Carbohydrate Metal Complexes as Ligands for Alkali Cations

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Vanadium(III) assembles six diacetoneglucose fragments in a pseudo-octahedral geometry, each pair of sugars making a cavity appropriate for binding alkali cations, as shown by the structural analysis.

Molecular design directed towards the construction of cavities for the complexation of alkali cations,[1] for trapping organic species *via* the establishment of weak interactions and to simulate the solvation sphere of a metal ion, has a variety of approaches in the literature ranging from crown ethers to more elaborate molecular architectures.[2] Here we report a substantially different approach. Transition metal ions, as a function of their coordination numbers and oxidation states, can assemble sugar units around themselves and thus shape cavities between two or more adjacent sugar ligands. Such oxygen-rich cavities should function, in principle, as binding sites for ions or for species bound *via* hydrogen bonding. Due to the enantiomeric nature of the ligand, such a process can go further for the eventual chiral recognition of the bound species. The monosaccharide used here is diacetoneglucose, 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (Hdag) (Fig. 1).

Homoleptic complexes $[M(dag)_n]$ (M = V, n = 3;[3] M = Ti, Zr, Hf, n = 4[4]) have been synthesized by protolysis of the corresponding metal-alkyl or metal-aryl complexes. Such compounds act as Lewis acids for a variety of bases, including the lithium {[Li(dag)] **1**†} and sodium {[Na(dag)] **2**‡} derivatives of Hdag. **1** (prepared from Bu^{n}Li in Et$_2$O) and **2** (prepared from NaH in Et$_2$O), which have never been described in the literature, are very useful starting materials for metal derivatization. Both are extremely soluble in hydrocarbons including *n*-hexane. They have been analytically, spectroscopically, and, in the case of **1**, structurally characterized. The X-ray structure of **1**§ is shown in Fig. 2 with a selection of structural parameters. The cubane structure has a D_2 non-crystallographic symmetry. Two Li$_4$ and O$_4$(1n) tetrahedra co-penetrate to form a slightly distorted cube. The Li–O distances within the cubic frame range from 1.86(1) to 1.99(1) Å, while the Li···Li distances vary from 2.52(2) to 2.61(2) Å. Each dag unit bridges four alternate edges of the cube, and functions as a bidentate ligand for each lithium *via* O(1) and O(6) (Fig. 2). The Li–O(6) distances (Fig. 2) are, however, significantly longer. All the six-membered rings Li–O(1)–C(1)–C(2)–C(8)–O(6) have a twisted-boat conformation with the torsional angle O(1)–Li–C(8)–C(2) varying from 8.0 (dag b) to 17.8° (dag c). The conformations of the dag units a, b and c are similar, while the significant difference observed for dag d derives essentially from the conformation of the C(8)–C(9)–O(5)–C(5)–C(10)–O(6) ring, which is differ-
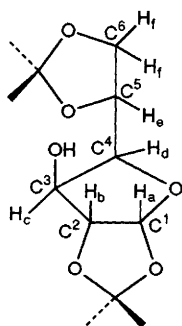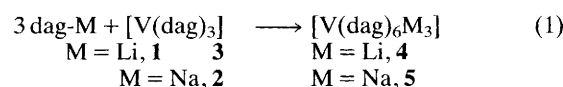
ent from that in the other dag units. There are a significant number of Li$_4$O$_4$ cubane-type structures[5] similar to **1** containing bidentate bridging ligands, forming five-, six- or seven-membered rings. Such rings usually possess an achiral S_4 symmetry around the cube. The arrangement of the four rings in **1** has the chiral D_2 symmetry.

The formation of Lewis acid–base adducts between **1** or **2** and a related dag transition metal complex is shown in eqn. (1). A purple solution of **3** was reacted in toluene with **1** or **2**

$$3\,dag\text{-}M + [V(dag)_3] \longrightarrow [V(dag)_6M_3] \quad (1)$$
$$M = Li, \mathbf{1} \qquad \mathbf{3} \qquad M = Li, \mathbf{4}$$
$$M = Na, \mathbf{2} \qquad\qquad M = Na, \mathbf{5}$$

leading to a green solution of **4**¶ and **5**,‡ which have been obtained in the form of green crystals and have been fully characterized including an X-ray analysis of both. Details are reported here on the structure of **4**,‖ shown in Fig. 3. Vanadium(III) binds the six oxygens O(1) from six different dag units in a slightly distorted octahedral geometry. Complex **4** has a crystallographic C_2 symmetry with the C_2 axis running through V and Li(1). The V–O distances are within a rather narrow range [2.021(4)–2.032(5) Å], much longer than in $[V(py)_2(dag)_3]$[3] but close to those in $[\{V(OPh)_6\}\{Li(dme)\}_3]$.[6] The coordination environment for each lithium cation is provided by two adjacent dag molecules with two O(1) and two O(6) oxygen atoms.
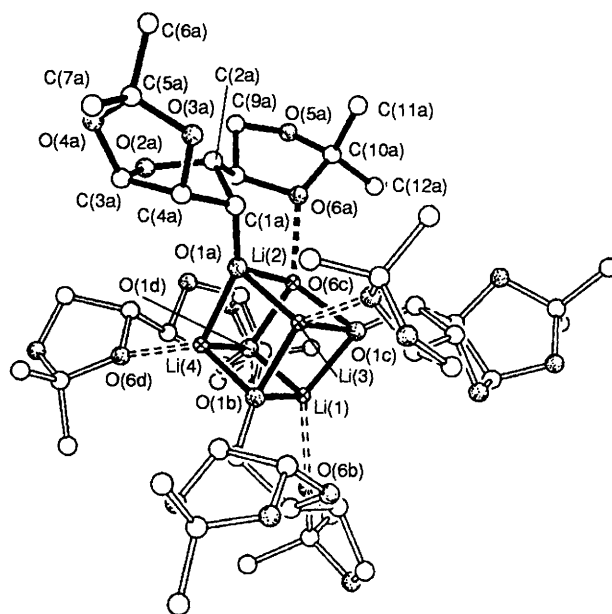
Each lithium cation with the two O(1) oxygen atoms should

