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Geometrical Isomerization of μ-Peroxo-bis[diethylenetriamine-(*R*)-propylenediaminecobalt(III)] Ions *via* Labile Cobalt(II) Species

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Synopsis. The title complex ion undergoes slow geometrical isomerization. A mechanism involving labile cobalt(II) species which is in equilibrium with the title ion, is suggested.

Cobalt(II) complexes of various amine ligands uptake dioxygen to give μ-peroxo-dicobalt(III) complexes in basic solutions.[1,2] Such a dioxygen uptake is often reversible; *i.e.* the μ-peroxo complex is in equilibrium with the cobalt(II) complexes and O_2, the equilibrium being in great favor of the μ-peroxo complexes. Unusually rapid ligand substitution reactions of such binuclear cobalt(III) complexes are interpreted by the existence of such equilibria.[2]

Peroxo bridged dicobalt(III) compelexes containing multidentate amine ligands can give many geometrical isomers with respect to the arrangement of chelate rings. Geometrical isomerization of such complexes would not be accompanied by a significant change in their electronic absorption spectra, but can be followed by circular dichroism (CD) spectra by use of an optically active ligand such as (*R*)-propylenediamine (*R*-pn). The CD spectrum of $[(\mathrm{dien})(R\text{-pn})\mathrm{Co^{III}}(\mu\text{-}O_2{}^{(2-)})\mathrm{Co^{III}}(R\text{-pn})(\mathrm{dien})]^{4+}$ (dien=diethylenetriamine), indeed changes slowly owing to geometrical isomerization.[3] This work is aimed at clarifying the mechanism of geometrical isomerization of this complex in relation to the deoxygenation equilibrium.

Experimental

Materials. *μ-Peroxo-bis[diethylenetriamine-*(R)*-propylenediamine-cobalt(III)] Perchlorate,* $[(\mathrm{dien})(\mathrm{R}\text{-}pn)Co^{III}(\mu\text{-}O_2{}^{(2-)})Co^{III}(\mathrm{R}\text{-}pn)(dien)](ClO_4)_4$: Two samples of the complex were obtained by modifying the previously reported method.[3] An aqueous solution (40 cm^3) of cobalt(II) nitrate hexahydrate (5.8 g) containing diethylenetriamine (2.1 g), (*R*)-propylenediamine dihydrochloride (2.9 g), and sodium hydroxide (1.6 g) was aerated at 0 °C, while aqueous solution of sodium perchlorate (20 g in *ca.* 30 cm^3) was slowly added. Brown hygroscopic precipitate was filtered off after 1 h, and dried *in vacuo* (sample A). The sample A was dissolved in a minimum amount of hot water (70 °C), cooled slowly (5—10 °C per hour) to room temperature and stored in a refrigerator overnight. The dark brown needles were filtered off and dried *in vacuo* (sample B). Found: C, 18.79; H, 5.03; N, 15.27%. Calcd for $C_{14}H_{46}N_{10}O_{18}Co_2Cl_4$: C, 18.64; H, 5.14; N, 15.52%.

Other Materials: Propylenediamine was resolved by Dwyer's method.[4] Special grade reagents of diethylenetriamine, ethylenediamine, and disodium dihydrogen ethylenediaminetetraacetate dihydrate, were used as received.

Measurements. Electronic absorption and circular dichroism spectra were recorded on a Hitachi 323 spectrophotometer and a JASCO J-40A automatic recording spectropolarimeter, respectively. The latter and a Hitachi 124 spectrophotometer with a Hitachi recorder QPD-34 were used for the kinetic measurements.

Results and Discussion

The Change in CD Spectra. Samples A and B gave almost identical absorption, but quite different CD spectra immediately after dissolution in water (Figs. 1 (a) and (b)). Their CD spectra changed slowly with time without any clear isosbestic point, and became almost identical with each other after 3 d at 15 °C (Fig. 1 (c)). No appreciable change in absorption spectra was accompanied. The plots of CD strengths at 510, 447, and 395 nm against time failed to give simple first-order decay curves (exemplified by Fig. 2 (d)). More than three geometrical isomers seem to be responsible for the CD change. Three

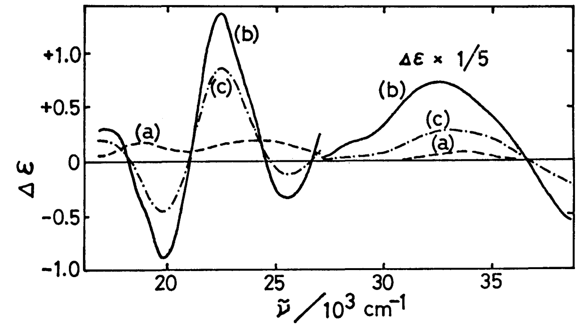

Fig. 1. Circular dichroism spectra of $[(\mathrm{dien})(R\text{-pn})\mathrm{Co^{III}}(\mu\text{-}O_2{}^{(2-)})\mathrm{Co^{III}}(R\text{-pn})(\mathrm{dien})]^{4+}$ in water at 15 °C; (a) fresh solution of sample A (----), (b) fresh solution of sample B (——), and (c) these solutions after 3 d (—·—·—).

