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Synthesis and X-ray crystal structures of two transition metal complexes based on functionalised 1,5-anhydro-2-deoxy-D-galactitol and methyl 2-deoxy-α-D-galactopyranoside

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Abstract—Two new ligands of transition metal cations based on galactose-derived scaffolds were synthesised: 1,5-anhydro-2-deoxy-3,4,6-tri-*O*-(2-picolyl)-D-galactitol and methyl 2-deoxy-3,4,6-tri-*O*-(2-picolyl)-α-D-galactopyranoside. These ligands permitted the isolation as single crystals of a Co(II) and a Ni(II) complex, respectively. The structures of both complexes were determined by X-ray crystallography showing a coordination sphere including sugar-bound oxygen atoms. The sugar-derived ligands were found to be in both cases in high energy conformations in the crystal structures of the complexes. These conformations contain an arrangement of sugar-bound oxygen atoms similar to those observed in polyol–metal and carbohydrate–metal complexes.

Keywords: Sugar-derived ligands; Sugar–metal complexes; Crystal structure; Pyranose-ring conformations

1. Introduction

The rationalisation of the coordinating properties of carbohydrates and cyclic polyols is a well-documented research topic. As OH groups are weak donors, two or three groups in favourable steric disposition are required bind metal ions in protic solvents. Different types of chelating sites and their preferences in terms of ionic radii of the metal cations are known. The binding sites found in six-membered rings in chair conformation with the highest affinity for metal cations are the axial–equatorial–axial *cis*,*cis*-1,2,3-triol and the rare triaxial 1,3,5-triol, which is found in *cis*-inositol. These sites provide an array of hydroxyl groups arranged as a nearly equilateral triangle, which constitutes a face of the coordination polyhedron of the metal cation.[1–7] On the other hand, synthetic modifications of carbohydrates to enhance their coordinating ability (functionalisation with Lewis bases) are also of interest[8] due to the potential applications of some of such compounds, for example, in the field of asymmetric catalysis[9] or in that of mass spectrometry.[10]

We have recently initiated a study of the metal complexes formed by ligands derived by functionalisation with Lewis bases of central monosaccharide scaffolds. Such *glycoligands* (with scaffolds derived from D-galactopyranose,[11,12] D-lyxofuranose,[13] D- and L-glucofuranose[13] and D-mannopyranose[14]) were found to form monometallic complexes with Co(II) and Ni(II) cations. The complexes contain coordinated sugar-bound ether oxygen atoms. The facial coordination by three ether moieties resembles the coordination by hydroxyl functions in the case of unfunctionalised carbohydrates and polyols in the necessity of having three coordinated oxygens on the same side of the mean pyranoid or furanoid plane and in a favourable steric arrangement.

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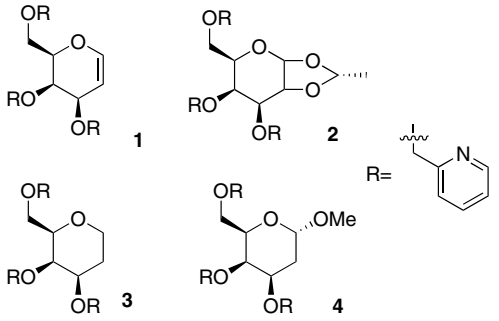

Figure 1. Sugar-derived ligands discussed in this work.

The two previously published glycoligands with *galacto* configuration[11]—namely, 3,4,6-tri-*O*-(2-picolyl)-D-galactal (**1**) and 1,2-*O*-(*R*)-ethylidene-3,4,6-tri-*O*-(2-picolyl)-α-D-galactopyranose (**2**) (Fig. 1)—included conformational locks: the double bond for **1** and the acetal ring for **2**. They induced well-defined coordination environments for the metal cation in both solid state and solution.[11,13] We describe here the synthesis of two new D-galactopyranose-derived ligands: 1,5-anhydro-2-deoxy-3,4,6-tri-*O*-(2-picolyl)-D-galactitol (**3**) and methyl 2-deoxy-3,4,6-tri-*O*-(2-picolyl)-α-D-galactopyranoside (**4**) (Fig. 1). Such ligands are expected to be less conformationally rigid than **1** and **2**. In their most stable chair conformation, they lack an arrangement of cofacial oxygen atoms compatible with chelation. The coordination to the metal cation is likely to enforce a less stable pyranoid ring conformation where the geometric requirements for coordination are fulfilled. The structural characterisation of the derived complexes [Co(**3**)]$(ClO_4)_2$ (**C3**$(ClO_4)_2$) and [Ni(**4**)]$(PF_6)_2$ (**C4**$(PF_6)_2$) is thus of interest.

