

# Peroxo-bridged dinuclear cobalt(III) complexes containing *N*-glycoside ligands from tris(2-aminoethyl)amine and *D*-glucose and their reversible dioxygen binding properties

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Peroxo-bridged dinuclear cobalt(III) complexes containing *N*-glycoside ligands from tris(2-aminoethyl)amine (tren) and *D*-glucose (*D*-Glc),  $[\{\text{Co}[(\text{D-Glc})_2\text{tren}]\}_2\text{O}_2]\text{X}_3 \cdot 5\text{H}_2\text{O}$  ( $\text{X} = \text{Cl}$  **2**,  $\text{Br}$  **3**), and their reversible dioxygen binding properties are reported  $[(\text{D-Glc})_2\text{tren} = \text{bis}(N\text{-D-glucosyl-2-aminoethyl})(2\text{-aminoethyl})\text{amine}]$ .

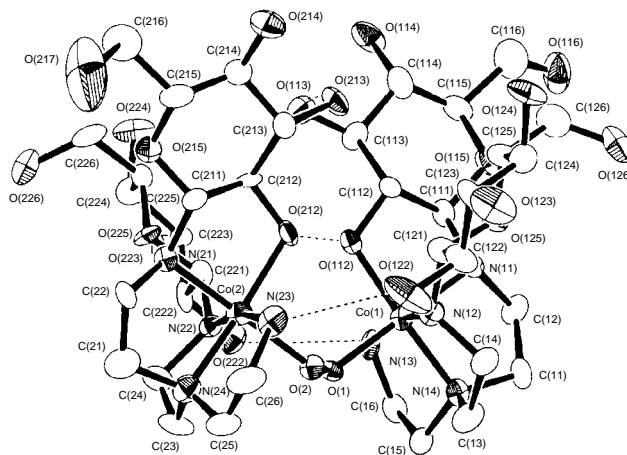
Interactions of carbohydrates with metal ions have become an important subject in bioinorganic chemistry, since many sugar-processing enzymes have been revealed to function with redox non-active metal ions such as  $\text{Mg}^{2+}$ ,  $\text{Mn}^{2+}$  and  $\text{Zn}^{2+}$  in the active sites.<sup>1</sup> Elucidation of reactivity and behavior of sugars around redox active metal ions is also potentially important in relevance to ribonucleotide reductases which utilize non-haem diiron or coenzyme B<sub>12</sub> functional units.<sup>2</sup>

We have recently reported mononuclear cobalt(II) complexes ligated by a heptadentate *N*-glycoside formed from tris(2-aminoethyl)amine (tren) and mannose-type aldohexoses,  $[\text{Co}\{(\text{aldose})_3\text{tren}\}]\text{X}_2$  **1**, where (aldose)<sub>3</sub>tren = tris(*N*-aldosyl-2-aminoethyl)amine, aldose = *D*-mannose (*D*-Man), *L*-rhamnose (*L*-Rha), and  $\text{X} = \text{Cl}$ ,  $\text{Br}$ ,  $1/2\text{SO}_4$ . Complex **1** showed a dynamic chiral inversion around the metal centre ( $\Delta \rightleftharpoons \Lambda$ ) induced by the interaction of sugars with the sulfate anion.<sup>3</sup> In general, mannose-type aldoses such as *D*-Man and *L*-Rha have 2,3-*cis* configuration and the sugar ring is axially oriented with respect to the chelate ring upon coordination through the 1,2-functional groups with the  $\beta$ -anomeric form being adopted.<sup>4</sup> The axial orientation of *D*-Man and *L*-Rha enables close sugar–sugar interactions around the metal centres.<sup>5</sup> The present study was carried out by utilizing *D*-glucose (*D*-Glc) as the sugar component, which has 2,3-*trans* configuration and was equatorially oriented on ligating through the 1,2-functional groups with the  $\beta$ -anomeric form being adopted.<sup>4</sup> We report herein novel  $\mu$ -peroxo dicobalt(III) complexes supported by  $\beta$ -*D*-glucosyl polyamine ligands and their reversible dioxygen binding properties.

