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Inversion of Configuration around the Seven-Coordinated Cobalt Center Induced by an Interaction between Sugars and Tetrahedral Oxoanions

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Carbohydrates have a widespread occurrence in nature and are indispensable compounds to living organisms.[1] Naturally rare carbohydrates have also proved to be involved in many glycoproteins, glycolipids, and antibiotics and play important roles in various biological processes.[2] Further, in some enzymatic reactions of carbohydrates, alkali, alkaline earth, and some of transition metal ions were suggested to act in cooperation with sugars.[3] In this regard, it is very important to investigate the interactions between sugars and metal ions including the stereochemical behavior of sugars in transition metal complexes. We have studied the synthesis and characterization of nickel(II) and cobalt(III) complexes containing *N*-glycosides derived from the reaction of sugars and diamines.[4] Here, we wish to report a synthesis of novel seven-coordinated cage-type cobalt complexes containing *N*-glycosides from mannose-type aldoses (D-mannose or L-rhamnose (=6-deoxy-L-mannose)) and tris(2-aminoethyl)amine (tren) and an unprecedented inversion of configuration around the metal center induced by an interaction between sugars and tetrahedral oxoanions.

A methanolic solution containing D-mannose (D-Man) or L-rhamnose (L-Rha) (4 equiv) and tren (1 equiv) was incubated at 60 °C for 1 h. Then, $CoX_2{\cdot}6H_2O$ ($X = Cl^-, Br^-$) (1 equiv) was added to the solution and the mixture was refluxed for 1 h. The resultant solution was purified on a Sephadex LH-20 gel permeation column. The wine-red major band was collected and concentrated, and an addition of ethanol gave microcrystals of [Co((aldose)$_3$-tren)]$X_2{\cdot}nH_2O$ (**1a**, aldose = D-Man, $X = Cl^-$; **1b**, aldose = L-Rha, $X = Cl^-$; **2a**, aldose = D-Man, $X = Br^-$; **2b**, aldose = L-Rha, $X = Br^-$), where (aldose)$_3$-tren is tris(*N*-aldosyl-2-aminoethyl)amine.[5] When $CoSO_4{\cdot}nH_2O$ was used as a metal source, similar complexes formulated as [Co((aldose)$_3$-tren)]$SO_4{\cdot}nH_2O$ (**3a**, aldose = D-Man; **3b**, aldose = L-Rha) were obtained.[5]

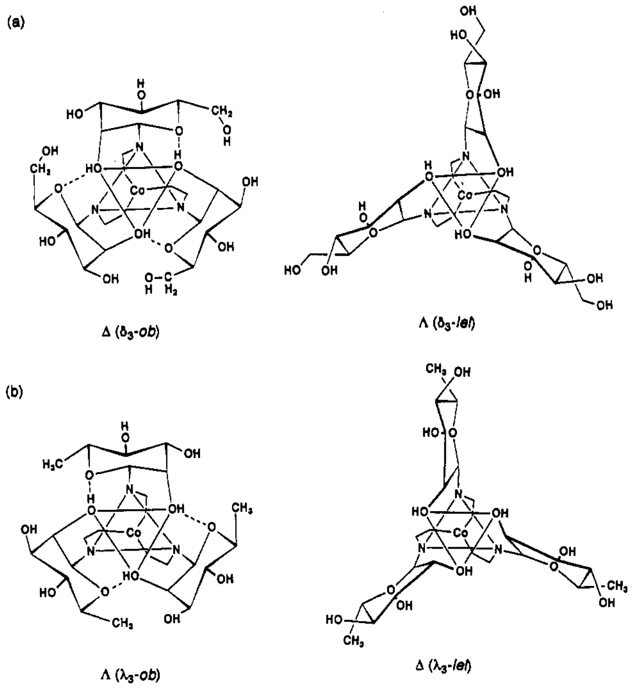

Figure 1. Possible structures of (a) [Co((D-Man)$_3$-tren)]$^{2+}$ and (b) [Co((L-Rha)$_3$-tren)]$^{2+}$.