The structural data will be compared to that of [Co(**1**)]$(PF_6)_2$ (**C1**$(PF_6)_2$) and [Ni(**2**)]$(PF_6)_2$ (**C2**$(PF_6)_2$), which possess isostructural binding sites (same conformation of the M/O-4/C-4/C-5/C-6 chelate cycle[12,13]) to those of **C3** and **C4**, respectively.

2. Experimental

2.1. Materials

Chemical reagents and solvents were purchased from Acros and used without further purification. 1,5-anhydro-2-deoxy-D-galactitol[15] was synthesised by catalytic hydrogenation of D-galactal.[16] Methyl 2-deoxy-α-D-galactopyranoside was synthesised by reaction of D-galactal with MeOH in the presence of anhydrous HCl.[15] NMR spectra were assigned by standard 2D techniques.

2.2. General methods

NMR spectra were recorded on a Bruker AV 360 spectrometer. Microanalysis was performed by the Service de Microanalyse de l'ICSN (Gif-sur-Yvette, France). ESI mass spectrometry analysis was performed with a Finnigan MAT95S spectrometer in a BE # mode in low resolution.

2.3. 3,4,6-Tri-*O*-(2-picolyl)-1,5-anhydro-2-deoxy-D-galactitol (3)

2-Picolyl chloride hydrochloride (591 mg, 3.64 mmol, 3.6 equiv) was suspended in toluene (5 mL). Its neutralisation and concomitant extraction in the toluene phase was performed by adding satd aq Na_2CO_3 (about 5 mL) on this suspension until gaseous evolution ceased. The aqueous phase was decanted and the organic phase was added to a solution of methyl 2-deoxy-α-D-galactopyranoside (150 mg, 1.01 mmol, 1 equiv) dissolved in dimethylsulfoxide (1 mL). 32.5 mg (0.1 mmol, 0.1 equiv) of tetrabutylammonium hydrogensulfate (TBAS), 0.05 mL of *t*-amyl alcohol and a ground mixture of 1 g K_2CO_3 and 0.25 g NaOH were added to the reaction mixture, which was vigorously stirred overnight after which TLC analysis (SiO_2, AcOEt/MeOH 9:1) showed the complete disappearance of the starting triol compound. The product was recovered by extraction (dichloromethane/water) followed by solvent evaporation and SiO_2 column chromatography (elution gradient: AcOEt→AcOEt/MeOH 9:1). Yield: 338 mg (79%) as a hygroscopic oil.

