

Diaqua[methyl 4-*O*-benzyl-2,3,6-tri-*O*-(2-picolyl)- α -D-mannopyranoside]-cobalt(II) bis(perchlorate) monohydrate: partial coordination of a ligand derived from D-mannose

Federico Cisnetti, Régis Guillot, Michel Thérissod and Clotilde Policar*

Université Paris-Sud, Institut de Chimie Moléculaire et des Matériaux d'Orsay, CNRS UMR 8182, F-91405 Orsay, France

Correspondence e-mail: cpolicar@icmo.u-psud.fr

Received 2 March 2007

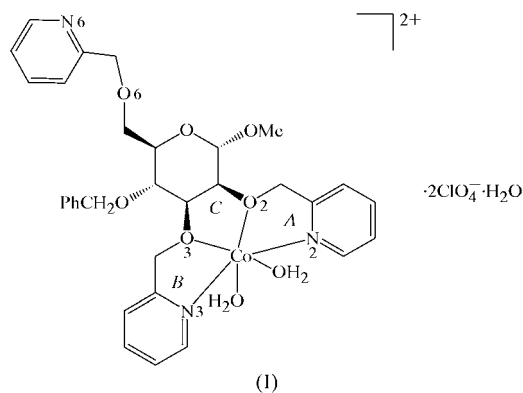
Accepted 21 March 2007

Online 21 April 2007

The title compound, $[\text{Co}(\text{C}_{32}\text{H}_{35}\text{N}_3\text{O}_6)(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$, contains a cationic complex with a novel facultative hexadentate sugar-derived ligand coordinated in a tetradentate fashion to give a CoN_2O_4 coordination. The partial coordination is imposed by the rigid conformation of the sugar. The pyridine group that is not bound to the metal is free to participate in intermolecular hydrogen bonding and π - π stacking interactions.

Comment

Designing inflexible ligands, *i.e.* ligands having a small number of low-energy conformations, is of interest in inorganic



chemistry as complexes containing such ligands have predetermined structural (conformational, stereochemical) properties (Comba & Schiek, 2003). Monosaccharides are known to display quite inflexible conformations, and this property has been used to design molecular scaffolds for the generation of bioactive molecules (Peri *et al.*, 2002). Ligands consisting of

monosaccharides functionalized with Lewis bases are of current research interest (Alexeev *et al.*, 2004). *Glycoligands* are ligands built on a central saccharide distribution frame by functionalization with Lewis bases, in the present case methyl α -D-mannopyranoside and 2-picolyl groups, respectively. We report here the structure of the title compound, (I) (Fig. 1).

The ligating methyl 4-*O*-benzyl-3,4,6-tri-*O*-(2-picolyl)- α -D-mannopyranoside (*L*) is bound to the metal cation by coordination of the N and O atoms of the picolyl ether groups (O2/N2 and O3/N3), as in previously published glycocomplex structures (Bellot *et al.*, 2005; Cisnetti *et al.*, 2007; Charron *et al.*, 2007) containing analogous ligands constructed on other monosaccharide frameworks (galactose, lyxose and glucose). In (I), the picolyl unit bonded to atom O6 remains uncoordinated to the Co atom. Thus *L*, which is a potentially hexadentate ligand, behaves here as a tetradentate ligand. Two water molecules are bonded to the metal cation in a *cis* fashion to achieve six-coordination. The cobalt coordination environment is of distorted octahedral geometry with longer Co—O distances for the coordinated ether groups than for the coordinated water molecules. The coordination environment is more open on the side of the water molecules because the chelate angles are less than 90° . The coordination distances and angles are given in Table 1. It should be noted that there are few examples of Co^{II} *cis*-diaqua complexes with a neutral tetradentate ligand (Pappalardo *et al.*, 1987; Hiller *et al.*, 1990; Castiñeiras *et al.*, 1991; Comba *et al.*, 2002).

