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Assembly of Carbohydrates on a Nickel(II) Center by Utilizing *N*-Glycosidic Bond Formation with Tris(2-aminoethyl)amine (tren). Syntheses and Characterization of [Ni{*N*-(aldosyl)-tren}(H$_2$O)]$^{2+}$, [Ni{*N*,*N*′-bis(aldosyl)-tren}]$^{2+}$ and [Ni{*N*,*N*′,*N*″-tris(aldosyl)-tren}]$^{2+}$

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Reactions of [Ni(tren)(H$_2$O)$_2$]X$_2$ (tren = tris(2-aminoethyl)amine; X = Cl (**1a**), Br (**1b**); X$_2$ = SO$_4$ (**1c**)) with mannose-type aldoses, having a 2,3-*cis* configuration (D-mannose and L-rhamnose), afforded {bis(*N*-aldosyl-2-aminoethyl)(2-aminoethyl)amine}nickel(II) complexes, [Ni(*N*,*N*′-(aldosyl)$_2$-tren)]X$_2$ (aldosyl = D-mannosyl, X = Cl (**2a**), Br (**2b**), X$_2$ = SO$_4$ (**2c**); aldosyl = L-rhamnosyl, X$_2$ = SO$_4$ (**3c**)). The structure of **1c** was confirmed by X-ray crystallography to be a mononuclear [Ni^{II}N$_4$O$_2$] complex with the tren acting as a tetradentate ligand (**1c**·2H$_2$O: orthorhombic, *Pbca*, $a = 15.988(2)$ Å, $b = 18.826(4)$ Å, $c = 10.359(4)$ Å, $V = 3118$ Å^3, $Z = 8$, $R = 0.047$, and $R_w = 0.042$). Complexes **2a**,**c** and **3c** were characterized by X-ray analyses to have a mononuclear octahedral Ni(II) structure ligated by a hexadentate *N*-glycoside ligand, bis(*N*-aldosyl-2-aminoethyl)(2-aminoethyl)amine (**2a**·CH$_3$OH: orthorhombic, $P2_12_12_1$, $a = 16.005(3)$ Å, $b = 20.095(4)$ Å, $c = 8.361(1)$ Å, $V = 2689$ Å^3, $Z = 4$, $R = 0.040$, and $R_w = 0.027$. **2c**·3CH$_3$OH: orthorhombic, $P2_12_12_1$, $a = 14.93(2)$ Å, $b = 21.823(8)$ Å, $c = 9.746(2)$ Å, $V = 3176$ Å^3, $Z = 4$, $R = 0.075$, and $R_w = 0.080$. **3c**·3CH$_3$OH: orthorhombic, $P2_12_12_1$, $a = 14.560(4)$ Å, $b = 21.694(5)$ Å, $c = 9.786(2)$ Å, $V = 3091$ Å^3, $Z = 4$, $R = 0.072$, and $R_w = 0.079$). The sugar part of the complex involves novel intramolecular sugar−sugar hydrogen bondings around the metal center. The similar reaction with D-glucose, D-glucosamine, and D-galactosamine, having a 2,3-*trans* configuration, resulted in the formation of a mono(sugar) complex, [Ni(*N*-(aldosyl)-tren)(H$_2$O)$_2$]Cl$_2$ (aldosyl = D-glucosyl (**4b**), 2-amino-2-deoxy-D-glucosyl (**5a**), and 2-amino-2-deoxy-D-galactosyl (**5b**)), instead of a bis(sugar) complex. The hydrogen bondings between the sugar moieties as observed in **2** and **3** should be responsible for the assembly of two sugar molecules on the metal center. Reactions of tris(*N*-aldosyl-2-aminoethyl)amine with nickel(II) salts gave the tris(sugar) complexes, [Ni(*N*,*N*′,*N*″-(aldosyl)$_3$-tren)]X$_2$ (aldosyl = D-mannosyl, X = Cl (**6a**), Br (**6b**); L-rhamnosyl, X = Cl (**7a**), Br (**7b**); D-glucosyl, X = Cl (**9**); maltosyl, X = Br (**10**); and melibiosyl, X = Br (**11**)), which were assumed to have a shuttle-type C_3 symmetrical structure with Δ helical configuration for D-type aldoses on the basis of circular dichroism and ^{13}C NMR spectra. When tris(*N*-rhamnosyl)-tren was reacted with NiSO$_4$·6H$_2$O at low temperature, a labile neutral complex, [Ni(*N*,*N*′,*N*″-(L-rhamnosyl)$_3$-tren)(SO$_4$)] (**8**), was successfully isolated and characterized by X-ray crystallography, in which three sugar moieties are anchored only at the N atom of the C-1 position (**8**·3CH$_3$OH·H$_2$O: orthorhombic, $P2_12_12_1$, $a = 16.035(4)$ Å, $b = 16.670(7)$ Å, $c = 15.38(1)$ Å, $V = 4111$ Å^3, $Z = 4$, $R = 0.084$, and $R_w = 0.068$). Complex **8** could be regarded as an intermediate species toward the C_3 symmetrical tris(sugar) complexes **7**, and in fact, it was readily transformed to **7b** by an action of BaBr$_2$.

Introduction

Carbohydrates are indispensable building blocks and energy sources to living organisms and play important roles in many biological functions.[1] Some enzymatic reactions have recently been elucidated to comprise interactions of sugars with metal ions. In this regard, the interactions of metal ions with carbohydrates are significant subjects in inorganic and bioinorganic fields, and the chemistry of sugar−metal complexes, however, has largely been unexplored owing to their complicated stereochemistry and hygroscopic properties.[2−5]

We have systematically studied the syntheses and characterizations of nickel(II) and cobalt(III) complexes containing *N*-glycosides derived from the reactions between sugars and diamines.[4] *N*-Glycosylamines derived from an aldose and diamines such as ethylenediamine (en) and trimethylenediamine (tn), *N*-aldosyl-en or *N*-aldosyl-tn, coordinate to the nickel atom in a tridentate manner through the oxygen atom of the hydroxyl group at the C-2 position of the sugar moiety and the two

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nitrogen atoms of the diamine part.[6−11] The similar *N*-glycosylamine from a ketose and a diamine acts as a tetradentate ligand *via* the two oxygen atoms of the hydroxyl groups at the C-1 and C-3 positions and the two nitrogen atoms of the diamine.[12−14] When *N*,*N′*-dimethylethylenediamine (*N*,*N′*-Me$_2$-en) and D-mannose were used as diamine and sugar parts, respectively, the dinuclear nickel(II) complex with a D-mannofuranoside residue of the *N*-glycoside ligand bridging the two metal ions was obtained.[15,16] Moreover, nickel(II) complexes of further N-methylated diamines, *N*,*N*,*N′*-trimethylenediamine and *N*,*N*,*N′*,*N′*-tetramethylethylenediamine, were shown to promote a novel stereospecific rearrangement of the carbon skeleton of sugars resulting in efficient C-2 epimerization of aldoses.[17−24] In the cobalt(III) complexes, *N*-aldosyl-en (aldosyl = D-mannosyl, L-rhamnosyl, and D-ribosyl) was ligated to the cobalt center in a tetradentate manner.[25−28] These results indicated that the structure of the sugar complexes is able to be modified by varying carbohydrates, diamines, and metal ions used.

Recently, a branched polyamine, tris(2-aminoethyl)amine (tren), having three primary amino groups, was introduced to our study in the hope of assembling three sugar units on the metal center in a symmetrical fashion. Reaction of cobalt(II) salts with tris(*N*-aldosyl-2-aminoethyl)amine from tren and aldoses afforded a C_3 symmetrical sugar complex, [Co(*N*,*N′*,*N″*-(aldosyl)$_3$-tren)]$^{2+}$ (aldosyl = D-mannosyl or L-rhamnosyl), the sugar pocket of which interestingly recognized tetrahedral oxo anions (SO$_4^{2-}$ and PO$_4^{2-}$) through the inversion of configuration around the cobalt center.[29] We wish to describe, herein, the assembly of aldoses on nickel(II) ion by utilizing the *N*-glycosidic bond formation with tren, mainly focusing on the syntheses and characterization of mono-, bis-, and tris(sugar) complexes, [Ni(*N*-(aldosyl)-tren)(H$_2$O)]$^{2+}$, [Ni(*N*,*N′*-(aldosyl)$_2$-tren)]$^{2+}$, and [Ni(*N*,*N′*,*N″*-(aldosyl)$_3$-tren)]$^{2+}$. Preliminary results have already appeared.[30,31]

Experimental Section

Materials. All reagents were of the best commercial grade and were used without further purification. [Ni(tren)(H$_2$O)$_2$]X$_2$ (X = Cl (**1a**), Br (**1b**)) was prepared by the known method,[32,33] and [Ni(tren)(H$_2$O)$_2$]SO$_4$ (**1c**) by a procedure similar to **1a**. The following abbreviations are used: tren, tris(2-aminoethyl)amine; D-Man, D-mannose; L-Rha, 6-deoxy-L-mannose (L-rhamnose); D-Glc, D-glucose; D-GlcN, 2-deoxy-2-amino-D-glucose (glucosamine); D-GalN, 2-deoxy-2-amino-D-galactose (galactosamine); Mal, α,D-glucopyranosyl-(1→4)-D-glucose (maltose); Mel, α,D-galactopyranosyl-(1→6)-D-glucose (melibiose); *N*,*N′*-(aldose)$_2$-tren, bis(*N*-aldosyl-2-aminoethyl)(2-aminoethyl)amine; *N*,*N′*,*N″*-(aldose)$_3$-tren, tris(*N*-aldosyl-2-aminoethyl)amine; *N*-(aldose)-tren, (*N*-aldosyl-2-aminoethyl)bis(2-aminoethyl)amine.

Measurements. Electronic absorption spectra were recorded on a Shimazu UV-3100 or a Hitachi Model 340 spectrometer, and circular dichroism spectra, on a Jasco J-720 or J-500 spectropolarimeter. Magnetic susceptibilities were measured at room temperature by the Faraday method using a Shimazu MB-100 or a Sherwood Scientific Ltd. Model MSB-MKI magnetic balance. Diamagnetic corrections were calculated from tables of Pascal's constants. ^{13}C NMR spectra of **10** and **11** (~0.15 M in DMSO-d_6) were measured at 100.40 MHz on a JEOL GX-400 spectrometer with broad-band ^{1}H decoupled and INEPT modes at 30 °C. The spectral width measured is 100 000 Hz (±500 ppm), and chemical shifts were calibrated with tetramethylsilane as an internal reference.

