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Chromate reduction: reduction of potassium chromate by D-glucose and D-fructose to form Cr(III)–saccharide complexes

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ABSTRACT

The reduction of chromate by saccharides is of paramount importance in the context of chromium transport in biological and ecological systems. Potassium chromate has been shown to be reduced by D-glucose and D-fructose to form Cr(III)–saccharide complexes via an intermediate Cr(V) species. These saccharide complexes have been isolated in the solid state for the first time and characterized by analytical, spectroscopic, magnetic and electrochemical methods. Bridged dinuclear saccharide complexes of Cr(III) have been proposed.

INTRODUCTION

Cr(VI) salts are reduced by various cellular components forming final cross-linked Cr(III) products which results in the impairment of normal cellular functions[1]. Soil components such as fulvic and humic acids are equally active in reducing Cr(VI) salts and perhaps provide entry for chromium into ecological and biological systems[2]. Among the various reductants, cysteine, glutathione, ascorbic acid, and saccharide molecules are found to be predominant[3]. In particular, saccharides are expected to promote chromium transport in biological and ecological cycles by being part of various molecular components of soil and cells of plants and animals. In a recent report Micera and coworkers demonstrated the reduction of dichromate with galacturonic acid in aqueous solution, but no solid compound was isolated[4]. Currently we are involved in studying the reductive capacities of various monosaccharides with chromate. Our studies indicate that the reduction of chromate occurs via soluble, reactive, and relatively long-lived Cr(V) intermediate species possessing different life times, depending upon the saccharide[5] and com-

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plex of the final Cr(III) product. In order to understand the basic interactions and the applicability of transition-metal–saccharide complexes, we have begun a systematic synthesis and characterization program and have had reasonable success[6]. In the present paper we demonstrate the synthesis, isolation, and characterization of Cr(III)–D-glucose [Cr(III)–D-Glc] and Cr(III)–D-fructose [Cr(III)–D-Fru] complexes that are formed as a result of chromate reduction by these saccharides, followed by complexation. To our knowledge, this is the first case whereby Cr(III)–saccharide complexes have been isolated and characterized in the solid state.

RESULTS AND DISCUSSION

Chromium(III)–saccharide complexes are soluble only in H_2O under normal conditions. However, in the presence of 18-crown-6, these dissolve in nonaqueous solvents such as MeOH, Me_2SO, and, to a lesser extent, in acetonitrile (MeCN), indicating that there exists strong intermolecular interactions mediated through K^+ ions. The final, purified products were characterized by several routine analytical, spectroscopic, magnetic, and electrochemical methods. These compounds are highly hygroscopic; hence, the need for special precautions while handling.

The reaction proceeded via the reduction of chromate by saccharide to give a final Cr(III) product that is bound to the saccharide. Absorption spectra measured during the reaction progress of the chromate–D-glucose system at different time intervals showed the disappearance of Cr(VI) bands (372 and 273 nm) and the appearance of the Cr(III) bands (580 and 410 nm). The reaction in this case is completed in 8–10 days. Fig. 1 shows the corresponding absorption changes as a function of time. This is similar to the case with D-fructose, except that the reaction is completed in a shorter period.

The final Cr(III)–D-Glc product in water showed two $d \rightarrow d$ transitions, one at 584 nm ($\epsilon = 85$, $A_{2g}(F) \rightarrow T_{2g}(F)$) and the other at 415 nm ($\epsilon = 27$, $A_{2g}(F) \rightarrow T_{1g}(F)$) with a weak shoulder at ~ 695 nm ($\epsilon = 27$) and one UV transition at 207 nm ($\epsilon = 9427$). The Cr(III)–D-Fru product in water showed transitions at 579 nm ($\epsilon = 86$), 408 nm ($\epsilon = 154$), 340 nm ($\epsilon = 292$), 203 nm ($\epsilon = 11\,413$), and a broad, weak shoulder around 690 nm ($\epsilon = 10$). In both cases, these bands are different from the Cr(III)–aquo species, indicating Cr(III) octahedral saccharide complexes having oxygens as the ligating atoms[7].

