Metallohosts Derived from the Assembly of Sugars around Transition Metals: The Complexation of Alkali Metal Cations

Umberto Piarulli, Andrew J. Rogers, and Carlo Floriani*

Institut de Chimie Minérale et Analytique, BCH, Université de Lausanne,
CH-1015 Lausanne, Switzerland

Giuliana Gervasio and Davide Viterbo

Dipartimento di Chimica, Università di Torino, I-10125 Torino, Italy

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The diacetone glucose (DAGH, 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose) monoanion DAG binds as a terminal alkoxo ligand to a variety of transition metals. When it is used in excess, with respect to the oxidation state of the metal, homoleptic anionic complexes $[M'(DAG)_6]^{3-}$ are formed. Such complexes contain oxygen-rich cavities between pairs of DAG ligands appropriate for binding alkali metal cations. The anionic complexes have been obtained by using [Li(DAG)], **1**, and [Na(DAG)], **2**, whose syntheses and characterization are reported here. The reaction of **1** and **2** with $[V(DAG)_3]$ gave $[V(DAG)_6Li_3]$, **3**, and $[V(DAG)_6Na_3]$, **4**, respectively. An alternative synthesis of **3** and **4** involves the metathesis reaction of **1** and **2** with $[VCl_3(thf)_3]$. This strategy also led to the synthesis of $[Cr(DAG)_6Li_3]$, **5**, and $[Ti(DAG)_6Li_3]$, **6**. Three pairs of DAG shape a cavity appropriate for three lithium cations in the case of complexes **3**, **5**, and **6**; a cavity is formed for three sodium cations in the case of **4**, where the alkali cation is in a tetrahedral O_4 environment. In the anionic manganese derivative $[Mn(Cl)(DAG)_4]^{3-}$, the four DAG units arrange in such a way as to bind four Li cations, which form a cationic cage $[Mn(Cl)(DAG)_4Li_4]^+$, and Cl^- is bound inside as $[Mn(Cl)(DAG)_4Li_4(\mu_4\text{-}Cl)]$, **7**. Crystallographic details: **4**, prism, $P2_1$, $a = 14.735(10)$ Å, $b = 15.033(9)$ Å, $c = 21.021(10)$ Å, $\beta = 107.34(2)°$, $V = 4445(5)$ Å^3, $Z = 2$, and $R = 7.60$; **5**, prismatic, $C2$, $a = 22.671(9)$ Å, $b = 18.785(5)$ Å, $c = 13.886(4)$ Å, $\beta = 126.39(2)°$, $V = 4761(3)$ Å^3, $Z = 2$, and $R = 7.32$; **6**, prismatic, $P2_1$, $a = 13.888(5)$ Å, $b = 18.750(5)$ Å, $c = 17.933(5)$ Å, $\beta = 91.84(2)°$, $V = 4667(2)$ Å^3, $Z = 2$, and $R = 8.75$; **7**, prismatic, $P2_1$, $a = 13.306(7)$ Å, $b = 21.311(11)$ Å, $c = 13.376(6)$ Å, $\beta = 95.01(2)°$, $V = 3779(3)$ Å^3, $Z = 2$, and $R = 9.33$.

Introduction

The rational design of cavities for the complexation of metal cations[1] and organic species *via* the establishment of weak interactions has been investigated by a number of substantially different approaches,[2] ranging from crown ethers to more sophisticated natural or synthetic architectures such as cyclic peptides etc. These systems have been implicated in metal transport through membranes and uptake and release processes of metals in living organisms.

Taking advantage of their coordination geometry, transition metals can organize around themselves rich donor atom ligands, creating binding cavities appropriate for hosting alkali metal or organic cations. A number of related, though quite different, approaches appeared recently in the literature, dealing with metallohosts[3] or metallacrowns.[4] Our entry in the area of inorganic analogues of polydentate ligands, specifically of open-chain polyethers, is part of a general interest in using protected sugars as ancillary ligands in both coordination and organometallic chemistry.[5,6]

The use of carbohydrates in the field of inorganic chemistry[6,7] has been on the whole limited, with a few exceptions, to aqueous solution studies. Carbohydrates should be considered particularly promising in that they are an inexpensive naturally occurring ligand source with a number of useful characteristics such as (a) an oxygen-rich periphery, (b) a variety of binding sites, and (c) steric demand and homochirality.

The different metals, with the coordination geometries imposed by their nature, electronic configuration, oxidation states, etc., could assemble around themselves a chiral oxygen-rich cavity able, in principle, of binding neutral or charged species such as organic molecules and metal cations. This ability could be further exploited in the fields of molecular recognition and asymmetric catalysis.[8]

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* To whom correspondence should be addressed.

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Diacetone glucose (DAGH, 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose) has been used in its deprotonated form DAG as the simplest monoprotic version of a sugar residue for binding transition metals. To this purpose, organometallic methods, which avoid protic conditions, have been developed. In this paper we report $[M'(DAG)_6]^{3-}$ (M′ = Ti, V, Cr) anionic complexes, acting as tris-open chain polyethers (metallapodands) in binding alkali metal cations, obtained *via* the corresponding [Li(DAG)] and [Na(DAG)] derivatives. Preliminary results have been briefly communicated.[5e]