Preparation of [Ni(*N*,*N′*-(D-Man)$_2$-tren)]Cl$_2$·CH$_3$OH (2a·CH$_3$OH). A methanolic solution (100 mL) containing [Ni(tren)(H$_2$O)$_2$]Cl$_2$ (**1a**) (0.94 g, 3.0 mmol), D-mannose (1.19 g, 6.6 mmol), and tren (0.04 g, 0.3 mmol) was refluxed for 1 h. The resultant violet reaction solution was chromatographed on a Sephadex LH-20 gel permeation column (4.0 cm × 90 cm) eluted with methanol. The violet main band was collected and was concentrated to give violet crystals of **2a**·CH$_3$OH in 87% yield (1.65 g). Slow evaporation of the solution afforded block-shaped crystals suitable for X-ray crystallography. Anal. Calcd for $C_{19}H_{42}N_4O_{11}Cl_2Ni$: C, 36.10; H, 6.70; N, 8.86; Cl, 11.22. Found: C, 35.85; H, 6.79; N, 8.81; Cl, 11.00. UV−vis (in DMSO): ν_{max} (ϵ) 10.0 (27.5), 12.4 (8.3)^{sh}, 17.3 (12.8), 27.1 (17.4) × 10^3 cm^{-1} (M^{-1} cm^{-1}). CD (in DMSO): ν_{max} ($\Delta\epsilon$) 10.9 (−0.152), 12.3 (−0.079)^{sh}, 16.0 (+0.036)^{sh}, 17.8 (+0.053), 26.5 (+0.039). μ_{eff}: 2.82 μ_B.

Preparation of [Ni(*N*,*N′*-(D-Man)$_2$-tren)]Br$_2$·H$_2$O (2b·H$_2$O). The reaction and workup similar to those for **2a,** by using [Ni(tren)(H$_2$O)$_2$]Br$_2$ (**1b**) instead of **1a**, gave violet crystals of **2b**·H$_2$O in 30% yield (0.64 g). Anal. Calcd for $C_{18}H_{40}N_4O_{11}Br_2Ni$: C, 30.58 H, 5.70; N, 7.92; Br, 22.60. Found: C, 30.81; H, 6.11; N, 7.63; Br, 22.58. UV−vis (in DMSO): ν_{max} (ϵ) 10.1 (26.1), 12.4 (8.2)^{sh}, 17.4 (12.6), 27.2 (17.5) × 10^3 cm^{-1} (M^{-1} cm^{-1}). CD (in DMSO): ν_{max} ($\Delta\epsilon$) 10.9 (−0.171), 12.3 (−0.091)^{sh}, 16.0 (+0.035)^{sh}, 17.8 (+0.053), 26.5 (+0.042). μ_{eff}: 3.11 μ_B.

Preparation of [Ni(*N*,*N′*-(D-Man)$_2$-tren)]SO$_4$·3CH$_3$OH (2c·3CH$_3$OH). A methanolic solution (100 mL) containing D-mannose (1.19 g, 6.6 mmol), tren (0.44 g, 3.0 mmol), and NH$_4$Cl (0.16 g, 3.0 mmol) was refluxed for 40 min, and then, NiSO$_4$·6H$_2$O (0.79 g, 3.0 mmol) dissolved in methanol (20 mL) was added to the solution. The reaction mixture was incubated at 57 °C for 30 min and cooled to room temperature. A white precipitate was removed by passing through a glass filter. The blue-violet filtrate was allowed to stand at room temperature for 2 days to afford violet crystals of **2c**·3CH$_3$OH in 13%

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yield. Complex **2c**·$3CH_3OH$ was also prepared by a method similar to that of **2a** by using $[Ni(tren)(H_2O)_2]SO_4$ (**1c**) as a starting complex in low yield. Anal. Calcd for $C_{21}H_{50}N_4O_{17}SNi$: C, 34.96; H, 6.99; N, 7.77. Found: C, 34.57; H, 6.37; N, 7.78. UV−vis (in ethylene glycol): ν_{max} (ϵ) 10.2 (22.4), 12.3 (8.4)^{sh}, 17.5 (12.8), 27.4 (20.1) × 10^3 cm^{-1} (M^{-1} cm^{-1}). CD (in ethylene glycol): ν_{max} ($\Delta\epsilon$) 11.0 (−0.214), 12.5 (−0.101)^{sh}, 17.7 (+0.069), 26.6 (+0.048). μ_{eff}: 3.04 μ_B. Complex **2c** could be recrystallized from a methanol/ethylene glycol (1:1) mixed solvent.

Preparation of $[Ni(N,N'\text{-}(L\text{-}Rha)_2\text{-}tren)]SO_4\cdot H_2O$ (3c·H_2O). A methanolic solution (100 mL) containing L-rhamnose monohydrate (1.19 g, 6.0 mmol) and tren (0.44 g, 3.0 mmol) was refluxed for 120 min, and then, $NiSO_4\cdot 6H_2O$ (0.79 g, 3.0 mmol) dissolved in methanol (20 mL) was added to the solution. The reaction mixture was cooled to room temperature and was concentrated to about 30 mL by a rotary evaporator. The concentrated solution was chromatographed on a Sephadex LH-20 column (4.0 cm × 90 cm) eluted with methanol. The blue main band was collected and concentrated, which was kept at room temperature for 12 h to give violet crystals of **3c**·H_2O in 40% yield. Complex **3c**·H_2O was also prepared by the similar method to that of **2c** by using L-rhamnose monohydrate as a sugar source in low yield. Anal. Calcd for $C_{18}H_{40}N_4O_{13}SNi$: C, 35.37; H, 6.60; N, 9.17. Found: C, 35.24; H, 6.81; N, 9.16. UV−vis (in methanol/ethylene glycol (1:1)): ν_{max} (ϵ) 10.3 (20.5), 12.5 (8.4)^{sh}, 17.6 (10.9), 27.6 (15.5) × 10^3 cm^{-1} (M^{-1} cm^{-1}). CD (in methanol/ethylene glycol (1:1)): ν_{max} ($\Delta\epsilon$) 11.2 (+0.144), 12.7 (+0.079)^{sh}, 18.0 (−0.036)^{sh}, 27.0 (−0.024). μ_{eff}: 3.02 μ_B.

Preparation of $[Ni(N,N'\text{-}(D\text{-}Glc)_2\text{-}tren)]Cl_2\cdot 2.5H_2O$ (4a·$2.5H_2O$). A methanolic solution (60 mL) containing D-glucose (1.08 g, 6.0 mmol) and tren (0.44 g, 3.0 mmol) was refluxed for 60 min, and then, $NiCl_2\cdot 6H_2O$ (0.71 g, 3.0 mmol) dissolved in methanol (10 mL) was added to the solution. The reaction mixture turned to blue and was further incubated at 63 °C for 25 min. The resultant solution was cooled to room temperature and was concentrated to ca. 30 mL by a rotary evaporator, followed by a Sephadex LH-20 gel permeation column chromatography eluted with methanol. The main bluish violet band was collected and purified by the same column three times. The purified solution was concentrated to ca. 10 mL, and an addition of ethanol gave **4a**·$2.5H_2O$ as a powder in 8% yield, which was highly hygroscopic and should be treated under a nitrogen atmosphere. Anal. Calcd for $C_{18}H_{43}N_4O_{12.5}Cl_2Ni$: C, 33.51; H, 6.72; N, 8.68. Found: C, 33.31; H, 6.94; N, 8.68. UV−vis (in methanol): ν_{max} (ϵ) 10.0 (22.3), 12.3 (6.6)^{sh}, 17.4 (11.5), 27.3 (18.1) × 10^3 cm^{-1} (M^{-1} cm^{-1}). CD (in methanol): ν_{max} ($\Delta\epsilon$) 11.1 (+0.356), 12.7 (+0.129)^{sh}, 13.4 (+0.051), 17.7 (−0.103), 26.6 (−0.059). μ_{eff}: 3.22 μ_B.

Preparation of $[Ni(N\text{-}(D\text{-}Glc)\text{-}tren)(H_2O)]Cl_2\cdot 0.5H_2O$ (4b·$0.5H_2O$). A methanolic solution (100 mL) containing $[Ni(tren)(H_2O)_2]Cl_2$ (**1a**) (0.94 g, 3.0 mmol), D-glucose (1.19 g, 6.6 mmol), and tren (0.04 g, 0.3 mmol) was refluxed for 1 h. The resultant blue reaction solution was concentrated to ca. 30 mL by a rotary evaporator and chromatographed on a Sephadex LH-20 gel permeation column (4.0 cm × 90 cm) eluted with methanol. The blue main band was collected and concentrated. Slow addition of ethanol to the solution gave blue crystals of **4**·$0.5H_2O$ in 5% yield (0.07 g). Anal. Calcd for $C_{12}H_{31}N_4O_{6.5}Cl_2Ni$: C, 31.00; H, 6.72; N, 12.05; Cl, 15.25. Found: C, 31.02; H, 6.91; N, 12.56; Cl, 14.95. UV−vis (in methanol): ν_{max} (ϵ) 10.3 (19.8), 12.6 (6.4)^{sh}, 17.5 (12.4), 27.5 (24.0) × 10^3 cm^{-1} (M^{-1} cm^{-1}). CD (in methanol): ν_{max} ($\Delta\epsilon$) 10.8 (+0.257), 12.6 (+0.102)^{sh}, 17.5 (−0.050), 26.8 (−0.032). μ_{eff}: 3.23 μ_B.

Preparation of $[Ni(N\text{-}(D\text{-}GlcN)\text{-}tren)(H_2O)]Cl_2$ (5a) and $[Ni(N\text{-}(D\text{-}GalN)\text{-}tren)(H_2O)]Cl_2\cdot H_2O$ (5b·H_2O). A methanolic solution (100 mL) containing $[Ni(tren)(H_2O)_2]Cl_2$ (**1a**) (0.94 g, 3.0 mmol), D-glucosamine hydrochloride (1.42 g, 6.6 mmol), and tren (0.04 g, 0.3 mmol) was refluxed for 1 h. The resultant violet reaction solution was concentrated to ca. 30 mL by a rotary evaporator, and a white powder of D-GlcN·HCl was removed by filtration. The violet solution was chromatographed on a Sephadex LH-20 gel permeation column (4.0 cm × 90 cm) eluted with methanol. The violet main band was collected and concentrated to give violet crystals of **5a**, which were recrystallized from hot methanol (52%, 0.71 g). Anal. Calcd for $C_{12}H_{31}N_5O_5Cl_2Ni$: C, 31.68; H, 6.87; N, 15.39; Cl, 15.58. Found: C, 31.29; H, 6.78; N, 15.31; Cl, 15.63. UV−vis (in methanol): ν_{max} (ϵ) 10.5 (16.6), 12.3 (9.3)^{sh}, 17.6 (11.1), 27.5 (17.0) × 10^3 cm^{-1} (M^{-1} cm^{-1}). CD (in methanol): ν_{max} ($\Delta\epsilon$) 10.7 (+0.117), 11.9 (+0.068)^{sh}, 15.5 (−0.055), 27.8 (−0.020). μ_{eff}: 2.99 μ_B. A similar preparation using $[Ni(tren)(H_2O)_2]Cl_2$ (**1a**) (0.47 g, 1.5 mmol), D-galactosamine hydrochloride (0.71 g, 3.3 mmol), and tren (0.05 g, 0.38 mmol) afforded violet crystals of **5b**·H_2O in 20% yield. Anal. Calcd for $C_{12}H_{33}N_5O_6Cl_2Ni$: C, 30.47; H, 7.03; N, 14.81. Found: C, 30.59; H, 7.15; N, 14.67. UV−vis (in methanol/ethylene glycol (1:1)): ν_{max} (ϵ) 11.2 (13.1), 12.5 (8.6)^{sh}, 18.5 (11.5), 28.3 (14.8) × 10^3 cm^{-1} (M^{-1} cm^{-1}). CD (in methanol/ethylene glycol (1:1)): ν_{max} ($\Delta\epsilon$) 10.3 (+0.039), 11.3 (−0.024)^{sh}, 12.3 (−0.056), 30.3 (−0.007). μ_{eff}: 3.20 μ_B.