The structure of (I) contains three five-membered metallacycles, *viz.* Co/O2/C20/C21/N2 (*A*), Co/O3/C30/C31/N3 (*B*) and Co/O2/C2/C3/O3 (*C*) (see scheme). The metallacycles can be described in terms of the Corey–Bailar δ, λ notation (Corey & Bailar, 1959) or by considering the torsion around the C—C

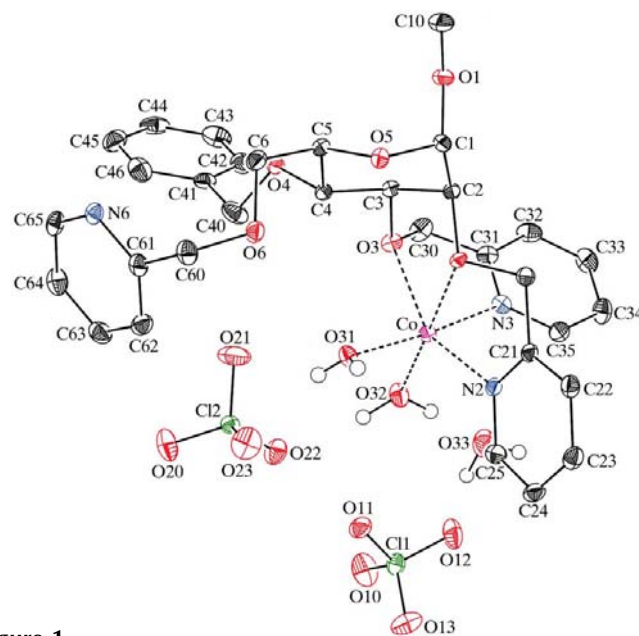


Figure 1
The molecular structure of (I), with displacement ellipsoids depicted at the 50% probability level. H atoms have been omitted for clarity, except those of water molecules, which are shown as small spheres of arbitrary radii.

bond. Metallacycles *A* and *B* are in an envelope conformation with, respectively, atoms C20 and C30 out of the envelope plane. The O2—C20—C21—N2 and O3—C30—C31—N3 torsion angles are, respectively, 33.9 (2) and 24.0 (2)°, and *A* and *B* are both of δ type. Metallacycle *C*, of λ type, adopts a twisted conformation, with atoms C2 and C3 out of the plane defined by the three other atoms. The O2—C2—C3—O3 torsion angle, which is common to both metallacycle *C* and the sugar ring, is -45.84 (19)°. This value is compatible with a slightly distorted 4C_1 chair conformation for the mannoside ring, as for methyl α -D-mannopyranoside (Gatehouse & Poppleton, 1970; Jeffrey *et al.*, 1977). The puckering amplitude of the glycoside ring is 0.53 Å for (I), which is very similar to the value for methyl α -D-mannopyranoside (0.55 Å). The methyl group at O1 is in an axial position, which is favourable in terms of the anomeric effect, and the greatest possible number of other substituents are in equatorial positions. The ligand in the complex is thus probably in the most stable conformation of the uncomplexed molecule.

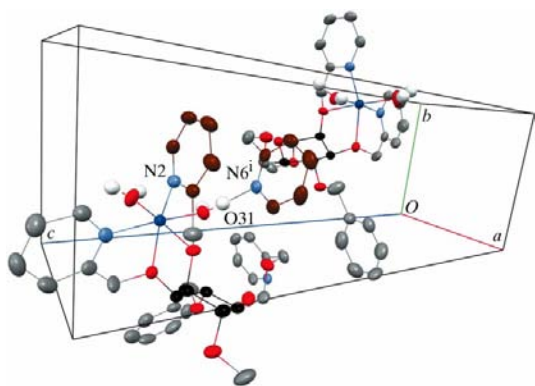


Figure 2
A partial view (perchlorate groups and solvent water molecules have been omitted for clarity) of the packing of (I), showing π - π stacking interactions and hydrogen bonds involving the dangling pyridine ring containing atom N6. The non-H atoms are shown with displacement ellipsoids drawn at the 80% probability level. H atoms have been omitted for clarity, except those of water molecules, which are shown as small spheres of arbitrary radii. [Symmetry code: (i) $-x + 2, y + \frac{1}{2}, -z + \frac{3}{2}$].