The electronic absorption (AB) spectra of **1**–**3** in solution showed a characteristic band around 20×10^3 cm^{-1}, corresponding to *d*–*d* transitions of Co(II) ions. The transmittance spectra (Nujol mull) also showed a similar absorption indicating no significant structural change around the metal on dissolution. In the circular dichroism (CD) spectra, a large Cotton effect was observed at about 20×10^3 cm^{-1}, suggesting the coordination of sugar moieties to the cobalt ion. Further, it should be noted that the sign of the Cotton effect of **1** and **2** containing halide counteranions is opposite to that of **3** with a SO_4^{2-} anion. In general, the absolute configuration around the metal center (configurational effect) has the major contribution to the circular dichroism rather than the minor contributions of the chelate ring conformation (conformational effect) and the chiral centers on the ligands (vicinal effect). Thus, the opposite sign between **1**–**2** and **3** was tentatively attributed to an inversion of the absolute configuration around the metal. By analogy with [Ni((py)$_3$-tren)]$^{2+}$ ((py)$_3$-tren = tris{1-(2-pyridyl)-2-azabuten-4-yl}amine),[6] two possible arrangements of the potentially heptadentate *N*-glycoside ligand (aldose)$_3$-tren around the metal are depicted in Figure 1. The complex cation was assumed to have a helical C_3 geometry from which two absolute configurations, Δ and Λ, arise. In the Δ configuration of [Co((D-Man)$_3$-tren)]$^{2+}$, the five-

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(5) Analytical data were deposited as supplementary material. Data for [Co((D-Man)$_3$-tren)]$Cl_2{\cdot}5H_2O$ (**1a**) are as follows. Yield: 56%. AB (in CH_3OH): $\nu_{max}/10^3$ cm^{-1} (ϵ) 9.80 (3.9), 19.84 (18.8). CD (in CH_3OH): $\nu_{max}/10^3$ cm^{-1} ($\Delta\epsilon$) 20.00 (−0.22). Data for [Co((L-Rha)$_3$-tren)]$Cl_2{\cdot}5H_2O$ (**1b**) are as follows. Yield: 34%. AB (in CH_3OH): $\nu_{max}/10^3$ cm^{-1} (ϵ) 9.70 (4.4), 19.69 (24.7). CD (in CH_3OH): $\nu_{max}/10^3$ cm^{-1} ($\Delta\epsilon$) 20.00 (+0.14). Data for [Co((D-Man)$_3$-tren)]$Br_2{\cdot}4H_2O$ (**2a**) are as follows. Yield: 75%. AB (in CH_3OH/ethylene glycol): $\nu_{max}/10^3$ cm^{-1} (ϵ) 9.62 (3.7), 19.96 (20.0). CD (in CH_3OH/ethylene glycol): $\nu_{max}/10^3$ cm^{-1} ($\Delta\epsilon$) 19.92 (−0.16). Data for [Co((L-Rha)$_3$- tren)]$Br_2{\cdot}H_2O$ (**2b**) are as follows. Yield: 40%. AB (in CH_3OH): $\nu_{max}/10^3$ cm^{-1} (ϵ) 9.65 (3.8), 19.74 (20.5). CD (in CH_3OH): $\nu_{max}/10^3$ cm^{-1} ($\Delta\epsilon$) 19.94 (+0.12). Data for [Co((D-Man)$_3$-tren)]$SO_4{\cdot}4H_2O$ (**3a**) are as follows. Yield: 77%. AB (in CH_3OH/ethylene glycol): $\nu_{max}/10^3$ cm^{-1} (ϵ) 9.62 (4.2), 19.65 (26.1). CD (in CH_3OH/ethylene glycol): $\nu_{max}/10^3$ cm^{-1} ($\Delta\epsilon$) 19.69 (+0.08). Data for [Co((L-Rha)$_3$-tren)]$SO_4{\cdot}3H_2O$ (**3b**) are as follows. Yield: 37%. AB (in CH_3OH/ethylene glycol): $\nu_{max}/10^3$ cm^{-1} (ϵ) 9.44 (6.4), 19.65 (30.8). CD (in CH_3OH/ethylene glycol): $\nu_{max}/10^3$ cm^{-1} ($\Delta\epsilon$) 19.80 (−0.25).