Preparation of $[Ni(N,N',N''\text{-}(D\text{-}Man)_3\text{-}tren)]Cl_2\cdot H_2O$ (6a·H_2O). The tris(*N*-glycoside) ligand, tris(*N*-D-mannosyl-2-aminoethyl)amine, was prepared in *situ* by reaction of tren (0.44 g, 3.0 mmol) with D-mannose (2.16 g, 12.0 mmol) in methanol (100 mL) at 50−55 °C for 3−4 h. The color of the solution changed to pale yellow. A methanolic solution (10 mL) of $NiCl_2\cdot 6H_2O$ (0.71 g, 3.0 mmol) was then added to the reaction mixture, which was cooled to room temperature and allowed to stand overnight. The resultant bluish green solution was concentrated to ca. 30 mL and chromatographed on a Sephadex LH-20 gel permeation column (4 cm × 90 cm) eluted with methanol. The blue main band was collected and concentrated to ca. 10 mL. An addition of diethyl ether afforded a blue powder of **6a**·H_2O, which was filtered out, washed with diethyl ether, and dried in vacuo (25%, 0.58 g). Anal. Calcd for $C_{24}H_{50}N_4O_{16}Cl_2Ni$: C, 36.94; H, 6.46; N, 7.18; Cl, 9.09. Found: C, 37.21; H, 6.62; N, 7.08; Cl, 8.94. UV−vis (in methanol): ν_{max} (ϵ) 9.9 (25.5), 12.5 (6.3)^{sh}, 17.0 (11.9), 26.6 (20.4) × 10^3 cm^{-1} (M^{-1} cm^{-1}). CD (in methanol): ν_{max} ($\Delta\epsilon$) 11.1 (+0.210), 12.2 (+0.061)^{sh}, 14.4 (+0.020), 17.2 (−0.008), 24.2 (−0.011), 27.5 (+0.011). μ_{eff}: 3.04 μ_B.

Preparation of $[Ni(N,N',N''\text{-}(D\text{-}Man)_3\text{-}tren)]Br_2\cdot H_2O$ (6b·H_2O). Complex **6b**·H_2O was prepared by the similar method as described for **6a**, $NiBr_2\cdot 3H_2O$ being used as a nickel salt. Yield: 48%. Anal. Calcd for $C_{24}H_{50}N_4O_{16}Br_2Ni$: C, 33.17; H, 5.80; N, 6.45; Br, 18.39. Found: C, 33.50; H, 5.89; N, 6.16; Br, 17.86. UV−vis (in methanol): ν_{max} (ϵ) 9.8 (23.1), 12.4 (6.3)^{sh}, 17.0 (12.0), 26.7 (22.8) × 10^3 cm^{-1} (M^{-1} cm^{-1}). CD (in methanol): ν_{max} ($\Delta\epsilon$) 11.0 (+0.184), 12.2 (+0.059)^{sh}, 14.4 (+0.026), 17.4 (−0.026), 25.2 (−0.010). μ_{eff}: 2.89 μ_B.

Preparation of $[Ni(N,N',N''\text{-}(L\text{-}Rha)_3\text{-}tren)]Cl_2\cdot 2CH_3OH\cdot H_2O$ (7a·$2CH_3OH\cdot H_2O$). Complex **7a**·$2CH_3OH\cdot H_2O$ was prepared by the similar method as described for **6a**, L-rhamnose monohydrate being used as a sugar source. Yield: 3%. Anal. Calcd for $C_{26}H_{58}N_4O_{15}Cl_2Ni$: C, 39.21; H, 7.34; N, 7.04. Found: C, 38.74; H, 7.62; N, 6.81; Br, 17.86. UV−vis (in methanol): ν_{max} (ϵ) 9.9 (26.5), 12.4 (7.2)^{sh}, 17.2 (11.4), 26.7 (18.8) × 10^3 cm^{-1} (M^{-1} cm^{-1}). CD (in methanol): ν_{max} ($\Delta\epsilon$) 10.9 (−0.117), 12.2 (−0.054)^{sh}, 14.5 (+0.023), 17.4 (+0.107), 25.9 (+0.046). μ_{eff}: 2.99 μ_B.

Preparation of $[Ni(N,N',N''\text{-}(D\text{-}L\text{-}Rha)_3\text{-}tren)]Br_2\cdot H_2O$ (7b·H_2O). Complex **7b**·H_2O was prepared by the similar method as described for **6b**, L-rhamnose monohydrate being used as a sugar source. Yield: 23%. Anal. Calcd for $C_{24}H_{50}N_4O_{13}Br_2Ni$: C, 35.10; H, 6.14; N, 6.82. Found: C, 34.81; H, 6.51; N, 6.58. UV−vis (in methanol): ν_{max} (ϵ) 10.0 (27.5), 12.4 (7.5)^{sh}, 17.3 (12.2), 26.7 (18.4) × 10^3 cm^{-1} (M^{-1} cm^{-1}). CD (in methanol): ν_{max} ($\Delta\epsilon$) 11.0 (−0.157), 12.2 (−0.067)^{sh}, 14.7 (+0.034), 17.5 (+0.139), 25.9 (+0.066). μ_{eff}: 2.79 μ_B.

Preparation of $[Ni(N,N',N''\text{-}(L\text{-}Rha)_3\text{-}tren)(SO_4)]\cdot 2H_2O$ (8·$2H_2O$). Complex **8**·$2H_2O$ was prepared by the similar method as described for **6a**, $NiSO_4\cdot 6H_2O$ and L-rhamnose monohydrate being used as nickel and sugar sources. After the addition of nickel salt, the reaction mixture was promptly cooled; otherwise complex **8** decomposed to **3c**. The purified methanolic solution of **8** was concentrated and kept in a refrigerator to give blue crystals of **8**·$2H_2O$ in 34% yield. Anal. Calcd for $C_{24}H_{52}N_4O_{18}SNi$: C, 37.17; H, 6.76; N, 7.23. Found: C, 36.70; H, 6.90; N, 7.23. UV−vis (in DMSO): ν_{max} (ϵ) 9.3 (16.7), 12.4 (3.6)^{sh}, 16.0 (10.1), 25.5 (15.1) × 10^3 cm^{-1} (M^{-1} cm^{-1}). CD (in DMSO): ν_{max} ($\Delta\epsilon$) 11.0 (+0.068), 12.9 (−0.027)^{sh}, 14.0 (−0.027), 17.1 (+0.057), 26.5 (+0.013). μ_{eff}: 3.05 μ_B.

Preparation of $[Ni(N,N',N''\text{-}(D\text{-}Glc)_3\text{-}tren)]Cl_2\cdot 3H_2O$ (9·$3H_2O$). The tris(*N*-glycoside) ligand, tris(*N*-D-glucosyl-2-aminoethyl)amine, was prepared in *situ* by reaction of tren (0.44 g, 3.0 mmol) with D-glucose (2.16 g, 12.0 mmol) in methanol (100 mL) at 65 °C for 70 min. A methanolic solution (10 mL) of $NiCl_2\cdot 6H_2O$ (0.71 g, 3.0 mmol) was

Table 1. Crystallographic and Experimental Data for **1c**·$2H_2O$, **2a**·CH_3OH, **2c**·$3CH_3OH$, **3c**·$3CH_3OH$, and **8**·$3CH_3OH$·H_2O

	compound				
	1c·$2H_2O$	**2a**·CH_3OH	**2c**·$3CH_3OH$	**3c**·$3CH_3OH$	**8**·$3CH_3OH$·H_2O
formula	$C_6H_{26}N_4SNi$	$C_{19}H_{42}N_4O_{11}Cl_2Ni$	$C_{21}H_{50}N_4O_{17}SNi$	$C_{21}H_{50}N_4O_{15}SNi$	$C_{27}H_{62}N_4O_{20}SNi$
fw	373.05	632.15	721.40	689.40	853.56
cryst syst	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic
space group	*Pbca* (No. 61)	$P2_12_12_1$ (No. 19)	$P2_12_12_1$ (No. 19)	$P2_12_12_1$ (No. 19)	$P2_12_12_1$ (No. 19)
a, Å	15.988(2)	16.005(3)	14.93(2)	14.560(4)	16.035(4)
b, Å	18.826(4)	20.095(4)	21.823(8)	21.694(5)	16.670(7)
c, Å	10.359(4)	8.361(1)	9.746(2)	9.786(2)	15.38(1)
V, $Å^3$	3118	2689	3176	3091	4111
Z	8	4	4	4	4
T, °C	23	23	23	23	23
D_{calcd}, g cm^{-1}	1.589	1.562	1.508	1.481	1.379
abs coeff, cm^{-1}	14.15	9.7	7.51	7.64	5.96
scan method	$\omega-2\theta$	ω ($2\theta < 30°$), $\omega-2\theta$ ($30 < 2\theta < 60°$)	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
2θ max, deg	50	60	50	50	50
no. of data[a]	3114	4422	3173	3106	4046
no. of obsd data	1094 ($I > 3\sigma(I)$)	2089 ($I > 3\sigma(I)$)	1537 ($I > 2.5\sigma(I)$)	1447 ($I > 2\sigma(I)$)	1752 ($I > 2.5\sigma(I)$)
solution	direct methods, MITHRIL	direct methods, MULTAN78	Patterson method, DIRDIF	Patterson method, DIRDIF	direct methods, MITHRIL
no. of params	181	503	368	350	324
data/param	6.04	4.15	4.18	4.13	5.41
R[b]	0.047	0.040	0.075	0.072	0.084
R_w[b]	0.042	0.027	0.080	0.079	0.068
GOF[c]	2.18	1.27	2.41	2.40	2.01
ρ_{max}, e $Å^{-3}$	0.52	0.40	0.71	0.65	0.71

[a] A unique octant of data was collected in each case. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ ($w = 1/\sigma^2(F_o)$). [c] GOF $= [\sum w(|F_o| - |F_c|)^2/(N_o - N_p)]^{1/2}$ (N_o = no. of data, N_p = no. of variables).

then added to the reaction mixture, which was cooled to room temperature. The resultant bluish green solution was concentrated to ca. 30 mL and chromatographed on a Sephadex LH-20 gel permeation column (4 cm × 90 cm) eluted with methanol. The blue main band was collected and purified by the same column three times. The solution was concentrated to ca. 8 mL, and an addition of ethanol afforded a blue powder of **9**·$3H_2O$ in 7% yield. Complex **4a** was crystallized from the mother liquor. Anal. Calcd for $C_{24}H_{54}N_4O_{18}Cl_2Ni$: C, 35.31; H, 6.67; N, 6.86. Found: C, 34.99; H, 6.89; N, 7.30. UV−vis (in methanol): ν_{max} (ϵ) 9.9 (29.7), 12.4 $(8.9)^{sh}$, 17.2 (15.7), 26.6 (24.9) × 10^3 cm^{-1} (M^{-1} cm^{-1}). CD (in methanol): ν_{max} ($\Delta\epsilon$) 10.9 (+0.248), 12.7 $(+0.096)^{sh}$, 17.3 (−0.098), 26.4 (−0.058). μ_{eff}: 3.28 μ_B.