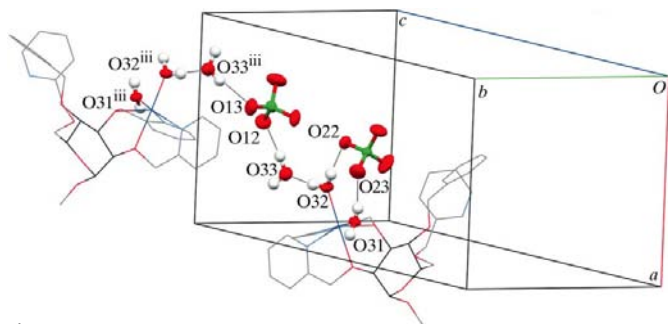


Figure 3
A partial view of the packing of (I), showing the network of hydrogen bonds linking two complex cations through water molecules and perchlorate anions. Non-H atoms of the perchlorate ions and water molecules are shown with displacement ellipsoids drawn at the 80% probability level. H atoms have been omitted for clarity, except those of water molecules, which are shown as spheres of arbitrary radii. [Symmetry code: (iii) $x - \frac{1}{2}, -y + \frac{3}{2}, -z + 2$].

The O2—O6 and O3—O6 distances depend on the sugar ring conformation. In the case of (I), these distances are larger than 4 Å, making the simultaneous coordination of atoms O2, O3 and O6 to a single metal centre impossible. The ligation of picolyl ether O6/N6 to the Co^{II} atom would entail a movement of C6 towards axially, which would result in a mannoside cycle deformation towards a less stable boat conformation.

Upon ligation, atoms O2 and O3 become stereocentres. Their asymmetry has been characterized by the sum of the oxygen bond angles (Mikata *et al.*, 2004, 2006). The values are 339.0° for O2 and 341.0° for O3, which are in the range that has been reported by us (Bellot *et al.*, 2005; Cisnetti *et al.*, 2007) and by Mikata *et al.* (2004, 2006) in the case of metal-bound sugar ethers.

The dangling pyridine ring containing atom N6 participates in hydrogen-bonding and π - π stacking interactions with another molecule of the complex. N6(*b*) is hydrogen bonded to O31(*a*) with a distance of 2.736 (2) Å [symmetry codes: (*a*) x, y, z ; (*b*) $-x + 2, y + \frac{1}{2}, -z + \frac{3}{2}$], which is indicative of a quite strong interaction [the mean value for the Co—OH₂···N distance over 110 structures in the Cambridge Structural Database (Allen, 2002), with the O—H···N angle in the range 120–180°, is 2.82 Å]. The pyridine ring containing N6(*a*) is stacked with the pyridine ring containing N2(*b*). The separation of the pyridine centroids is 3.63 (1) Å and the angle between the two ring planes is 9.01° (Fig. 2).

The perchlorate anion containing Cl2 bridges atoms O31 and O32 through hydrogen bonding (Table 2). There is a network of hydrogen bonds bridging each part of the complex cation to the others *via* hydrogen bonding with the perchlorate anions containing O13 and O12 and the solvent water molecule containing O33 (Fig. 3).