Fig. 1 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose, Hdag

Fig. 2 Molecular diagram of [{Li(dag)}$_4$], **1**, with the atom labelling scheme. Selected bond distances (Å): Li–Li (avg.) 2.550(14), Li(1)–O(1b) 1.972(12), Li(1)–O(6b) 1.987(10), Li(1)–O(1c) 1.890(10), Li(1)–O(1d) 1.910(12), Li(2)–O(1a) 1.953(13), Li(2)–O(1c) 1.909(12), Li(2)–O(6a) 1.991(11), Li(2)–O(1d) 1.890(10), Li(3)–O(1a) 1.919(10), Li(3)–O(1b) 1.863(10), Li(3)–O(1c) 1.995(12), Li(3)–O(6c) 2.000(10), Li(4)–O(1a) 1.919(9), Li(4)–O(1b) 1.948(12), Li(4)–O(1d) 1.957(12), Li(4)–O(6d) 2.051(12).
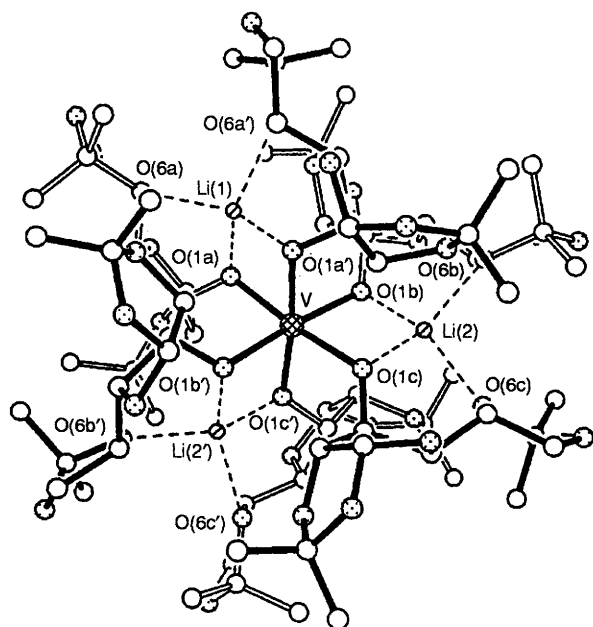
Fig. 3 Molecular diagram of $[V(dag)_6Li_3]$ **4**, with the labels of the most relevant atoms (labelling scheme of sugar ligands in the same as that of Fig. 1). Selected bond distances (Å): V–Li(1) 2.817(16), V–Li(2) 2.862(10), V–O(1a) 2.028(4), V–O(1b) 2.032(5), V–O(1c) 2.021(4), Li(1)–O(6a) 2.061(11), Li(1)–O(1a') 1.884(12), Li(2)–O(6b) 2.078(12), Li(2)–O(1c) 1.922(15), Li(2)–O(1b) 1.896(11), Li(2)–O(6c) 2.078(12). The primed atoms are symmetry equivalent of the corresponding unprimed atoms.

be regarded as a bidentate chelating unit for vanadium(III). Accordingly, **4** should be considered as an octahedral complex containing three bidentate ligands (three blade propellers) with a Λ configuration. Stereochemical similarities with **4** can be found in vanadium(III)-tris(amino acid) derivatives,[7] for which complexes belonging to the same configuration as **4** show the same sign and similar magnitudes for $[\alpha]_D^{298}$. Another striking similarity as far as these properties are concerned can be found with $[V(dag)_3]^3$ and its pyridine adduct, which both show the same Λ configuration and exhibit similar optical rotatory values ($[\alpha]_D^{293}$ -200.7, -226, respectively). This can be rationalized in terms of 'stereochemical correspondence'[8] of tris chelate octahedral complexes and complexes which show a propeller-like conformation.

We wish to emphasize how much our complexes differ from those reported in the very-active area of mixed transition metal alkali or alkaline earth metal alkoxides.[9] Structural analysis has shown that those systems are generally polynuclear, or they contain extra ligands when monomeric. In contrast, the sugar residues provide intramolecularly the solvation type environment for the alkali cations.

Footnotes

27.4, 28.2, 69.6, 76.5, 79.7, 86.0, 91.3, 107.3, 110.5, 111.8. $[\alpha]_D$ -21.2 (*c* 4.86, THF). $M_r = 889$ (by cryoscopy in benzene).

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