FTIR spectra of both complexes showed an almost symmetric broad band ($\Delta\nu_{1/2} \sim 450$ cm^{-1}) centered around 3346 cm^{-1} with a weak shoulder around 3266 cm^{-1} that indicates the breakage of several intermolecular H-bonds originally present in the free solid glucose[8] and fructose[9]. However, the shape, position, and the width of the ν_{O-H} band of the complex is further indicative of secondary interactions through its free hydroxyl groups. The stretching vibration of the O–H of water is also expected to overlap in this region. Though the comparison of the

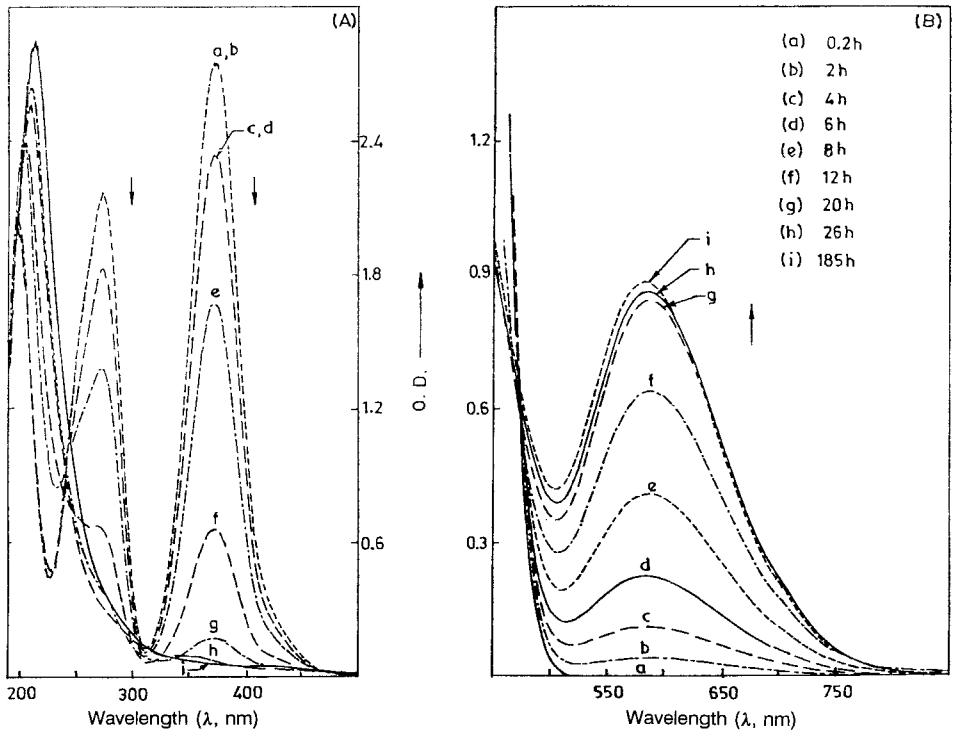

Fig. 1. Absorption spectra of the reaction between potassium chromate and D-glucose as a function of time; A, disappearance of the Cr(VI) bands (372 and 273 nm); B, appearance of the Cr(III) bands (580 and 410 nm).

bands between the free ligands and their complexes in the 900–1400 cm^{-1} region exhibited a good correspondence, the bands in the latter were broad with small shifts that correspond to the formation of both α and β isomers in the final product. This conclusion is further supported from NMR studies.

The reaction between chromate and saccharide showed initially a sharp EPR signal ($g = 1.978$, $\Delta H_{PP} = 0.23$ mT) characteristic of Cr(V), with an increase in intensity for a few hours after the reaction was allowed to take place, followed by a decrease to form a new broad signal assignable to the formation of a Cr(III) species. The intensity of the latter increases as a function of time and approaches a limiting value when the reaction is complete (8–10 days). The changes observed in the intensity of the Cr(V) and Cr(III) signals as a function of time for the D-glucose reaction are shown in Fig. 2. The reaction between chromate and D-fructose follows a similar trend except that the total reaction in this case was completed within 4–5 days. The reactions were allowed to take place until no further growth of the Cr(III) peak was observed.