Experimental

For the synthesis of *L*, methyl 4-*O*-benzyl- α -D-mannopyranoside, (II), was prepared according to a published four-step synthesis (Rao & Roy, 1980). The picolylation to obtain *L* was performed on a 3 mmol scale by a phase transfer procedure adapted from Szeja's protocol for benzylation (Szeja *et al.*, 1989). Picolyl chloride hydrochloride (3.6 equivalents), NBu₄⁺·HSO₄⁻ (0.1 equivalent) and (II) (1 equivalent) were dissolved in a biphasic system composed of toluene (7 ml), 50% aqueous NaOH (5 ml) and 0.1 ml of *tert*-amyl alcohol. The mixture was stirred vigorously at room temperature overnight. *L* was recovered in 65% yield by extraction (CH₂Cl₂/H₂O) followed by SiO₂ column chromatography (eluent: AcOEt/methanol 19:1). ¹H NMR (CDCl₃, 360 MHz): δ 8.5 (*m*, 3H), 7.5 (*m*, 6H), 7.2 (*m*, 5H), 7.1 (*m*, 3H) (aromatic H); 4.9 (*m*, 9H, O—CH—OCH₃, O—CH₂—C_{Ar}); 3.9 (*m*, 6H, other sugar CH); 3.31 (*s*, 3H, CH₃). ¹³C NMR (CDCl₃, 90 MHz): δ 158.6 (2C), 158.5 (quaternary and phenyl C); 148.9, 148.8, 148.7, 136.6 (2C), 136.5, 122.2 (2C), 122.1, 121.5, 121.2, 121.1 (pyridine C); 138.3 (quaternary and phenyl C); 128.3 (2C), 127.8 (2C), 127.6 (phenyl C); 98.7 (C1); 75.0, 74.1, 73.5, 72.6, 69.9 (C6, O—CH₂—C_{Ar}); 80.2, 75.8, 74.6, 71.5 (other sugar CH); 54.8 (CH₃). ESI-MS: *m/z* 558.3 ([*L*+H]⁺). Crystals of the title compound were prepared by mixing 100 mg of *L* and 1 equivalent of Co(ClO₄)₂·6H₂O in 5 ml of 96% ethanol. Mixing resulted in a hyperchrome effect. The crystals were grown by slow evaporation over approximately one week and were recovered by filtration (yield 55%). Microanalysis (calculated/found): C 44.2/44.0, H 4.6/4.5, N 4.8/4.8, Cl 8.2/8.4, Co 6.8/6.6%.

Crystal data

[Co(C₃₂H₃₅N₃O₆)(H₂O)₂]
(ClO₄)₂·H₂O
M_r = 869.51
Orthorhombic, P2₁2₁2₁
a = 10.7451 (4) Å
b = 11.0327 (4) Å
c = 31.2265 (12) Å

V = 3701.8 (2) Å³
Z = 4
Mo Kα radiation
μ = 0.69 mm⁻¹
T = 100 (1) K
0.28 × 0.17 × 0.11 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: ψ scan (SADABS; Bruker, 2000)
T_{min} = 0.852, T_{max} = 0.923

18042 measured reflections
9372 independent reflections
8339 reflections with I > 2σ(I)
R_{int} = 0.023

Refinement

R[F² > 2σ(F²)] = 0.032
wR(F²) = 0.070
S = 1.00
9372 reflections
520 parameters
6 restraints

H atoms treated by a mixture of independent and constrained refinement
Δρ_{max} = 0.47 e Å⁻³
Δρ_{min} = -0.34 e Å⁻³
Absolute structure: Flack (1983), 538 Friedel pairs
Flack parameter: 0.015 (8)

Table 1

Selected geometric parameters (Å, °).

Co—O31	2.0457 (13)	Co—N3	2.1330 (15)
Co—O32	2.0459 (14)	Co—O3	2.1627 (13)
Co—N2	2.0742 (16)	Co—O2	2.2028 (13)
O31—Co—O32	93.96 (6)	N2—Co—O3	149.92 (6)
O31—Co—N2	91.70 (6)	N3—Co—O3	77.14 (6)
O32—Co—N2	106.19 (6)	O31—Co—O2	86.99 (5)
O31—Co—N3	175.22 (7)	O32—Co—O2	177.41 (6)
O32—Co—N3	86.78 (6)	N2—Co—O2	76.17 (5)
N2—Co—N3	92.63 (6)	N3—Co—O2	92.08 (5)
O31—Co—O3	98.08 (5)	O3—Co—O2	76.02 (5)
O32—Co—O3	101.44 (6)		
O2—C2—C3—O3	-45.84 (19)	O3—C30—C31—N3	24.0 (2)
O2—C20—C21—N2	33.9 (2)		

Table 2

Hydrogen-bond geometry (Å, °).

D—H...A	D—H	H...A	D...A	D—H...A
O31—H31A...N6 ⁱ	1.00 (2)	1.74 (3)	2.736 (2)	173 (2)
O31—H31B...O23	0.75 (2)	2.12 (2)	2.860 (2)	168 (3)
O32—H32A...O22	0.89 (2)	2.04 (2)	2.912 (2)	168 (3)
O32—H32B...O33	0.89 (3)	1.79 (3)	2.677 (2)	171 (3)
O33—H33A...O12	0.97 (2)	1.94 (2)	2.885 (2)	165 (3)
O33—H33B...O13 ⁱⁱ	0.81 (3)	2.11 (3)	2.919 (3)	176 (3)

Symmetry codes: (i) -x + 2, y + 1/2, -z + 3/2; (ii) x + 1/2, -y + 3/2, -z + 2.