Experimental Section

General Procedure. All manipulation were performed under an inert atmosphere of purified nitrogen using modified Schlenk glassware which was oven-dried prior to use and cooled under vacuum. Solvents were dried according to standard procedures and stored under nitrogen atmosphere. IR spectra were recorded on a Perkin-Elmer 1600 FT infrared spectrophotometer (Nujol mulls, using KBr plates) and UV−vis spectra on a Hewlett-Packard 8452 A diode array spectrophotometer. NMR spectra were obtained using a Bruker AC 200 instrument [200.13 MHz (^{1}H), 50.33 (^{13}C)] or a Bruker DPX 400 instrument [400.13 MHz (^{1}H), 100.6 (^{13}C)]. Magnetic susceptibility measurements were made with a Quantum Design MPMS 5 SQUID magnetometer. $[VCl_3(thf)_3]$, $[TiCl_3(thf)_3]$, $[CrCl_3(thf)_3]$, and $MnCl_2{\cdot}thf_{1.5}$ were prepared by following a published procedure.[9] The synthesis of $[V(DAG)_3]$ was performed as reported.[5a]

Preparation of [Li(DAG)], 1. Bu^{n}Li (1.6 M in *n*-hexane, 154 mmol) was added dropwise to a stirred suspension of DAGH (40.0 g, 154 mmol) in diethyl ether (200 mL) at *ca.* −20 °C. When the mixture was allowed to warm to room temperature, an immediate reaction ensued, a gas was given off, and a pale yellow solution formed, which was stirred for a further 6 h. The solvent was evaporated under reduced pressure, and the resulting oily off-white solid was washed with *n*-hexane (150 mL) and dried under vacuum to afford white [Li(DAG)] (33.5 g, 82%). X-ray-quality crystals were obtained by cooling a saturated ether solution to 4 °C. Anal. Calcd for $C_{12}H_{19}LiO_6$: C, 54.19; H, 7.19. Found: C, 54.46; H, 7.45. ^{1}H NMR (200 MHz, C_6D_6, 298 K): δ 1.21 (s, 3H, Me), 1.39 (s, 3H, Me), 1.46 (s, 3H, Me), 1.49 (s, 3H, Me), 3.99 (m, 1H, H_f), 4.15 (m, 1H, H_f), 4.35 (m, 1H, H_d), 4.38 (d, 1H, H_b, $J_{H_aH_b} = 3.4$ Hz), 4.70 (m, 1H, H_e), 4.72 (d, 1H, H_c, $J_{H_cH_d} = 3.2$ Hz), 6.22 (d, 1H, H_a, $J_{H_aH_b} = 3.4$ Hz). ^{13}C NMR (50 MHz, C_6D_6, 298 K): δ 26.4, 27.1, 27.4, 28.2, 69.6, 76.5, 79.7, 86.0, 91.3, 107.3, 110.5, 111.8. $[\alpha]^{25}_D$ (thf, 4.86 g dm^{-3}): −21.2°. Molecular weight determination by cryoscopy in benzene: 884, $[Li(DAG)]_{3.4}$.

Preparation of [Na(DAG)], 2. NaH (2.82 g, 117.7 mmol) was added in small aliquots to a suspension of DAGH (30.64 g, 117.7 mmol) in diethyl ether (250 mL). The resulting suspension was then heated at reflux overnight. The resulting cloudy solution was filtered and the solvent evaporated under reduced pressure. Hexane (150 mL) was then added to the yellowish oily residue and the resulting suspension stirred for 2 h. The precipitate was collected on a filter and dried under vacuum (30.2 g, 90%). Anal. Calcd for $C_{12}H_{19}NaO_6$: C, 51.00; H, 6.73. Found: C, 51.37; H, 6.84. ^{1}H NMR (200 MHz, C_7D_8, 325 K): δ 1.50 (s, 3H, Me), 1.68 (s, 3H, Me), 1.71 (s, 3H, Me), 1.72 (s, 3H, Me), 4.36 (m, 1H, H_f), 4.43 (m, 1H, H_d), 4.51 (m, 1H, H_f), 4.58 (d, 1H, H_b, $J_{H_aH_b} = 3.6$ Hz), 4.72 (m, 1H, H_e), 4.81 (d, 1H, H_c, $J_{H_cH_d} = 2.6$ Hz), 6.34 (d, 1H, H_a, $J_{H_aH_b} = 3.6$ Hz). ^{13}C NMR (50 MHz, C_7D_8, 325 K): δ 28.1, 26.6, 26.9, 27.3, 68.9, 74.5, 78.9, 85.1, 90.2, 106.1, 110.2, 111.3. $[\alpha]^{25}_D$ (thf, 3.42 g dm^{-3}): −10.5°.

Preparation of $[V(DAG)_6Li_3]$, 3. [Li(DAG)] (2.37 g, 8.92 mmol) was added in one portion to a solution of $[V(DAG)_3]$ (2.46 g, 2.97 mmol) in toluene (60 mL). The resulting purple solution was stirred at room temperature for 48 h, during which the solution turned bright green. The solvent was evaporated under reduced pressure and the green residue washed with *n*-hexane (70 mL) and dried *in vacuo* (3.3 g, 68%). Crystals suitable for X-ray diffraction were grown by slow diffusion of heptane into a toluene solution. Anal. Calcd for $C_{72}H_{114}Li_3O_{36}V$: C, 53.08; H, 7.00. Found: 53.13; 7.02. IR (KBr, Nujol): 1217 m, 1167 s, 1124 m, 1057 vs, 838.6 s, 804 w, 601.6 w, 496.7 cm^{-1} w. μ_{eff} (μ_B): 2.60. $[\alpha]^{25}_D$ (c = 1.01 in toluene): −172°.

