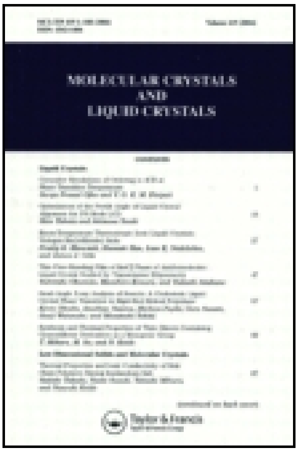

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INTELLIGENT SUGAR COMPLEXES

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Abstract The structure of $[Co((L\text{-}Rha)_3\text{-}tren)]Br_2.2CH_3OH$, where $(Rha)_3$-tren is tris(*N*-rhamnosyl-2-aminoethyl)amine, was elucidated by X-ray crystallography, which confirmed the unprecedented configurational inversion of $[Co((Rha)_3\text{-}tren)]^{2+}$, around the metal center reversibly by an addition and a removal of sulfate.

INTRODUCTION

Studies constructing artificial metal sites for molecular recognition and asymmetric reaction by the use of carbohydrate ligands are very interesting in connection with metal containing enzymes. Naturally rare carbohydrates have also proved to be involved in many glycoproteins, glycolipids, and antibiotics and play important roles in various biological processes.[1] Further, in some enzymatic reactions of carbohydrates, alkali, alkaline earth, and some of transition metal ions were suggested to act in cooperation with sugars.[2] 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.[3] Recently, we reported that a synthesis of novel seven-coordinated containing *N*-glycosides from mannose-type aldoses (D-mannose or L-rhamnose (Rha = 6-deoxy-L-mannose)) and tris(2-aminoethyl)-amine (tren) and an unprecedented inversion of configuration around the metal center induced by an addition and a removal of sulfate as shown in Figure 1. The Δ strucure of $[Co((L\text{-}Rha)_3\text{-}tren)]SO_4{\cdot}3H_2O{\cdot}CH_3OH$ (**1**)[4] was elucidated by X-ray crystallography. On the other hand, in the light of the CD spectral data, the Λ helical configuration of $[Co((L\text{-}Rha)_3\text{-}tren)]X_2$ ($X = Cl^-, Br^-$) was assigned, tentatively. Now, in order to confirm this unprecedented inversion, we have determined the molecular structure of [Co((L-Rha)$_3$-tren)]Br$_2$·2CH$_3$OH (**2**) by X-ray crystallography. Here, we wish to report a preliminary account on this work.

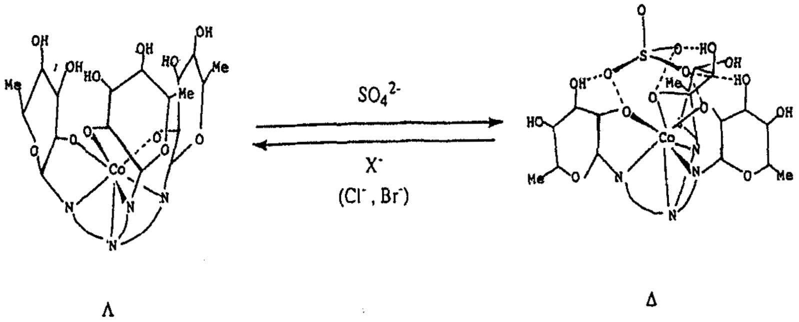

Figure 1. Configurational inversion around the metal center.

EXPERIMENTAL

Crystal data for [Co((L-Rha)$_3$-tren)]Br$_2$·2CH$_3$OH (**2**) : monoclinic, space group $P2_1$, a = 11.045(2) Å, b = 17.283(6) Å, c = 10.996(3) Å, β = 10.996(3)°, V = 1864(1) Å^3, Z = 2, μ (linear absorption coefficient) = 26.65 cm^{-1}. From 2792 independent reflections with $I > 4\sigma(I)$ collected with Mo Kα radiation (λ = 0.7107 Å) within the sphere of $2\theta < 50°$ on a Rigaku R-AXIS II CS instrument. The structure was solved by direct methods and refined with full-matrix least squares techniques to R = 0.073 and Rw = 0.193.

