

Review

INTELLIGENT METAL COMPLEXES CONTAINING N-GLYCOSIDES FORMED FROM TRIS(2-AMINOETHYL)AMINE AND ALDOSES, HAVING MOLECULAR RECOGNITION ABILITY

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Abstract Assembly of carbohydrates on nickel (II) center by utilizing N-glycosidic bond formation with a branched amine: tris(2-aminoethyl)amine (tren), an unprecedented chiral inversion around the metal center (Co or Mn) induced by an interaction between sugars and sulfate anions, peroxo-bridged dinuclear cobalt (III) complex containing N-glycoside ligands from tren and D-glucose and its reversible dioxygen binding property, and novel trimanganese complexes with a linear Mn_3 (II, III, II) assemblage bridged by carbohydrates are described.

Keywords Intelligent sugar complex; Molecular recognition; N-glycoside complex

INTRODUCTION

Carbohydrates have a wide spread occurrence in nature and are indispensable compounds to living organisms^[1]. Naturally rare carbohydrates have also been shown to be involved in many glycoproteins, glycolipids and antibiotics, and play important roles in various biological processes^[2]. 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 the transition metal complexes. The detailed coordination behavior of sugar molecules, however, has not been well established due to their complicated stereochemistry and extremely hygroscopic properties. Non-covalent interactions are vital in the 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. In contrast with many studies on interactions between side-chains of amino acids contained in transition metal complexes^[4], those concerning the structural details of sugar-sugar interactions around a metal center are very few. The synthetic efforts to construct artificial metal sites for molecular recognition by utilizing carbohydrate ligands are, therefore, very interesting subjects.

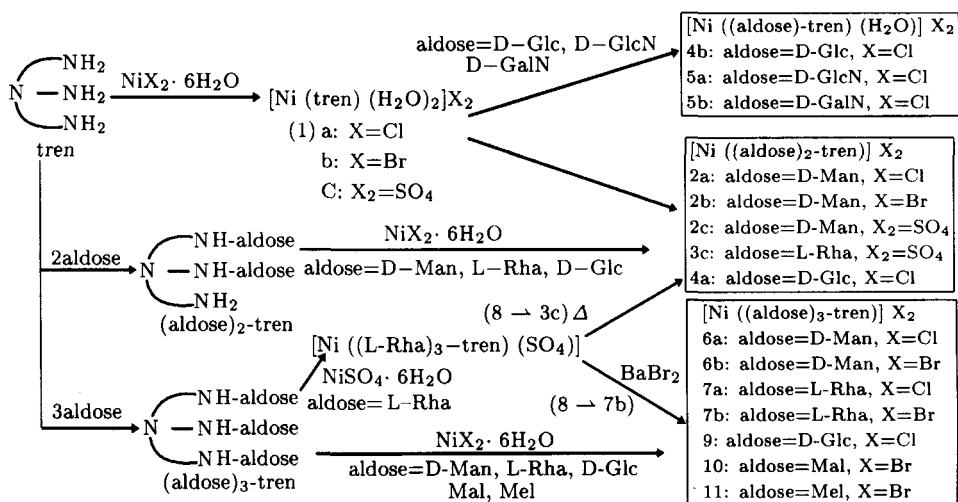
We have extensively studied the synthesis and characterization of nickel (II) and cobalt (III) complexes containing N-glycosides derived from the reaction of sugars and diamines^[5~9], the results of which suggested that the stereo structure of the sugar complexes can be modified by varying diamines and metal ions used. During our studies, we fortunately discovered the new sugar transformation reactions by the cooperative effects between metal ions and amines^[10~17]. We have also developed the antitumor^[18,19] or antifungal^[20] metal complexes containing amino sugars. 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 a metal center in a symmetrical fashion with effective sugar-sugar interactions. In particular, when the mannose-type aldoses having 2,3-*cis* configuration, D-mannose (D-Man) and L-rhamnose (L-Rha) were used as a sugar part, structures of the nickel (II)-N-glycoside complexes, $[\text{Ni}(\text{aldose}_2\text{-tren})]^{2+}$ (aldose=D-Man, L-Rha), exhibited novel intramolecular sugar-sugar interactions around the metal center, which facilitate the assemblage of sugars on the metal center^[7]. The pyranose ring of the mannose-type sugars, on coordinating to the metal, was oriented nearly perpendicular with respect to the five membered chelate ring, which enables sugar ligands to contact each other, whereas the pyranose ring of the glucose-type sugars having 2,3-*trans* configuration lies in the same plane of the five-membered chelate ring, preventing intramolecular sugar-sugar interaction on a metal center.

We wish to describe a short review herein mainly focusing on the mono-, bis- and tris-sugar complexes, $[\text{Ni}(\text{N}-(\text{aldosyl})\text{-tren})(\text{H}_2\text{O})]^{2+}$, $[\text{Ni}(\text{N}, \text{N}'-(\text{aldosyl})_2\text{-tren})]^{2+}$ and $[\text{Ni}(\text{N}, \text{N}', \text{N}''-(\text{aldosyl})_3\text{-tren})]^{2+}$ ^[21,22], an unprecedented chiral inversion around the metal center (Co ^[23~25] or Mn ^[27]) induced by an interaction between sugars and sulfate anions, peroxo-bridged dinuclear cobalt (III) complex containing N-glycoside ligands from tris(2-aminoethyl)amine and D-glucose and its reversible dioxygen binding property^[28], and novel trimanganese complexes with a linear Mn_3 (II, III, II) assemblage bridged by carbohydrates.