Pure Cr(III)–D-Glc and Cr(III)–D-Fru complexes exhibited broad signals both in the solid state ($g = 1.9853$, $\Delta H_{PP} = 61$ mT; $g = 1.9849$, $\Delta H_{PP} = 63$ mT) and in

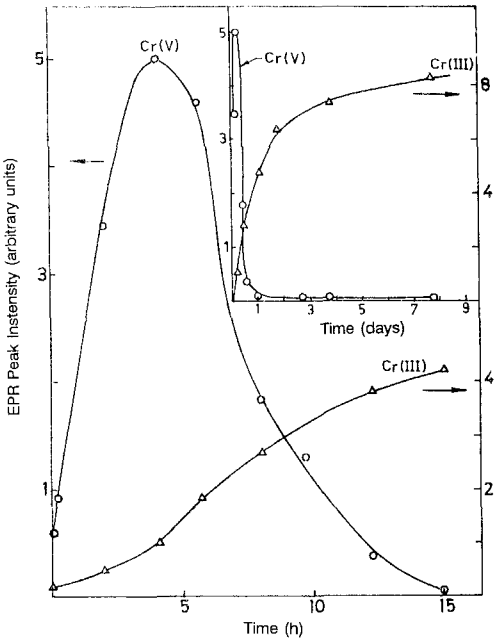

Fig. 2. EPR peak intensities of Cr(V) and Cr(III) species as a function of time in the potassium chromate–D-glucose reacton.

aqueous solution ($g = 1.9468$, $\Delta H_{PP} = 57$ mT; $g = 1.9596$, $\Delta H_{PP} = 60$ mT), which correspond to the presence of Cr(III) in an oxygen environment. Large line widths ranging from 20–40 mT have been noted for various Cr(III)–aquo species, unlike those predicted, and these were attributed to zero field splitting (zfs) as these could not be fitted with other possible relaxation mechanisms[10]. In the Cr(III)–saccharide complexes, we observed larger line widths than these, which perhaps may be associated with a more definite zfs component arising from geometric distortions at the metal centers.

^{1}H NMR spectra of the Cr(III)–Glc complex measured in D_2O and Me_2SO-d_6 were compared with the spectra of pure D-glucose in corresponding solvent systems in order to deduce the binding nature of D-glucose with the Cr(III) species. The spectral lines were broad due to the paramagnetic behaviour of the metal ion. The disappearance of the HO-2 and HO-3 proton resonances in Me_2SO-d_6 spectra indicated that the binding occurs through O^- groups of these carbon atoms of D-glucose. Hydrogens bound to these carbons showed downfield shifts of 0.207 and 0.175 ppm, respectively, in their α isomers and 0.322 and 0.225 ppm, respectively, in their β isomers. Formation of complexes with D-glucose in both anomeric forms is further justified as the starting material itself possesses both anomeric pyranoses in solution. The situation is more complicated in case of the D-fructose complex, as D-fructose substantially exists in at least four different forms arising from its furanose and pyranose structures and also anomers.

