

Reaction of Metal Complexes with Carbohydrates: Synthesis and Characterization of an Unprecedented μ -Mannofuranoside Binuclear Nickel(II) Complex Containing *N*-Glycosides

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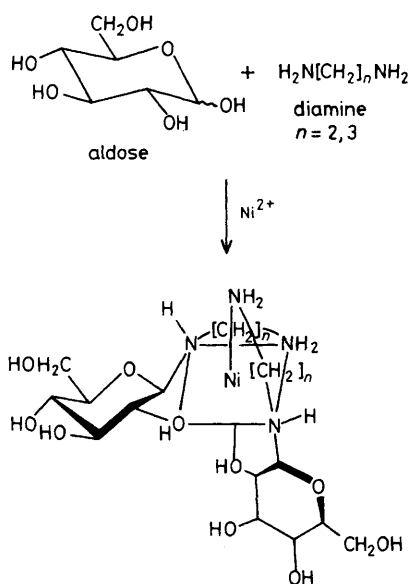
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The X-ray crystal structure of the novel μ -mannofuranoside binuclear nickel(II) complex, μ -Man-[Ni₂(MeOH)(*N*-D-Man-*N,N'*-Me₂en)(*N,N'*-D-Man₂-*N,N'*-Me₂en)]Cl₂ · MeOH · 5H₂O containing three *N*-glycosides derived from the reaction of D-mannose (D-Man) and *N,N'*-dimethylethylenediamine (*N,N'*-Me₂en) is reported.

The interaction of carbohydrates with metals has been of much interest in recent years, in particular in industry and biochemistry. In order to study carbohydrate-transition metal interactions, we have systematically studied the synthesis and characterization of transition metal complexes containing *N*-glycosides derived from the reaction of sugars and diamines. We have already determined the structure of [Ni(L-Rha-tn)₂]Br₂ · 2H₂O · MeOH¹ and [Ni(D-GlcN-en)₂]Br₂ · 4H₂O² (en = ethylenediamine, tn = trimethylenediamine, Rha = rhamnose, GlcN = 2-deoxy-2-amino-glucose) by X-ray crystallography, the results of which suggested that an *N*-glycoside from an aldose and a primary diamine are attached to nickel through the oxygen atom of the hydroxy group on C-2 of the sugar moiety and through the two nitrogen atoms of the diamine residues³ (Scheme 1). It is often observed that *N*-alkyl groups on co-ordinating nitrogen atoms influence strongly the stereochemistry of metal complexes, and we have thus used *N,N'*-Me₂en as a diamine component in the hope of verifying the co-ordination behaviour of *N*-glycoside ligands. Of many aldoses studied, only in the case of D-mannose have we obtained a binuclear solid complex containing *N*-glycosides. To clarify the stereochemistry of this unprecedented Ni^{II} complex, we have undertaken an X-ray crystal structure determination.

To a methanolic solution of [Ni(H₂O)₂(*N,N'*-Me₂en)₂]Cl₂ (2.90 mmol) was added D-mannose (8.70 mmol). The stirred



Scheme 1. Reaction of aldoses with nickel(II)-primary diamine complexes.

solution was heated at 65 °C for 15 min. Chromatography on Sephadex LH-20 led to separation of the coloured materials into two blue-green bands and each was collected and concentrated. Blue-green crystals of the title compound were obtained from the faster eluting band† (yield 38% based on the starting nickel complex). Crystals suitable for X-ray analysis were obtained from hot methanol. The other fraction readily decomposed into starting materials.

In the air, the crystals decomposed within a few hours, so diffraction data were obtained from crystals sealed in a Lindemann capillary in the presence of a droplet of mother liquor. **Crystal data:** C₂₇H₅₆Cl₂N₄Ni₂O₁₆ · CH₃OH · 5H₂O, orthorhombic, space group *P*2₁2₁2₁, *a* = 19.647(35), *b* = 17.169(8), *c* = 13.247(4) Å, *Z* = 4, *D*_m = 1.471 g cm⁻³, *D*_c = 1.472 g cm⁻³, Mo-*K*_α radiation. About 4000 reflections were measured and, of these, 2199 independent reflections with $|F_o| > 3\sigma|F_o|$ were used in the structure refinement. No absorption

