Sugar vanadates: Synthesis and characterization of a mannopyranoside ester incorporating VO$^{3+}$

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Received 12 April 1999

The reaction of methyl-4,6-dimethoxy-$\alpha$-D-mannopyranoside (H$_2$man) with [V$^{IV}$O(L)(H$_2$O)] (L$^2-$, deprotonated salicylaldimine of glycine) in air has afforded [VVO(Hman)(L)] in which the sugar ligand is chelated to the metal via alkoxydic and alcoholic oxygen atoms, the V-O lengths being 1.799(7) Å and 2.366(8) Å respectively.

Sugar vanadates are of interest as analogues of sugar phosphates$^{1-10}$. Such species are, however, sparsely known in the crystalline state and only a pair have so far been structurally characterized; both contain VO$_2^+$ binucleated by diionised sugars as in $^{11,12}$ and as part of our programme on the study of oxovanadium alkoxides$^{13,14}$ we have initiated studies on sugar vanadates and herein we describe the first authentic carbohydrate ester (a mannopyranoside) incorporating VO$_2^+$ chelated as in 2.

Experimental

1

2

Spectra were measured using Perkin-Elmer 783 (IR, KBr disk) and Bruker FT 300 MHz ('H NMR, CDCl$_3$) instruments. X-ray structure was determined using a Nicolet R3m/V diffractometer (Mo K$_\alpha$ radiation, $\lambda=0.71073$ A) and SHEXTL-ver. 5.03 program$^{15}$. Crystal data are: space group, $P2_1$; $a=9.789\,(3)\,$Å, $b=18.534\,(5)\,$Å, $c=13.689\,(4)\,$Å, $\alpha=91.64\,(2)\,$º, $V=2483\,(1)\,$Å$^3$; Z=4; $R=6.49\%$, $wR=13.96\%$. Further details can be had from the author (AC).

Methyl-4,6-dimethoxy-$\alpha$-D-mannopyranoside, H$_2$man, was synthesized from the parent glycoside via protection of two hydroxyl groups as isopropylidene derivative followed by exhaustive methylation and subsequent hydrolysis of the isopropylidene function. The reaction of [V$^{IV}$O(L)(H$_2$O)]$^{16}$ with slight excess of H$_2$man in methanol in air afforded [V$^\circ$(Hman)(L)] as a dark coloured solid. Crystallization from benzene- hexane mixture afforded single crystals of composition [V$^\circ$(Hman)(L)].1/2C$_6$H$_6$ in 80% yield. Analytical data: Found (Calc.): C, 50.09 (50.00); H, 5.41 (5.36); N, 2.73(2.78).

Results and discussion

The mannopyranoside ligand (3) has been so methylated that only an axial-equatorial cis pair of vicinal hydroxyl groups is free for potential metal binding. The Schiff base 4 is employed for blocking three coordination position of VO$_2^+$ setting aside two for possible sugar binding. The reaction of [V$^{IV}$O(L)(H$_2$O)] with H$_2$man has indeed afforded [V$^\circ$(Hman)(L)] in excellent yield.

The complex is diamagnetic ($d^0$) and displays characteristic IR stretches: V=O, 1290 cm$^{-1}$; CO$_2^-$, 1615, 1650 and 1290 cm$^{-1}$.

The structure of [V$^\circ$(Hman)(L)] is shown in Fig.1. The conformation of the V(Hman) fragment is further clarified in 5. The Hman ligand is chelated at the alkoxydic (axial) and alcoholic (equatorial) oxygen atoms lying trans to the azomethine nitrogen atom of L$^2-$ and the oxo-oxygen atom respectively. The five V-O bonds in the distorted octahedral VO$_3$N coordination sphere span the range 1.57-2.37 Å; the V-O (alkoxide) and V-
Fig. 1—Perspective view and atom-labeling scheme for [VO(Hman)(L)].

(alcoholic) lengths being 1.799(7) Å and 2.366(8) Å respectively. Two metrically similar but crystallographically distinct molecules constituting the asymmetric unit form a cyclic (average cavity diameter, 4.5 Å) supramolecular dimer via carboxylate-alcohol hydrogen bonds of lengths 2.70(1) and 2.64(1) Å.

The ^1^H NMR results are consistent with the preservation of the gross [VO(Hman)(L)] structure in solution. The alkoxide and alcoholic functions are at C(2) and C(3)

respectively - the C(2)H(5.42δ, multiplet) signal is shifted downfield from the C(3)H(4.33δ, doublet of doublets) signal by ~ 1 ppm. The anomeric proton (C(1)H occurs as a singlet, the weak equatorial-equatorial coupling with C(2)H being unresolved. The chemical shift of alcoholic OH signal (broad) is 7.41δ.

The general applicability of our synthetic strategy is under scrutiny and there are good indications that VO^3+ esters of methyl 2,6-dimethoxy-β-D-galactopyranoside and methyl-5-methoxy-β-D-ribofuranoside can be isolated.

Acknowledgement

We thank the Indian National Science Academy, Department of Science and Technology and the Council of Scientific and Industrial Research, New Delhi for financial support. Affiliation with the Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore, India, is acknowledged.

References