^{1}H NMR ($CDCl_3$): δ {8.54 (d, 2H, $J_{6py,5py}$ 4.7 Hz), 8.48 (d, 1H, $J_{3py,4py}$ 4.8 Hz), H-6py}, 7.65 (m, 3H, H-4py), {7.58, 7.46, 7.40} (3 × d, 3 × 1H, $J_{3py,4py}$ 7.8 Hz, H-3py), 7.2 (m, 3H, H-5py), {5.11, 4.81} (2 × d, 2 × 1H, ^2J 13.2 Hz, CH_2-py), 4.75 (s_{large}, 2 × 1H, CH_2-py), {4.67, 4.60} (2 × d, 2 × 1H, ^2J 13.4 Hz, CH_2-py), 4.12 (ddd, 1H, $J_{1b,1a}$ 11.7 Hz, $J_{1b,2a}$ 4.8 Hz, $J_{1b,2b}$ 1.8 Hz H-1b), 4.06 (m, 1H, H-4), 3.7 (m, 3H, H-6a, H-6b and H-3), 3.63 (td, $J_{5,6a} \approx J_{5,6b} \approx 6$ Hz, $J_{5,4}$ 1.0 Hz, H-5), 3.50 (td, 1H, $J_{1a,2a} \approx J_{1a,1b} \approx 12$ Hz, $J_{1a,2b}$ 2.3Hz, H-1a), 2.25 (qd, 1H, $J_{2a,2b} \approx J_{2a,3} \approx J_{2a,1a} \approx 12$ Hz, $J_{2a,1b}$ 4.8 Hz, H-2a), 1.87 (dm, 1H, $J_{2a,2b} \approx 12.5$ Hz, H-2b); ^{13}C NMR ($CDCl_3$): δ 159.1, 158.5, 158.1 (C-2py), {149.0, 148.9, 148.6} (C-6py), {136.7, 136.6, 136.5} (C-4py), {122.3 (2C), 122.1, 121.7, 121.4, 121.2} (C-3py, C-5py), 78.9 (C-5), 77.8 (C-3), {75.5, 74.2, 71.2} (*C*H_2-py), 74.8 (C-4), 70.4 (C-6), 66.1 (C-1), 27.2 (C-2); ES-MS: *m*/*z*, (intensity, %): 444.1 (100%, $[M+Na]^+$). Anal. Calcd for $C_{24}H_{27}N_3O_4 \cdot 2/3H_2O$: C, 66.50; H, 6.59; N, 9.69. Found: C, 66.39; H, 6.61; N, 9.71.

2.4. Methyl 3,4,6-tri-*O*-(2-picolyl)-2-deoxy-α-D-galactopyranoside (4)

The synthesis and isolation of **4** was performed as for **3**, starting from methyl 2-deoxy-α-D-galactopyranoside

(400 mg, 2.24 mmol). Yield: 898 mg (89%) as a hygroscopic oil.

^{1}H NMR ($CDCl_3$): {8.50 (m, 2H), 8.49 (d, 3H, $J_{6py,5py}$ 4.5 Hz,), H-6py}, 7.60 (m, 3H, H-4py), {7.57, 7.55, 7.41} (3 × d, 3 × 1H, $J_{3py,4py}$ 7.8 Hz, H-3py), 7.20 (m, 3H, H-5py), {5.10, 4.82} (2 × d, 2 × 1H, ^2J 13.2 Hz, CH_2-py), 4.94 (d, 1H, $J_{1,2a}$ 3.1 Hz, H-1), 4.75 (m, 2H, CH_2-py), {4.69, 4.61} (2 × d, 2 × 1H ^2J 13.3 Hz, CH_2-py), 4.10 (m, 1H, H-4), 4.0 (m, 2H, H-3 and H-5), 3.7 (m, 2H, H-6a and H-6b), 3.26 (s, 3H, Me), 2.27 (td, $J_{2a,2b} \approx J_{2a,3} \approx 13$ Hz, $J_{2a,1}$ 3.1 Hz, H-2a), 2.07 (dd, $J_{2a,2b}$ 12.5 Hz, $J_{2b,3}$ 4.6 Hz, H-2b); ^{13}C NMR ($CDCl_3$): {159.2, 158.7, 158.4} (C-2py), {149.0, 148.9, 148.6} (C-6py), {136.6, 136.5, 136.4} (C-4py), {122.2(2C), 122.1, 121.6, 121.2, 121.1} (C-3py, C-5py), 98.8 (C-1), {75.4, 74.1, 71.2} (*C*H_2-py), 74.8 (C-3), 74.2 (C-4), 70.1 (C-6), 69.5 (C-5), 54.8 (Me), 31.1 (C-2); ES-MS: *m*/*z* (intensity, %): 474.2 (100%, $[M+Na]^+$), 452.2 (5.8, $[M+H]^+$). Anal. Calcd for $C_{25}H_{29}N_3O_5 \cdot 1/5H_2O$: C, 65.98; H, 6.51; N, 9.23. Found: C, 65.77; H, 6.11; N, 9.22.