Preparation of [Ni(*N,N′,N″*-Mal$_3$-tren)]Br$_2$·3H$_2$O (10·3H$_2$O). The tris(*N*-glycoside) ligand, tris(*N*-maltosyl-2-aminoethyl)amine, was prepared in *situ* by reaction of tren (0.44 g, 3.0 mmol) with maltose monohydrate (3.60 g, 10.0 mmol) in methanol (100 mL) at 65 °C for 1.5 h. A methanolic solution (10 mL) of $NiBr_2$·$3H_2O$ (0.82 g, 3.0 mmol) was then added to the reaction mixture, which was cooled to room temperature. The resultant bluish green solution was concentrated to ca. 30 mL and chromatographed on a Sephadex LH-20 gel permeation column (4 cm × 90 cm) eluted with methanol. The blue main band was collected and purified by the same column three times. The solution was concentrated to ca. 8 mL, and an addition of ethanol afforded a blue powder of **10**·$3H_2O$ in 17% yield (0.72 g). Anal. Calcd for $C_{42}H_{84}N_4O_{33}Br_2Ni$: C, 36.25; H, 6.08; N, 4.03; Br, 11.48. Found: C, 36.49; H, 6.49; N, 4.36; Br, 11.21. UV−vis (in DMSO): ν_{max} (ϵ) 10.0 (30.3), 12.3 $(8.5)^{sh}$, 17.1 (14.3), 27.9 (44.1) × 10^3 cm^{-1} (M^{-1} cm^{-1}). CD (in DMSO): ν_{max} ($\Delta\epsilon$) 10.5 (+0.148), 12.0 $(+0.069)^{sh}$, 15.0 $(-0.022)^{sh}$, 17.5 (−0.073), 26.5 (−0.045). μ_{eff}: 3.00 μ_B.

Preparation of [Ni(*N,N′,N″*-Mel$_3$-tren)]Br$_2$·3H$_2$O (11·3H$_2$O). The tris(*N*-glycoside) ligand, tris(*N*-melibiosyl-2-aminoethyl)amine, was prepared in *situ* by reaction of tren (0.44 g, 3.0 mmol) with melibiose monohydrate (3.60 g, 10.0 mmol) in ethylene glycol (100 mL) at 60−65 °C for 30 min. A solution of ethylene glycol (10 mL) containing $NiBr_2$·$3H_2O$ (0.82 g, 3.0 mmol) was then added to the reaction mixture, which was cooled to room temperature. The resultant bluish green solution was concentrated to ca. 30 mL and chromatographed on a Sephadex LH-20 gel permeation column (4 cm × 90 cm) eluted with methanol. The blue main band was collected and concentrated to give a blue powder of **11**·$3H_2O$ in 18% yield (0.75 g). Anal. Calcd for $C_{42}H_{84}N_4O_{33}Br_2Ni$: C, 36.25; H, 6.08; N, 4.03; Br, 11.48. Found: C, 35.88; H, 6.18; N, 4.33; Br, 11.34. UV−vis (in DMSO): ν_{max} (ϵ) 10.0 (29.8), 12.3 $(9.4)^{sh}$, 17.3 (14.3), 28.6 $(68.7)^{sh}$ × 10^3 cm^{-1} (M^{-1} cm^{-1}). CD (in DMSO): ν_{max} ($\Delta\epsilon$) 10.6 (+0.224), 11.9 $(+0.126)^{sh}$, 15.0 $(-0.041)^{sh}$, 17.4 (−0.075), 26.4 (−0.061). μ_{eff}: 3.09 μ_B.

Crystal Data and Intensity Measurements for [Ni(H$_2$O)$_2$(tren)]SO$_4$·2H$_2$O (1c·2H$_2$O), [Ni(*N,N′*-(D-Man)$_2$-tren)]Cl$_2$·CH$_3$OH (2a·CH$_3$OH), [Ni(*N,N′*-(D-Man)$_2$-tren)]SO$_4$·3CH$_3$OH (2c·3CH$_3$OH), [Ni(*N,N′*-(L-Rha)$_2$-tren)]SO$_4$·3CH$_3$OH (3c·3CH$_3$OH), and [Ni(*N,N′,N″*-(L-Rha)$_3$-tren)(SO$_4$)]·3CH$_3$OH·H$_2$O (8·3CH$_3$OH·H$_2$O). Careful crystallizations from methanol in a refrigerator yielded block-shaped crystals of **1c**·$2H_2O$, **2a**·CH_3OH, **2c**·$3CH_3OH$, **3c**·$3CH_3OH$, and **8**·$3CH_3OH$·H_2O, which were suitable for X-ray crystallography. The crystals used in data collection were sealed into a glass tube capillary (0.7 mm o.d.) with mother liquor, since they lost clearness when picked up from the mother liquor. Crystal data and experimental conditions are summarized in Table 1. All data were collected on Rigaku AFC4 (**2a**·CH_3OH) and Rigaku AFC5S (**1c**·$2H_2O$, **2c**·$3CH_3OH$, **3c**·$3CH_3OH$, and **8**·$3CH_3OH$·H_2O) diffractometers equipped with graphite monochromatized Mo Kα (λ = 0.710 69 Å) radiation. The cell constants were obtained from least squares refinement of 20−25 reflections with $20 < 2\theta < 30°$. Three standard reflections were monitored every 150 reflections and showed no systematic decrease in intensity. Reflection data were corrected for Lorentz−polarization and absorption effects (ψ-scan method).

Structure Solution and Refinement. The structure of **1c**·$2H_2O$ was solved by direct methods with MITHRIL.[34] The nickel atom was located in the initial *E* map, and subsequent Fourier syntheses gave the positions of other non-hydrogen atoms. The coordinates of C−H and N−H hydrogen atoms were calculated at ideal positions with a distance of 0.95 Å and were not refined. The structure was refined with the full-matrix least-squares techniques minimizing $\sum w(|F_o| - |F_c|)^2$. Final refinement with anisotropic thermal parameters for non-hydrogen atoms converged to $R = 0.047$ and $R_w = 0.042$, where $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ ($w = 1/\sigma^2(F_o)$). The structure of **2a**·CH_3OH was solved by direct methods with MULTAN78.[35] The coordinates of all hydrogen atoms were determined by difference Fourier syntheses. Final full-matrix least-squares refinement with anisotropic thermal parameters for non-

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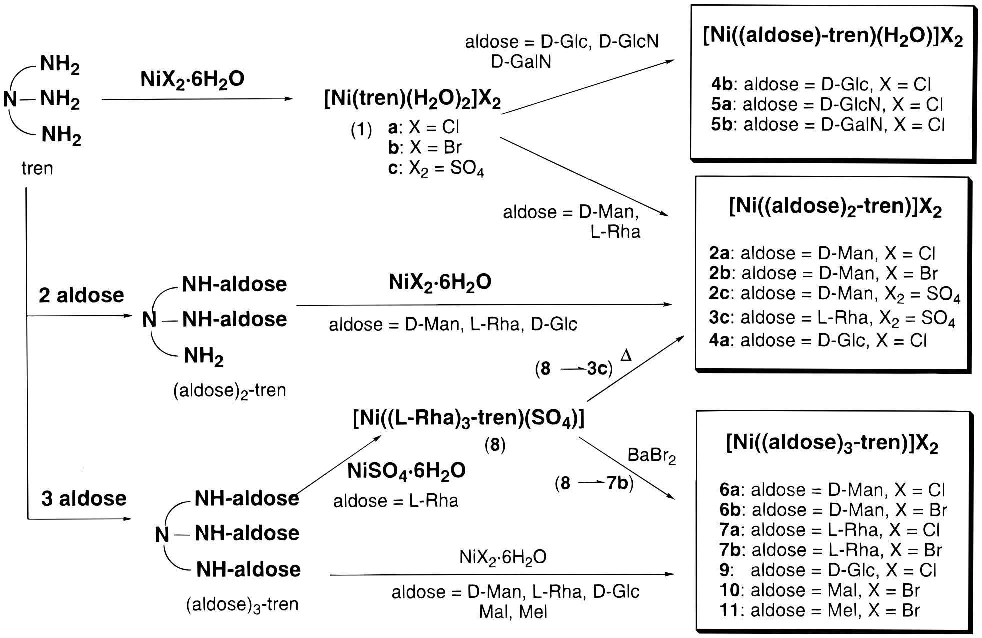
Scheme 1



hydrogen atoms and isotropic ones for hydrogen atoms converged to $R = 0.040$ and $R_w = 0.027$. The structures of **2c**$\cdot$3CH$_3$OH and **3c**$\cdot$3CH$_3$OH were solved by Patterson methods with DIRDIF[36] and direct methods with SAPI,[37] respectively. The coordinates of C−H and N−H hydrogen atoms were calculated at ideal positions with a distance of 0.95 Å and were not refined. Final full-matrix least-squares refinement with anisotropic thermal parameters for non-hydrogen atoms (solvent methanol molecules were refined isotropically) converged to $R = 0.075$ and $R_w = 0.080$ for **2c**$\cdot$3CH$_3$OH and $R = 0.072$ and $R_w = 0.079$ for **3c**$\cdot$3CH$_3$OH. The structure of **8**$\cdot$3CH$_3$OH$\cdot$H$_2$O was solved by the similar procedures described for **1c**$\cdot$2H$_2$O. Final full-matrix least-squares refinement with anisotropic thermal parameters for Ni, Cl, S, O, and N atoms and isotropic temperature factors for C atoms and solvent molecules converged at $R = 0.084$ and $R_w = 0.068$.

Atomic scattering factors and values of f' and f'' for Ni, Cl, S, O, N, and C were taken from the literature.[38,39] All calculations were carried out on a Digital VAX Station 3100 with the TEXSAN program package[40] and a FACOM M-380 with the UNICS III program.[41] The perspective views were drawn by using the program ORTEP.[42] A compilation of final atomic parameters for all non-hydrogen atoms is supplied as supporting information.

Results and Discussion

Synthetic routes to the nickel(II)−sugar complexes described in this report are summarized in Scheme 1.