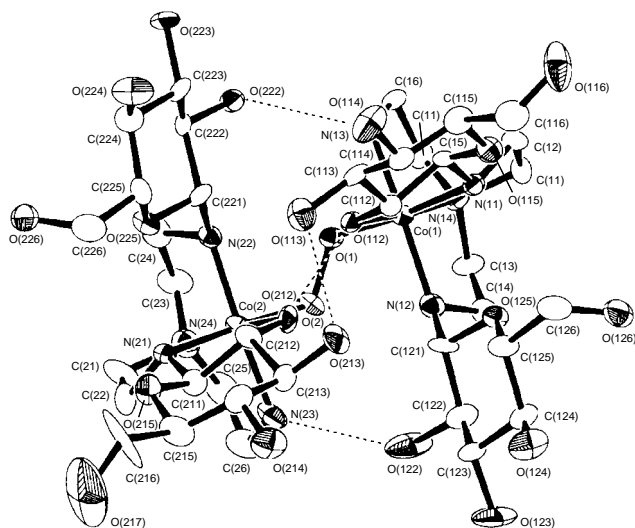
A methanolic solution of  $\text{Co}^{\text{II}}\text{X}_2 \cdot 6\text{H}_2\text{O}$  ( $\text{X} = \text{Cl}$ ,  $\text{Br}$ ) was treated in air with tris(*N*-*D*-glucosyl-2-aminoethyl)amine  $[(\text{D-Glc})_3\text{tren}]$ , which was prepared from *D*-glucose (*D*-Glc) and tris(2-aminoethyl)amine (tren) *in situ*. The resultant dark brown solution was chromatographed on a Sephadex LH-20 gel permeation column, eluted with methanol, and the brown band was collected. Slow evaporation of the solution yielded brown crystals formulated as  $[\{\text{Co}[(\text{D-Glc})_2\text{tren}]\}_2\text{O}_2]\text{X}_3 \cdot 5\text{H}_2\text{O}$  ( $\text{X} = \text{Cl}$  **2**,  $\text{Br}$  **3**) in low yields, where  $(\text{D-Glc})_2\text{tren}$  is bis(*N*-*D*-glucosyl-2-aminoethyl)(aminoethyl)amine.<sup>†</sup> Elemental analyses indicated that complexes **2** and **3** contained a *N*-glycoside ligand,  $(\text{D-Glc})_2\text{tren}$ , formed by a loss of one *D*-glucose residue from  $(\text{D-Glc})_3\text{tren}$ , per metal. The presence of a peroxo bridge between the two cobalt ions is demonstrated by the intense electronic absorption band around 400 nm ( $\log \epsilon$  3.46–3.58), corresponding to a peroxo–metal charge-transfer band, and the IR peak at  $888\text{ cm}^{-1}$  assignable to  $\nu_{\text{O-O}}$ . Two environmentally different *D*-glucose moieties were confirmed by the <sup>1</sup>H and <sup>13</sup>C

NMR spectra of **3** in  $\text{D}_2\text{O}$  assignments being carried out by combination of <sup>1</sup>H–<sup>1</sup>H and <sup>13</sup>C–<sup>1</sup>H COSY, HMBC, and HMQC NMR spectra. The *N*-glycosidic bond formation was unambiguously determined by the isotopic multiplets observed in the <sup>13</sup>C NMR spectrum in  $\text{D}_2\text{O}$ – $\text{H}_2\text{O}$  (1 : 1). 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.<sup>6†</sup>

