The Dioxygen Carrier Properties of the Dicobalt–Obistren† Cryptate in Aqueous Solution

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Spectrophotometric studies of the oxygenation, deoxygenation, and degradation of the binuclear cobalt complex of the cryptand ligand obistren reveal that it is potentially an excellent reagent for chemical separation of oxygen from gaseous mixtures.

During the past several years there has been renewed interest in the use of dioxygen carriers for the chemical separation of dioxygen from other gases, and several metal chelate systems have been developed for this purpose.[1] The cobalt dioxygen complexes having polyamines as ligands have in general not been considered because of their very high stabilities and their tendencies to undergo oxidative attack of the co-ordinated

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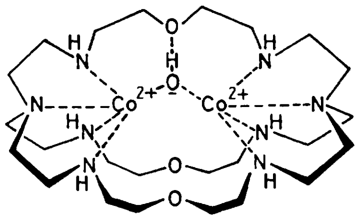
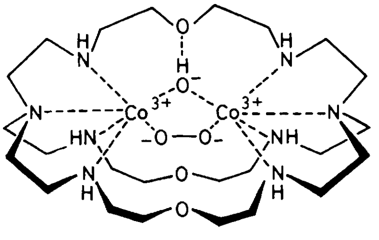
† Obistren = 7,19,30-trioxa-4,10,16,22,27,33-hexa-azabicyclo-[11,11,11]pentatriacontane.



(**1**) μ-Hydroxo-dicobalt obistren cryptate



(**2**) μ-Hydroxo-μ-peroxo dicobalt obistren cryptate

ligands by co-ordinated dioxygen.[2—4] It has been noted, however, that the dicobalt–obistren cryptate (**1**) forms a dioxygen complex (**2**) having an oxygenation constant which is more than three orders of magnitude lower than the value predicted by analogy with other cobalt(II) polyamine chelates.[5] It was therefore decided to study the effectiveness of (**1**) as an oxygen carrier. On the basis of the evidence presented here, this complex surprisingly ranks among the best of the dioxygen carriers reported thus far for oxygen separation.

Complex (**2**) has the intense charge transfer band at 380 nm characteristic of cobalt–polyamine–dioxygen complexes.[6] Yellow–brown dilute aqueous solutions of this complex (*ca.* 2×10^{-4} M) lose their colour on heating, but regain it on cooling. The u.v.–visible absorption spectra of the solutions of this complex between 25 and 75 °C are illustrated in Figure 1. The absorbance at 25.0 °C, together with its concentration calculated from stability data,[2,5] allowed calculation of its extinction coefficient as $6110\,\mathrm{dm^3\,mol^{-1}\,cm^{-1}}$. At 95 °C a solution of (**2**) showed virtually no absorbance due to the dioxygen complex, in a cell open to the atmosphere. Reduction of the temperature to 25.0 °C restored the original spectrum at its original intensity. In separate parallel experiments a 2×10^{-4} M solution of the dioxygen complex (**2**) was heated to 75 °C in a tightly sealed cell, with an air space above the solution. Again, the solution lost all its 380 nm absorbance at the high temperature but regained its full intensity when cooled. The cycle was repeated several times, with no measurable loss in the low-temperature absorbance.

The experimental evidence described above demonstrates reversibility of the oxygenation process during cycling of temperature. Reversibility resulting from decrease of equilibrium pressure of dioxygen was demonstrated at 25.0 °C. When purified nitrogen was bubbled through the solution for 12 h, about two-thirds of the original absorbance was lost. Subsequent treatment with pure dioxygen restored the spectrum to its full intensity.

It is well known that all dioxygen complexes undergo some type of degradation to form inert complexes. For (**2**) it was necessary to raise the temperature above 90 °C to detect a slow irreversible metal-centred degradation. The ultimate change of absorbance, illustrated in Figure 2, is essentially a conversion of the spectrum of (**1**) to that ot its $\mathrm{Co^{III}}$ analogue. Here only a trace of dioxygen complex is present. With time, this complex is gradually but completely converted to the corresponding binuclear $\mathrm{Co^{III}}$ complex (**3**) presumably with one or two hydroxo bridges; the reactions occurring in solution which give rise to the absorbance curves in Figure 2 are interpreted as reactions (1)—(3).

