *cis*-MoO_2^{2+}–saccharide complexes. Some of the OH groups present on carbons are not shown for clarity.

^{13}C spectra indicated a fast dissociation of complex **2** in aqueous solution. Considering the chelating affinity of the monosaccharides in accordance with the ^{13}C NMR shift values, O-3–O-4 chelation is proposed for all the complexes. Based on the shifts observed with the carbons, a weak bridging is proposed through O-1 and O-4 for **1** and **6** and O-3 and O-4 in case of **3, 4**, and **5**. Considering all these aspects, four possible types of structures (a), (b), (c) and (d) were proposed, as shown in Fig. 6. Among these, structure (a) is best fitted with **1** and **6**, structure (b) with **3**, structure (c) with **5**, and structure (d) with **4**.

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