Preparation of $[V(DAG)_6Na_3]$, 4. [Na(DAG)] (1.87g, 6.62 mmol) was added in one portion to a solution of $[V(DAG)_3]$ (1.87 g, 2.21 mmol) in toluene (70 mL). The resulting purple solution was stirred at room temperature overnight. Slowly, the solution turned green and a green crystalline solid precipitated. The solvent was then evaporated under reduced pressure, and the solid was washed with *n*-hexane (50 mL) and dried *in vacuo* (2.92 g, 80% yield). Crystals suitable for X-ray diffraction were grown from a saturated toluene solution at room temperature. Anal. Calcd for $C_{72}H_{114}Na_3O_{36}V$: C, 51.55; H, 6.80. Found: C, 51.69; H, 6.98. IR (KBr, Nujol): 1225 s, 1166 s, 1044 vs, 839 s, 801 m, 726 w, 586 w, 512 cm^{-1} w. μ_{eff} (μ_B): 2.50. $[\alpha]^{25}_D$ (c = 0.75 in toluene): −237.3°.

Preparation of $[V(DAG)_6Li_3]$ *via* Metathetical Exchange from $[VCl_3(thf)_3]$. $[VCl_3(thf)_3]$ (1.3 g, 3.4 mmol) was added portionwise to a suspension of [Li(DAG)] (5.4 g, 20.4 mmol) in *n*-hexane (150 mL). The resulting reddish suspension was stirred for 48 h to give a green precipitate in a reddish solution. The green solid was isolated, dried under reduced pressure, and suspended in toluene (200 mL). After 3 h, the suspension was filtered to eliminate insoluble LiCl and the solvent evaporated *in vacuo*. *n*-Hexane (80 mL) was then added and the green solid collected on a filter and dried *in vacuo* (3.58 g, 65%). Anal. Calcd for $C_{72}H_{114}Li_3O_{36}V$: C, 53.08; H, 7.00. Found: C, 53.25; H, 6.96.

Preparation of $[V(DAG)_6Na_3]$ *via* Metathetical Exchange from $[VCl_3(thf)_3]$. $[VCl_3(thf)_3]$ (1.36 g, 3.64 mmol) was added portionwise to a suspension of [Na(DAG)] (6.2 g, 22.0 mmol) in *n*-hexane (200 mL). The resulting reddish suspension was stirred for 24 h to give a green precipitate in a reddish solution. The green solid was isolated, dried under reduced pressure, and suspended in toluene (200 mL). After 3 h, the suspension was filtered to eliminate insoluble NaCl and the solvent evaporated *in vacuo*. *n*-Hexane (100 mL) was then added and the green solid collected on a filter and dried under reduced pressure (1.43 g, 24%). Anal. Calcd for $C_{72}H_{114}Na_3O_{36}V$: C, 51.55; H, 6.80. Found: C, 52.39; H, 6.90.

Preparation of $[Cr(DAG)_6Li_3]$, 5. $[CrCl_3(thf)_3]$ (0.941 g, 2.51 mmol) was added to a cooled (−20 °C) solution of [Li(DAG)] (4.01 g, 15.1 mmol) in toluene (100 mL). Warming to room temperature gave a green solution, which was then stirred overnight. A white solid precipitated and was filtered off; the filtrate was reduced *in vacuo* to 20 mL, and heptane (70 mL) was added. A green microcrystalline solid precipitated, which was collected on a filter and dried *in vacuo* (2.79 g, 65%). Crystals suitable for X-ray structural determination were grown from a saturated toluene solution at room temperature. Anal. Calcd for $\mathbf{5}{\cdot}C_7H_8$, $C_{79}H_{122}CrLi_3O_{36}$: C, 55.15; H, 7.15. Found: C, 55.70; H, 7.43. $\mu_{eff} = 3.82\ \mu_B$ at 310 K.

Preparation of $[Ti(DAG)_6Li_3]$, 6. $TiCl_3(thf)_3$ (0.942 g, 2.55 mmol) was added to a cold (−20 °C) solution of [Li(DAG)] (4.067 g, 15.28 mmol) in toluene (100 mL). Warming to room temperature gave a brownish solution, which was then stirred overnight. A white solid precipitated and was filtered off. The solvent was then reduced *in vacuo* to 20 mL, and *n*-hexane (70 mL) was added. A pale pink microcrystalline solid precipitated, which was collected on a filter and dried *in vacuo* (2.53 g, 60%). Crystals suitable for X-ray determination were grown by slow diffusion of heptane into a concentrated toluene solution. Anal. Calcd for $\mathbf{6}{\cdot}0.5C_7H_8$, $C_{75.5}H_{118}Li_3O_{36}Ti$: C, 54.23; H, 7.06. Found: C, 54.56; H, 7.54. $\mu = 1.76\ \mu_B$ at 310 K.

Preparation of $[V(DAG)_6Li_3]$ *via* $[V(DAG)_6Na_3]$. Anhydrous lithium chloride (0.16 g, 3.8 mmol) was added in one portion to a solution of $NaBPh_4$ (1.29 g, 3.76 mmol) in THF (80 mL). An immediate reaction ensued, and a pale precipitate formed. The white suspension was stirred overnight and filtered. $[V(DAG)_6Na_3]$ (1.1 g, 0.63 mmol) was then added in one portion and the resulting purple solution stirred overnight. The solvent was removed under reduced pressure and toluene (50 mL) added to the residue. A green solution with a pale precipitate was obtained; the mixture was filtered, and the