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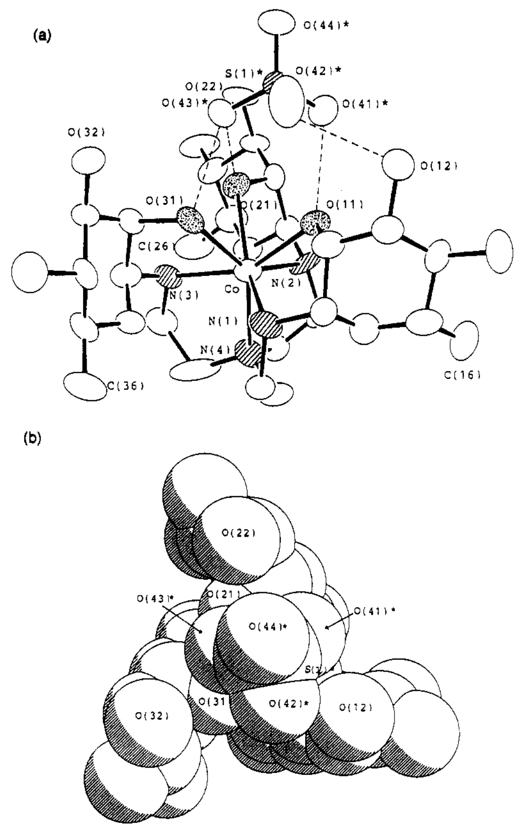

Figure 2. Perspective drawings of [Co((L-Rha)$_3$-tren)]SO$_4$ (**3b**) (a) with thermal ellipsoids and (b) with the van der Waals radii viewed down along the *pseudo* C_3 axis. Selected bond distances (Å) and angles (deg): Co(1)–O(11) = 2.26(1), Co(1)–O(21) = 2.38(1), Co(1)–O(31) = 2.39(1), Co(1)–N(1) = 2.13(1), Co(1)–N(2) = 2.15(2), Co(1)–N(3) = 2.13(1), Co(1)–N(4) = 2.31(2); O(11)–Co(1)–N(1) = 75.7(5), O(21)–Co(1)–N(2) = 73.3(5), O(31)–Co(1)–N(3) = 75.0(4), N(1)–Co(1)–N(4) = 78.8(6), N(2)–Co(1)–N(4) = 76.6(6), N(3)–Co(1)–N(4) = 78.9(6); O(11)···O(41)* = 2.70(2), O(12)···O(42)* = 2.80(2), O(21)···O(43)* = 2.69(2), O(31)···O(43)* = 2.67(2).

membered chelate rings [CoNC$_2$O] of the sugar moiety (adopting *δ-gauche* conformation) were rather perpendicular to the C_3-axis (*ob* form) and the hydrogen-bonding network between the hydroxy group on the C-2 position of D-Man and the cyclic oxygen atom on the C-5 position was inferred from the crystal structure of [Ni((D-Man)$_2$-tren)]Cl$_2$·CH$_3$OH (**4**).[4d] Contrary, in the Λ configuration, the five-membered chelate rings of the sugar moieties are nearly parallel to the C_3 axis (*lel* form) and the hydrogen bondings could not be expected. The structures of [Co-((L-Rha)$_3$-tren]$^{2+}$ in the Δ and Λ configurations were assumed to be the mirror images of the corresponding structures of [Co-((D-Man)$_3$-tren)]$^{2+}$, because D-Man and L-Rha (6-deoxy-L-mannnose) are almost enantiomeric to each other.