RESULTS AND DISCUSSIONS

In the circular dichroism (CD) spectra, a large Cotton effect was observed at about 20 - 103 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** with a SO$_4^{2-}$ anion is opposite to that of and **2** and **3** containing halide counteranions (Fugure 2). 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** and **2-3** was tentatively attributed to an inversion of the absolute configuration around the metal. By analogy with $[Ni(py)_3\text{-tren})]^{2+}$ ($(py)_3$-tren = tris{1-(2-pyridyl)-2-azabuten-4-yl}amine),[5] two possible arrangements of the potentially heptadentate *N*-glycoside ligand (aldose)$_3$-tren around the metal. The complex cation was assumed to have a helical C_3 geometry from which two absolute configurations, Δ and Λ, arise. In the Λ configuration of $[Co((L\text{-}Rha)_3\text{-tren})]^{2+}$, the five- membered chelate rings [$CoNC_2O$] of the sugar moiety (adopting λ-gauche conformation) were rather perpendicular to the C_3 axis (*ob* form) and the hydrogen-bonding network between the hdroxy group on the C-2 position of L-Rha and the cyclic oxygen atom on the C-5 position was inferred from the crystal structure of $[Ni((D\text{-}Man)_2\text{-tren})]Cl_2{\cdot}CH_3OH$ (4).[3d] Contrary, in the Δ 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.

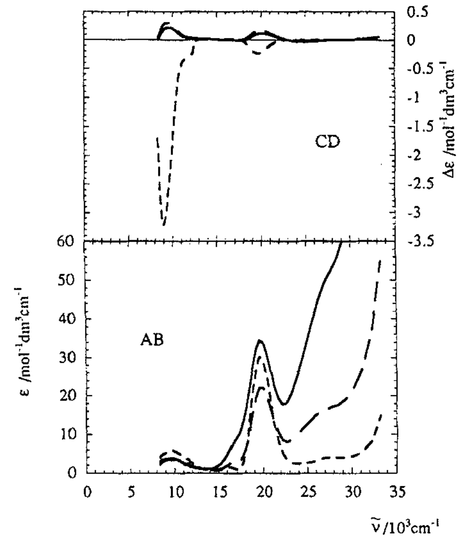

Figure 2. (—) $[Co((L\text{-}Rha)_3\text{-tren})]Cl_2$
(......) $[Co((L\text{-}Rha)_3\text{-tren})]Br_2$
(- - -) $[Co((L\text{-}Rha)_3\text{-tren})]SO_4$

A view of cation of $[Co((L\text{-}Rha)_3\text{-tren})]Br_2.2CH_3OH$ (2) was shown in Figure 3. 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 Λ, which may stabilized by an interligand hydrogen-bonding network of the sugar units and the CC vectors in the [$CoNC_2O$] rings are nearly perpendicular to the C_3 axis (λ_3-*ob* form). In the case of the complex cation of 1[4], a heptadentate (L-Rha)$_3$-tren ligand also completes a monofacecapped octahedron having a *pseudo* C_3 symmetry in the Δ (λ_3-*lel*).

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-}.

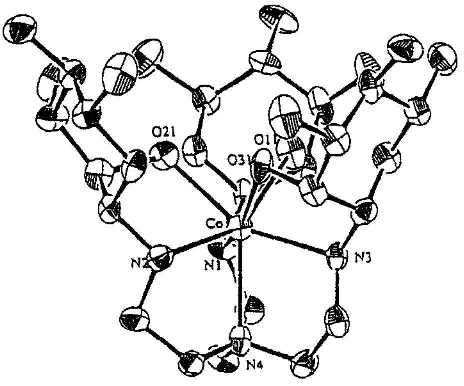

Figure 3. A perspective drawing of a complex cation of $[Co((L\text{-}Rha)_3\text{-}tren)]Br_2.2CH_3OH$ (**2**)

In the light of the two X-ray structures of **1**[4] and **2**, the inversion of sign of the CD spectra is corresponding to a configurational inversion around the cobalt center (Figure 1). Thus we could confirm that the unprecedented configurational inversion is preceded reversibly by an addition and a removal of sulfate, just like flowers open and close.

The present work could be regarded as a seminal contribution to a new aspect of artificial molecular recognition, and as a fundamental model for "induced fit" in biology.

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