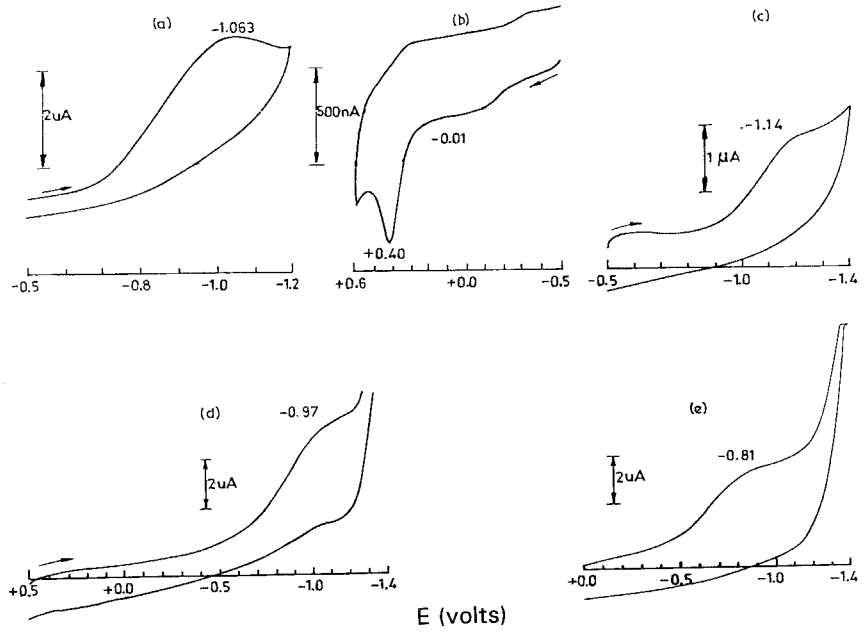

Fig. 3. Cyclic voltammogram of: (a) and (b) 1 mM Cr–D-Glc complex in Me_2SO (solubilized using 18-crown-6) with 0.3 M Me_4NCl as the supporting electrolyte; (c) 1 mM Cr(III)–D-Fru complex in Me_2SO (solubilized using 18-crown-6); (d) 1 mM Cr(III)–D-Fru complex; (e) 1 mM Cr(III)–D-Glc complex both in 50:1 (v/v) of Me_2NCHO–H_2O mixture using 0.1 M Me_4NCl as the supporting electrolyte; scan speed: 100 mV/s.

Solution redox properties of these complexes were studied in Me_2SO (solubilized using 18-crown-6; 0.3 M Me_4NCl as the supporting electrolyte) and 50:1 (v/v) mixture of Me_2NCHO and H_2O (0.1 M Me_4NCl as the supporting electrolyte), under an N_2 atmosphere using cyclic voltammetry at the Pt electrode. Corresponding voltammograms are shown in Fig. 3. In the case of the Cr(III)–D-Glc complex in Me_2SO solution, one irreversible cathodic reduction peak corresponding to a Cr(III)/Cr(II) couple was observed around -1.063 V (Fig. 3a), and two consecutive anodic oxidations of the ligand were seen around -0.01 and $+0.40$ V (Fig. 3b), respectively. The reduction potential of Cr(III) observed in our case is in agreement with that found in the literature[11] and also in our studies with $CrCl_3(THF)_3$. Both of the oxidation potentials of the bound glucose observed in the present case were at more positive values compared to free glucose as studied in basic solution at the Au electrode[12]. This suggests that the oxidation of glucose is facilitated in the Cr(III) complex as compared to that for free glucose. In the case of the Cr(III)–D-Fru complex in Me_2SO, the corresponding Cr(III)/Cr(II) reduction peak was shifted to more negative potentials by about 77 mV as compared to its glucose counterpart (Fig. 3c). In a Me_2NCHO–H_2O mixture, irreversible reduction peaks were observed around -0.97 V (Fig. 3d) and -0.81 V (Fig. 3e) in the D-fructose and D-glucose complexes, respectively. The electrochemical data observed for the Cr(III)–saccharide complexes in the Me_2SO and

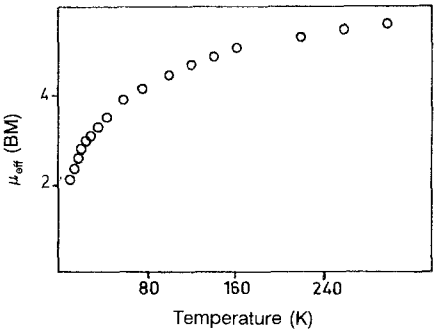

Fig. 4. Magnetic moment (μ_{eff}, BM) of the Cr(III)–D-glucose complex as a function of (K).

$Me_2NCHO-H_2O$ system indicate that the reduction of Cr(III) to Cr(II) is easier in the case of the Cr(III)–D-Glc complex than in the Cr(III)–D-Fru complex. This observation is further consistent with the higher negative charge found in the case of Cr(III)–D-Fru (4^-) as compared to the Cr(III)–D-Glc complex (3^-). Our molar conductance values also reflected the fact that the fructose complex possesses more ions than the glucose one.

Room temperature magnetic susceptibility measurements performed in the case of the Cr(III)–D-Glc complex gave a μ_{eff} of 5.43 BM that is comparable with a calculated magnetic moment for a dinuclear Cr(III) centre ($\mu_{eff}^{calcd} = 5.48$ BM). The measured χ_M^{-1}, exhibited a strong nonlinear behaviour with respect to the temperature in the range 8–300 K, indicating deviation from simple paramagnetic behaviour. A plot of μ_{eff} vs. T (Fig. 4) indicated a $\sim 60\%$ decrease in the observed μ_{eff} in the same temperature range. This behaviour can be explained as characteristic of an antiferromagnetically coupled dinuclear system at low temperature through a bridging species. The Cr(III)–D-Fru complex exhibited a μ_{eff} value of 5.22 BM at room temperature, which is also consistent with a dinuclear Cr(III) center.