Nickel(II) Bis(sugar) Complexes, [Ni(*N*,*N*′-(aldose)$_2$-tren)]$^{2+}$ (2 and 3). Reactions of [Ni(tren)(H$_2$O)$_2$]X$_2$ (**1**) with D-mannose and L-rhamnose (6-deoxy-L-mannose), having a 2,3-*cis* configuration, in the presence of a catalytic amount of tren yielded nickel(II) bis(sugar) complexes formulated as [Ni(*N*,*N*′-(aldose)$_2$-tren)]X$_2$ (aldose = D-Man, X = Cl (**2a**), Br (**2b**), X$_2$ = SO$_4$ (**2c**); aldose = L-Rha, X$_2$ = SO$_4$ (**3c**). Reactions without the additional amount of tren did not give complexes **2** and **3**. The magnetic susceptibilities, ranging 2.8−3.1 μ_B, indicated that the nickel(II) ions have two unpaired electrons and octahedral geometry.[43] Electronic absorption (AB) and circular dichroism (CD) spectra are shown in Figure 1. The positions of the absorption maxima in AB are almost identical for **2** and **3** and closely similar to those of [Ni(*N*-aldosediamine)$_2$]$^{2+}$ (**12**) (diamine = ethylenediamine (en) and trimethylenediamine (tn)), which have the [Ni^{II}N$_4$O$_2$] octahedral structure.[8,11] The coordination of halide and sulfate anions could be ruled out, because

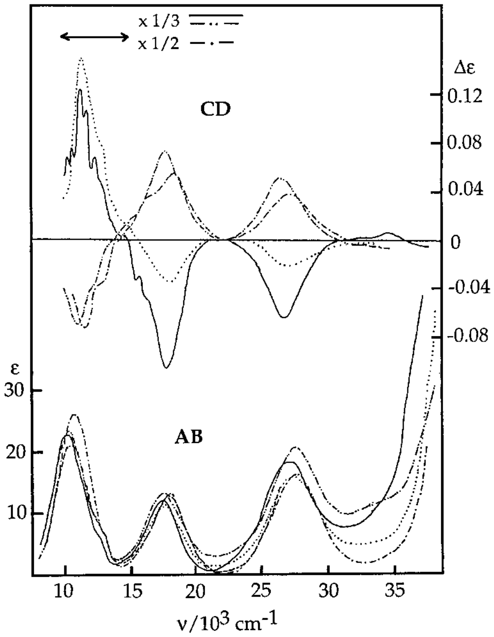


Figure 1. UV−vis absorption (AB) and circular dichroism (CD) spectra of (a, —) [Ni(*N*,*N*′-(D-Glc)$_2$-tren)]Cl$_2$ (**4a**) in MeOH, (b, —•—) [Ni(*N*,*N*′-(D-Man)$_2$-tren)]Cl$_2$ (**2a**) in DMSO, (c, —••—) [Ni(*N*,*N*′-(D-Man)$_2$-tren)]SO$_4$ (**2c**) in ethyleneglycol, and (d,- -) [Ni(*N*,*N*′-(L-Rha)$_2$-tren)]SO$_4$ (**3c**) in MeOH/ethyleneglycol.

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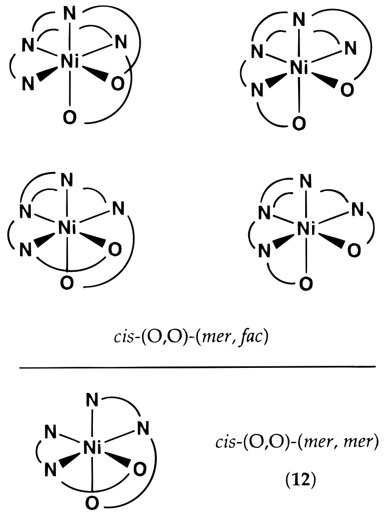

Figure 2. Coordination modes of the *N*-glycoside ligand *N*,*N*′-bis(aldosyl)-tren.

of the independence of AB spectra on the counteranions. The AB spectra consist of three principal bands with comparatively low intensities (<30 M^{-1} cm^{-1}), which are also characteristic of octahedral nickel(II) complexes and assigned to the three spin-allowed transitions ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$, and ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$.[44] In the CD spectra, large Cotton effects are observed in the range of d−d transitions (9−28 kcm^{-1}), suggesting the coordination of sugar moieties to the nickel(II) center. The spectral patterns are almost mirror image between **2** and **3**, which is consistent with the fact that D-mannose and L-rhamnose are enantiomeric except for C-6 hydroxyl groups. The counteranions did not have any influence on the CD spectral patterns. On the basis of analytical, magnetic, and spectroscopic data, complexes **2** and **3** were assumed to consist of an octahedral nickel(II) atom ligated by bis(*N*-aldosyl-2-aminoethyl)(2-aminoethyl)amine, *N*,*N*′-(aldose)$_2$-tren. A coordination of the C-2 hydroxyl group of sugar moieties can be expected by analogy with the structure of [Ni(*N*-aldosediamine)$_2$]$^{2+}$, leading to the four possible configurational isomers with *cis*-(O,O)-(*mer*, *fac*) geometry as depicted in Figure 2. The *cis*-(O,O)-(*mer*, *mer*) structure observed in **12** cannot be accommodated by the branched polyamine tren.

The structure of the starting complex [Ni(tren)(H$_2$O)$_2$]SO$_4$·2H$_2$O was confirmed by X-ray crystallography to have a distorted octahedral geometry coordinated by a tetradentate tren and two water molecules (Figure 3). The smallest *trans* angle is 163.7(4)° (N(2)−Ni(1)−N(3)). All the five-membered chelate rings of tren adopt the gauche conformation with an average bite angle of 83.2°. Selected bond lengths and angles are listed in Table 2.

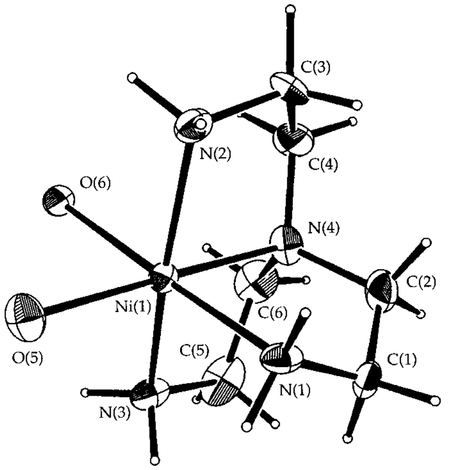

Figure 3. ORTEP plot of the complex cation of **1c**, [Ni(tren)(H$_2$O)$_2$]$^{2+}$.

Table 2. Selected Bond Lengths and Angles of **1c**·2H$_2$O[a]

Bond Length (Å)			
Ni(1)−O(5)	2.066(6)	Ni(1)−O(6)	2.181(8)
Ni(1)−N(1)	2.10(1)	Ni(1)−N(2)	2.098(9)
Ni(1)−N(3)	2.11(1)	Ni(1)−N(4)	2.066(8)
Bond Angles (deg)			
O(5)−Ni(1)−O(6)	86.9(4)	O(5)−Ni(1)−N(1)	95.4(5)
O(5)−Ni(1)−N(2)	96.8(4)	O(5)−Ni(1)−N(3)	96.7(4)
O(5)−Ni(1)−N(4)	178.2(5)	O(6)−Ni(1)−N(1)	177.7(3)
O(6)−Ni(1)−N(2)	85.2(4)	O(6)−Ni(1)−N(3)	86.5(3)
O(6)-Ni(1)-N(4)	95.0(4)	N(1)−Ni(1)−N(2)	94.4(4)
N(1)−Ni(1)−N(3)	93.4(4)	N(1)−Ni(1)−N(4)	82.7(5)
N(2)−Ni(1)−N(3)	163.7(4)	N(2)−Ni(1)−N(4)	83.4(4)
N(3)−Ni(1)−N(4)	83.4(4)		

[a] Estimated standard deviations are in parentheses. See Figure 3 for atom labels.

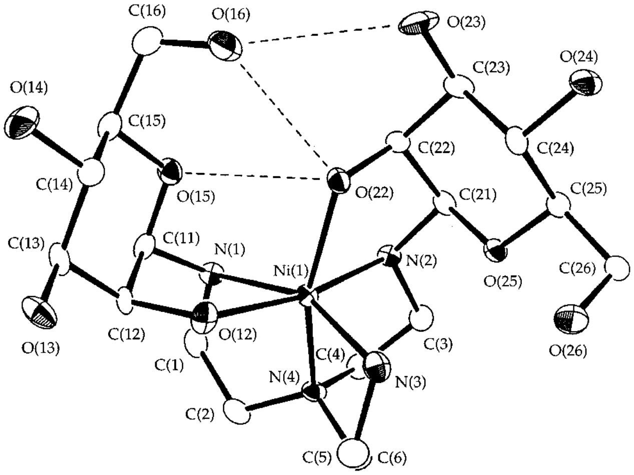

Figure 4. ORTEP view of the complex cation of **2a**, [Ni(*N*,*N*′-(D-Man)$_2$-tren)]$^{2+}$.

Crystal Structures of [Ni(*N*,*N*′-(D-Man)$_2$-tren)]Cl$_2$·CH$_3$OH (2a·CH$_3$OH), [Ni(*N*,*N*′-(D-Man)$_2$-tren)]SO$_4$·3CH$_3$OH (2c·3CH$_3$OH), and [Ni(*N*,*N*′-(L-Rha)$_2$-tren)]SO$_4$·3CH$_3$OH (3c·3CH$_3$OH). Complex **2a** is composed of a mononuclear nickel(II) complex cation and two chloride counteranions. A perspective drawing of the complex cation of **2a** with the atomic numbering scheme is illustrated in Figure 4, and some selected bond lengths and angles are summarized in Table 3. The nickel atom is octahedrally coordinated by N$_4$O$_2$ donor atoms of a hexadentate *N*-glycoside ligand, *N*,*N*′-(D-Man)$_2$-tren, which contains two mannose residues. The two oxygen atoms lie in a *cis* arrangement. The octahedron around the nickel atom is considerably distorted with smallest *trans* and *cis* angles of 153.9(2)° (N(1)−Ni(1)−N(3)) and 76.6(2)° (O(12)−Ni(1)−N(1)). Both sugar moieties adopt the stable β-${}^4C_1$-pyranose form and attach to the nickel through the glycosidic nitrogen atom and the oxygen atom of the C-2 hydroxyl group as observed in [Ni(*N*-(L-Rha)-tn)$_2$]Br$_2$·H$_2$O·CH$_3$OH (**12a**).[7,11] The one *N*-glycoside residue chelates in a meridional mode (N(4)-N(2)O(22)) with respect to the tertiary nitrogen atom N(4), and the other, in a facial mode (N(4)(N(1)O(12)); the former fashion was observed in **12a**, and the latter, in the dinuclear complex [Ni$_2$(CH$_3$OH)(*N*-(D-Man)-*N*,*N*′-Me$_2$en)(*N*,*N*′-(D-Man)$_2$-*N*,*N*′-Me$_2$-en)]$^{2+}$ (**13**).[15,16] The absolute configuration of the *N*-glycosidic nitrogen atom, N(1), is found to be *S* in the notation of Cahn, Ingold, and Prelog, and that of the N(2) atom is *R* (Figure 5).

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(44) Sacconi, L. *Transition Met. Chem.* **1968**, *4*, 199.