The structure of [Co((L-Rha)$_3$-tren)]SO$_4$·3H$_2$O·CH$_3$OH (**3b**) was elucidated by X-ray crystallography (Figure 2).[7] The complex cation consists of a cobalt atom coordinated by a heptadentate (L-Rha)$_3$-tren ligand to produce a monocapped octahedron having a *pseudo* C_3 symmetry. The three L-rhamnosyl moieties form *β-N*-glycosidic linkages with three primary amino groups of tren. The five-membered chelate rings of the sugar parts adopt the *λ-gauche* conformation. The absolute configuration around the metal with respect to the helical axis is Δ and the $\overline{CC}$ vectors in the [CoNC$_2$O] rings are nearly parallel to the C_3 axis (λ$_3$-*lel* form). The most remarkable feature is the interaction between the complex cation and the SO$_4^{2-}$ anion. The other facial site of the complex cation is capped by the SO$_4^{2-}$ anion along the C_3 axis, which is presumably supported by hydrogen bondings between the hydroxy groups on the C-2 and C-3 positions of L-Rha and the three oxygen atoms of SO$_4^{2-}$. Figure 2b with the van der Waals radii clearly shows a fit of the SO$_4^{2-}$ anion to the shallow cavity composed of three L-rhamnosyl units.

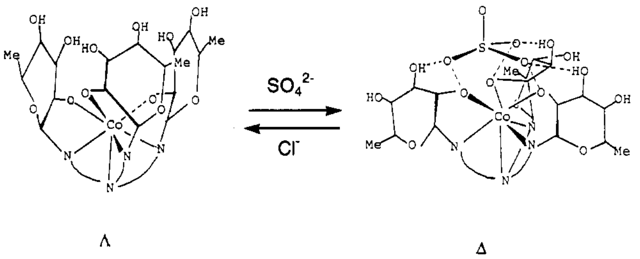

Figure 3. Configurational inversion around the metal center in [Co-((L-Rha)$_3$-tren)]$^{2+}$ induced by an interaction between sugars and SO$_4^{2-}$.

In the light of the X-ray structures of **3b** and **4** and the CD spectral data, the inversion of sign of the CD spectra is assumed to be corresponding to a configurational inversion around the cobalt center (Figure 3). [Co((L-Rha)$_3$-tren)]X$_2$ (**1b**, X = Cl$^-$, **2b**, X = Br$^-$) has the Λ (λ$_3$-*ob*) helical configuration (**1a** and **2a**: Δ (δ$_3$-*ob*)), which may stabilized by an interligand hydrogen-bonding network of the sugar units as observed in **4**. The facial site is blocked by the carbohydrate residues resulting in a small-size deep cavity. On the other hand, [Co((L-Rha)$_3$-tren)]SO$_4$ (**3b**) adopts the Δ (λ$_3$-*lel*) helical configuration (**3a**: Λ (δ$_3$-*lel*)), where the SO$_4^{2-}$ anion is fitted to the large-size shallow cavity at the facial site. The configurational inversion was preceded reversibly by an addition of excess amount of SO$_4^{2-}$ or X$^-$, just like flowers open and close. Phosphate anions were also effective in the configurational change, implying further development of the present system involving biological compounds such as nucleotides and sugar phosphates.

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Supplementary Material Available: Listings of crystallographic data, positional and thermal parameters, atomic parameters of hydrogen atoms, and bond lengths and angles for **3b**, listings of analytical and spectral data for **1–3**, figures showing electronic absorption and CD spectra for **1–3**, and a figure showing an additional ORTEP view of **3b** (11 pages). Ordering information is given on any current masthead page.

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(7) Crystal data for [Co((L-Rha)$_3$-tren)]SO$_4$·3H$_2$O·CH$_3$OH (**3b**): orthorhombic, space group $P2_12_12_1$, a = 14.836(2) Å, b = 22.489(2) Å, c = 12.181(3) Å, V = 4064(1) Å^3, Z = 4. For 2010 independent reflections with $I > 3\sigma(I)$, the structure was solved by direct methods and refined with full-matrix least squares techniques to R = 0.077 and R_w = 0.086 ($w = 1/\sigma^2(F_o)$).