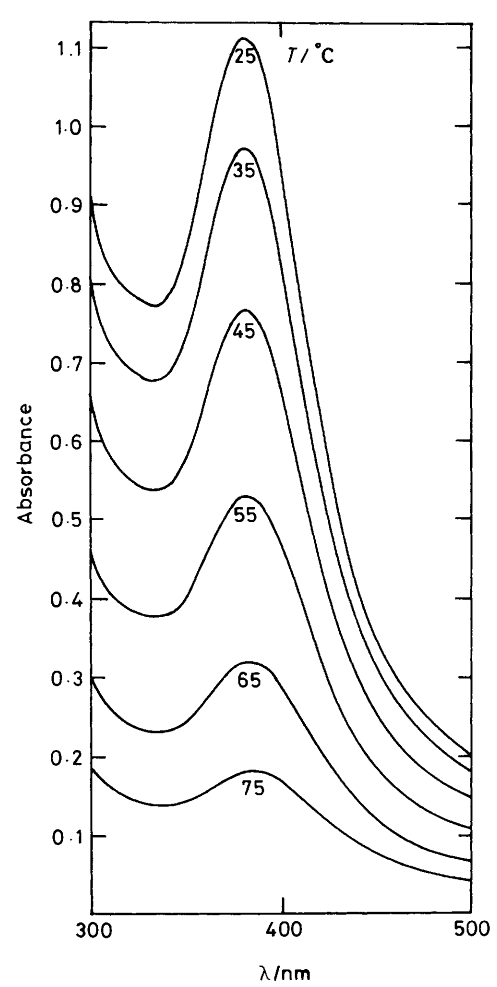


Figure 1. U.v.–visible absorbance spectra of the equilibrium system (**1**) + $O_2 \rightleftharpoons$ (**2**) for the temperatures (°C) indicated. [L] = 1/2[Co] = 2.00×10^{-4} M, $\mu = 0.100$ M (KCl); pH = 8.6.

$$\mathrm{Co_2(OH)(obistren)^{3+} + O_2 \overset{\text{fast}}{\rightleftharpoons} Co_2(OH)O_2(obistren)^{3+}} \tag{1}$$

$$\mathrm{Co_2(OH)O_2(obistren)^{3+} + 2H^+ \xrightarrow{\text{slow}} Co_2(OH)(obistren)^{5+} + H_2O_2} \tag{2}$$

$$\mathrm{H_2O_2 \rightarrow H_2O + 1/2O_2} \tag{3}$$

The initial absorbance curve of Figure 2 is that of the dinuclear cobalt(II) obistren cryptate (**1**) at 95 °C, and corresponds closely to the absorbance curve at 75 °C, illustrated in Figure 1. Thus the final spectrum in Figure 2 is that of the inert binuclear cobalt(III) complex, $\mathrm{Co_2(OH)(obistren)^{5+}}$, formed by irreversible metal-centred oxidation of the corresponding dioxygen complex (**2**). The cobalt(III) complex formed is inert and does not react with dioxygen. Neither does it dissociate in the presence of excess of concentrated HCl. The data represented by Figure 2 provide no information on the disproportionation of the hydrogen peroxide formed, but

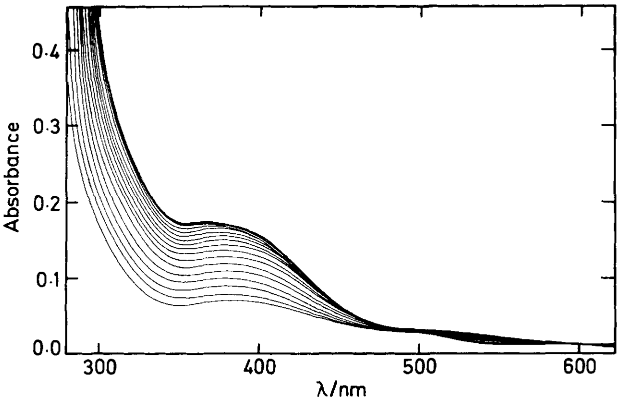


Figure 2. U.v.-visible absorbance curves (30 min apart) illustrating the autoxidation of $Co_2(OH)(L)^{3+}$ to $Co_2(OH)(L)^{5+}$ (with dioxygen complex as intermediate). L = obistren, [L] = 2.00×10^{-4} M; [Co] = 4.00×10^{-4} M; μ = 0.100 M (KCl); T = 95.0 °C; pH = 8.6; $P(O_2)$ = 0.0349 atm. First-order rate constant determined from plot of log of absorbance found to be $3.7 \times 10^{-5}\,s^{-1}$.

catalase-like activity of cobalt(II) complexes has been reported.[7] The binuclear cobalt(II) cryptate (**1**), its dioxygen complex (**2**), and its cobalt(III) analogue (**3**) are clearly characterized by their electronic absorption spectra illustrated in Figures 1 and 2. The dicobalt(III) cryptate is being investigated further to determine the number of hydroxo bridges in the complex.

The observation reported for the first time in this paper, that oxygen may be recycled with a binuclear cobalt(II) polyamine complex without detectable degradation to inert complexes, provides a new perspective on the potential of such complexes as oxygen carriers. So far, all reports on cobalt(II) polyamine complexes indicate that their dioxygen adducts undergo facile, and in some cases rapid, degradation to give inert oxidation product.[4,7,8] The only obstacle to widespread application for oxygen production is the expense of the ligand resulting from the multistep synthesis required for its preparation.[9,10] We are attempting to develop a less expensive synthetic method.

This research was supported by a research grant, A-259, from the Robert A. Welch Foundation. The authors thank Professor Ichiro Murase, Kyushu University, for synthesis of obistren, and Professor J.-M. Lehn, Universite Louis Pasteur, Strasbourg, for many helpful discussions.

Received, 7th March 1988; Com. 8/00891D

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