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LETTER

Homoleptic glucose complexes of VO^{2+} and Cr^{3+}

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Transition metal–saccharide complexes are expected to play important roles in various fields such as catalysis, biology and medicine due to the unique interaction of their hydroxyl groups. The impetus for this study is generated from their inherent optical activity and versatile solubility factors and essentially the coexistence of transition metal ions and saccharide-containing molecules in different biological systems. Though there are several reports available in the literature regarding the interaction between these two in solution, no solid complexes of soluble, small molecular weight, homoleptic metal–saccharides have been isolated. Some of these solution interactions include reduction of V(V) with galacturonic acid [1], vanadate–polyol interactions to give mono- and binuclear vanadium complexes [2], reaction of monosaccharides with $CrCl_3(Pyridine)_3$ to give metal complexes only through replacing neutral pyridine ligands [3], manganese–polyol interactions to give complexes of Mn(II, III and IV) which are biologically important [4]. Of course there are certain complexes of Ni and Co as studied by single crystal X-ray diffraction with modified ethylenediamine-*N*-glycoside ligands formed due to the reaction between the respective metal–amines and saccharide molecules [5]. Hence, in the present paper we report the synthesis, isolation and characterization of glucose complexes of VO^{2+} and Cr^{3+} ions in an unprecedented manner.

Experimental

The green solid vanadyl–glucose complex was synthesized by reacting $VOSO_4 \cdot 2H_2O$ with Na–β-D(+)-glucose (generated from equimolar ratios of sodium metal and saccharide in a minimum amount of MeOH) in a 1:2 mole ratio in MeOH. The final green product was isolated by concentrating the reaction filtrate and separating the product and further washing the solid and drying under vacuum. The chromium counterpart was prepared by reacting $CrCl_3(THF)_3$ [6] with Na_2–D(+)-glucose in a 1:3 ratio in MeOH. The methanol insoluble glucose product was isolated by filtration followed by washing two times with MeOH and ether and then drying under vacuum.

Results and discussion

Though the preliminary identification of metal ion–glucose complexation has been made by following the colour changes during the reaction and the loss of halides in the case of chromium, the nature of the complex is studied further by using UV–Vis, FT-IR, EPR and ^1H NMR techniques. All the intermolecular hydrogen bonds present in the solid of free glucose (3200–3400 cm^{-1}) are broken upon complexation with VO^{2+} and Cr^{3+} and an almost symmetric band results at 3380 cm^{-1} for the VO^{2+} complex and at 3405 cm^{-1} for the Cr^{3+} complex with a small shoulder around 3270 ± 10 cm^{-1} corresponding to intermolecular hydrogen bonding interaction with at least one free OH, conceivably C6(OH), from each molecule of the complex. All the sharp bands observed in the case of glucose in the regions 1340–1460 cm^{-1} (δ(OCH, CH, CCH)), 990–1140 cm^{-1} (ν(CO, CC)) and 770–840 cm^{-1} (δ(CCH, CH), ν(CC, CO)) [7] are merged and become broad due to the complex formation and also due to the mixture of compounds present in the product. FT-IR showed the presence of $\nu(V{=}O)$ 995 cm^{-1} and the disappearance of the SO_4^{2-} vibration bands [8] conforming to a final neutral product possessing the VO^{2+} group. A broad, one line EPR spectrum obtained for $VOSO_4 \cdot 2H_2O$ ($g = 2.0116$, $\nu_{1/2} = 135$ G) is converted to an eight-line spectrum upon complexation ($g = 1.953$, $\nu_{1/2} = 19$ G, $a = 16.5$ G) retaining the V(IV) state intact during the reaction. The absorption spectrum of the final product exhibits both d → d (490(sh), 720(br), 830(br) nm) and LMCT bands (250 nm) characteristic of VO^{2+} complexes having an oxygen environment in their primary coordination shell [9]. Proton NMR spectra are indicative of a mixture of products in the case of VO^{2+} and Cr^{3+}. While the ^1H NMR spectrum measured in D_2O provided the information regarding the carbon-bound hydrogens, the DMSO spectrum provided information regarding the OH groups. The δ values of C-1(H) and C-1(OH) showed upfield shifts of

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0.130 and 0.180 ppm, respectively, C-2(H) showed a downfield shift of 0.102 ppm and the C-2(OH) signal was found to be absent. Such shifts were not observed with the sodium salt of β-D(+)-glucose. The spectra also revealed resonances corresponding to the free ligand. All this information is consistent with the formation of a five-membered chelate via O^- of C-2 and OH of C-1 groups to give the VO[β-D(+)-glu$^-$]$_2$ product whose proposed structure is provided in Fig. 1(a).

The absorption spectrum of the chromium–glucose reaction (bands at λ_{max} 260, 333(sh), 655 and 735(sh) nm) is clearly indicative of the complex formation by being different from the spectra of its precursor compounds as well as Cr^{3+}–aquo species. The spectrum observed in the range 600–800 nm showed asymmetry in the Cr^{3+} octahedral band which can be attributed to a mixture of α and β products formed in the reaction in addition to any possible asymmetry involved with the coordination sphere. Comparison of ^1H NMR data of the chromium product in D_2O with that of the free ligand revealed that δ of C-1(H) of α and β products are shifted upfield by 0.053 and 0.104 ppm, respectively, and that of C-2(H) are shifted downfield by 0.230 and 0.110 ppm for the same isomers. Such shifts are not observed for the disodium salt of glucose. Since major shifts are observed with C-1(H) and C-2(H), it is thus reasonable to assume the formation of a five-membered chelate ring through deprotonated oxygens of C-1 and C-2 atoms of both α- and β-isomers. Since, the final product shows only the saccharide ligands and no halide, the product may correspond to the formula $Na_3[Cr(glu)_3]$. The proposed structure of the corresponding β-isomer is shown in Fig.1(b).

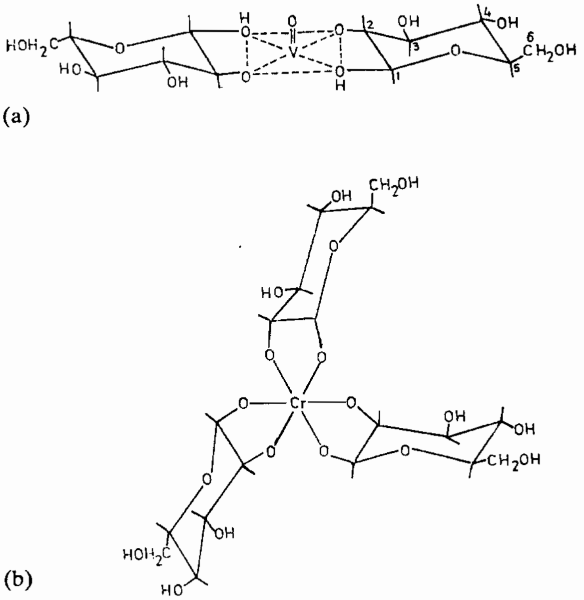

Fig.1. Schematic representation of proposed structures for the complexes (a) VO^{2+}–β-D(+)-glucose and (b) Cr^{3+}–β-D(+)-glucose.

Conclusions

Homoleptic glucose complexes of vanadium and chromium have been synthesized, isolated in the solid state, characterized and the structures are proposed for the first time. We are currently focussing on the separation of the isomers formed in the reaction and establishing their three-dimensional structures using single crystal X-ray diffraction wherever possible.

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