CHEMISTRY LETTERS, pp. 2153-2156, 1987.

A Novel Sugar-sugar Interaction in a Transition Metal Complex. X-Ray Crystal Structure of N,N-Di(N-D-mannosyl-2-aminoethyl)-ethylenediamine Nickel(II) Dichloride Methanol, $[Ni(N,N'-(D\text{-}Man)_2\text{-}tren)]Cl_2 \cdot CH_3OH$

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The synthesis and crystal structure of the nickel(II) complex, $[Ni(N,N'-(D\text{-}Man)_2\text{-}tren]Cl_2 \cdot CH_3OH$ containing two N-glycosides derived from the reaction of D-mannose (D-Man) and N,N-di(2-aminoethyl)ethylenediamine (tren) are reported. The suagr part in the complex involves novel intramolecular sugar-sugar hydrogen bondings around the metal center.

Noncovalent interactions are vital in processes of biological recognition of molecules. The enzyme-substrate, hormone-receptor, and antigen-antibody interactions are among the most important in biological systems, and are achieved mainly by the specific side-chain groups of amino acids and sugar chains involved in proteins. Although with regard to interactions between the side-chains of amino acids contained in transition metal complexes, many excellent studies have been made in connection with metal-containing enzymes,[1] the literatures concerning the structural details of sugar-sugar interactions around a metal center are very few.

We have already reported the structures of transition metal complexes containing N-glycosides derived from the reaction of carbohydrates and diamines.[2] These complexes gave us very important information as to metal-sugar interactions, but none of them showed distinct sugar-sugar interactions around the metal center. In this study, we used N,N-di(2-aminoethyl)ethylenediamine (tren) as a polyamine part in order to prepare the nickel(II)-N-glycoside complex involving some intramolecular sugar-sugar hydrogen bonding networks around the metal center, and when D-mannose was used as a starting sugar, we obtained good crystals for X-ray crystallographic analysis.

To a methanolic solution of $[Ni(H_2O)_2(tren)]Cl_2$[3] (1.0 mmol) were added D-mannose (D-Man) (2.0 mmol) and tren (0.3 mmol). The solution was incubated at 65 °C for 30 min with stirring. The excessive addition of tren ligand accelarated the N-glycoside complex formation dramatically. Chromatography on Sephadex LH-20

led to separation of coloured material into the major blue and minor yellow bands. The blue band was collected and concentrated to give blue single crystals of the title compound[4] (1) (yield 87% based on the starting nickel complex), which were suitable for X-ray crystallography.

Crystal data; $C_{19}H_{42}Cl_2O_{11}N_4Ni$, M=632.15, orthorhombic, space group $P2_12_12_1$, a = 16.005(3), b = 20.095(4), c = 8.361(2) Å, V = 2689(1) Å^3, D(obsd) = 1.55 g cm^{-3}, D(calcd) = 1.56 g cm^{-3}, Mo-Kα radiation (λ = 0.7107 Å), μ(linear absorption coefficient) = 9.7 cm^{-1}. Of the 4422 reflections collected by using the ω ($2<2\theta<30°$) and ω-2θ ($30<2\theta<60°$) method, 2287 ($|Fo| > 3\sigma(|Fo|)$) were considered to be observed. An absorption correction was applied. The structure was solved by direct methods[5] and atomic parameters were refined using block-diagonal least-squares techniques[6] to R = 0.049 (Rw = 0.053). The absolute configuration was determined using the known asymmetric carbon atoms of D-mannose as an internal reference of asymmetric center.

A perspective drawing of the complex cation is given in Fig. 1. The nickel atom is octahedrally coordinated with a cage-type hexadentate N-glycosides ligand (N,N'-(D-Man)$_2$-tren),[7] which contains two mannose moieties. Both adopt the stable β-$^4C_1$-pyranose form and attach to nickel through the glycosidic nitrogen atom and the oxygen atom of the C-2[8] hydroxyl group as observed in [Ni(L-Rha-tn)$_2$]Br$_2$·H$_2$O·CH$_3$OH[2c] (Rha = 6-deoxy-mannose, tn = trimethylenediamine), but one of the N-