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Table 1. Crystal Data and Data Collection and Refinement Parameters for **4**−**7**

	complex **4**	complex **5**	complex **6**	complex **7**
empirical formula	$C_{74}H_{114}Na_3O_{36.5}V$	$C_{79}H_{114}CrLi_3O_{36}$	$C_{72}H_{114}Li_3O_{36}Ti$	$C_{69}H_{100}Cl_2Li_4MnO_{24}$
color; habit	green; prismatic	green; prismatic	colorless; prismatic	colorless; prismatic
crystal size, mm	0.28 × 0.40 × 0.64	0.32 × 0.40 × 0.52	0.32 × 0.34 × 0.72	0.30 × 0.45 × 1.00
space group	$P2_1$	$C2$	$P2_1$	$P2_1$
unit cell dimens				
a, Å	14.735(10)	22.671(9)	13.888(5)	13.306(7)
b, Å	15.033(9)	18.785(5)	18.750(5)	21.311(11)
c, Å	21.021(10)	13.886(4)	17.933(5)	13.376(6)
β, deg	107.34(2)	126.39(2)	91.84(2)	95.01(2)
V, Å^3	4445(5)	4761(3)	4667(2)	3779(3)
Z	2	2	2	2
fw	1707.6	1712.5	1624.4	1467.1
d(calcd), Mg/m^3	1.276	1.195	1.156	1.289
abs coeff, mm^{-1}	0.210	0.199	0.169	0.319
temp, K	120	293	150	120
2θ range, deg	2.0−48.0	2.0−50.0	2.0−50.0	2.0−55.0
scan type	ω	ω	ω	$\theta-2\theta$
no. of indep reflns	7165 (R_{int} = 4.19%)	4335 (R_{int} = 2.84%)	8520 (R_{int} = 1.52%)	6923 (R_{int} = 9.60%)
no. of obsd reflns	5142 ($F > 4.0\sigma(F)$)	3055 ($F > 4.0\sigma(F)$)	5011 ($F > 4.0\sigma(F)$)	4939 ($F > 4.0\sigma(F)$)
weighting scheme	$w^{-1} = \sigma^2(F) + 0.0050F^2$	$w^{-1} = \sigma^2(F) + 0.0130F^2$	$w^{-1} = \sigma^2(F) + 0.0146F^2$	$w^{-1} = \sigma^2(F) + 0.0300F^2$
no. of params refined	1018	510	511	715
final R indices (obsd data)	R = 7.60%, R_w = 10.61%	R = 7.32%, R_w = 10.20%	R = 8.75%, R_w = 12.59%	R = 9.33%, R_w = 13.70%
goodness-of-fit	1.23	0.82	0.89	0.78

solvent was removed under reduced pressure. *n*-Hexane (70 mL) was then added, and the green precipitate was collected by filtration and dried *in vacuo* (0.6 g, 59%). Anal. Calcd for $C_{72}H_{114}Li_3O_{36}V$: C, 53.08; H, 7.00. Found: C, 53.25; H, 6.96.

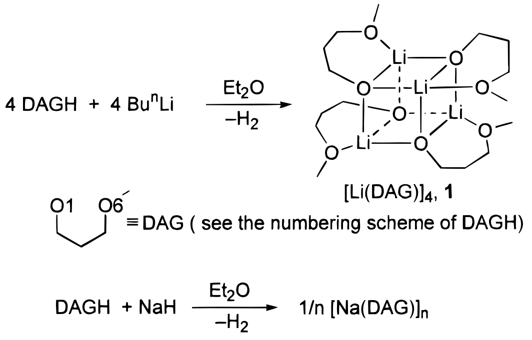
Preparation of [Mn(Cl)(DAG)$_4$Li$_4$Cl], 7. MnCl$_2$·1.5thf (2.55 g, 10.9 mmol) was added portionwise to a solution of [Li(DAG)] (11.62 g, 43.63 mmol) in toluene (150 mL). Stirring overnight gave a colorless solution. The solvent was evaporated under reduced pressure and the residue washed with *n*-hexane (100 mL). The resulting white microcrystalline solid was collected and dried (12.3 g, 95%). Crystals suitable for an X-ray analysis were grown from a saturated toluene solution at room temperature, and were found to contain C_7H_8 of crystallization. The solid dried *in vacuo* lost solvent of crystallization. Anal. Calcd for $C_{48}H_{76}Cl_4Li_2MnO_{24}$: C, 48.24; H, 6.36. Found: C, 48.16; H, 6.51. IR (Nujol; ν_{max}/cm^{-1}, selected values): 1266 m, 1220 s, 1164 m, 1130 s, 1065 s, 1019 s, 930 m, 808 s, 811 s, 583 m, 537 m.

X-ray Analysis for 4−7. Crystal data and data collection and refinement parameters are summarized in Table 1 for all four compounds. The crystals were enclosed in Lindemann glass capillaries which where then sealed under nitrogen. The measurements were performed on a Siemens P4 diffractometer, using Mo Kα radiation (λ = 0.710 69 Å) monochromatized by a graphite crystal. The data were collected at low temperature for all complexes except **5**, the crystals of which gave good diffraction at room temperature. For this complex, the intensities were corrected for absorption (minimum/maximum transmission factors 0.89/0.93) using the ψ-scan method.[10] The structures were solved by direct methods[11] and refined using the SHELXTL-IRIS system.[12] The hydrogen atoms were located in calculated positions and refined by a riding model with fixed U_{iso} values. Some compounds also contain crystallization solvent molecules; in particular, complex **4** contains disordered (occupation factor 0.5) ethyl ether molecules, complex **6** includes a well-defined toluene molecule and a disordered benzene moiety, and complex **7** contains three toluene molecules. The absolute configuration was defined by the known chirality of the diacetone glucose molecule. The final atomic coordinates are listed in the Supporting Information for complexes **4**−**7**.

Results and Discussion

Alkali Metal Derivatives of Diacetone Glucose. The lithium derivative **1** was obtained by deprotonating DAGH with

Scheme 1



Bu^{n}Li in cold (−20 ° C) diethyl ether (Scheme 1). The standard workup procedure allowed the isolation of the desired product in good yields.