Table 3. Some Selected Bond Lengths (Å) and Angles (deg) of **2a**·CH_3OH, **2c**·$3CH_3OH$, and **3c**·$3CH_3OH$[a]

	2a	2c	3c
Ni(1)−O(12)	2.093(4)	2.10(1)	2.08(1)
Ni(1)−O(22)	2.183(3)	2.10(1)	2.08(1)
Ni(1)−N(1)	2.147(5)	2.10(1)	2.12(1)
Ni(1)−N(2)	2.061(4)	2.08(1)	2.05(1)
Ni(1)−N(3)	2.077(5)	2.04(1)	2.05(1)
Ni(1)−N(4)	2.086(4)	2.09(1)	2.09(1)
O(12)−Ni(1)−O(22)	94.0(1)	95.3(4)	91.5(4)
O(12)−Ni(1)−N(1)	76.6(2)	79.6(4)	79.5(4)
O(12)−Ni(1)−N(2)	168.6(2)	171.8(5)	169.3(4)
O(12)−Ni(1)−N(3)	86.5(2)	89.2(4)	90.1(4)
O(12)−Ni(1)−N(4)	104.5(2)	98.8(5)	101.9(5)
O(22)−Ni(1)−N(1)	106.3(2)	100.0(5)	96.4(5)
O(22)−Ni(1)−N(2)	78.6(1)	80.3(5)	80.0(5)
O(22)−Ni(1)−N(3)	94.4(2)	95.2(5)	97.7(5)
O(22)−Ni(1)−N(4)	161.2(2)	165.7(5)	166.5(5)
N(1)−Ni(1)−N(2)	97.0(2)	94.2(5)	94.8(5)
N(1)−Ni(1)−N(3)	153.9(2)	161.9(5)	162.7(5)
N(1)−Ni(1)−N(4)	81.7(2)	84.7(5)	85.0(5)
N(2)−Ni(1)−N(3)	102.6(2)	98.0(5)	97.5(5)
N(2)−Ni(1)−N(4)	83.7(2)	85.9(5)	86.5(5)
N(3)−Ni(1)−N(4)	83.6(2)	82.9(5)	83.7(5)

[a] Estimated standard deviations are in parentheses. See Figures 4, 6, and 7 for atom labels.

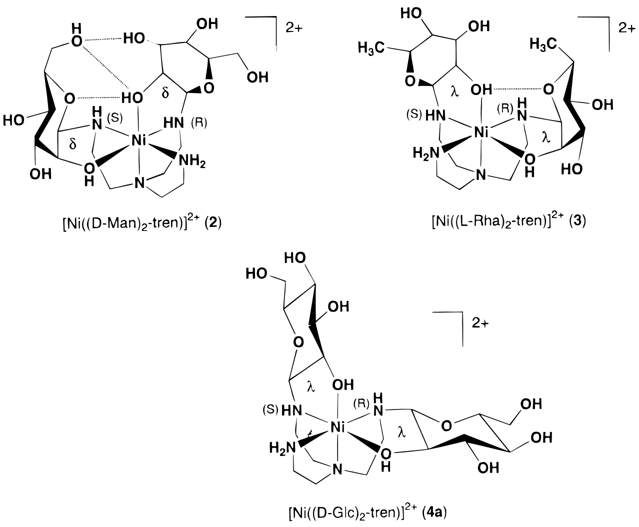


Figure 5. Structures of nickel(II) bis(sugar) complexes **2**, **3**, and **4a**.

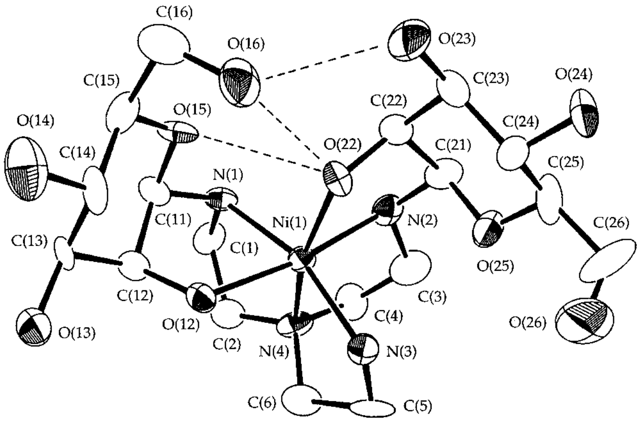


Figure 6. ORTEP view of the complex cation of **2c**, [Ni(*N*,*N*′-(D-Man)$_2$-tren)]$^{2+}$.

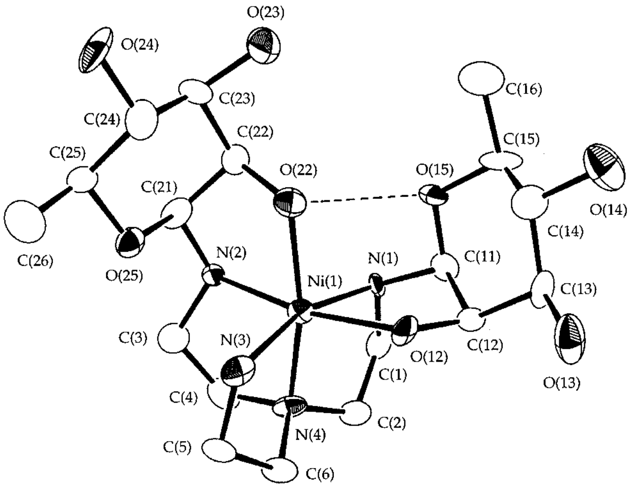


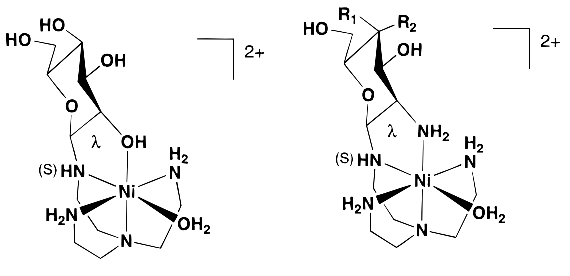
Figure 7. ORTEP view of the complex cation of **3c**, [Ni(*N*,*N*′-(L-Rha)$_2$-tren)]$^{2+}$.

The [NiNCCO] five-membered chelate rings comprising the sugar units have δ-gauche conformations with an average bite angle of 77.6°, comparable to the value observed in **12a** (average 78.7°). The three [NiNCCN] five-membered rings take a set of $\lambda\lambda\lambda$ gauche comformations with an average N−Ni−N angle of 83.0°. This form is different from the $\lambda\lambda\delta$ or $\delta\delta\lambda$ sets in **1c** suggesting that the polyamine chelates of tren were flexible so as to accommodate sugar units on the metal center. The similar behavior of *N*,*N*′-Me_2en was observed in **13**.

The salient feature is found in the interaction between the two sugar parts. The tetradentate tren ligand directs two mannose residues to the same side of the complex, resulting in the intramolecular sugar−sugar hydrogen bondings, O(15)···O(22) = 2.979(5) Å, O(16)···O(22) = 2.858(6) Å, and O(16)···O(23) = 3.047(7) Å. On the basis of interatomic distance, the interaction between the O(16) and O(23) atoms is assumed to be weak. The complex cation of **2a** can be divided into two blocks, a hydrophobic polyamine part and a hydrophilic sugar part, the latter involving distinct sugar−sugar hydrogen-bonding interactions. Noncovalent interactions are vital in the processes of biological recognitions involving the enzyme−substrate, hormone−receptor, and antigen−antibody interactions, and thus, the structural features of **2a** might give fundamental information in designing artificial molecular recognition complex by utilizing carbohydrates.

An ORTEP plot of the complex cation of **2c** with the atomic numbering scheme is given in Figure 6. Selected bond lengths and angles are listed in Table 3. The complex structure is identical to that of **2a**, and the SO_4^{2-} anion does not have any influence on the coordination behavior of *N*,*N*′-(D-Man)$_2$-tren at all. The intramolecular sugar−sugar hydrogen bondings are also observed with O(15)···O(22) = 2.88(2) Å, O(16)···O(22) = 2.79(2) Å, and O(16)···O(23) = 2.74(2) Å, which are shorter than those found in **2a**, although the reason is not clear.

A perspective drawing of the complex cation of **3c** with the atomic numbering scheme is shown in Figure 7, and some selected bond lengths and angles are summarized in Table 3. The complex cation is nearly enantiomeric to **2a**,**c** except for the C-6 substituents as expected (Figure 5). The *N*-glycoside *N*,*N*′-(L-Rha)$_2$-tren acts as a hexadentate ligand, and the two L-rhamnosyl residues take the stable β-$^4C_1$-pyranose form. The absolute configurations of the *N*-glycosidic nitrogen atoms, N(1) and N(2), are *R* and *S*, respectively, and the sugar chelate rings adopt λ gauche conformation (Figure 5). The three diamine chelates involved in the tren part take a set of $\delta\delta\delta$ gauche forms. The C-2 hydroxyl group of the facial sugar interacts with the ring oxygen atom of the meridional sugar moiety by a hydrogen bonding (O(15)···O(22) = 2.81(1) Å), while the other parts of sugars do not contact each other.



[Ni((D-Glc)-tren)(H_2O)]$^{2+}$ (**4b**)

[Ni((aldose)-tren)(H_2O)]$^{2+}$

(**5a**): aldose = D-GlcN, R_1 = OH, R_2 = H
(**5b**): aldose = D-GalN, R_1 = H, R_2 = OH

Figure 8. Possible structures of nickel(II) mono(sugar) complexes **4b** and **5**.

Complexes **2** and **3** were also prepared by the reactions of bis(*N*-aldosyl)-tren, generated from tren and aldose (2 equiv) in *situ*, with nickel salts. By this procedure, [Ni((D-Glc)$_2$-tren)]-Cl_2•2.5H_2O (**4a**•2.5H_2O) was barely isolated in 8% yield. On the basis of the structure of **2** and **3**, a possible structure of **4a** is illustrated in Figure 5, which involves a *cis*-(O,O)-(*mer*, *fac*) geometry with the hexadentate *N*-glycoside ligand, (D-Glc)$_2$-tren. This structure prohibits two glucose residues from interacting with each other, which might be responsible for its low yield.

Nickel(II) Mono(sugar) Complexes, [Ni(*N*-(aldosyl)-tren)-(H_2O)]Cl_2 (Aldose = D-Glucose (4b), D-Glucosamine (5a), and D-Galactosamine (5b)). Reaction of [Ni(tren)(H_2O)$_2$]Cl_2 with an excess of D-glucose, having a 2,3-*trans* configuration, in the presence of a catalytic amount of tren resulted in the formation of a nickel(II) mono(sugar) complex, [Ni(*N*-(D-Glc)-tren)(H_2O)]Cl_2•0.5H_2O (**4**•0.5H_2O), in low yield, and a bis(sugar) complex, [Ni(*N*,*N*′-(D-Glc)$_2$-tren)]Cl_2 (**4a**), was not obtained. The similar reactions of **1a** with D-glucosamine (2-amino-2-deoxy-D-glucose) and D-galactosamine (2-amino-2-deoxy-D-galactose) also gave the mono(sugar) complexes [Ni(*N*-(D-GlcN)-tren)(H_2O)]Cl_2 (**5a**, 52%) and [Ni(*N*-(D-GalN)-tren)(H_2O)]Cl_2•H_2O (**5b**•H_2O, 20%). The analytical, magnetic, and electronic absorption spectroscopic data of **4** and **5** indicated the octahedral nickel(II) complex is ligated by a pentadentate *N*-glycoside ligand, (*N*-aldosyl-2-aminoethyl)bis(2-aminoethyl)-amine. The sugar moiety is expected to be meridionally oriented with respect to the tertiary nitrogen atom, on the basis of the structure of [Ni(*N*-(D-GlcN)-en)$_2$]Br_2•4H_2O (**14**)[9] in which the *N*-(D-GlcN)-en ligand coordinates to the metal in a *mer* fashion through the C-2 amino group and the two nitrogen atoms of the diamine part and the absolute configuration of the glycosidic nitrogen atom is *S*, and the sugar and diamine chelates take the λ- and δ-gauche conformations, respectively. One of the possible structures for **4** and **5** is depicted in Figure 8.