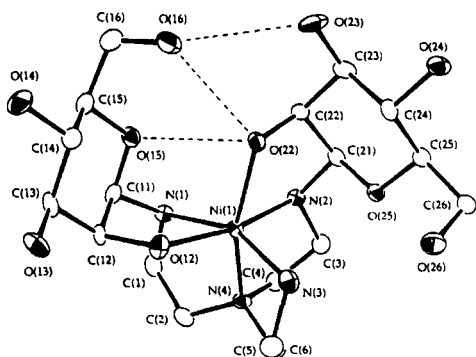
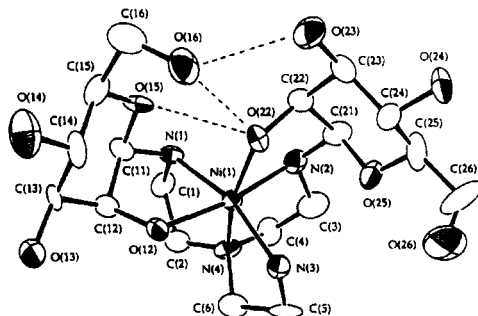
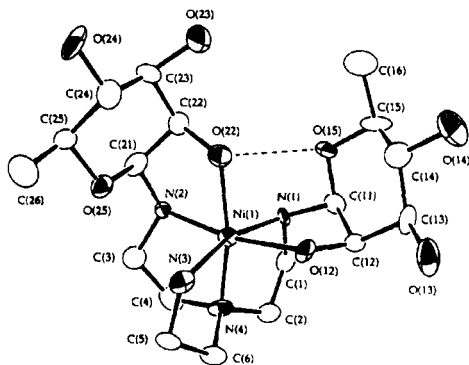
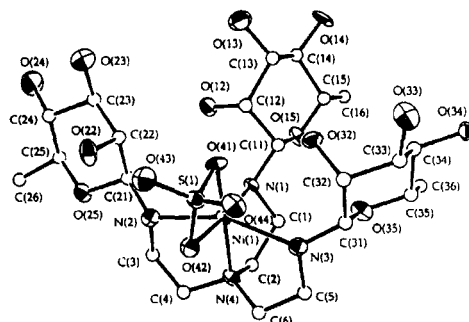
ASSEMBLY OF CARBOHYDRATES ON NICKEL (II) CENTER BY UTILIZING N-GLYCOSIDIC BOND FORMATION WITH TRIS(2-AMINOETHYL)AMINE^[21,22]. SYNTHESSES AND CHARACTERIZATION OF $[\text{Ni}\{\text{N}-(\text{ALDOSYL})-\text{TREN}\}(\text{H}_2\text{O})]^{2+}$, $[\text{Ni}\{\text{N}, \text{N}'\text{-DI}(\text{ALDOSYL})-\text{TREN}\}]^{2+}$ AND $[\text{Ni}\{\text{N}, \text{N}', \text{N}''\text{-TRI}(\text{ALDOSYL})-\text{TREN}\}]^{2+}$

Synthetic routes to the nickel(II)-sugar complexes are summarized in Scheme 1.

1. Reactions of $[\text{Ni}(\text{tren})(\text{H}_2\text{O})_2]\text{X}_2$ (tren=tris(2-aminoethyl)amine; X=Cl (1a), Br (1b), and $\text{X}_2=\text{SO}_4$ (1c)) with mannose-type aldoses, having 2,3-*cis* configuration (D-mannose and L-rhamnose), afforded { bis(N-aldosyl-2-aminoethyl) (2-aminoethyl)amine } nickel (II) complexes, $[\text{Ni}(\text{N}, \text{N}'-(\text{aldosyl})_2-\text{tren})]\text{X}_2$ (aldosyl=D-mannosyl, X=Cl (2a), Br (2b), $\text{X}_2=\text{SO}_4$ (2c); aldosyl=L-rhamnosyl, $\text{X}_2=\text{SO}_4$ (3c)). The structure of 1c was confirmed by X-ray crystallography to be a mononuclear $[\text{Ni}^{\text{II}}\text{N}_4\text{O}_2]$ complex with the tren acting as a tetradentate ligand. Complexes 2a, 2c, 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 (Fig. 1~3). 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 2,3-*trans* configuration, resulted in the formation of monosugar complex, $[\text{Ni}(\text{N}-(\text{aldosyl})-\text{tren})(\text{H}_2\text{O})_2]\text{Cl}_2$ (aldosyl=D-glucosyl (4b), 2-amino-2-deoxy-D-glucosyl (5a) and 2-amino-2-deoxy-D-galactosyl (5b)) instead of bissugar 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, $[\text{Ni}(\text{N}, \text{N}', \text{N}''-(\text{aldosyl})_3-\text{tren})]\text{X}_2$ (aldosyl=D-mannosyl, X=Cl (6a), Br (6b); L-rhamnosyl, X=Cl (7a), Br (7b); D-glucosyl, X=Cl (9); maltosyl, X=Br (10); 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 $\text{NiSO}_4 \cdot 6 \text{H}_2\text{O}$ at low temperature, a labile neutral complex, $[\text{Ni}(\text{N}, \text{N}', \text{N}''-(\text{L-rhamnosyl})_3-\text{tren})(\text{SO}_4)]$ (8), was successfully isolated and characterized by X-ray crystallography, in which three sugar moieties are anchored only at the N atom of C-1 position (Fig. 4). 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

BaBr₂.