The product is tetrameric in solution as shown by MW determination (cryoscopy in benzene). ^{1}H and ^{13}C NMR analyses revealed only one sugar species even at low temperature. A comparison with the NMR spectrum of DAGH reveals a pronounced deshielding of the protons H3 and H1, 0.3 ppm for the anomeric proton and 0.45 ppm for the proton directly bound to the carbon which bears O1 binding lithium (see O1 in Figure 1). A deshielding of 0.3 ppm is observed for proton H8 which we attribute to the Li−O6 interaction (see O6 in Figure 1). Figure 1 refers to the DAG fragment taken from the structure of **1**,[5e] where lithium is chelated by O1 and O6. The methyl groups of the protecting groups are not affected by the presence of the metal. Details of the synthesis of **1** are reported here, while its crystal structure is described in ref 5e.

The sodium derivative [Na(DAG)], **2**, was obtained by adding NaH to a chilled (−40 °C) suspension of DAGH in diethyl ether (Scheme 1) and could be obtained in pure form by recrystallization from cold *n*-hexane. The ^{1}H NMR spectrum (298 K) shows broad signals which sharpen upon an increase in temperature to 325 K. In contrast, a decoalescence of the signals was not observed at low temperature. The spectrum at 325 K shows a clear deshielding of the anomeric proton H3 (0.4 ppm) compared to that of the free DAGH, but the effect of the H substitution on H1 is less remarkable (0.2 ppm) than it is in the case of **1**. The [α]$^{25}_{D}$ values for complexes **1** and **2** did not differ greatly from that of free DAGH. The absence of an X-ray

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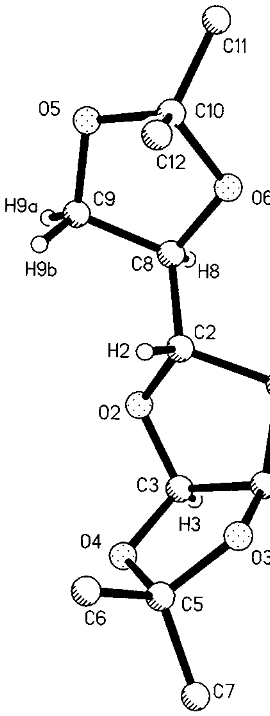


Figure 1. Atom-labeling scheme for the DAG ligand, 1,2:5,6-di-*O*-isopropylidene-D-glucofuranose.

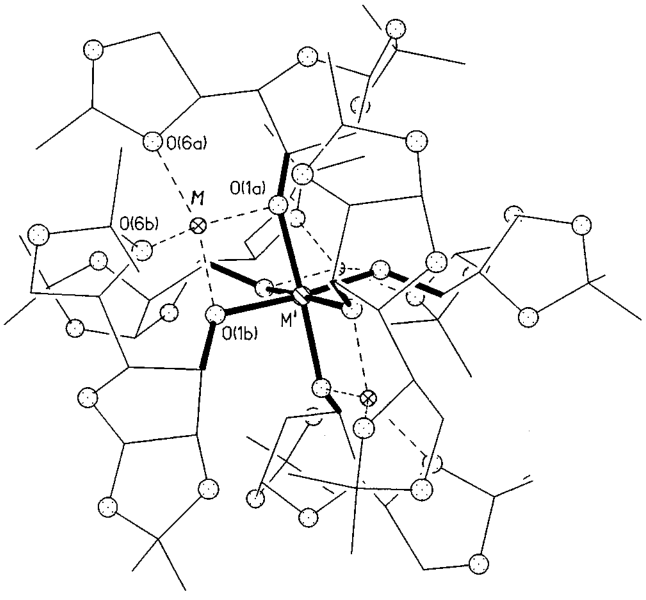
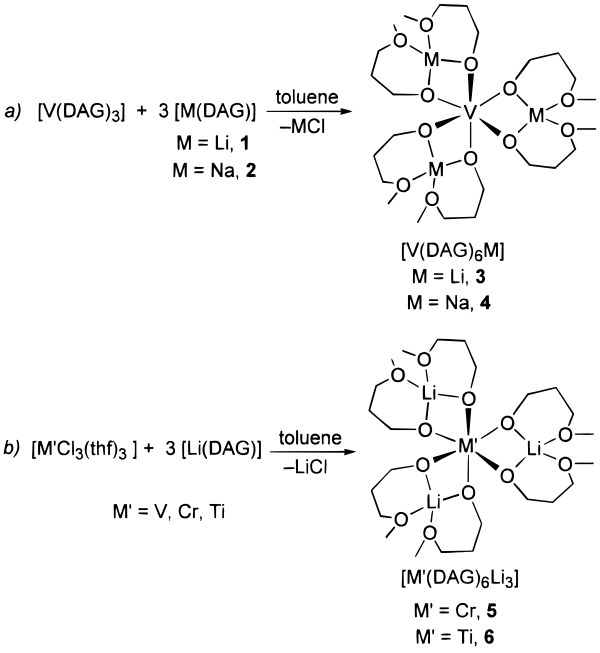


Figure 2. Structural skeleton common to complexes **3**−**6** (M = Li, Na; M′ = Ti, V, Cr).

Scheme 2



analysis for **2** means that we have no evidence of its molecular complexity in the solid state. Further, its poor solubility in benzene prevented the MW determination in solution. It is well-known that alkali metal alkoxides[13,14] display a variety of aggregation degrees both in the solid state and in solution depending, among other things, on the presence of additional bonding sites on the alkoxo residue. This is particularly true for DAG. Compounds **1** and **2** cannot be compared to any previously reported alkali metal carbohydrate derivatives, which are usually obtained from aqueous solution and contain the protic form of the sugar along with water molecules.[7,15] Compounds **1** and **2** are particularly suitable in metathesis reactions with transition metal salts under nonprotic conditions.

Alkali Metal Cation Complexation by Anionic $[M'(DAG)_6]^{3-}$ Complexes. The title compounds are accessible *via* two different synthetic routes illustrated in Scheme 2, reactions a and b.