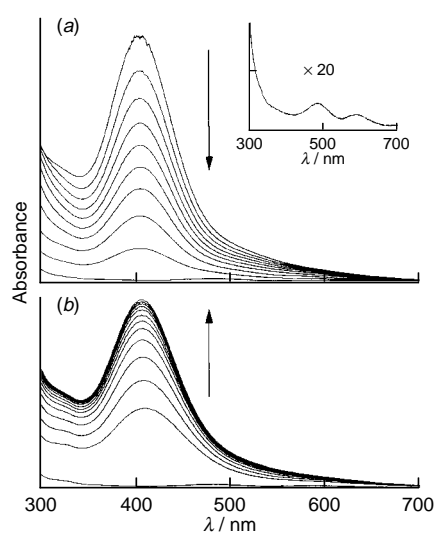
ORTEP diagrams for the complex cation of **2** are illustrated in Fig. 1 and 2.<sup>‡</sup> The complex cation consists of two  $\text{Co}^{\text{III}}$  ions bridged by a peroxo unit  $[\text{O}(1)\text{--O}(2)\ 1.452(10)\ \text{\AA}]$ . The cation has a pseudo-*C*<sub>2</sub> symmetry with respect to an axis passing through the middle of the O–O bond (Fig. 2). The metal–metal separation is  $4.114(2)\ \text{\AA}$ . Each cobalt ion is ligated by the *N*-glycoside,  $(\text{D-Glc})_2\text{tren}$ , through the four nitrogen atoms and the C(2) oxygen atom of a sugar moiety together with the peroxide to give distorted *cis*-(O,O)- $[\text{CoN}_4\text{O}_2]$  octahedral geometry. The other *D*-glucose residue is anchored on the metal by only the *N*-glycosidic nitrogen atom; hydroxyl groups of the sugar lie away from the coordination sphere of the metal.<sup>5</sup> The  $\text{Co}^{\text{III}}_2(\mu\text{-O}_2)$  core is supported by hydrogen bonds between the sugar moieties  $[\text{O}(112)\cdots\text{O}(212)\ 2.42(1)\ \text{\AA}$ ,  $\text{O}(113)\cdots\text{O}(213)\ 2.70(1)\ \text{\AA}$ ,  $\text{O}(122)\cdots\text{N}(23)\ 2.95(1)\ \text{\AA}$ ,  $\text{O}(222)\cdots\text{N}(13)\ 2.92(1)$



**Fig. 1** ORTEP diagram of the complex cation of **2**,  $[\{\text{Co}[(\text{D-Glc})_2\text{tren}]\}_2\text{O}_2]^{3+}$ . Selected bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ );  $\text{Co}(1)\text{--O}(1)\ 1.895(7)$ ,  $\text{Co}(1)\text{--O}(112)\ 1.910(7)$ ,  $\text{Co}(1)\text{--N}(11)\ 1.963(9)$ ,  $\text{Co}(1)\text{--N}(12)\ 1.999(9)$ ,  $\text{Co}(1)\text{--N}(13)\ 1.977(8)$ ,  $\text{Co}(1)\text{--N}(14)\ 1.918(9)$ ,  $\text{Co}(2)\text{--O}(2)\ 1.916(7)$ ,  $\text{Co}(2)\text{--O}(212)\ 1.973(7)$ ,  $\text{Co}(2)\text{--N}(21)\ 1.954(9)$ ,  $\text{Co}(2)\text{--N}(22)\ 1.993(9)$ ,  $\text{Co}(2)\text{--N}(23)\ 1.98(1)$ ,  $\text{Co}(2)\text{--N}(24)\ 1.95(1)$ ,  $\text{O}(1)\text{--O}(2)\ 1.452(10)$ ;  $\text{O}(1)\text{--Co}(1)\text{--O}(112)\ 92.1(3)$ ,  $\text{O}(112)\text{--Co}(1)\text{--N}(11)\ 87.6(3)$ ,  $\text{N}(11)\text{--Co}(1)\text{--N}(14)\ 87.2(4)$ ,  $\text{N}(12)\text{--Co}(1)\text{--N}(14)\ 86.7(4)$ ,  $\text{N}(13)\text{--Co}(1)\text{--N}(14)\ 84.6(4)$ ,  $\text{O}(2)\text{--Co}(2)\text{--O}(212)\ 92.9(3)$ ,  $\text{O}(212)\text{--Co}(2)\text{--N}(21)\ 87.2(3)$ ,  $\text{N}(21)\text{--Co}(2)\text{--N}(24)\ 87.6(4)$ ,  $\text{N}(22)\text{--Co}(2)\text{--N}(24)\ 87.6(4)$ ,  $\text{N}(23)\text{--Co}(2)\text{--N}(24)\ 84.4(4)$ ,  $\text{Co}(1)\text{--O}(1)\text{--O}(2)\ 118.1(5)$ ,  $\text{Co}(2)\text{--O}(2)\text{--O}(1)\ 115.8(5)$ ,  $\text{O}(1)\text{--Co}(1)\text{--N}(11)\ 175.7(3)$ ,  $\text{O}(112)\text{--Co}(1)\text{--N}(14)\ 173.8(3)$ ,  $\text{N}(12)\text{--Co}(1)\text{--N}(13)\ 167.5(4)$ ,  $\text{O}(2)\text{--Co}(2)\text{--N}(21)\ 177.8(4)$ ,  $\text{O}(212)\text{--Co}(2)\text{--N}(24)\ 173.2(4)$ ,  $\text{N}(22)\text{--Co}(2)\text{--N}(23)\ 167.6(4)$ .