2.5. Co(II) complex of 3 (C3(ClO$_4$)$_2$)

Compound **3** (100 mg, 0.24 mmol, 1 equiv) in 2 mL absolute ethanol and $Co(ClO_4)_2 \cdot 6H_2O$ (87 mg, 0.24 mmol, 1 equiv) in 2 mL of absolute ethanol were mixed, which resulted in immediate precipitation of **C3**$(ClO_4)_2$. The precipitate was redissolved by addition of a minimal volume of acetone (ca. 1 mL). The resulting solution yielded 112 mg (69% yield) of **C3**$(ClO_4)_2$ as crystals (pink-purple plates) suitable for X-ray diffraction by slow evaporation.

Safety note: although no particular problems were encountered during the preparation of the complex **C3**, perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled with care.

ES-MS: *m*/*z*, (intensity, %): 444.1 (100, $[\mathbf{3}+H]^+$). Anal. Calcd for $CoC_{24}H_{27}N_3O_4(ClO_4)_2$: C, 42.43; H, 4.01; N, 6.19. Found: C, 42.44; H, 4.08; N, 6.18.

2.6. Ni(II) complex of 4 (C4(PF$_6$)$_2$)

Compound **4** (100 mg, 0.22 mmol, 1 equiv) in 2 mL absolute ethanol and $Ni(NO_3)_2 \cdot 6H_2O$ (64 mg, 0.22 mmol, 1 equiv) were mixed which resulted in immediate colour change. NH_4PF_6 (2.5 equiv) was dissolved in 1 mL absolute ethanol and this solution added to the solution of the complex, which resulted in precipitation of **C4**$(PF_6)_2$. The precipitate was redissolved by addition of a minimal volume of acetone (ca. 5 mL). The resulting solution yielded 125 mg (71% yield) of **C4**$(PF_6)_2$ as crystals (blue cubes) suitable for X-ray diffraction by slow evaporation.

ES-MS: *m*/*z* (intensity, %): 254.5 (5.8, $[\mathbf{C4}]^{2+}$), 474.2 (100%, $[\mathbf{4}+Na]^+$). Anal. Calcd for $NiC_{25}H_{29}N_3O_5(PF_6)_2$: C, 37.53; H, 3.65; N, 5.25. Found: C, 37.55; H, 3.33; N, 5.77.

Table 1. Crystal data for **C3**$(ClO_4)_2$ and **C4**$(PF_6)_2$

Complex	**C3**$(ClO_4)_2$	**C4**$(PF_6)_2$
Empirical formula	$C_{24}H_{27}Cl_2CoN_3O_{12}$	$C_{25}H_{29}F_{12}N_3NiO_5P_2$
Molecular mass	679.32	800.14
Crystal system, space group	Monoclinic $P2_1$	Tetragonal $P4_34_12$
a (Å)	8.8901(7)	10.3498(2)
b (Å)	10.1373(7)	10.3498(2)
c (Å)	14.9943(11)	56.593(2)
α (°)	90	90
β (°)	90.7140(10)	90
γ (°)	90	90
V (Å^3)	1351.21(17)	6062.2(3)
Z	2	8
F(000)	698	3248
(Mg m)	1.67	1.753
μ(MoK$_\alpha$) (mm)	0.904	0.862
Crystal size (mm)	0.22 × 0.16 × 0.08	0.11 × 0.11 × 0.11
No. reflections measured (R_{int})	17,589 (0.0158)	42,932 (0.0679)
No. of unique reflections	11,309	9229
No. of observed reflections $I > 2\sigma(I)$	10,422	6696
θ Range (°)	$2.29 < \theta < 38.93$	$1.44 < \theta < 30.53$
hkl ranges	−14, 14; −16, 17; −23, 23	−14, 7; −13, 14; −60, 80
No. parameters	397	436
R_1[a]	0.0362	0.0550
wR_2[b]	0.0959	0.0935
Max. and min. Fourier difference [e/Å^3]	0.757; −0.595	0.507; −0.469
Flack parameters	0.003(7)	0.035(14)

[a] $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o|$.
[b] $wR_2 = \sum(w(F_o^2 - F_c^2)^2)/(2 \cdot \sum[w(F_o^2)^2])$.