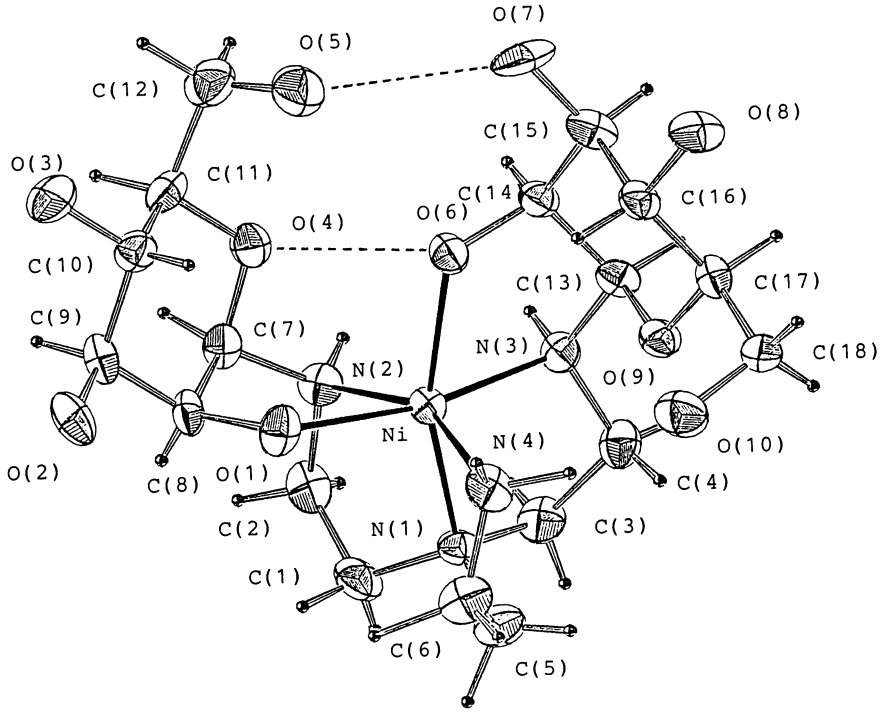

Fig. 1. An ORTEP drawing of the complex cation, [Ni(N,N'-(D-Man)$_2$-tren)]$^{2+}$. Selected bond distances (Å); Ni-O(1) 2.109(5), Ni-O(6) 2.181(5), Ni-N(1) 2.099(7), Ni-N(2) 2.148(7), Ni-N(3) 2.069(6), Ni-N(4) 2.086(7); selected bond angles (deg); O(1)-Ni-N(2) 77.2(2), O(1)-Ni-N(3) 168.5(3), O(6)-Ni-N(1) 161.2(2), O(6)-Ni-N(3) 78.5(2), N(1)-Ni-N(2) 81.8(3), N(1)-Ni-N(3) 83.8(3), N(1)-Ni-N(4) 83.6(3), N(2)-Ni-N(4) 153.9(3).

glycoside residues is in the facial mode (N(1), N(2), O(1)) and the other in the meridional mode (N(1), N(3), O(6)). Further the tetradentate tren ligand directs two mannose residues to the same side in the complex, and this brings about the desired intramolecular sugar-sugar hydrogen bondings (O(5)···O(7), 3.026(10) Å; O(4)····O(6), 2.969(8) Å) around the metal center, the pair of C-6[8] oxygen and cyclic oxygen being combined with the cis oxygen pair on C-2 and C-3.[8]

On the other hand, when D-glucose (D-Glc) was used instead of D-mannose, no $[Ni(N,N'\text{-}(Sug)_2\text{-tren})]^{2+}$ (Sug = aldose moiety) type complex was obtained, and the complex containing only one sugar moiety, $[Ni(N\text{-}(D\text{-Glc})\text{-tren})(H_2O)]Cl_2 \cdot 1/2H_2O$[9] (2) was formed in a very low yield (an estimated structure is presented in Fig. 2). D-Glucose is not expected to complete a intramolecular hydrogen bonding network because of its trans arrangement of C-1(β),[10] C-2, and C-3 hydroxyl groups. Thus, the intramolecular hydrogen bondings around the metal center are thought to be a significant driving force to complete the N-glycoside complexes involving two sugar moieties.

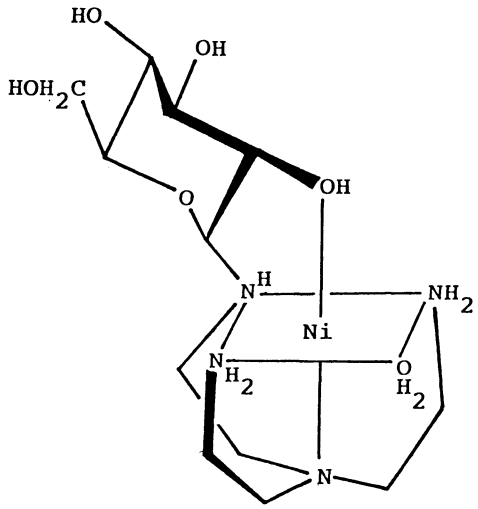

Fig. 2. An estimated structure of the complex (2).