Scheme 1

Fig. 1 ORTEP view of the complex cation of 2a, [Ni (N, N'-(D-Man)₂-tren)]²⁺Fig. 2 ORTEP view of the complex cation of 2c, [Ni (N, N'-(D-Man)₂-tren)]²⁺Fig. 3 ORTEP view of the complex cation of 3c, [Ni (N, N'-(L-Rha)₂-tren)]²⁺Fig. 4 ORTEP view of the complex cation 8, [Ni (N, N', N''-(L-Rha)₃-tren) (SO₄)]

CHIRAL INVERSION AROUND THE SEVEN-COORDINATED METAL CENTER INDUCED BY AN INTERACTION BETWEEN SUGARS AND SULFATE ANIONS

Cobalt (II) center^[23~25]

Novel seven-coordinated cage-type cobalt (II) complexes containing N-glycosides from mannose-type aldoses and tris(2-aminoethyl)amine (tren), $[\text{Co}((\text{aldose})_3\text{-tren})]\text{X}_2 \cdot n\text{H}_2\text{O}$ (1a $\cdot$ 5H H_2O : aldose=D-mannose (D-Man), $\text{X}=\text{Cl}^-$; 1b $\cdot$ 5H $_2\text{O}$: aldose=6-deoxyl-L-mannose (L-Rha), $\text{X}=\text{Cl}^-$; 2a $\cdot$ 4H $_2\text{O}$: aldose=D-Man, $\text{X}=\text{Br}^-$; 2b $\cdot$ H $_2\text{O}$: aldose=L-Rha, $\text{X}=\text{Br}^-$) and $[\text{Co}((\text{aldose})_3\text{-tren})]\text{SO}_4 \cdot n\text{H}_2\text{O}$ (3a $\cdot$ 4H $_2\text{O}$: aldose=D-Man; 3b $\cdot$ 3H $_2\text{O}$: aldose=L-Rha) were prepared and characterized by elemental analysis, electronic absorption and circular dichroism spectroscopies, and X-ray crystallography, where (aldose) $_3$ -tren is tris (N-aldosyl-2-aminoethyl)amine. The complex cation of 2b consists of a cobalt atom coordinated by a heptadentate (L-Rha) $_3$ -tren ligand to produce a mono face-capped octahedron having a pseudo C_3 symmetry with the Λ (λ_3 -ob form) configuration around the metal (Fig. 5). The complex cation of 3b has a mono face-capped octahedron coordinated by a heptadentate (L-Rha) $_3$ -tren ligand having a pseudo C_3 symmetry with the Δ (λ_3 -lel form) configuration (Fig. 6). The other facial site of the complex cation is capped by the SO_4^{2-} anion through hydrogen bondings with the hydroxy groups of L-rhamnose residues. The C_3 helical-configurational inversion around the cobalt(II) center, $\Delta \leftrightarrow \Lambda$, induced by an interaction between the sugars and the SO_4^{2-} anion, was monitored by circular dichroism spectroscopy in which the sign of the Cotton effect of 1 and 2 having halide counter anions is opposite to that of 3 having sulfate counter anions,

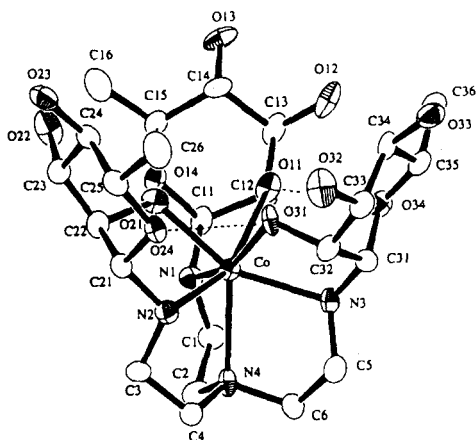


Fig. 5 ORTEP drawing of the complex cation of $[\text{Co}((\text{L-Rha})_3\text{-tren})]\text{Br}_2$ (2b)