In the first case (reaction a), the preformed homoleptic neutral diacetone glucose complex is reacted with the DAG alkali metal salt [M(DAG)] [M = Li, Na]. For vanadium, the reaction between $[V(DAG)_3]$[5a] and the alkali metal−DAG salt was carried out in toluene, from which **3** or **4** could be recovered after removal of the solvent. Both compounds **3** and **4** have been obtained as crystals suitable for the X-ray analysis (see Experimental Section). Complexes **3** and **4** along with **5** and **6** are accessible also *via* the more straightforward metathesis reaction (reaction b in Scheme 2).

The Cr and Ti derivatives **5** and **6** were obtained by reacting 6 equiv of [Li(DAG)] with $[CrCl_3(thf)_3]$ and $[TiCl_3(thf)_3]$, respectively, in toluene. An initial solubilization of the metal chlorides is noticed accompanied by the formation of green (Cr) and violet (Ti) solutions from which LiCl slowly precipitates. Filtration of LiCl followed by concentration of the resulting solutions causes the precipitation of the Cr complex whereas addition of heptane is necessary to obtain complex **6**. Attempts to prepare the analogous vanadium species **3** or **4** using $[VCl_3(thf)_3]$ were not as successful, as LiCl did not precipitate in toluene. However, when the reaction was carried out in *n*-hexane followed by extraction of the products in toluene, pure **3** and **4** were obtained.

Complexes **3**−**6** have similar structures, details of which are reported here for **4**−**6** only, while the structure of **3** is given in the preliminary communication.[5e] A comprehensive picture of the structure of the three complexes is given in Figure 2.

In complexes **4**−**6**, the metal atom has a slightly distorted octahedral coordination involving six DAG moieties. The most relevant structural parameters of the three complexes are summarized in Table 2. With respect to the three main axes of the octahedron, the sugar moieties are all *syn*, with C1−O1−M−O1′−C1′ atoms adopting a U shape. A molecular super-

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Table 2. Relevant Distances (Å) and Angles (deg) for Complexes **3**−**6**

	3 (M = Li, M′ = V)	**4** (M = Na, M′ = V)	**5** (M = Li, M′ = Cr)	**6** (M = Li, M′ = Ti)
M′−O1$_{av}$	2.027(11)	2.048(10)	2.009(6)	2.056(8)
O1−M′−O1$_{range}$	83.7(2)−92.2(2)	87.0(4)−92.7(4)	83.1(3)−93.1(3)	82.1(3)−92.7(3)
M′−O1−C1$_{av}$	125.4(3)	127.0(9)	125.0(6)	126.5(7)
M···M′$_{av}$	2.84(1)	3.17(1)	2.86(2)	2.89(2)
M···O1$_{av}$	1.90(1)	2.26(1)	1.91(2)	1.91(2)
M···O6$_{av}$	2.07(1)	2.32(1)	2.07(2)	2.05(2)
O1···M···O6$_{av}$	92.4(5)	83.6(4)	93(1)	92(1)
	146.3(5)	131.9(5)	147(1)	147(1)
		157.9(5)		
O1···M···O1$_{av}$	91.0(7)	79.6(4)	89(1)	90(1)
O6···M···O6$_{av}$	103.4(7)	119.3(4)	104(1)	104(1)

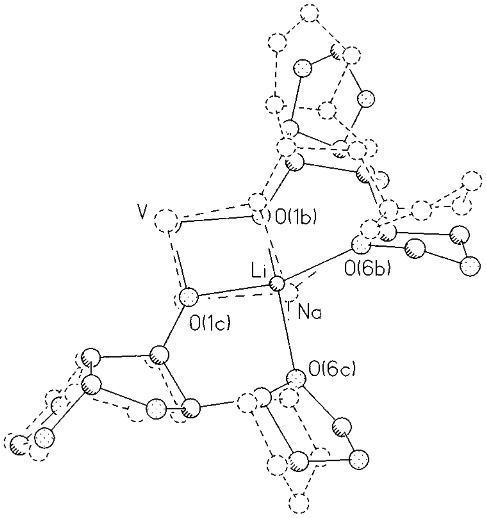

Figure 3. Comparison of the alkaline metal ion cavities in complexes **3** and **4**, showing the deformation induced by the larger Na^+ cation.

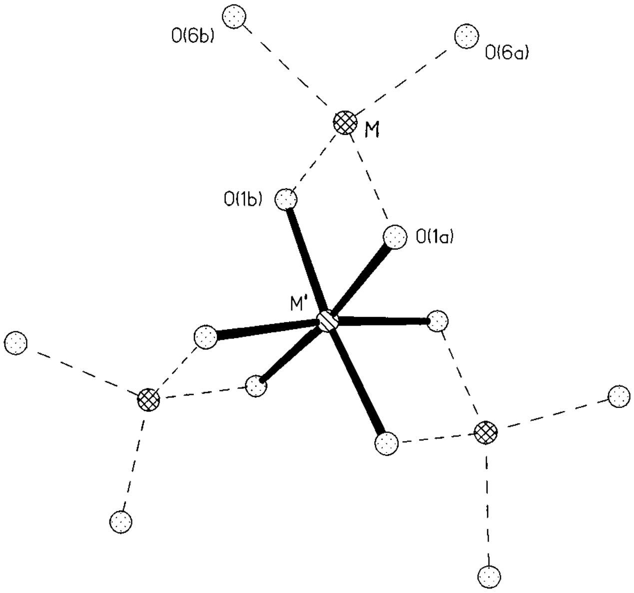

Figure 4. Atomic arrangement around the transition metal center in complexes **3**−**6**, showing a Λ configuration.

position of the four structures obtained by fitting the metal, the alkali metal ions, and all O1*n* and C1*n* atoms indicates an almost perfect overlap between **3**^{5e} and **5**, which are isomorphous with very close cell dimensions, and with **6**. The overlap of **4** with the other three structures is rather poor, due to the presence of Na^+ which widens the cavity determined by the two DAG moieties (Figure 3). Each alkali metal atom is tetracoordinated to a pair of adjacent sugar molecules through O1 and O6 and thus forms two six-membered rings M−O6−C8−C2−C1−O1. The three Na^+ ions in complex **4** show an additional, though weaker, coordination, to O3 of a third sugar with the Na^+···O3 distances ranging from 2.75(1) to 3.13(1) Å.