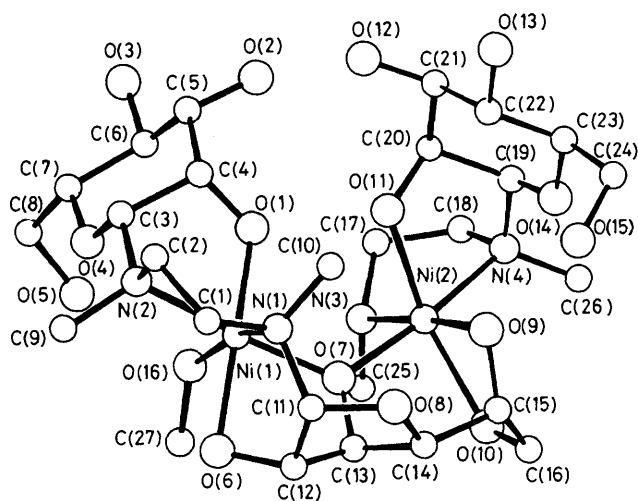


Figure 2. Perspective drawing and atomic numbering scheme for the μ -Man-[Ni₂(MeOH)(*N*-D-Man-*N,N'*-Me₂en)(*N,N'*-D-Man₂-*N,N'*-Me₂en)]²⁺ ion, Man = mannose. Selected bond lengths (Å) and angles (°): Ni(1) ··· Ni(2) 3.596(4), Ni(1)-O(1) 2.02(1), Ni(1)-O(6) 2.12(2), Ni(1)-O(7) 2.02(1), Ni(1)-O(16) 2.15(2), Ni(1)-N(1) 2.19(2), Ni(1)-N(2) 2.13(2), Ni(2)-O(7) 2.02(1), Ni(2)-O(9) 2.09(1), Ni(2)-O(10) 2.16(2), Ni(2)-O(11) 2.04(1), Ni(2)-N(3) 2.10(2), Ni(2)-N(4) 2.19(2); O(1)-Ni(1)-N(2) 83.2(6), O(6)-Ni(1)-O(7) 82.1(5), O(6)-Ni(1)-N(1) 79.5(6), N(1)-Ni(1)-N(2) 84.0(6), O(7)-Ni(2)-O(10) 89.3(6), O(9)-Ni(2)-O(10) 77.9(6), O(11)-Ni(2)-N(4) 79.7(6), N(3)-Ni(2)-N(4) 82.8(7).

† Satisfactory elemental analyses for C, H, N, Cl, and Ni were obtained; ν_{\max} (MeOH): 9450 (ϵ 16.9), 16 330 (13.3), and 26 330 (28.3) cm⁻¹; c.d. (MeOH): ν_{\max} 10 250 ($\Delta\epsilon$ +23.0), 16 620 ($\Delta\epsilon$ -13.3), and 25 640 ($\Delta\epsilon$ -8.4) cm⁻¹.

correction was made since μ (10.7 cm^{-1}) was low. The structure was solved by direct methods⁴ and all hydrogen atoms except for those of hydroxy groups and solvent molecules were placed in calculated positions assuming tetrahedral co-ordination. Atomic parameters were refined using block-diagonal least-squares techniques to $R = 0.077$ ($R_w = 0.087$).[‡]

A perspective drawing of the complex cation is given in Figure 1. The metal centre of the complex is surprisingly binuclear with one of the mannose residues linking the two nickel atoms. So far as we know, this is the first report of an *X*-ray crystal structure determination of a binuclear nickel(II) complex containing sugar moieties. The complex cation contains three mannose residues forming *N*-glycosides with *N,N'*-Me₂en. Two of them adopt the β -⁴C₁-pyranose form and co-ordinate to nickel through the glycosidic nitrogen atom and the oxygen atom of the C-2 hydroxy group in a similar manner to that in $[\text{Ni}(\text{L-Rha-tn})_2]\text{Br}_2 \cdot 2\text{H}_2\text{O} \cdot \text{MeOH}$.¹ The other mannose residue adopts the unusual furanose form and links two nickel atoms with an oxygen bridge *via* the C-3 hydroxy group. Furthermore it is attached to two nickel atoms through the glycosidic nitrogen atom and the oxygen atoms of the C-2, C-5, and C-6 hydroxy groups. This co-ordination behaviour of *D*-mannose is fairly rare as far as we know but it seems to be the most suitable form for linking two nickel atoms, because in the furanose form all donor atoms are pushed out of the ring

plane in the same direction. It is probably for this reason that a stable binuclear complex was obtained only using *D*-mannose. These structural features will be dealt with in detail elsewhere.⁶ The result of this *X*-ray crystal structure determination suggests the possibility of selective complexation for mannose-type sugars *via* modification of the diamine component in $[\text{Ni}(\text{H}_2\text{O})_2(\text{diamine})_2]^{2+}$ salts, and investigations along these lines are now in progress.[§]

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

§ Recently we have surprisingly observed that *D*-glucose reacted with $[\text{Ni}(\text{H}_2\text{O})_2(\text{N,N}'\text{-Me}_2\text{en})_2]^{2+}$ to give an *N*-glycoside complex containing *D*-mannose in low yield.