2.7. X-ray crystallography

X-ray diffraction data were collected using a Kappa X8 APPEX II Bruker diffractometer with graphite-monochromated MoK$_\alpha$ radiation ($\lambda = 0.71073$ Å). The temperature of the crystal was maintained at 100 K by means of a 700 series Cryostream cooling device to within an accuracy of ±1 K. The data were corrected for Lorentz, polarisation and absorption effects. The structures were solved by direct methods using SHELXS-97[17] and refined against F^2 by full-matrix least-squares techniques using SHELXL-97[18] with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were located on a difference Fourier map and introduced into the calculations as riding model with isotropic thermal parameters. All calculations were performed using the Crystal Structure crystallographic software package WINGX[19] (Table 1).

3. Results and discussion

3.1. Synthesis of the ligands and complexes

The synthesis of the picolyl-functionalised sugar-derivatives was performed by a phase transfer catalysis (PTC) protocol as for previously published glycoligands.[13] This synthetic pathway is based on an efficient PTC benzylation protocol (Fig. 2).[20] NMR data is in agreement with a pure $^4C_1$ chair conformation for both ligands **3** and **4** (Fig. 5).

Complexes **C3** and **C4** were obtained by reacting equimolar amounts of the ligand and the metal salt in ethanol. **C3**$(ClO_4)_2$ and **C4**$(PF_6)_2$ were isolated as single crystals in ethanol/acetone solution by slow evaporation.

3.2. X-ray crystal structures

ORTEP-III[21] views of the cationic complexes **C3** and **C4** are shown in Figures 3 and 4, respectively.

Selected structural parameters for **C1**–**4** are presented in Table 2. The coordination bond lengths and angles

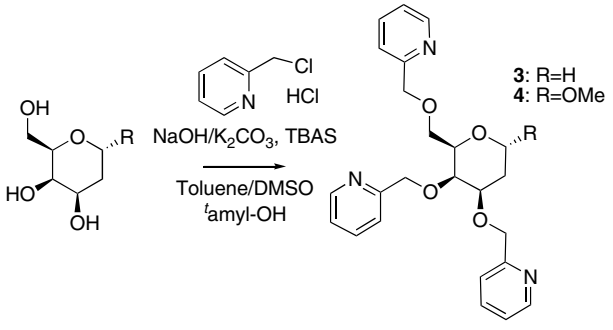

Figure 2. Synthesis of **3** and **4**.

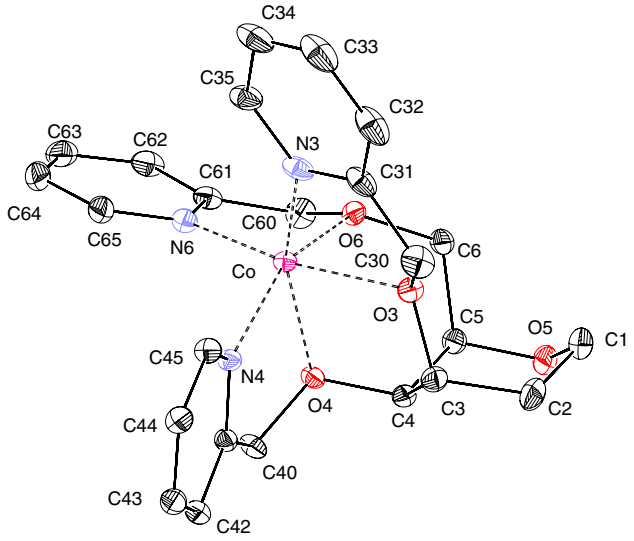

Figure 3. ORTEP-III[21] view of the cationic complex **C3** (hydrogen atoms have been omitted for clarity).

