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The Reaction of $[Ni(tn)_3]^{2+}$ (tn = trimethylenediamine) with Carbohydrates: *X*-Ray Crystal Structure of Bis{1-[(3-aminopropyl)-amino]-1,6-dideoxy-L-mannose}nickel(II) Dibromide Dihydrate Methanol Solvate: {$[Ni(L\text{-}rham\text{–}tn)_2]Br_2{\cdot}2H_2O{\cdot}CH_3OH$ (rham = rhamnose)}

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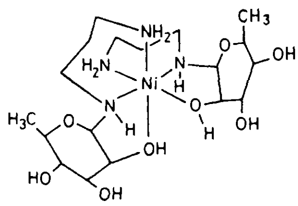
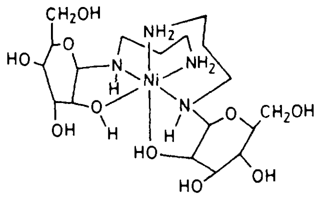
The *X*-ray crystal structure of the octahedral nickel(II) complex $[Ni(L\text{-}rham\text{–}tn)_2]Br_2{\cdot}2H_2O{\cdot}CH_3OH$ (**1**) (rham = rhamnose and tn = trimethylenediamine) containing two *N*-glycosides derived from the reaction of L-rham and tn is reported.

The interaction of carbohydrates with metals is of current interest for various reasons: it has application in analysis (in electrophoresis, chromatography, and in n.m.r. shift reagents), in industry (sequestration of metal ions), and in medicine and biochemistry. The isolation and structure determination of metal complexes containing sugar derivatives should provide useful information to aid in the interpretation of this interaction.

Recently, we have studied the synthesis and characterisation of transition metal complexes containing *N*-glycosides, the latter being formed by the reaction of sugars and amines.[1] The structures of both $[Ni(en)(D\text{-}fru\text{–}en)]Cl_2{\cdot}CH_3OH$[2] (2) and $[Ni(D\text{-}N\text{-}gl\text{-}en)_2]Br_2{\cdot}4H_2O$[3] (3) (en = ethylenediamine, fru = fructose, and gl = glucose) were determined by *X*-ray crystallography, the results of which suggested that an *N*-glycoside from an aldose and a diamine co-ordinates to the nickel ion through the oxygen atom of the hydroxy-group on C-2 of the sugar moiety and through the two N atoms of the diamine. The *gauche* conformation of the chelate ring, then, will depend on the orientation of the C-2 hydroxy-group and this makes a significant contribution to the circular dichroism (c.d.). The latter is very important as a reference by which the co-ordination in complexes containing aldoses can be assigned by correlation of their c.d. spectra. Accordingly, it is interesting to examine the relationship between the *X*-ray crystal structures and the c.d. spectra of metal complexes of the C-2 epimers D-glucose and D-mannose (D-man). However, it is difficult to predict the preferred conformation of a pyranoside of D-man and its derivatives in their complexes because an aqueous solution of D-man contains 69% of the α-pyranose and 31% of the β-pyranose in equilibrium. When we used L-rhamnose (L-rham) as the sugar component, we obtained good crystals for an *X*-ray crystallographic study. Though the sugar is L-type and has no hydroxy-group on C-6, the co-ordination behaviour of *N*-glycosides derived from L-rham is expected to be similar to that for complexes of D-man.



$[Ni(L\text{-}rham\text{-}tn)_2]^{2+}$
(1)



$[Ni(D\text{-}man\text{-}tn)_2]^{2+}$
(4)

$[Ni(en)(D\text{-}fru\text{-}en)]Cl_2 \cdot CH_3OH$
(2)

$[Ni(D\text{-}N\text{-}gl\text{-}en)_2]Br_2 \cdot 4H_2O$
(3)

$[Ni(tn)_3]Br_2{\cdot}2H_2O$ (tn = trimethylenediamine) (1.0 equiv.) was treated with L-rham (3.0 equiv.) in methanol to give a blue solution, which was purified by chromatography on SEPHADEX LH-20 and evaporated to give blue crystals of the title compound. These were recrystallised from hot methanol to give crystals suitable for *X*-ray analysis. Good elemental analyses were obtained.

Crystal data: $C_{19}H_{48}Br_2O_{11}N_4Ni$, $M = 727.11$, orthorhombic, space group $P2_12_12_1$, $a = 12.373(1)$, $b = 21.614(2)$, $c = 11.272(1)$ Å, $U = 3214.5(5)$ Å^3, $D_m = 1.62$ g cm^{-3}, $D_c = 1.60$ g cm^{-3}, $Z = 4$, Mo-K_α radiation, $\lambda = 0.7107$ Å, $\mu = 39.71$ cm^{-1}. Of the 3920 reflections collected by using the θ–2θ scan method, 2657 had $F_o > 3\sigma(F_o)$ and were considered to be

