

## Carbohydrate Metal Complexes as Ligands for Alkali Cations

Umberto Piarulli,<sup>a</sup> David N. Williams,<sup>a</sup> Carlo Floriani,<sup>\*a</sup> Giuliana Gervasio<sup>b</sup> and Davide Viterbo<sup>b</sup>

<sup>a</sup> Institut de Chimie Minérale et Analytique, Université de Lausanne, Place du Château 3, CH-1005 Lausanne, Switzerland

<sup>b</sup> Dipartimento di Chimica Inorganica, Chimica Fisica e Chimica dei Materiali, Università di Torino, Via P. Giuria 7, I-10125 Torino, Italy

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,<sup>1</sup> 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.<sup>2</sup> 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- $\alpha$ -D-glucufuranose (Hdag) (Fig. 1).

Homoleptic complexes [M(dag)<sub>n</sub>] (M = V, n = 3;<sup>3</sup> M = Ti, Zr, Hf, n = 4<sup>4</sup>) 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<sup>†</sup>} and sodium {[Na(dag)] 2<sup>‡</sup>} derivatives of Hdag. **1** (prepared from Bu<sup>n</sup>Li in Et<sub>2</sub>O) and **2** (prepared from NaH in Et<sub>2</sub>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<sub>2</sub> non-crystallographic symmetry. Two Li<sub>4</sub> and O<sub>4</sub>(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-

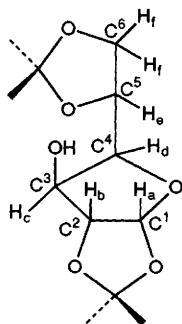
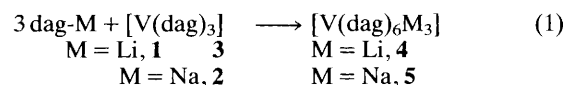


Fig. 1 1,2:5,6-di-*O*-isopropylidene- $\alpha$ -D-glucufuranose, Hdag

ent from that in the other dag units. There are a significant number of Li<sub>4</sub>O<sub>4</sub> cubane-type structures<sup>5</sup> similar to **1** containing bidentate bridging ligands, forming five-, six- or seven-membered rings. Such rings usually possess an achiral S<sub>4</sub> symmetry around the cube. The arrangement of the four rings in **1** has the chiral D<sub>2</sub> 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**



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<sub>2</sub> symmetry with the C<sub>2</sub> 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)<sub>2</sub>(dag)<sub>3</sub>]<sup>3</sup> but close to those in {[V(OPh)<sub>6</sub>]{Li(dme)}<sub>3</sub>}.<sup>6</sup> 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

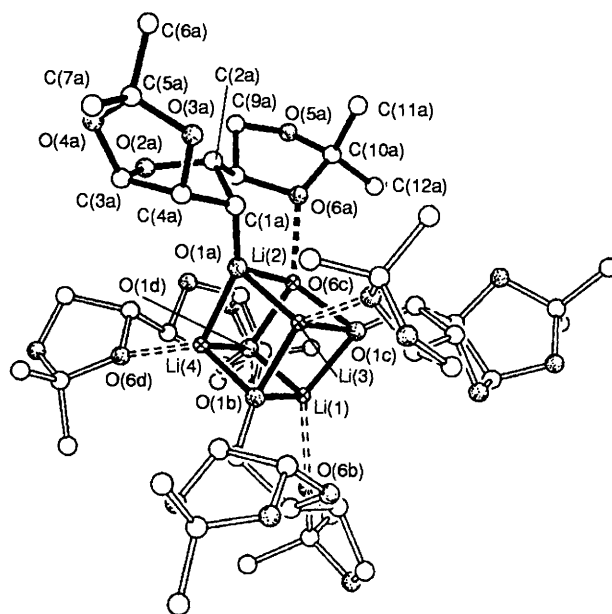
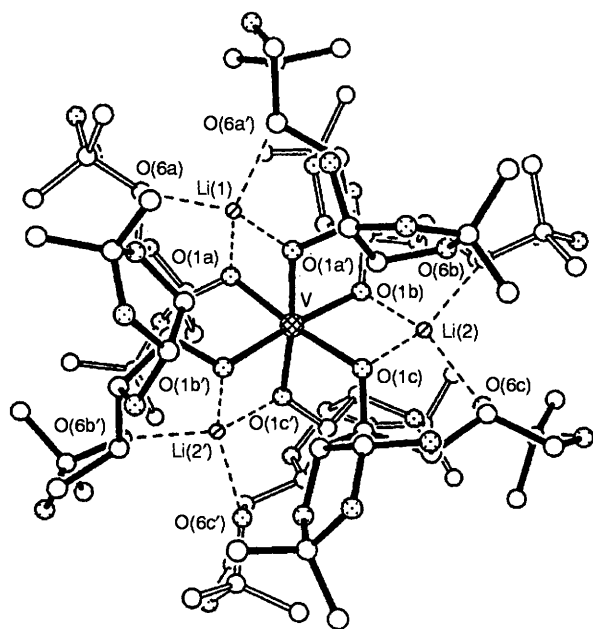