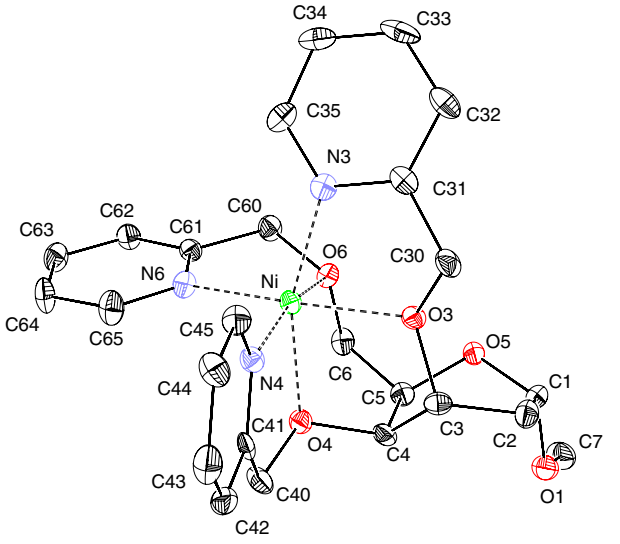

Figure 4. ORTEP-III[21] view of the cationic complex **C4** (hydrogen atoms have been omitted for clarity).

for **C3** and **C4** are very close to those of their conformationally rigidified counterparts **C1** and **C2**, respectively.

Contrarily to **1** and **2**, strong modifications of the pyranoid ring conformations of **3** and **4** occurred upon complexation (see below). They are depicted in Figure 5.

A comparison between complexes containing conformationally constrained sugar-derivatives (**C1** and **C2**) and complexes containing relatively more flexible ligands (**C3** and **C4**) shows that the arrangement of chelating oxygen atoms is quite similar in all cases: O-3, O-4 and O-6 are organised as a nearly equilateral triangle and define a face of the distorted coordination octahedron. It is to be noted that such an arrangement is impossible in the chair conformation of the ligand

Table 2. Coordination bond lengths and angles, Cremer–Pople ring puckering parameters[22,23] in Co(II) complexes **C1** and **C3** and in Ni(II) complexes **C2** and **C4**

	M–O[a] (Å)	M–N[a] (Å)	O–M–O[b] (°)	O–M–O[c] (°)	O–M–N[a,d]	ϕ_2 (°)	QT (Å)	θ (°)	Reference
C1	2.121	2.067	79.4	77.4	77.6	50.8(8)	0.493(6)	−161.4(9)	11
C3	2.122	2.073	77.7	81.1	78.0	83(3)	0.553(2)	176.7(2)	This work
C2	2.092	2.046	77.8	83.5	78.6	115.5(4)	0.665(4)	81.9(4)	12
C4	2.077	2.032	81.7	85.7	80.0	16.5(3)	0.718(3)	89.5(3)	This work

[a] Average value.
[b] In the five-membered chelate cycle M/O-3/C-3/C-4/O-4.
[c] In the six-membered chelate cycle M/O-4/C-4/C-5/C-6/O-6.
[d] In five-membered O,N chelate cycles (2-picolyl groups).

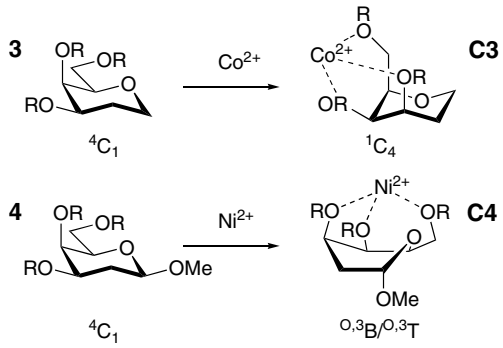

Figure 5. Schematic view of the conformational changes of the ligands occurring upon complexation.

as it is apparent in the crystal structures of methyl β-D-galactopyranoside[24] and 1,5-anhydro-D-galactitol,[25] where the distance between O-4 and O-6 is >6 Å.

C1 and **C3** are formally related by hydrogenation of the C-1–C-2 double bond of **C1**. The release of the constraint induced by the presence of two sp^2 carbons in the pyranoid cycle induces a relaxation of its conformation from $^5H_4$ in **C1**[11] to a slightly distorted $^1C_4$ chair conformation in **C3** (see Table 2 for Cremer–Pople puckering parameters[22,23] and Table 3 for torsion angles). O-3 and C-6 are in axial position. This allows O-3, O-4 and O-6 to be arranged in relative positions suitable for facial coordination.