Nickel(II) Tris(sugar) Complexes, [Ni(*N*,*N*′,*N*″-tris(aldosyl)-tren)]$^{2+}$ (Aldose = D-Mannose (6), L-Rhamnose (7), D-Glucose (9), Maltose (10), and Melibiose (11)). Tris(sugar) complexes formulated as [Ni(*N*,*N*′,*N*″-tris(aldosyl)-tren)]X_2 were prepared by the reaction of nickel(II) salts with *N*,*N*′,*N*″-tris(aldosyl)-tren ligands (Scheme 1). The labile *N*,*N*′,*N*″-tris(aldosyl)-tren was prepared by the reaction between tren and aldose without metal ions and could be stabilized by the coordination to a nickel(II) ion. Isolated and characterized compounds were [Ni(*N*,*N*′,*N*″-(D-Man)$_3$-tren]X_2 (**6a**, X = Cl, 25%; **6b**, X = Br, 48%), [Ni(*N*,*N*′,*N*″-(L-Rha)$_3$-tren]X_2 (**7a**, X = Cl, 3%; **7b**, X = Br, 23%), [Ni(*N*,*N*′,*N*″-(D-Glc)$_3$-tren]Cl_2 (**9**, 7%), [Ni(*N*,*N*′,*N*″-Mal$_3$-tren]Br_2 (**10**, 17%), and [Ni(*N*,*N*′,*N*″-Mel$_3$-tren]Br_2 (**11**, 18%). These complexes could not be obtained by the reactions of [Ni(tren)(H_2O)$_2$]$^{2+}$ (**1**) with excess amounts of aldoses. Elemental analysis indicated the presence of nickel, tren, and aldose in a ratio of 1:1:3. The magnetic susceptibilities, ranging 2.8−3.3 μ_B, indicated that the nickel(II) ions have two unpaired electrons and an octahedral geometry. Electronic absorption (AB) and circular dichroism (CD) spectra are shown in Figure 9. The AB spectra consist of three principal bands with comparatively low intensities (<30 M^{-1} cm^{-1}), characteristic of octahedral nickel(II) complexes, and the energy of the first band maxima (9.9−10.0 kcm^{-1}), corresponding to $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ transition, shifted toward the low-energy side in comparison with those of *cis*-(*O*,*O*)-[$Ni^{II}N_4O_2$] sugar complexes **2** and **3** (10.0−10.7 kcm^{-1}). Recently, we have prepared the C_3-symmetrical Co(II)−sugar complexes [Co(*N*,*N*′,*N*″-(aldosyl)$_3$-tren)]X_2 (**15**)[29] (aldose = D-mannose (**15**), L-rhamnose (**16**); X = Cl, Br; X_2 = SO_4) by a method similar to the present one. The X-ray analyses of **16a** (aldose = L-Rha, X = Br) and **16c** (aldose = L-Rha, X_2 = SO_4) clearly demonstrated that the monomeric cobalt(II) center is ligated by the *N*,*N*′,*N*″-(L-Rha)$_3$-tren *N*-glycoside ligand in a heptadentate manner through three C-2 hydroxyl groups of the sugars, three *N*-glycosidic nitrogen atoms, and the tertiary nitrogen atom of tren. By analogy, the nickel(II) tris(sugar) complexes **6**, **7**, and **9**−**11** were assumed to have a C_3-symmetrical structure with the *N*,*N*′,*N*″-tris(aldosyl)-tren ligand, although the coordination of the tertiary nitrogen atom of tren is not clear. ^{13}C NMR spectra of **10** and **11** were measured to confirm the C_3-symmetrical structure (Table 4). While the ^{13}C NMR spectra of **6**, **7**, and **9** involving monosaccharides were featureless, the ^{13}C NMR spectra of **10** and **11** involving disaccharides showed six peaks as shown in Figure 10. The six resonances could be assigned to a set of carbon atoms in the nonreducing terminal unit (α,D-glucosyl or galactosyl residue), on the basis of the INEPT method and the chemical shifts in comparison with those of the nonreducing terminal units of free maltose and melibiose (Table 4 and Figure 11).[45] The peaks at δ ~100 and ~60 were assigned to C1 and C6 carbons of the nonreducing unit, respectively, whereas the other four peaks were not unambiguously assigned. The resonances for C1 were considerably broad, relative peak heights referenced to the C6 resonance being 0.28 (the degree of line-broadening

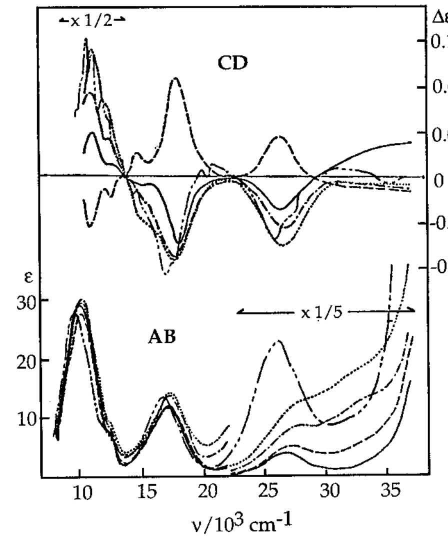


Figure 9. UV−vis absorption (AB) and circular dichroism (CD) spectra of (a, —) [Ni(*N*,*N*′,*N*″-(D-Man)$_3$-tren)]Br_2 (**6b**) in MeOH, (b, − −) [Ni(*N*,*N*′,*N*″-(L-Rha)$_3$-tren)]Br_2 (**7b**) in MeOH, (c, −•−) [Ni(*N*,*N*′,*N*″-Mal$_3$-tren)]Br_2 (**10**) in DMSO, (d, - -) [Ni(*N*,*N*′,*N*″-Mel$_3$-tren)]Br_2 (**11**) in DMSO, and (e, −••−) [Ni(*N*,*N*′,*N*″-(D-Glc)$_3$-tren)]Cl_2 (**9**) in MeOH.

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(45) Christfides, J. C.; Davies, D. B. *J. Am. Chem. Soc.* **1983**, *105*, 5099.

Table 4. ^{13}C NMR Chemical Shifts of Nickel(II) Tris(sugar) Complexes **10** and **11**[a] and Nonreducing Residues of β-Maltose and β-Melibiose[b]

compd	δ, ppm[c,d]					
[Ni(*N*,*N*′*N*″-Mal$_3$-tren)]$^{2+}$ (**10**)	102.76 (28), C1	72.63 (48), C2	73.04 (81), C3	69.76 (93), C4	73.41 (91), C5	60.69 (100), C6
β-maltose (α,D-glucosyl residue)	100.81, C1	72.68, C2	73.45, C3	70.05, C4	73.51, C5	61.02, C6
[Ni(*N*,*N*′*N*″-Mel$_3$-tren)]$^{2+}$ (**11**)	98.81 (42), C1	68.28 (95), C2	69.44 (86), C3	68.72 (134), C4	70.91 (73), C5	60.53 (100) C6
β-melibiose (α,D-glucosyl residue)	99.10, C1	68.44, C2	69.56, C3	68.89, C4	70.98, C5	60.59, C6

[a] In DMSO-d_6. [b] Reference 53. [c] Referenced to tetramethylsilane. Relative peak heights are shown in parentheses.

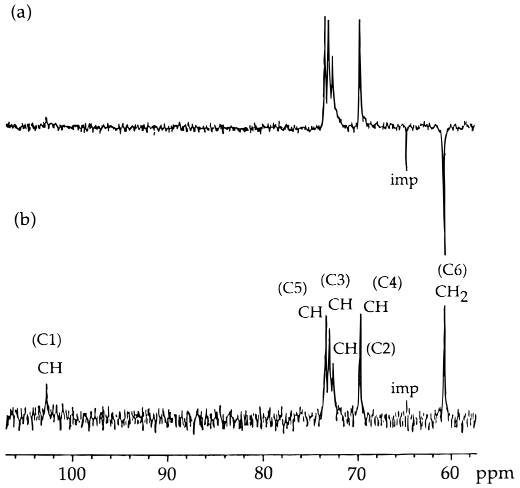


Figure 10. ^{31}C NMR spectra of [Ni(*N*,*N*′,*N*″-Mal$_3$-tren)]Br$_2$ (**10**) in DMSO-d_6: (a) INEPT spectrum with $\tau = {}^3/_4{}^1J_{CH}$; (b) low-power broadband proton-decoupled spectrum.

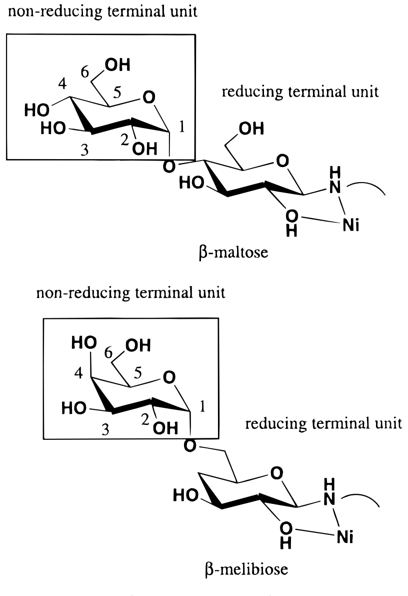


Figure 11. Structures of β-maltose and β-melibiose residues.