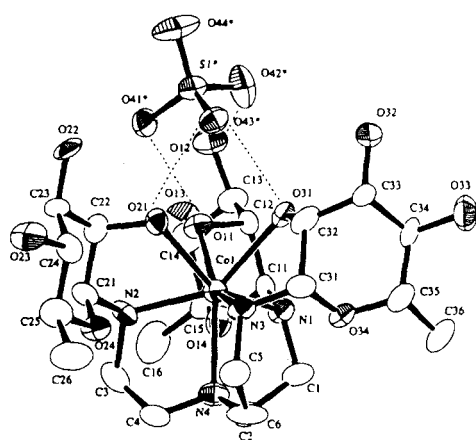


Fig. 6 ORTEP drawing of $[\text{Co}((\text{L-Rha})_3\text{-tren})]\text{SO}_4$ (3b)

and was reversibly proceeded by an addition and a removal of sulfate anions (Fig. 7). The intensities of circular dichroism spectra for $[\text{Co}((\text{L-Rha})_3\text{-tren})]^{2+}$ and $[\text{Co}((\text{D-Man})_3\text{-tren})]^{2+}$ were appreciably changed with an addition of sulfate ions. The spectral changes were interpreted in terms of the ion-pair formation. By using electrostatic theories of ion association^[26], the closest distance between the sulfate ions and the $[\text{Co}((\text{D-Man or L-Rha})_3\text{-tren})]^{2+}$ cations was estimated as ~ 0.5 nm, which is consistent with the Co-S distance of 0.4697 (6) nm observed in the crystal structure of 3b. The sulfate ion was suggested to fit into the cavity comprised of the sugar hydroxyl group through hydrogen bonds even in solution state.

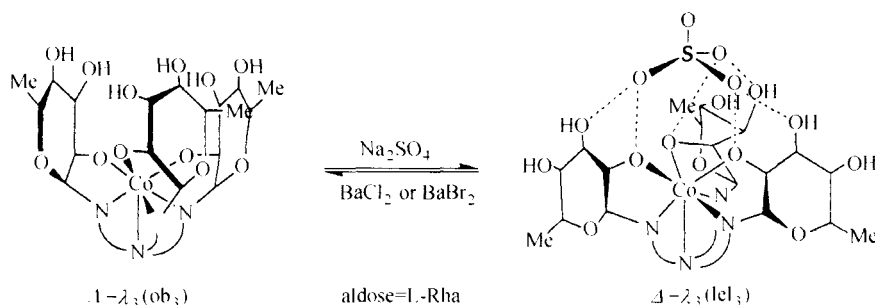


Fig. 7 Configurational inversion around the metal center in $[\text{Co}((\text{L-Rha})_3\text{-tren})]^{2+}$ induced by an interaction between sugars and SO_4^{2-}

Manganese (II) center^[27]

To a methanolic solution of tris(N-aldosyl-2-aminoethyl)amine formed from tren and D-mannose or L-rhamnose (6-deoxy-L-mannose) in situ, was added Mn (II) $\text{X}_2 \cdot 4\text{H}_2\text{O}$ ($\text{X}=\text{Br}$ and $1/2 \text{SO}_4$). The resultant solution was chromatographed on a Sephadex LH-20 gel permeation column and the pale pink major band was collected and concentrated to afford colorless microcrystals formulated as $[\text{Mn}(\text{aldose}_3\text{-tren})]\text{X}_2 \cdot 4\text{H}_2\text{O}$ (2: aldose=D-Man, $\text{X}=\text{Br}$; 3: aldose=D-Man, $\text{X}=1/2\text{SO}_4$; 4: aldose=L-Rha, $\text{X}=1/2\text{SO}_4$) in 34 ~ 82% yields. The elemental analysis showed a mononuclear manganese ion to be ligated by the potentially heptadentate N-glycoside ligand, $\text{aldose}_3\text{-tren}$, and the efficient magnetic moments (5.62 ~ 5.89 B.M.) indicated the high-spin Mn(II) state.

The complex cation possesses a crystallographically imposed C_3 symmetry with the axis passing through the Mn(1) and N(1) atoms and comprises a mononuclear Mn(II) ion ligated by a heptadentate N-glycoside ligand, $(\text{D-Man})_3\text{-tren}$, similar to the structure of $[\text{Co}((\text{L-Rha})_3\text{-tren})]\text{Br}_2$ (1a) except the C-6 hydroxyl groups (Fig. 8a)^[25]. The ligand coordinates to the metal through four nitrogen atoms and three C-2 hydroxyl groups of sugar moieties to complete a considerably distorted mono-face-capped octahedral geometry, the tertiary amino nitrogen of the tren part

binds to the facial site with Mn-N distance being 0.2375 (9) nm. The bite angles of O (2)–Mn (1)–N(2) and N (1) –Mn(1)–N (2) are 74.7 (2)° and 75.9 (1)°, respectively. The five-membered chelate rings take δ -gauche conformation and are arranged in ob-form with respect to the C₃ axis, resulting in the Δ –C₃ helical configuration around the metal. The relatively crowded Δ – δ_3 (ob₃) structure is stabilized by inter-sugar hydrogen bonding network, O (2) $\cdots$ O (5)* = 0.2746 (6) nm and O (3) $\cdots$ O (6)* = 0.2753 (8) nm. The sugar-sugar interactions in 2 should be stronger than those found in 1b owing to the presence of C-6 hydroxyl groups. Further, a water molecule is loosely trapped into the narrow cavity composed of the three D-mannose residues (O (6) $\cdots$ O (12)=0.3273 (6) nm).