The three [M(DAG)$_2$] moieties in complexes **3**−**6** give rise to a unit having the Λ absolute configuration (Figure 4). In order to establish a structural correlation between the solid state and its solution, a study of the optical properties of complexes **3**−**6** was undertaken.

Absorption spectra of toluene solutions were measured, and their salient features are summarized as follows. For complexes **3** and **4**, three absorption bands are observed and are attributed to a MLCT transition (the first one) and to the two d^2 transitions (see Table 3). Their values are in good agreement with literature values for the octahedral hexaaquo complexes (526 and 500 nm). The absorption spectrum of complex **4** in THF shows a shift of the two bands assigned to d^2 transition (430 and 668 nm) to 368 and 552 nm, respectively. We ascribe the shift to an increased electron density on the metal due to the formation of a separated ion pair, with the Na ions being outside the cavity and being complexed by THF molecules. The same considerations hold for the Cr^{3+} and Ti^{3+} complexes **5** and **6**, for which the literature values for hexaaquo complexes are also 581 and 390 nm and 490 nm respectively.[16] Circular dichroism curves were determined for complexes **3**−**6**, and several common features deserve comment. For complexes **3**−**6**, the MLCT transition gives rise to a small positive Cotton effect. The d^n transitions have a correspondingly more pronounced negative Cotton effect for the lower value transition and in the case of V^{3+} a second negative Cotton effect, whereas for Cr^{3+} a large positive Cotton effect is found corresponding to the $^3T_{2g} \rightarrow {}^3T_{1g}$ and $^4T_{2g} \rightarrow {}^4A_{2g}$ transitions, respectively. A comparison of these stereochemical properties with those of V^{3+}−α-amino acid[17] complexes having the same configuration as **3** and **4** shows the same sign and similar magnitudes for $[\alpha]^{25}{}_D$. Another striking similarity, as far as these properties are concerned, applies to [V(DAG)$_3$] and its pyridine adduct,[5a] which showed similar optical rotatory values ($[\alpha]^{25}{}_D = -200.7$ and $-226°$, respectively) and which were assigned the same Λ configuration.

A vanadium anionic complex, [V(OPh)$_6$Li$_3$(dme)$_3$],[18] with some structural similarities to complex **3**, has been reported. In this complex, each lithium cation is complexed to a pair of oxygens from two phenoxo groups. This anionic complex should not be considered a metallacrown, since the alkali metal cation is complexed by the important intervention of the DME solvent. It has been emphasized that in the anionic complexes $[M'(DAG)_6]^{3-}$ the three pairs of DAG determine three oxygen-

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Table 3. Absorption and CD Maxima for Complexes **3**−**6**

complex	UV, nm	activity	ϵ	transition in $M(H_2O)_6^{3+}$	CD, nm	molar ellipticity	sign
3	284	0.35	95.6	MLCT	284	2300	positive
	412	0.108	29.5	$^3T_{2g} \rightarrow {}^3T_{1g}$	417	−5973	negative
	622	0.05	13.7	$^3T_{1g} \rightarrow {}^3T_{1g}$	616	−6409	negative
4	288	0.186	115.4	MLCT	288	2300	positive
	430	0.07	42.7	$^3T_{2g} \rightarrow {}^3T_{1g}$	440	−5977	negative
	668	0.34	21.4	$^3T_{1g} \rightarrow {}^3T_{1g}$	660	−6401	negative
5	298	0.33	73.8	MLCT	275	272	positive
	464	0.16	35.8	$^4T_{2g} \rightarrow {}^4A_{2g}$	480	−3460	negative
	615	0.14	31.8	$^4T_{1g} \rightarrow {}^4A_{2g}$	609	16439	positive
6	287	1.04	218.5	MLCT	288	272	positive
	525	0.03	6.3	$^3T_{2g} \rightarrow {}^3T_{1g}$	558	−596	negative

rich cavities, the size of which depends on the ionic radius of the transition metal ion. Changes in the coordination number and coordination geometry would generate other cavities and allow the design of appropriate receptors for alkali metal and organic cations as a function of the transition metal parameters. In this context, a number of observations have been made during the synthesis of complexes **3**−**6**. The synthesis of [M′(DAG)$_6$Na$_3$] was successful but only in the case of vanadium. In the case of Cr and Ti, the reaction between [M′Cl$_3$(thf)$_3$] and [Na(DAG)] led to formation of a honey-like suspension and no solid could be isolated. This could suggest that the sodium cation is not completely encapsulated within the two pairs of DAG, due to the unsuitable cavity size. In order to complete its coordination sphere, Na$^+$ uses, very probably, oxygen donor atoms from other [M′(DAG)$_6$]$^{3-}$ units. Formation of a polymeric form was also observed for reactions involving the potassium cation. All reactions, which employed K(DAG), with [M′Cl$_3$(thf)$_2$] never led to any discrete [M′(DAG)$_6$K$_3$] forms. This reflects the fact that the cavity provided by two DAG units is too small. The results outlined above, in the case of sodium and potassium, leave open the possibility of shaping the cavity of the receptor according to the size or to other parameters of the guest cation.