In this study, it was revealed that even though the polydentate tren is used as an amine part, the nickel(II) complex containing N-glycosides derived from the reaction of tren and D-mannose is obtained in a good yield, and the complex has unique structural features owing to the effect of polydentate tren ligand. That is, the complex can be said to consist of two large blocks; a hydrophobic polyamine part and a hydrophilic sugar part, the later involving distinct intramolecular sugar-sugar hydrogen bondings. The present X-ray crystallography could provide some fundamental informations with regard to interactions between oligosaccharide chains in glycoproteins, and the hydrogen bonding network in the complex might be useful in recognition of chiral organic compounds having polar groups. Studies to explore such possibility are now in progress.

This work has been supported in part by a grant-in-aid from Mitsubishi Foundation.

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3) The starting complex, $[Ni(H_2O)_2(tren)]Cl_2$, was prepared by the known method (C. K. Jorgensen, Acta Chem. Scand., 10, 887(1956); O. Bostrup, C. K. Jorgensen, ibid., 11, 1223(1957)).

4) Found: C, 35.85; H, 6.79; N, 8.81; Cl, 11.00%. Calcd for $[Ni(N,N'\text{-}(D\text{-}Man)_2\text{-}tren)]Cl_2\cdot CH_3OH$ ($C_{19}H_{42}O_{11}N_4Cl_2Ni$): C, 36.10; H, 6.70; N, 8.86; Cl, 11.22%. Near-infrared and visible spectral data in DMSO : $\nu_{max}/10^3cm^{-1}$ 10.1 (ε 25.8), 12.5(7.3) (sh), 17.5(12.1), 27.4(16.8). Circular dichroism spectral data in DMSO : $\nu_{max}/10^3cm^{-1}$ 10.7($\Delta\varepsilon$ /10^2 -21.7), 12.4(-8.8) (sh), 15.5(+4.4) (sh), 17.6(+7.3), 26.7(+5.3).

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6) The hydrogen atoms of hydroxyl groups and the methanol were not included in this X-ray crystallography. Among other hydrogen atoms, 28 were determined by differential Fourier techniques and 2 were placed at idealized positions. The calculations were carried out on a FACOM M-780 computer at the Institute of Physical and Chemical Research with the Universal Computation Program System UNICS III (T. Sakurai, K. Kobayashi, Rikagaku Kenkyusho Hokoku, 55, 69(1979)).

7) The fully systematic name is N,N-di(N-D-mannosyl-2-aminoethyl)ethylenediamine.

8) C-2, C-3, or C-6 hydroxyl group means the hydroxyl group on C-1, C-2, or C-6 carbon of the aldohexose unit in the conventional notation of carbohydrates.

9) Found: C, 31.02; H, 6.91; N, 12.56; Cl, 14.95%. Calacd for $[Ni(N\text{-}(D\text{-}Glc)\text{-}tren)(H_2O)]Cl_2\cdot 1/2H_2O$ ($C_{12}H_{31}O_{6.5}N_4Cl_2Ni$): C, 31.00; H, 6.72; N, 12.05; Cl, 15.25%. Near-infrared and visible spectral data in methanol, $\nu_{max}/10^3cm^{-1}$ 10.3(ε 19.8), 12.6(6.4) (sh), 17.5(12.4), 27.5(24.0). Circular dichroism spectral data in methanol, $\nu_{max}/10^3cm^{-1}$ 10.8($\Delta\varepsilon$ /10^2 +25.7), 12.6(+10.2) (sh), 17.5(-5.0), 26.8(-3.2). N-(D-Glc)-tren = N,N-di(2-aminoethyl)-N'-(D-glucosyl)ethylenediamine.

10) C-1(β) hydroxyl group means the hydroxyl group on C-1 carbon atom of β-glucopyranose. In our previous studies, it was revealed that D-glucose in β-N-glycopyranoside form predominantly coordinates to nickel through the glycosidic nitrogen atom and the oxygen atom of C-2 hydroxyl group (Refs. 2a, 2b, and 2e).

(Received August 1, 1987)