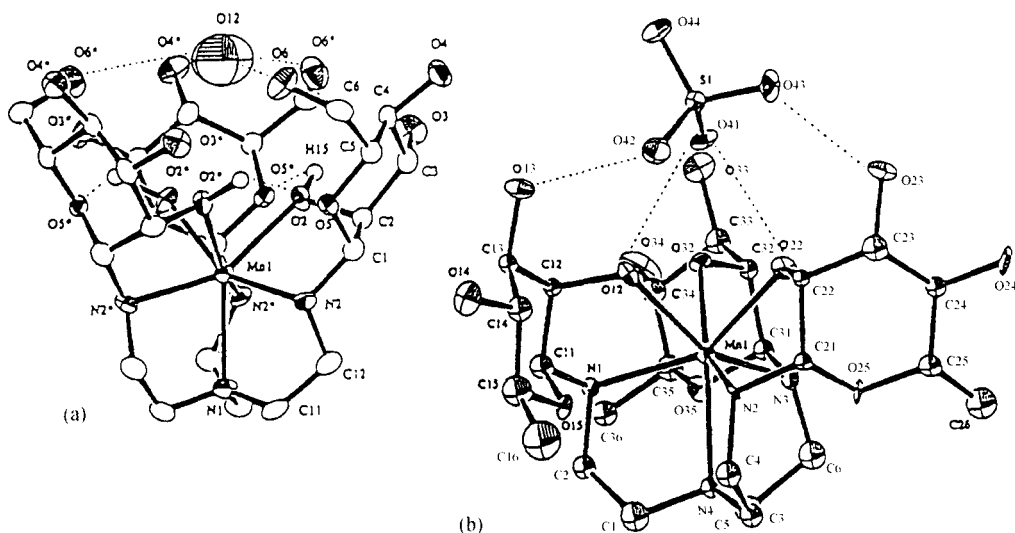


Fig. 8 (a) ORTEP diagram of the complex cation of 2, $[\text{Mn}((\text{D-Man})_3\text{-tren})]^{2+}$ and a trapped water molecule; (b) ORTEP diagram of the complex 4, $[\text{Mn}((\text{L-Rha})_3\text{-tren})]\text{SO}_4$

The complex cation of 4 has a pseudo C₃ symmetry, consisting of a Mn(II) ion with the cage-type ligand, (L-Rha)₃-tren, just like $[\text{Co}((\text{L-Rha})_3\text{-tren})]\text{SO}_4$ (1b) (Fig. 8b)^[25]. The N-glycoside acts as a heptadentate ligands with the tertiary amino nitrogen capping a facial site with Mn-N distance of 0.244 (1) nm. The C₃ helical configuration is Δ (lel₃) with three λ -gauche sugar chelations. The other facial site composed of three C-2 hydroxyl groups of sugar moieties is electrostatically capped by a sulfate anion supported by hydrogen bondings (O (12) $\cdots$ O (41)=0.278 (1) nm, O (22) $\cdots$ O (41)=0.278 (1) nm, O (13) $\cdots$ O (42)=0.277 (1) nm and O (23) $\cdots$ O (43)=0.264 (1) nm). The sulfate anion is considerably distorted from a C₃ symmetrical structure in comparison with that found in 1b. The Mn (1) $\cdots$ S (1) interatomic distance is 0.5237 (5) nm which is significantly longer than what is

found in 1b ($\text{Co} \cdots \text{S} = 0.4697$ (6) nm) and indicates a weaker ion-pair interaction than in 1b.

The two types of C_3 helical configurations, $\Delta - \lambda_3$ (ob_3) and $\Delta - \lambda_3$ (lel_3), should be considered, in general, for the D-mannose-containing complex, $[\text{Mn}((\text{D-Man})_3\text{-tren})]^{2+}$ as depicted in Fig. 8b. The structures of $[\text{Mn}((\text{L-Rha})_3\text{-tren})]^{2+}$ are essentially enantiomeric to the corresponding D-mannose complexes because L-Rha is an enantiomer to D-Man except the C-6 substituent group. The present structural analyses clearly revealed that the configurational switch of the metal center proceeds depending on the counter anions; the ob_3 -form, found with bromide anions, bears a small and deep cavity on the sugar-facial site which is stabilized by hydrogen bonds between the sugar ligands, and on the other hand, the lel_3 -form has a wide and shallow cavity which is capped by a sulfate anion.

PEROXO-BRIDGED DINUCLEAR COBALT (III) COMPLEX CONTAINING N-GLYCOSIDE LIGANDS FROM TRIS(2-AMINOETHYL)AMINE AND D-GLUCOSE AND ITS REVERSIBLE DIOXYGEN BINDING PROPERTY^[28]