In order to clarify the selectivity of the cavities for differently sized metal cations, a few cation exchange reactions were undertaken. As already noticed by Armstrong (see above), dramatic color changes from green to purple in the case of complex **4** and to violet blue for **3** occur on dissolution of the complexes in THF, owing to a probable destruction of the VLi$_3$ and VNa$_3$ cores. The reactions are nevertheless reversible, and the original complexes are restored by replacing THF with toluene or heptane. To capitalize on this property, we dissolved complexes **3**, **5**, and **6** in THF and added a 2-fold excess of NaBPh$_4$ in order to prepare the analogous sodium derivatives. However, no reaction occurred. On the contrary, treatment of a THF solution of complex **4** with LiBPh$_4$ (formed *in situ* by reacting NaBPh$_4$ and anhydrous LiCl in THF) led to the quantitative formation of complex **3**, as confirmed by elemental analysis and absorption spectra. This is also shown by the structural data (*vide infra*) from which it is evident that the cavity complexing the sodium ion is widened because of the size of the cation. The preferred complexation of lithium cation forming a six-membered metallacycle is in agreement with the several reports in the literature.[19]

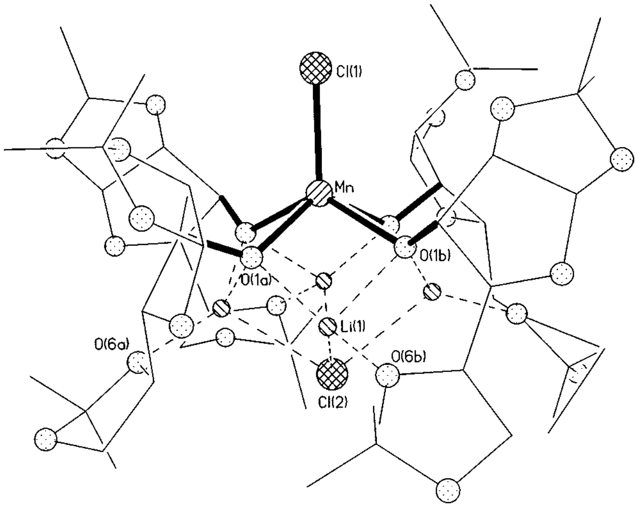
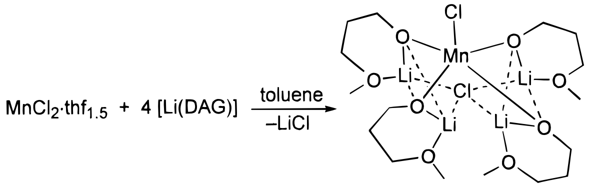


Figure 5. Structure of complex **7**.

Scheme 3



7

A remarkable change, though only substantiated by a single example, has been observed on moving to a nonhomoleptic anionic complex, like [Mn(DAG)$_4$(Cl)]$^{3-}$. Its synthesis was performed as outlined in Scheme 3.

When the insoluble MnCl$_2$·1.5thf was reacted with a toluene solution of [Li(DAG)], **1**, complete solubilization was observed without any precipitation of the expected LiCl. However, concentration followed by addition of *n*-hexane gave complex **7** in good yield. The toluene solution, cooled to 4 °C, gave crystals suitable for X-ray analysis. The structure is shown in Figure 5.

Manganese is five-coordinate in a square-pyramidal coordination geometry. The four DAG moieties are arranged around the Mn atom [average Mn−O1 distance 2.181(8) Å] like the legs of a spider, capturing the four lithium cations through their O1 and O6 atoms. On the side opposite to these bonds, a chloride anion is directly linked to Mn [Mn−Cl1 = 2.325(4) Å]. Each Li$^+$ is linked to two adjacent O1 atoms at different distances [average shortest Li−O1 distance 1.86(2) Å, average longest Li−O1 distance 1.96(2) Å] and to only one O6 atom [average Li−O6 distance 1.98(2) Å]. Each O1 coordinates two Li$^+$ cations. Three of the four coordination sites of Li$^+$ are thus completed by oxygen atoms, and the coordination sphere of each Li$^+$ is saturated by a chloride anion [average Li−Cl2

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distance 2.48(2) Å] shared by all four cations. Thus the resulting coordination geometry around each Li^+ ion is that of a tetrahedron distorted toward a trigonal pyramid.

In complex **7**, unlike in complexes **3**−**6**, all four cavities determined by the four adjacent DAG units are involved in binding four lithium cations. The resulting monocationic cavity is able to bind the Cl^- anion, which is shared equally by the four alkali metal cations. The result in Scheme 3 and the structure of **7** show how the different geometrical arrangements of the DAG residues around the metal can be tuned for binding not only cations but also anions or, in general, for carrying salts.

Conclusions

Assembling transition metals and sugars led to the generation of a novel class of metallohosts or metallacrowns. This has been achieved in a preliminary approach by using diacetone glucose (DAGH) as a monoprotic alkoxo group. In the anionic complexes $[M'(DAG)_6]^{3-}$, each pair of DAG ligands functions as an oxygen-rich cage for binding alkali metal cations. Shaping the binding cavity can be achieved by changing the nature and/or the parameters (oxidation state, coordination number, etc.) of the transition metal. The homochirality and the oxygen-rich nature of DAG introduce some characteristic features into the metallohosts reported here, which are able to mimic the coordination environment experienced by the guest cations in aqueous solutions.

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Supporting Information Available: Tables giving full details of X-ray data collections and refinements, atomic coordinates and isotropic displacement parameters, anisotropic displacement parameters, and bond distances and angles for complexes **4**−**7** (52 pages). Ordering information is given on any current masthead page.

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