Fig. 2 Molecular diagram of {[Li(dag)]<sub>4</sub>}, **1**, with the atom labelling scheme. Selected bond distances (Å): Li–Li (avg.) 2.550(14), Li(1)–O(1b) 1.972(12), Li(1)–O(6b) 1.987(10), Li(1)–O(1c) 1.890(10), Li(1)–O(1d) 1.910(12), Li(2)–O(1a) 1.953(13), Li(2)–O(1c) 1.909(12), Li(2)–O(6a) 1.991(11), 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  $[V(\text{dag})_6\text{Li}_3]$  **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 ( $\text{\AA}$ ): 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  $\Lambda$  configuration. Stereochemical similarities with **4** can be found in vanadium(III)-tris(amino acid) derivatives,<sup>7</sup> 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  $[V(\text{dag})_3]^3$  and its pyridine adduct, which both show the same  $\Lambda$  configuration and exhibit similar optical rotatory values ( $[\alpha]_D^{293} -200.7$ ,  $-226$ , respectively). This can be rationalized in terms of 'stereochemical correspondence'<sup>8</sup> 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.<sup>9</sup> 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.

We thank the Fonds National Suisse de la Recherche Scientifique (Grant No. 20-33420-92), Italian CNR and MURST for financial support.

Received, 17th March 1994; Com. 4/01617C

### Footnotes

† Satisfactory elemental analysis has been obtained. *Spectroscopic data* for **1**:  $^1\text{H}$  NMR ( $\delta$ , 200 MHz,  $\text{C}_6\text{D}_6$ , 298 K): 1.21 (s, 3 H, Me), 1.39 (s, 3 H, Me), 1.46 (s, 3 H, Me), 1.49 (s, 3 H, Me), 3.99 (m, 1 H,  $\text{H}_f$ ), 4.15 (m, 1 H,  $\text{H}_f$ ), 4.35 (m, 1 H,  $\text{H}_d$ ), 4.38 (d, 1 H,  $\text{H}_b$ ,  $J_{\text{Ha,Hb}}$  3.4 Hz), 4.70 (m, 1 H,  $\text{H}_e$ ), 4.72 (d, 1 H,  $\text{H}_c$ ,  $J_{\text{Hc,Hd}}$  3.2 Hz), 6.22 (d, 1 H,  $\text{H}_a$ ,  $J_{\text{Ha,Hb}}$  3.4 Hz).  $^{13}\text{C}$  NMR ( $\delta$  50 MHz,  $\text{C}_6\text{D}_6$ , 298 K): 26.4, 27.1,

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).

‡ Satisfactory analytical and spectroscopic data have been obtained. § *Crystal data* for **1**:  $\text{C}_{48}\text{H}_{76}\text{Li}_4\text{O}_{24}$ ,  $M = 1064.8$ , monoclinic, space group  $P2_1$ ,  $a = 12.149(8)$ ,  $b = 21.363(15)$ ,  $c = 12.634(11)$   $\text{\AA}$ ,  $\beta = 117.32(2)^\circ$ ,  $U = 2913(4)$   $\text{\AA}^3$ ,  $Z = 2$ ,  $D_c = 1.214$   $\text{g cm}^{-3}$ , Mo-K $\alpha$  radiation ( $\lambda = 0.71069$   $\text{\AA}$ ),  $\mu(\text{Mo-K}\alpha) = 0.95$   $\text{cm}^{-1}$ , crystal dimensions  $0.30 \times 0.42 \times 0.62$  mm. The structure was solved by direct methods and anisotropically refined by full-matrix least-squares for all the non-hydrogen atoms. No absorption correction was applied. The correct absolute configuration was assigned by assuming the  $\text{D}$ -configuration of the dag molecule and confirmed by refining the chirality parameter.<sup>10</sup> For 4381 unique observed structure amplitudes [ $I > 2\sigma(I)$ ] collected at 120 K on a Siemens P4 diffractometer in the range  $2 < 2\theta < 50^\circ$ , the current  $R$  value is 0.0638. Attempts to solve the structure with data collected at room temperature failed.