A methanolic solution of $\text{Co(II)} \cdot \text{X}_2 \cdot 6\text{H}_2\text{O}$ ($\text{X} = \text{Cl}, \text{Br}$) was treated in air with tris(N-D-glucosyl-2-aminoethyl)amine ($(\text{D-Glc})_3\text{-tren}$), which was prepared from D-glucose (D-Glc) and tris(2-aminoethyl)amine (tren) in situ. The resultant dark brown solution was chromatographed on a Sephadex LH-20 gel permeation column eluted by methanol and the brown band was collected. A slow evaporation of the solution yielded brown crystals formulated as $\{[\text{Co}((\text{D-Glc})_2\text{-tren})]_2\text{O}_2\} \cdot \text{X}_2 \cdot 5\text{H}_2\text{O}$ ($\text{X} = \text{Cl}$ (2), Br (3)) in low yields, where $\text{tren}-(\text{D-Glc})_2$ is bis(N-D-glucosyl-2-aminoethyl) (aminoethyl) amine. Elemental analyses indicated that complexes 2 and 3 contain a N-glycoside ligand, $\text{tren}-(\text{D-Glc})_2$, formed by a loss of one D-glucose residue from $\text{tren}-(\text{D-Glc})_3$ per metal. The presence of peroxo bridge between the two cobalt ions are demonstrated by the intense electronic absorption band around 400 nm ($\lg \epsilon$ 3.46~3.58), corresponding to a peroxo-metal charge transfer band, and the IR peak at 888 cm^{-1} assignable to $\nu_{\text{O-O}}$. Two environmentally different D-glucose moieties were confirmed by the ^1H and ^{13}C -NMR spectra of 3 in D_2O ; assignments being carried out by combinations of ^1H ^1H and ^{13}C ^1H COSY, HMBSC, and HMQC spectra. The N-glycosidic bond formation was unambiguously determined by the isotopic multiplets observed in the ^{13}C -NMR spectrum in a $\text{D}_2\text{O}/\text{H}_2\text{O}$ (1:1) mixed solvent. Two resonances for the C-1 carbon atoms of D-glucose were observed as doublets owing to the isotope induced shifts of the neighboring N H

and N-D species^[30].

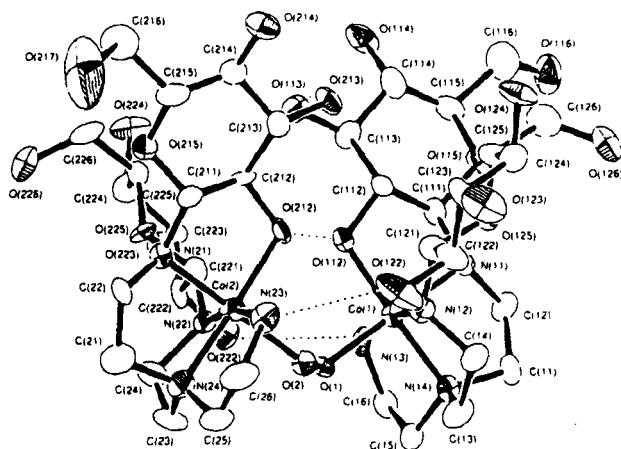


Fig. 9 ORTEP diagram of the complex cation of 2, $[\{Co[(D-Glc)_2tren]\}_2O_2]^{3+}$

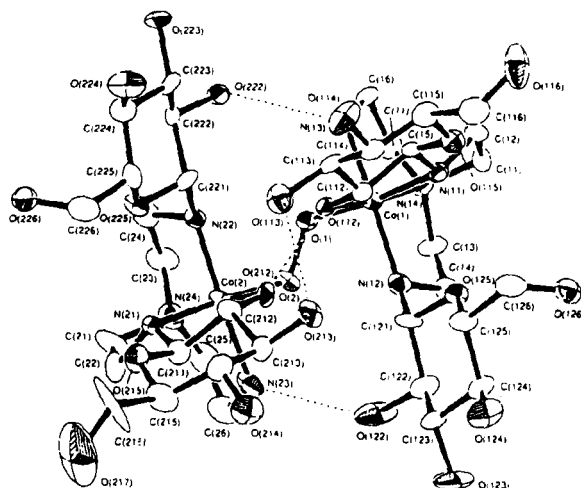


Fig. 10 ORTEP plot of the complex cation of 2, $[\{Co[(D-Glc)_2tren]\}_2O_2]^{3+}$, viewed along the pseudo- C_2 axis.

ORTEP diagrams for the complex cation of 2 are illustrated in Fig.9 and Fig.10. The complex cation consists of two Co(III) ions bridged by a peroxo unit (O (1)–O (2)=0.1452 (10) nm). The cation has a pseudo C_2 symmetry with respect to an axis passing through the middle of O–O bond. The metal-metal separations is 0.4114 (2) nm. Each cobalt ion is ligated by the N-glycoside, tren-(D-Glc)₂, through the four nitrogen atoms and the C-2 oxygen atom of a sugar moiety together with the peroxide to form a distorted *cis*-(O, O)-[CoN₄O₂] octahedral geometry. The other D-glucose residue is anchored on the metal by the N-glycosidic nitrogen atom only; hydroxyl groups of the sugar are away from the coordination sphere