These data, together with the elemental analyses (see Experimental section), can be fitted with a formula of a novel μ-hydroxy bridged dinuclear Cr(III)–D-Glc complex $[K_3Cr_2(\mu\text{-}OH)(D\text{-}Glc)_4(H_2O)_3]$. Additional evidence for the formation of the compound has been provided through the measured molar conductance of 150 cm^2 ohm^{-1} M^{-1} that is characteristic of a 3:1 electrolyte[13].

In case of the Cr(III)–D-Fru complex, all the spectroscopic data, together with the elemental analyses (see Experimental section) can be fitted with a dinuclear Cr(III) complex of the type $[K_4Cr_2(\mu\text{-}OH)_2(D\text{-}Fru)_4(H_2O)]$. The molar conductivity value of 236 cm^2 ohm^{-1} M^{-1} gives further evidence for the presence of a 4:1 type of electrolyte[13].

CONCLUSIONS

Chromium(III) products of chromate reduction by D-glucose and D-fructose have been isolated by an unprecedented synthetic procedure. These complexes

may be important in understanding the role of saccharides in chromate reduction activity and in the transport of toxic chromium in ecological and biological cycles. The compounds have been thoroughly characterized by analytical, spectroscopic, magnetic and electrochemical techniques, and novel bridged dinuclear saccharide complexes of Cr(III) have been proposed for the first time.

EXPERIMENTAL

General methods.—Absorption spectra of reactions between chromate and saccharides, and also the final Cr(III)–saccharide compounds were measured on a Shimadzu UV-260 spectrophotometer in aqueous solution. FTIR spectra of the compounds and starting materials were measured on a Nicolet spectrometer in a matrix of KBr. EPR spectra of chromate–saccharide reactions in solution were recorded on a Varian ESR-112 spectrometer with tetracynoethylene (TCNE) as the field marker ($g = 2.00277$). EPR spectra of the final products were measured both in solution and in the solid state. ^{1}H NMR spectra were recorded on a Varian XL-300 spectrometer both in D_2O and in Me_2SO-d_6. Electrochemical studies were performed on a BAS-100A Electrochemical Analyzer at the Pt electrode in dimethylsulfoxide (Me_2SO) and in a *N*,*N*-dimethylformamide–H_2O mixture, using Me_4NCl as the supporting electrolyte and an Ag/AgCl reference electrode.

Cr(III)–Glc complex.—A mixture of K_2CrO_4 (1.942 g, 10 mmol) and D-glucose (10.8 g, 60 mmol) were added to 100 mL of double-distilled water (purged for 20 min with N_2 before use) and stirred at 40–45°C for 8–10 days, followed by filtration and concentration of the filtrate. Completion of the reaction was monitored through absorption (see Fig. 1) and EPR (see Fig. 2) spectra measured at various time intervals. The concentrated solution was precipitated with cold MeOH to give a green solid, and the solid collected upon filtration was washed with three portions of warm MeOH. The solid was redissolved in 20 mL of H_2O and reprecipitated and washed with MeOH. This procedure was repeated three times. The solid thus obtained was stirred for one day in 25 mL of hexane and filtered. This procedure was repeated for a second time. The compound was finally washed with diethyl ether and dried under N_2. The final product was obtained in a yield of 70%, based on the metal. *Anal.* Calcd for $[K_3Cr_2(\mu\text{-OH})(\text{D-Glc})_4(H_2O)_3]$: C, 28.69; H, 4.68; Cr, 10.36; K, 11.65. Found: C, 28.20; H, 4.52; Cr, 10.54; K, 11.89.

Cr(III)–Fru complex.—The procedure for the Cr(III)–Glc complex was adapted, by reduction of the reaction time to 4–5 days, to produce the Cr(III)–Fru complex, which was isolated in 76% yield. *Anal.* Calcd for $[K_4Cr_2(\mu\text{-OH})_2(\text{D-Fru})_4(H_2O)]$: C, 28.13; H, 4.30; Cr, 10.16; K, 15.23. Found: C, 27.93; H, 4.49; Cr, 10.21; K, 15.46.

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