¶ Correct elemental analysis for **4**,  $\text{C}_{72}\text{H}_{114}\text{Li}_3\text{O}_{36}\text{V}\cdot\text{C}_7\text{H}_8$ .  $\mu_{\text{eff}} = 2.60$   $\mu_B$  at 300 K.  $[\alpha]_D -172$  (c 1.01, toluene).

|| *Crystal data* for **4**:  $\text{C}_{70}\text{H}_{122}\text{Li}_3\text{O}_{36}\text{V}$ ,  $M = 1719.6$ , monoclinic, space group  $C2$ ,  $a = 22.456(6)$ ,  $b = 18.559(6)$ ,  $c = 13.791(5)$   $\text{\AA}$ ,  $\beta = 126.93(2)^\circ$ ,  $U = 4594(3)$   $\text{\AA}^3$ ,  $Z = 2$ ,  $D_c = 1.243$   $\text{g cm}^{-3}$ , Mo-K $\alpha$  radiation ( $\lambda = 0.71069$   $\text{\AA}$ ),  $\mu(\text{Mo-K}\alpha) = 1.90$   $\text{cm}^{-1}$ , crystal dimensions  $0.24 \times 0.32 \times 0.74$  mm. The structure was solved by direct methods and anisotropically refined by full-matrix least-squares for all the non-hydrogen atoms. No absorption correction was applied. The correct absolute configuration was assigned by assuming the  $\text{D}$ -configuration of the dag molecule and confirmed by refining the chirality parameter.<sup>10</sup> The toluene molecule of crystallization was found to be disordered. For 5134 unique observed structure amplitudes [ $I > 2\sigma(I)$ ] collected at 120 K on a Siemens P4 diffractometer in the range  $2 < 2\theta < 50^\circ$ , the current  $R$  value is 0.0622. All calculations were carried out on an Indigo Silicon Graphics work station using SIR92 and SHELXTL/IRIS. For both structures, atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

### References

- D. E. Fenton, in *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, Oxford, 1987; vol. 3, ch. 23.
- G. W. Gokel, *Crown Ethers and Cryptands*, RSC, Cambridge, 1991; F. Vögtle, *Supramolecular Chemistry*, Wiley, New York, 1993; *Molecular Recognition: Chemical and Biochemical Problems*, ed. S. M. Roberts, RSC, Cambridge, 1989; *Crown Ethers and Analogs*, ed. S. Patai and Z. Rappoport, Wiley, New York, 1989; R. M. Izah, K. Pawlak, J. S. Bradshaw and R. L. Bruening, *Chem. Rev.*, 1991, **91**, 1721.
- J. Ruiz, C. Floriani, A. Chiesi-Villa and C. Guastini, *J. Chem. Soc., Dalton Trans.*, 1991, 2467, and references cited therein.
- D. N. Williams, U. Piarulli, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *J. Chem. Soc., Dalton Trans.*, 1994, 1243.
- G. Boche, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 277; D. Seebach, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1624; H. Gais, U. Dingerdissen, C. Krüger and K. Angermund, *J. Am. Chem. Soc.*, 1987, **109**, 3775; E. M. Arnett, M. A. Nichols and A. T. McPhail, *J. Am. Chem. Soc.*, 1990, **112**, 7059; O. Graalmann, U. Klingebiel, W. Clegg, M. Haase and G. M. Sheldrick, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 891; D. Schmidt-Bäse and U. Klingebiel, *Chem. Ber.*, 1989, **122**, 815.
- W. C. A. Wilisch, M. J. Scott and W. H. Armstrong, *Inorg. Chem.*, 1988, **27**, 4333.
- C. P. Magill, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *Inorg. Chem.*, 1993, **32**, 2729.
- K. Mislow, *Acc. Chem. Res.*, 1976, **9**, 26; D. Gust and K. Mislow, *J. Am. Chem. Soc.*, 1973, **95**, 1535.
- K. G. Caulton and L. G. Hubert-Pfalzgraf, *Chem. Rev.*, 1990, **90**, 969; M. J. Hampden Smith, D. S. Williams and A. L. Rheingold, *Inorg. Chem.*, 1990, **29**, 4076; A. P. Purdy, C. F. George and J. H. Callahan, *Inorg. Chem.*, 1991, **30**, 2812; B. A. Vaarastra, J. C. Huffman, W. E. Streib and K. G. Caulton, *J. Chem. Soc., Chem. Commun.*, 1990, 1750; M. H. Chisholm and I. P. Rothwell, *Alkoxides and Aryloxides*, in *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon Press, Oxford, 1981, vol. 2, ch. 15.3.
- D. Rogers, *Acta Crystallogr., Sect. A*, 1981, **37**, 734.