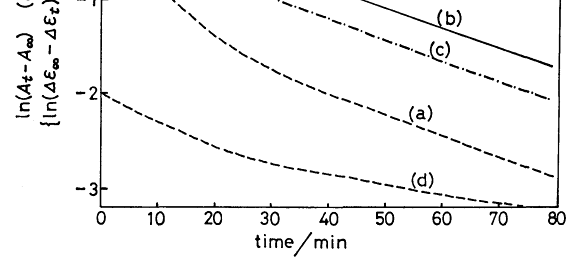

Fig. 2. First-order plots for the decrease in absorbance at 303 nm of $[(\mathrm{dien})(R\text{-pn})\mathrm{Co^{III}}(\mu\text{-}O_2{}^{(2-)})\mathrm{Co^{III}}(R\text{-pn})(\mathrm{dien})]^{4+}$ on addition of Na_2H_2edta to (a) fresh solution of sample A (----), (b) fresh solution of sample B (——), and (c) these solutions after 3 d (—·—·—), and (d) first-order plot for the change in CD strength at 447 nm of the fresh solution of sample A (----).

solutions represented by the three different CD curves in Fig. 1 should have different compositions of geometrical isomers.

Deoxygenation Kinetics. The deoxygenation can be followed by adding EDTA⁵⁾ to basic solutions of μ-peroxo complexes, EDTA scavenging cobalt(II) species to prevent reformation of μ-peroxo complexes.²⁾ Figure 2 shows the first-order plots of decrease in absorbance at 303 nm (common peak position of geometrical isomers of $[(\text{dien})(R\text{-pn})\text{Co}^{\text{III}}(\mu\text{-O}_2{}^{(2-)})\text{Co}^{\text{III}}(R\text{-pn})(\text{dien})]^{4+}$) at 40 °C on addition of $\text{Na}_2\text{H}_2\text{edta}$ to basic solutions of the complex in various isomer compositions (pH, *ca.* 8). Two conclusions can be deduced from the plots: (i) Comparison of cruve (a) for the deoxygenation of sample A with curve (d) for the change in CD strength of the same solution, clearly indicates that the deoxygenation occurs much more rapidly than geometrical isomerization. (ii) The deoxygenation rate constants are significantly different among geometrical isomers, since solutions with different isomer compositions give significantly different first-order plots.

The fresh solution of sample B gave a good straight line with the first-order rate constant, $3.5\times10^{-4}\,\text{s}^{-1}$ (40.0 °C, I=0.1 M (NaCl) (1 M=1 mol dm^{-3})), indicating that B is composed of only one geometrical isomer.⁶⁾ Fresh solution of sample A and aged solutions of both samples (3 d at 15 °C) gave curved plots, which can be analyzed as representing parallel deoxygenations of more than two geometrical isomers.⁷⁾ The last parts of these plots are linear with identical slopes to that of the fresh solution of sample B. The same isomer as that in sample B should be responsible at this stage. Namely the isomer in sample B decomposes at the smallest rate among the isomers. The contents of this isomer were estimated from the plots to be *ca.* 35 and 65% for the fresh and aged solutions of sample A, respectively. The initial rapid decomposition of the fresh solution of sample A gave a rate constant, $2.4\times10^{-3}\,\text{s}^{-1}$, about one order of magnitude greater than that of sample B.

Ligand Substitution Reaction. When sample B was dissolved in water ([B]=0.0006 M) containing 0.029 M ethylenediamine (en) (pH, 7.9 (ammonia buffer), I=0.05 M (NaCl)), the CD spectrum gradually disappeared without appreciable change in absorption spectrum. The first-order plot of the decrease in CD strength at 447 nm gave a straight line. The slope ($3.3\times10^{-4}\,\text{s}^{-1}$ at 39.8 °C) is almost identical with that for its deoxygenation under similar conditions. Thus en should replace the coordinated *R*-pn through rate-determining deoxygenation process. The formation of $[(\text{en})(\text{dien})\text{Co}^{\text{III}}(\mu\text{-O}_2{}^{(2-)})\text{Co}^{\text{III}}(\text{dien})(\text{en})]^{4+}$ from $[\text{Co}^{\text{II}}(\text{dien})(\text{en})(\text{H}_2\text{O})]^{2+}$ and O_2, as well as the ligand substitution at cobalt(II) state, should be rapid.

Mechanism of the Geometrical Isomerization. The deoxygenation occurs much more rapidly than the CD change in the solution of sample A. Thus, the geometrical isomerization can take place at labile cobalt(II) state which is in equilibrium with the μ-peroxo complex. Such a view is supported by the complete replacement of en for the coordinated *R*-pn with rate-determining deoxygenation.

Rate of the formation of μ-peroxo complexes from cobalt(II) complexes and O_2 are similar to one another (second-order rate constants, 10^5—$10^6\,\text{M}^{-1}\,\text{s}^{-1}$ at 25 °C) for even those with different ligands such as $[\text{Co}^{\text{II}}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+}$ and $[\text{Co}^{\text{II}}(\text{tetren})(\text{H}_2\text{O})]^{2+}$ (tetren= tetraethylenepentamine).⁸⁾ Thus the formation rates of the μ-peroxo complexes would not be significantly different among the geometrical isomers of $[\text{Co}^{\text{II}}(\text{dien})(R\text{-pn})(\text{H}_2\text{O})]^{2+}$. The initial product of the μ-peroxo complex, sample A, can be a mixture of various isomers. The small CD strength may result from the cancellation of CD spectra of various isomers. The deoxygenation rates are, on the other hand, significantly different among geometrical isomers (Fig. 2). Such a difference would result in the geometrical isomerization in the solution of sample A. Isomers with small deoxygenation rates should accumulate gradually to give thermally equilibrated isomer distribution, of which the deoxygenation pattern is represented by the curve (c) in Fig. 1.

The present results show that the deoxygenation rather than the formation rate is important in determining the stability of μ-peroxo complexes.

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5) EDTA represents variously protonated forms of ethylenediaminetetraacetate ion, $\text{H}_n\text{edta}^{(4-n)-}$, and is used when the degree of protonation need not to be specified.

6) An alternative possibility that sample B is composed of more than two isomers with identical deoxygenation rate, is much less likely.

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