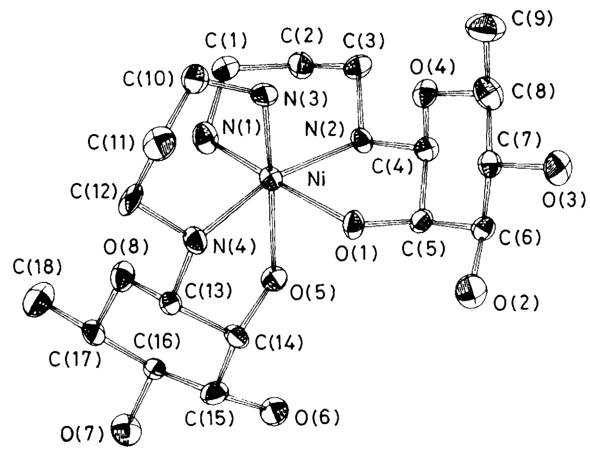


Figure 1. ORTEP drawing and atomic numbering scheme for the $[Ni(\text{L-rham-tn})_2]^{2+}$ ion except for the hydrogen atoms. Selected bond distances (Å): Ni–N(1) 2.08(1), Ni–N(2) 2.11(1), Ni–O(1) 2.17(1), Ni–N(3) 2.09(1), Ni–N(4) 2.09(1), Ni–O(5) 2.18(1). Selected bond angles (°): N(1)–Ni–N(2) 92.3(2), N(3)–Ni–N(4) 90.9(2), N(2)–Ni–O(1) 78.1(2), N(4)–Ni–O(5) 79.1(2), N(1)–Ni–O(1) 168.7(2), N(2)–Ni–N(4) 165.7(2), N(3)–Ni–O(5) 168.1(2).

observed. An absorption correction was applied. The structure was solved by heavy-atom methods and atomic parameters were refined using block-diagonal least-squares except for those of three hydrogen atoms to a final R value of 0.044.†

Figure 1 shows the *X*-ray crystal structure of the complex cation in (**1**), where the two *N*-glycoside molecules complete an octahedral co-ordination around the nickel atom; the complex has approximately C_2 symmetry. The absolute configuration of the two co-ordinated chiral nitrogen atoms is *S*. Each pyranose ring of the sugar moieties has the β-$^1C_4$ chair conformation. The hydroxy-group on C-2, which co-ordinates to the nickel atom, is axial with respect to the pyranose ring. Each sugar residue forms a five-membered chelate ring with the nickel atom in a *gauche* conformation. It is also λ in the case of (**3**); the δ-*gauche* conformation occurs when D-man is the original sugar. These structural features are evident in the c.d. spectra. The c.d. curves of (**1**)‡ and $[Ni(\text{D-man-tn})_2]Cl_2 \cdot 1.5H_2O$ (**4**)‡ are nearly mirror images of each other and that of (**3**)‡ has the opposite sign to those of (**1**) or (**4**) in the first absorption region.

Each diamine residue forms a six-membered chelate ring with a chair conformation. The ring angles at the central atom for the diamine rings, namely N(1)–Ni–N(2) and N(3)–Ni–N(4), are *ca.* 90°. The values are significantly larger than those reported for the five-membered diamine rings in (**2**) and (**3**). In (**1**) the average angle between the terminal co-ordinated atoms of the *N*-glycoside ligands at the nickel atom, *i.e.* N(1)–Ni–O(1) and N(3)–Ni–O(5), is 168.4°. The corresponding value in (**3**) is 160.7°. Clearly, the *N*-glycoside ligands in (**1**) are almost strain-free. The amelioration of such a distortion in (**1**) is presumably due to the strain-relieving effects of the six-membered ring relative to the five-membered ring in (**3**). These structural features support the view that six-membered diamine chelates are an aid in the preparation of metal complexes with *N*-glycosides.§ The results suggest that some of the co-ordination pattern of D-man and its derivatives in their complexes is predictable by correlation of their c.d. spectra.

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† The calculations were carried out on the HITAC M-200H computer at Tokyo University with the Universal Computation Program System UNICS III (T. Sakurai and K. Kobayashi, *Rikagaku Kenkyusho Hokoku*, 1979, **55**, 69).

The atomic co-ordinates are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

‡ For (**1**) c.d. (methanol): $10^{-3} \times \nu_{max}$ ($\Delta\epsilon \times 10^2$) 10.6 (−18.7), 16.6 (+ 6.1), 25.2 (+ 1.5), 27.4 (−0.8), and 35.0 (+ 4.8) cm^{-1}. For (**4**) c.d. (methanol): 10^{-3} ν_{max} ($\Delta\epsilon \times 10^2$) 10.1 (+10.0), 14.8 (+ 1.3), 16.8 (−2.5), 21.6 (+ 0.2), 25.2 (−1.1), 28.0 (+ 1.5), and 33.8 (−1.5) cm^{-1}. For (**3**) c.d. (methanol): 10^{-3} ν_{max} ($\Delta\epsilon \times 10^2$) 11.8 (+ 8.5), 12.6 (+ 7.7), 18.4 (+ 2.6), 26.3 (−0.4), and 29.0 (+ 2.1) cm^{-1}.

§ Recently we have observed that sugars reacted with $[Ni(tn)_3]^{2+}$ to give good yields of the *N*-glycoside complexes in a short time (unpublished results).