**Fig. 2** ORTEP plot of the complex cation of **2**,  $[\text{Co}\{(\text{D-Glc})_2\text{tren}\}]_2\text{O}_2^{3+}$ , viewed along the pseudo- $C_2$  axis.



**Fig. 3** (a) An electronic absorption spectral change of **2** in  $\text{CH}_3\text{OH}$  upon irradiation with a high-pressure mercury lamp at room temp. 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.

$\text{\AA}$ ). In particular, the short interatomic distance  $\text{O}(112)\cdots\text{O}(212)$  suggests the presence of  $\text{O}\cdots\text{H}\cdots\text{O}$  type strong hydrogen bond, similar to that observed in the dinuclear nickel(II) complex bridged by a  $\beta$ -D-mannofuranoside residue.<sup>7</sup> This hydrogen-bonding system distorts the  $\text{Co}\text{--}\text{O}\text{--}\text{O}\text{--}\text{Co}$  torsional angle from planarity to  $100.4(6)^\circ$ , between  $0\text{--}65^\circ$  found in  $\text{Co}^{\text{III}}_2(\mu\text{-O}_2)(\mu\text{-X})$  double-bridged complexes ( $\text{X} = \text{OH}, \text{NH}$ ) and  $145\text{--}180^\circ$  in  $\text{Co}^{\text{III}}_2(\mu\text{-O}_2)$  single-bridged structures.<sup>8</sup>

The electronic absorption spectrum of **2** in methanol rapidly changed upon irradiation with a high-pressure mercury lamp at room temp. under a nitrogen atmosphere [Fig. 3(a)]. The absorption intensity around 400 nm, characteristic of a  $\mu$ -peroxo dicobalt(III) complex, decreased and finally very weak absorptions around 480 and 590 nm were observed. This spectral change could correspond to deoxygenation of **2** leading to a cobalt(II) species and  $\text{O}_2$ , by analogy with the photolysis of  $[(\text{en})_2\text{Co}^{\text{III}}(\mu\text{-OH})(\mu\text{-O}_2)\text{Co}^{\text{III}}(\text{en})_2]^{3+}$  ( $\text{en} = 1,2\text{-diaminoethane}$ ).<sup>9</sup>

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 [Fig. 3(b)]. These spectral changes clearly indicated an almost reversible dioxygen binding through the  $\mu$ -peroxo dimer **2**.

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

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## Footnotes and References

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† Synthetic procedures and analytical and spectral data for **2** and **3**, and the  $^{13}\text{C}$  NMR spectra of **3** in  $\text{D}_2\text{O}$  and in  $\text{D}_2\text{O}\text{--}\text{H}_2\text{O}$  (1:1) are available as supplementary materials upon request to the authors.

‡ Crystal data for  $2\cdot 4\text{H}_2\text{O}\cdot\text{CH}_3\text{OH}$ : orthorhombic, space group  $P2_12_12_1$  (no. 19),  $a = 19.384(8)$ ,  $b = 23.468(5)$ ,  $c = 13.195(5)$   $\text{\AA}$ ,  $U = 6002(2)$   $\text{\AA}^3$ ,  $Z = 4$ ,  $D_c = 1.440$   $\text{g cm}^{-3}$ ,  $T = -99$   $^\circ\text{C}$ ,  $R = 0.078$ ,  $R_w = 0.085$  [ $w = 1/\sigma^2(F_o)$ ] for 4961 reflections with  $I > 3\sigma(I)$ . The structure was solved and refined with teXsan program package. CCDC 182/605.

§ Detailed photochemistry and kinetic parameters will be reported elsewhere.

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