The conformation of the pyranoid ring of **C4** is intermediate between boat and twist-boat ($^{O,3}B$, $^{O,3}T$). The conformation is quite similar to the $^{O,3}B$ conformation of **C2**[12] despite the absence of the cyclic acetal conformational lock. The conformation of the sugar ring allows the C-6O-6 ring substituent to be distorted towards axiality thus allowing O-6 to come in proximity of O-3 and O-4. The chelating site is again based on a nearly equilateral triangle of oxygen atoms. The inter-oxygen distances for **C1**–**4** are reported in Table 4.

The difference in the pyranoid ring conformation in **C3** and **C4** can be understood by stabilisation through the anomeric effect of the axial methoxy group (see Fig. 4) in the boat-like conformation of **C4**.

The chelating site found in the glycocomplexes described in this paper is reminiscent of a chelating site found in polyols. A site consisting of a *cis*-diol with the participation of an exocyclic hydroxymethyl group has been postulated in the case of furanoid polyols such as methyl α-D-lyxofuranoside and 2,5-anhydro-D-galactitol.[5] Such a site contains a six-membered chelate ring. The presence of six-membered chelate rings was shown to favour the chelation of smaller metal cations compared to complexes containing only five-membered chelate rings.[4,26] Thus, polyols which possess the 1,3,5-triaxial site (three six-membered chelate rings) can facially coordinate cations with an ionic radius smaller than the ones preferred by polyols containing an axial–equatorial–axial site (three five-membered chelate rings). The former polyols can thus form complexes even with small 3d metal cations.[26,7] Due to these properties of cyclic polyol ligands, no crystal structure containing the axial–equatorial–axial site complexed to 3d transition metal cations has been reported so far, whereas there are some examples of structurally characterised lanthanide complexes (with coordination numbers >6) with such a site (see Ref. 27 and references therein for 1:1 D-ribose-lanthanide complexes). On the other hand, 10 crystal structures containing the 1,3,5-triaxial site in ligands complexed with uncharged oxygen atoms to 5- or 6-coordinated divalent transition metal cations or cations with similar ionic radii[28] (Mg,[29,30] Fe,[31] Co,[32] Ni,[33,34] Cu,[33,34] Zn[34]) have been published. The mean

Table 3. Pyranoid ring torsion angles in complexes **C3** and **C4**

Bond	Torsion angle in **C3**	Torsion angle in **C4**
O-5–C-1	56.9(2)	19.1(4)
C-1–C-2	−52.3(2)	55.3(3)
C-2–C-3	51.4(2)	19.1(4)
C-3–C-4	−54.8(2)	−56.9(4)
C-4–C-5	57.7(2)	14.6(4)
C-5–O-5	−58.1(2)	46.8(3)

Table 4. Interoxygen distances in complexes **C1**–**4**

	O-3–O-4	O-3–O-6	O-4–O-6	Average value	Reference
C1	2.704	2.814	2.686	2.734	11
C2	2.648	2.937	2.728	2.771	12
C3	2.774	2.846	2.655	2.758	This work
C4	2.699	2.768	2.849	2.772	This work

value for the interoxygen distances over the 10 crystal structures is 2.82 Å (st. dev. 0.05 Å). The average interoxygen distances measured in the crystal structures of **C3** and **C4** (2.758 and 2.772 Å, respectively) are close to this figure. Moreover, the mean value for the O–M–O angles for the same 10 crystal structures is 86.81° (st. dev. 1.68°) to be compared with 81.13 for **C3** and 85.71 for **C4**. The more constrained ligands **1** and **3** enforce somewhat smaller O–M–O angles.

This structural study stresses the similarity of the facial coordination by the 1,3,5-triaxial site in polyols with the one offered by the three sugar-bound ether atoms in the glycoligand family. The conclusions of the extensive literature in the field of polyol–metal complexes may thus be useful to rationalise the coordinating properties of this new family of compounds.

Acknowledgement

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Supplementary data

Tables S1–S18 of atomic coordinates, bond angles, bond lengths and other structural parameters are supplied as supplementary data. Complete crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 648925 and 648926. Copies of this information may be obtained free of charge from the Director, Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033, e-mail: deposit@ccdc.cam.ac.uk or via: www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carres.2007.11.031.

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