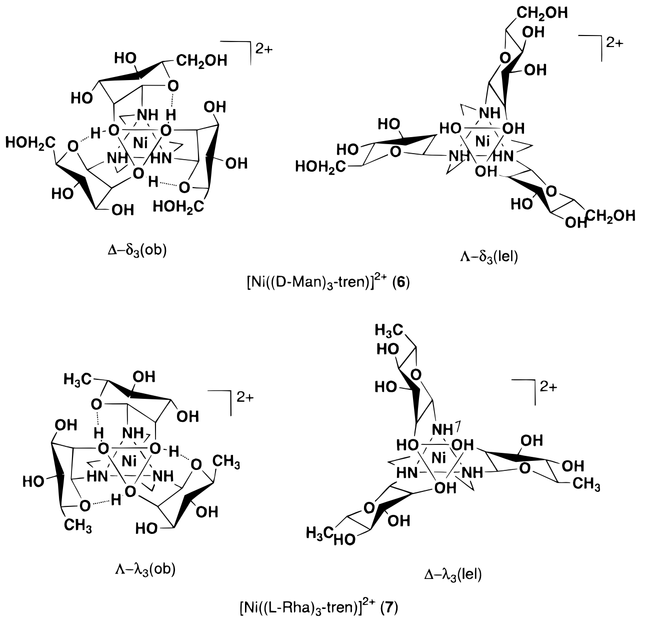
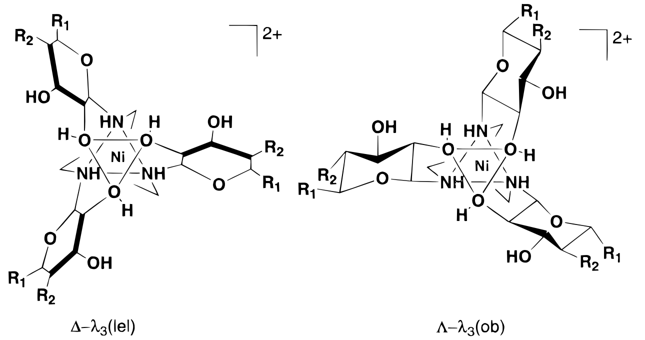


Figure 12. C_3 helical structures of [Ni(*N*,*N*′,*N*″-(D-Man)$_3$-tren)]$^{2+}$ (**6**) and [Ni(*N*,*N*′,*N*″-(L-Rha)$_3$-tren)]$^{2+}$ (**7**).



9: R_1 = CH$_2$OH, R_2 = OH: D-glucose
10: R_1 = OH, R_2 = α,D-glucopyranosyl: maltose
11: R_1 = α,D-galactopyranosyl, R_2 = OH: melibiose

Figure 13. C_3 helical structures of [Ni(*N*,*N*′,*N*″-(D-Glc)$_3$-tren)]$^{2+}$ (**9**), [Ni(*N*,*N*′,*N*″-Mal$_3$-tren)]$^{2+}$ (**10**), and [Ni(*N*,*N*′,*N*″-Mel$_3$-tren)]$^{2+}$ (**11**).

is a good indicator for the distance (r) between the paramagnetic nuclei and the observed nuclei, because the dipole–dipole interaction correlating to $1/r^6$ is mainly responsible for the paramagnetic reluxation).[46] The ^{13}C spectral data strongly suggested that the three sugar moieties are equivalent, consistent with the C_3 symmetrical structure.

On the event that the tris(sugar) complexes **6**, **7**, and **9**–**11** take a C_3-symmetrical structure, two helical absolute configurations around the nickel center, Δ and Λ, are accommodated as shown in Figures 12 and 13. In detail, complexes **9**–**11**, which contain D-glucose as the reducing terminal, can adopt Δ-λ_3(lel) and Λ-λ_3(ob) configurations (Figure 13), where the five-membered chelate rings are rather perpendicular to the C_3-axis in the ob structure and the five-membered chelate rings are nearly parallel to the C_3-axis in the lel structure. The λ-gauche conformation of the β,D-glucosylamine unit has already been confirmed in the crystal structures of [Ni(*N*-(D-GlcN)-en)$_2$]$^{2+}$ and [Ni(*N*-Mal-en)$_2$]$^{2+}$.[9,10] The absolute configuration around the metal center (configurational effect) is a major contributer to the circular dichroism (CD) rather than the chelate ring conformation (conformational effect) and the chiral centers on the ligands (vicinal effect). The sign of the CD spectra is thus very informative as to the helical configuration. Wilson et al. reported the synthesis and characterization of a C_3 helical nickel(II) complex, [Ni(py$_3$-tren)]$^{2+}$ (py$_3$-tren = tris{1-(2-pyridyl)-2-azabuten-4-yl}amine), which was shown to have Δ helical configuration with a plus sign for the Cotton effects around the

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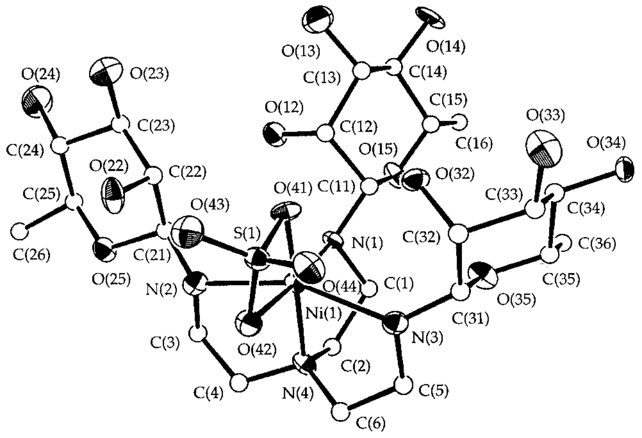

Figure 14. ORTEP diagram of complex **8**, [Ni(*N*,*N*′,*N*″-(L-Rha)$_3$-tren)(SO$_4$)]. Carbon atoms are illustrated with an arbitrary circle for clarity.

first d−d transition in the CD spectrum.[47,48] The CD spectra of **9**−**11** also exhibited plus-sign Cotton effects in the region of the first d−d transition band (10.5−10.9 k cm^{-1}) (Figure 9), strongly suggesting that the C_3 helical configuration is Δ with a lel arrangement of three λ conformation comprising sugar moieties. The Δ-λ_3(lel) structure is more favorable than the Λ-λ_3(ob) structure on the basis of CPK models. The corresponding sign of the CD spectra of **6** is plus (11.0−11.1 kcm^{-1}), indicating Δ-δ_3 (ob) arrangement, which might be stabilized by hydrogen-bonding interactions between the sugar moieties as observed in **2** (Figure 12). Complexes **7** were assumed to have the enantiomeric structure of **6**, Λ-λ_3 (ob), since the CD spectral pattern is almost a mirror image of those of **6**. The analogous cobalt(II) complex, [Co(*N*,*N*′,*N*″-(L-Rha)$_3$-tren)]Br$_2$ has recently been characterized by X-ray crystallography.[49]

Preparation and Reactions of [Ni(*N*,*N*′,*N*″-(L-Rha)$_3$-tren)(SO$_4$)]·2H$_2$O (8·2H$_2$O). A counteranion-induced inversion of C_3 helical configuration, $\Delta \rightleftharpoons \Lambda$, was observed in the Co(II) tris(sugar) complexes [Co((aldose)$_3$-tren)]$^{2+}$ (aldose = D-Man, L-Rha). The CD spectral sign of the Ni(II) tris(sugar) complexes **6** and **7**, however, would not change by the addition of sulfate anions, and the reaction of *N*,*N*′,*N*″-(aldose)$_3$-tren (aldose = D-Man, L-Rha) with NiSO$_4$·6H$_2$O resulted in the formation of the bis(sugar) complexes **2c** and **3c** *via* a hydrolytic cleavage of one of the *N*-glycosidic bonds. When the reaction of *N*,*N*′,*N*″-(L-Rha)$_3$-tren with NiSO$_4$·6H$_2$O was carried out at low temperature instead, a neutral complex [Ni(*N*,*N*′,*N*″-(L-Rha)$_3$-tren)(SO$_4$)]·2H$_2$O (**8**·2H$_2$O) was isolated in 34% yield. The intensity of the CD spectrum of **8** is less than half of those for the tris(sugar) complexes **7a**,**b**. The structure of **8** was determined by X-ray crystallography as shown in Figure 14, and some selected bond distances and angles are listed in Table 5. Complex **8** comprises a fairly distorted octahedral nickel(II) cation ligated by a bidentate sulfate anion and the *N*-glycoside ligand, *N*,*N*′,*N*″-tris(β,L-rhamnosyl)-tren, which acts as a tetradentate ligand through the four nitrogen atoms. The smallest *cis* and *trans* angles are 67.7(5)° (O(41)−Ni(1)−O(42)) and 158.0(6)° (N(2)−Ni(1)−N(3)), respectively. The sugar moieties are anchored on the metal center by only the glycosidic nitrogen atom on the C-1 position, all hydroxyl groups of the sugar residues being out of coordination although this ligand is potentially heptadentate as observed in [Co(*N*,*N*′,*N*″-(L-Rha)$_3$-tren)]$^{2+}$.[29,49] The O(22) and O(32) atoms intramolecularly interact, respectively, with the O(43) and O(41) atoms by hydrogen bondings (O(22)−O(43) = 2.76(2) Å, O(32)−O(41) = 2.64(2) Å), and the O(12) atom interacts with the O(42) atom of the neighboring complex cation ($^1/_2 - x, -y, z - {}^1/_2$). Complex **8** is able to be regarded as an intermediate species to the C_3 symmetrical tri-sugar complexes, and in fact, treatment of **8** with BaBr$_2$·2H$_2$O led to the formation of **7b**.

Table 5. Selected Bond Lengths and Angles of **8**·3CH$_3$OH·H$_2$O[a]

Bond Length (Å)

Ni(1)−O(41)	2.07(1)	Ni(1)−O(42)	2.18(1)
Ni(1)−N(1)	2.13(1)	Ni(1)−N(2)	2.23(2)
Ni(1)−N(3)	2.36(2)	Ni(1)−N(4)	2.04(2)
S(1)−O(41)	1.54(1)	S(1)−O(42)	1.47(1)
S(1)−O(43)	1.47(1)	S(1)−O(44)	1.45(1)
N(1)−C(11)	1.44(3)	N(2)−C(21)	1.42(2)
N(3)−C(31)	1.48(2)		

Bond Angles (deg)

O(41)−Ni(1)−O(42)	67.7(5)	O(41)−Ni(1)−N(1)	107.6(6)
O(41)−Ni(1)−N(2)	98.1(6)	O(41)−Ni(1)−N(3)	92.0(6)
O(41)−Ni(1)−N(4)	164.9(6)	O(42)−Ni(1)−N(1)	174.6(6)
O(42)−Ni(1)−N(2)	81.8(6)	O(42)−Ni(1)−N(3)	84.1(6)
O(42)-Ni(1)-N(4)	98.5(6)	N(1)−Ni(1)−N(2)	96.7(6)
N(1)−Ni(1)−N(3)	98.8(6)	N(1)−Ni(1)−N(4)	86.5(7)
N(2)−Ni(1)−N(3)	158.0(6)	N(2)−Ni(1)−N(4)	85.4(7)
N(3)−Ni(1)−N(4)	80.1(7)	O(41)−S(1)−O(42)	103.8(8)
O(41)−S(1)−O(43)	109.3(9)	O(41)−S(1)−O(44)	110.3(9)
O(42)−S(1)−O(43)	110.9(9)	O(42)−S(1)−O(44)	109.8(8)
O(43)−S(1)−O(44)	112(1)		

[a] Estimated standard deviations are in parentheses. See Figure 14 for atom labels.

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Supporting Information Available: Tabulations of crystallographic data, positional and thermal parameters, and bond lengths and angles of non-hydrogen atoms for **1c**·2H$_2$O, **2a**·CH$_3$OH, **2c**·CH$_3$OH, **3c**·3CH$_3$OH, and **8**·3CH$_3$OH·H$_2$O (36 pages). Ordering information is given on any current masthead page.

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