of the metal. The $(\mu\text{-O}_2)\text{Co(III)}_2$ core is supported by some hydrogen bondings between the sugar moieties ($\text{O (112)} \cdots \text{O (212)} = 0.242 (1) \text{ nm}$, $\text{O (113)} \cdots \text{O (213)} = 0.270 (1) \text{ nm}$, $\text{O (122)} \cdots \text{N (23)} = 0.295 (1) \text{ nm}$ and $\text{O (222)} \cdots \text{N (13)} = 0.292 (1) \text{ nm}$). In particular, the $\text{O (112)} \cdots \text{O (212)}$ short interatomic distance suggests the presence of $\text{O}^- \cdots \text{H-O}$ type strong hydrogen bond which is similar to that observed in the dinuclear Ni (II) complex bridged by $\beta\text{-D-mannofuranoside}$ residue^[31]. These hydrogen bonding system deviates the Co-O-O-Co torsional angle from planarity to an intervening value of $100.4 (6)^\circ$ between $0 \sim 65^\circ$ found in $(\mu\text{-O}_2)(\mu\text{-X}) \text{Co (III)}_2$ double bridged complexes ($\text{X}=\text{OH}, \text{NH}$) and $145 \sim 180^\circ$ in $(\mu\text{-O}_2)\text{Co(III)}_2$ single bridged structures^[32]. The electronic absorption spectrum of **2** in methanol was rapidly changed on irradiation by a high-pressure mercury lamp at room temperature under nitrogen atmosphere (Fig. 11a). The absorption intensity around 400 nm, characteristic of $\mu\text{-peroxo}$ dicobalt (III) complex, decreased and finally to very weak absorptions around 480 nm and 590 nm were observed. This spectral change could correspond to deoxygenation of **2** leading to Co (II) species and O_2 , by analogy with the photolysis of $[(\text{en})_2\text{Co}^{\text{III}}(\mu\text{-OH})(\mu\text{-O}_2)\text{Co}^{\text{III}}(\text{en})_2]^{3+}$ ($\text{en}=1, 2\text{-diaminoethane}$)^[33].

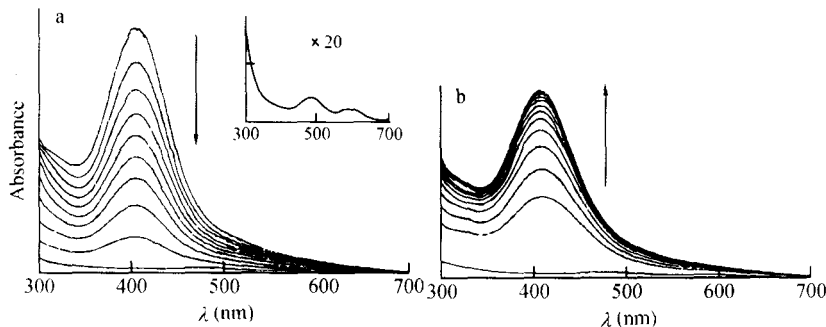


Fig. 11 (a) An electronic absorption spectral change of **2** in CH_3OH upon irradiation with a high-pressure mercury lamp at room temperature under a nitrogen atmosphere, monitored every 5 min. The final spectrum is expanded in the upper-right; (b) Absorption spectral changes measured in air every 5 min after the irradiation

When the resultant solution was exposed to air after irradiation, the absorption peak at 400 nm was immediately restored, and finally, almost 80% of complex **2** was recovered on the basis of its absorbance. These spectral changes clearly indicated an almost reversible dioxygen binding through the $\mu\text{-peroxo}$ dimer **2**.

The sugar units dramatically influence the redox property of the cobalt center, which was demonstrated by the differential reactivity toward dioxygen molecule between the complex with mannose-type aldoses (D-Man and L-Rha) and that with D-glucose.

TRIMANGANESE COMPLEXES WITH A LINEAR Mn_3 (II, III, II) ASSEMBLAGE BRIDGED BY CARBOHYDRATES^[29]

The potentially heptadentate N-glycoside ligands, tris((N-aldosyl) aminoethyl) amine ((aldose)₃-tren), prepared by the reaction between tris(aminoethyl)amine (tren) with aldose (D-mannose (D-Man) or L-rhamnose (L-Rha=6-deoxyl-L-Man)) in situ, were treated with manganese (II) salts ($\text{MnX}_2 \cdot 4\text{H}_2\text{O}$, X=Cl, Br, NO_3) in methanol. The workup of the resultant solutions afforded reddish-orange crystals formulated as $\{[\text{Mn}(\text{aldose})_3\text{-tren}]_2\text{Mn}(\text{H}_2\text{O})\} \text{X}_3 \cdot n\text{H}_2\text{O}$ in 10% ~ 42% yield (1·11 H_2O : aldose=L-Rha, X=Cl; 2·10 H_2O : aldose=L-Rha, X=Br; 3·8 H_2O : aldose=L-Rha, X= NO_3 ; 4·2 H_2O : aldose=D-Man, X=Cl). These trimanganese-sugar complexes were assumed to have an almost identical structure to each other on the basis of electronic absorption and circular dichroism spectra and magnetic susceptibilities, $\mu_{\text{eff}} = 15.1 \sim 16.0 \text{ BM per Mn}_3$ (23°C, solid state).