H atoms of the ligand were positioned geometrically and refined using a riding model. H atoms of water molecules O31, O32 and O33

were located in a difference Fourier map and refined using DFIX instructions in which the O—H distances were restrained to 0.96 (3) Å and H...H distances to 1.52 (3) Å according to the ideal molecular geometry of water. The absolute configuration was unambiguous because the starting material for the ligand synthesis was pure methyl α-D-mannopyranoside and none of the synthetic steps could have led to any racemization.

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Bruker, 2001); program(s) used to refine structure: SHELXTL; molecular graphics: ORTEP-3.2 (Brueggemann & Schmid, 1990) and Mercury (Macrae *et al.*, 2006); software used to prepare material for publication: SHELXTL.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3097). Services for accessing these data are described at the back of the journal.

References

Alexeev, Y. E., Vasilchenko, I. S., Kharisov, B. I., Blanco, L. M., Garnovskii, A. D. & Zhdanov, Y. A. (2004). *J. Coord. Chem.* **57**, 1447–1517.
Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
Bellot, F., Hardré, R., Pelosi, G., Thérissod, M. & Policar, C. (2005). *Chem. Commun.* pp. 5414–5416.
Brueggemann, R. & Schmid, G. (1990). ORTEP-3.2. PC version. University of Ulm, Germany.
Bruker (2000). SADABS. Version 2.03. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2001). SMART (Version 5.624), SAINT (Version 6.04) and SHELXTL. Bruker AXS Inc., Madison, Wisconsin, USA.
Castiñeiras, A., Carballo, R., Hiller, W. & Strähle, J. (1991). *Acta Cryst.* **C47**, 1725–1727.
Charron, G., Bellot, F., Cisnetti, F., Pelosi, G., Rebilly, J.-N., Rivière, E., Barra, A.-L., Mallah, T. & Policar, C. (2007). *Chem. Eur. J.* **13**, 2774–2782.
Cisnetti, F., Guillot, R., Desmadril, M., Pelosi, G. & Policar, C. (2007). *Dalton Trans.* pp. 1473–1476.
Comba, P., Kersch, M., Merz, M., Muller, V., Pritzkow, H., Remenyi, R., Schiek, W. & Xiong, Y. (2002). *Chem. Eur. J.* **8**, 5750–5760.
Comba, P. & Schiek, P. (2003). *Coord. Chem. Rev.* **238–239**, 21–29.
Corey, E. J. & Bailar, J. C. J. (1959). *J. Am. Chem. Soc.* **81**, 2620–2629.
Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
Gatehouse, B. M. & Poppleton, B. J. (1970). *Acta Cryst.* **B26**, 1761–1765.
Hiller, W., Strähle, J., Castiñeiras, A., Carballo, R. & Bermejo, M. R. (1990). *An. Quim.* **86**, 506–511.
Jeffrey, G. A., McMullan, R. K. & Takagi, S. (1977). *Acta Cryst.* **B33**, 728–737.
Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453–457.
Mikata, Y., Sugai, Y., Obata, M., Harada, S. & Yano, S. (2006). *Inorg. Chem.* **45**, 1543–1551.
Mikata, Y., Sugai, Y. & Yano, S. (2004). *Inorg. Chem.* **43**, 4778–4780.
Pappalardo, S., Bottino, F., Finocchiaro, P., Mamo, A. & Fronczek, F. R. (1987). *J. Inclusion Phenom. Macrocycl. Chem.* pp. 153–156.
Peri, F., Cipolla, L., Forni, E. & Nicotra, F. (2002). *Monatsh. Chem.* **133**, 369–382.
Rao, A. S. & Roy, N. (1980). *Indian J. Chem. Sect. B*, **19**, 161–162.
Szeja, W., Fokt, I. & Gryniewicz, G. (1989). *Recl. Trav. Chim. Pays Bas*, **108**, 224–226.