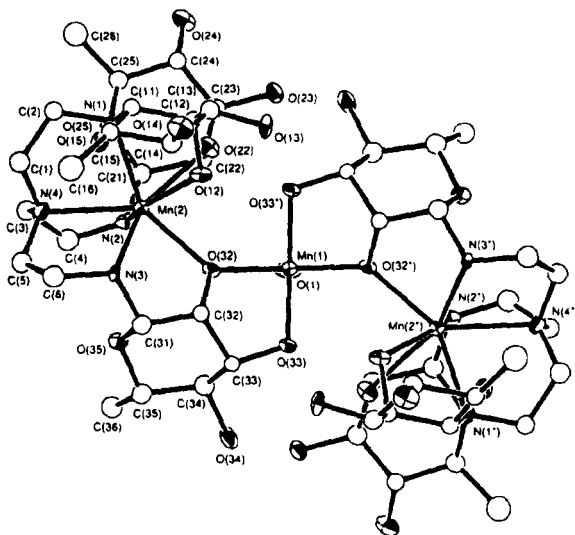


Fig. 12 ORTEP diagram of the complex cation of 3, $\{[\text{Mn}((\text{L-Rha})_3\text{-tren})]_2\text{Mn}(\text{H}_2\text{O})\}^{3+}$, viewed down vertical to the central square plane

The structures of 3 and 4 were determined by X-ray crystallography to reveal a linearly ordered trimanganese core bridged by two carbohydrate residues with a Mn-Mn separation of 0.3846 (2) nm (3) and av. 0.3911 (5) nm (4) and a Mn-Mn-Mn angle of 180.0° (3) and 171.0 (1)° (4) (Fig. 12). The terminal Mn atoms are seven-coordinate with a distorted mono-face-capped octahedral geometry ligated by the (aldose)₃-tren ligand through three oxygen atoms of C-2 hydroxyl groups, three N-glycosidic nitrogen atoms and a tertiary amino nitrogen atom, just as observed in $[\text{Co}((\text{L-Rha})_3\text{-tren})](\text{SO}_4)$ (6)^[25]. The C₃ helical configurations and the NO chelate

conformations are denoted as Δ -1el (λ_3) and Λ -1el (δ_3), respectively, for 3 and 4^[25]. The central Mn atoms are five-coordinate ligated by four oxygen atoms of carbohydrate residues in the (aldose)₃-tren ligands and one water molecule, resulting in a square-pyramidal geometry. On the basis of the bond lengths, the oxidation states of the terminal and central manganese atoms are assumed to be Mn(II) and Mn(III), respectively. This formulation of Mn oxidation states is also consistent with the relatively nitrogen-rich coordination sphere on the terminal Mn atoms. The C-2 and C-3 hydroxyl groups of the bridging sugar moieties are also estimated to be deprotonated from the short bond lengths to the central Mn atom (0.188~0.196 nm). Alternatively, the complex cations can be viewed as two seven-coordinate Mn(II) complexes, $[\text{Mn}((\text{aldose})_3\text{-tren})]^{2+}$, trapping a Mn(III) ion through a sugar tentacle. To our knowledge, the present trimanganese complex is the first example of Mn₃ (II, III, II) linear assemblage, whereas many Mn₃ (II, II, II)^[33] and Mn₃(III, II, III)^[34] compounds have already been reported.

The structurally characterized examples of dimetal complexes with bridging carbohydrates are extremely rare. Only two structures have been reported, namely, $[\text{Mo}_2\text{O}_5(\text{D-Lyx})]$ (7)^[35] (Lyx=lyxose) and $[\text{Ni}_2(\text{N}, \text{N}'\text{-(D-Man)}_2\text{-N}, \text{N}'\text{-Me}_2\text{en}) (\text{N}(\text{D-Man})\text{-N}, \text{N}'\text{-Me}_2\text{en})(\text{CH}_3\text{OH})]\text{Cl}_2$ (8)^[31], both of which involve a β -furanose bridging system. In complexes 3 and 4, a β -mannopyranosyl skeletal unit with a chair conformation bridges the two manganese ions with the C-2 μ -alkoxo group joining

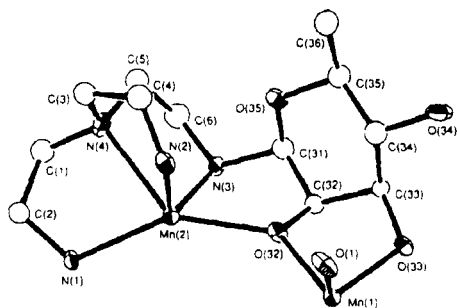


Fig. 13 A perspective drawing of the sugar bridging part in 3

two metal ions and the C-1 N-glycosidic amino and the C-3 alkoxo groups coordinating to each metal centre (Fig. 13). These structural features could lead to a new general equatorial-axial-equatorial bridging system of sugars and suggested stronger affinity of the mannose-type aldoses, having 2,3-*cis* configuration, to dimetal centres than that of the glucose-type aldoses which possess a 2,3-*trans* configuration.

The present study reports the unprecedented mixed-valence trimanganese (II, III, II) complexes with N-glycoside ligands, which could provide useful insight into the interaction of carbohydrates with dimetal ions and interesting physical properties in the multinuclear manganese chemistry.

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