

### Conclusions

These results further illustrate the utility of thermochemically derived bond enthalpy data in understanding organotransition-metal bonding and reactivity patterns. In the present, archetypical early transition metal systems, it can be seen that many distinctive characteristics can be understood on the basis of the electropositive nature and redox properties of the metal centers vis-à-vis those of later transition elements.

**Acknowledgment.** We are grateful to the NSF for support of this research under grant CHE8306255. L.E.S. thanks Dow Chemical Co. for a fellowship. We thank Dr. G. E. Kellogg for assistance with some of the graphics.

**Registry No.** Cp<sub>2</sub>ZrCl<sub>2</sub>, 54039-38-2; Cp<sub>2</sub>ZrMe<sub>2</sub>, 67108-80-9; Cp<sub>2</sub>Zr(OH)<sub>2</sub>, 91294-93-8; Cp<sub>2</sub>ZrPh<sub>2</sub>, 79847-76-0; Cp<sup>+</sup>Zr(Ph)(η<sup>5</sup>-

CH<sub>2</sub>C<sub>5</sub>Me<sub>4</sub>), 105501-02-8; Cp<sub>2</sub>Zr(CO)<sub>2</sub>, 61396-31-4; Cp<sub>2</sub>Zr(H)(NH<sub>2</sub>), 91295-10-2; Cp<sub>2</sub>HfCl<sub>2</sub>, 85959-83-7; Cp<sub>2</sub>HfH<sub>2</sub>, 81956-87-8; Cp<sub>2</sub>HfI<sub>2</sub>, 92786-75-9; Cp<sup>+</sup>ZrMe<sub>3</sub>, 81476-64-4; Cp<sub>2</sub>ZrMe<sub>2</sub>, 12636-72-5; Cp<sub>2</sub>ZrI<sub>2</sub>, 1298-41-5; Cp<sub>2</sub>ZrH<sub>2</sub>, 61396-34-7; Cp<sup>+</sup>Zr(H)Ph, 112532-20-4; Cp<sup>+</sup>Zr(OH)Ph, 116436-94-3; Cp<sup>+</sup>ZrCH<sub>2</sub>CH<sub>2</sub>-o-C<sub>6</sub>H<sub>4</sub>, 116436-95-4; Cp<sup>+</sup>ZrCH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>, 116558-25-9; Cp<sup>+</sup>Zr(H)(O-*t*-Bu), 116436-96-5; Cp<sup>+</sup>Zr(Me)(OC<sub>6</sub>H<sub>5</sub>), 116436-97-6; Cp<sup>+</sup>ZrI<sub>2</sub>, 68209-12-1; Cp<sup>+</sup>Zr(OC<sub>6</sub>F<sub>5</sub>)<sub>2</sub>, 116436-98-7; Cp<sup>+</sup>Zr(OC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>, 116436-99-8; Cp<sup>+</sup>Zr(OCH<sub>2</sub>CF<sub>3</sub>), 116437-00-4; Cp<sup>+</sup>HfMe<sub>2</sub>, 116437-01-5; Cp<sup>+</sup>Hf(*n*-Bu)<sub>2</sub>, 116437-02-6; Cp<sup>+</sup>Hf(OC<sub>6</sub>F<sub>5</sub>)<sub>2</sub>, 116437-03-7; Cp<sup>+</sup>HfMe<sub>3</sub>, 113161-86-7; Cp<sup>+</sup>Hf(OC<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, 116437-04-8; Cp<sup>+</sup>HfCl<sub>3</sub>, 75181-08-7.

**Supplementary Material Available:** A table giving bond disruption enthalpy data used in deriving the present *D*(M-R) and *D*(M-L) results (1 page). Ordering information is given on any current masthead page.

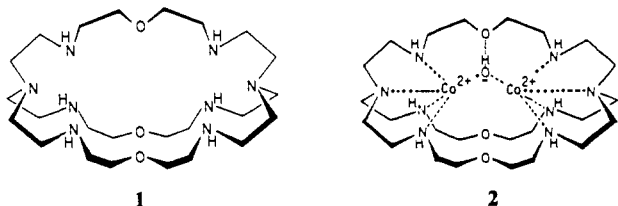
## Dicobalt-O-BISTREN Cryptate as a Reversible Dioxygen Carrier for Oxygen Separation and Transport

Ramunas J. Motekaitis and Arthur E. Martell\*

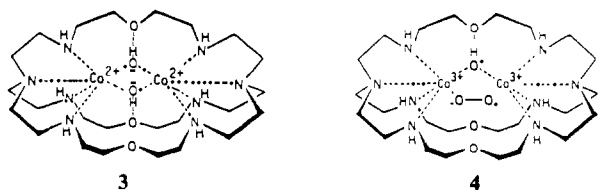
Contribution from the Department of Chemistry, Texas A&M University, College, Station, Texas 77843-3255. Received March 31, 1988

**Abstract:** Spectrophotometric studies of the dioxygen complex of the dicobalt-O-BISTREN cryptate have been carried out over the temperature range 25–95 °C. The dioxygen complex is nearly completely formed at low temperature and nearly completely dissociated at 95 °C. No degradation of the dioxygen complex to inert complexes was observed below 65 °C. At the highest temperature studied (95.0 °C), slow metal-centered degradation of the dioxygen complex to the inert binuclear cobalt(III) cryptate was observed. The facile formation and dissociation of the dioxygen complex from 35 to 75 °C indicates that the dicobalt(II) complex of O-BISTREN would be an effective and efficient oxygen carrier for oxygen separation and transport.

The binuclear cobalt(II) complex of the cryptand ligand O-BISTREN (1) was first prepared by Lehn et al.,<sup>1</sup> and its intensely colored brown dioxygen complex was mentioned in a review by Lehn.<sup>2</sup> The dioxygen complex was first prepared in aqueous



solution, and the corresponding dioxygen formation constants were reported by Motekaitis et al.<sup>3</sup> Potentiometric equilibrium studies, which resulted in the equilibrium constants listed in Table I, showed that the simple binuclear complex Co<sub>2</sub>(O-BISTREN)<sup>4+</sup> is never more than a minor species in aqueous solution but is further stabilized by hydroxide ion bridging, resulting in conversion to the major hydrolyzed species Co<sub>2</sub>(OH)(O-BISTREN)<sup>3+</sup> (2) and Co<sub>2</sub>(OH)<sub>2</sub>(O-BISTREN)<sup>2+</sup> (3) at neutral and high pH. The



(1) Lehn, J. M.; Pine, S. H.; Watanabe, E.; Willard, A. K. *J. Am. Chem. Soc.* 1977, 99, 6766.

(2) Lehn, J. M. *Pure Appl. Chem.* 1980, 52, 2441.

(3) Motekaitis, R. J.; Martell, A. E.; Lehn, J. M.; Watanabe, E. *Inorg. Chem.* 1982, 21, 4253.

**Table I.** Equilibrium Constants<sup>a</sup> for the O-BISTREN-Cobalt(II)-Dioxygen System

equilibrium quotient <sup>b</sup>	log <i>K</i>	equilibrium quotient <sup>b</sup>	log <i>K</i>
[HL <sup>+</sup> ]/[L][H <sup>+</sup> ]	9.89	[CoL <sup>2+</sup> ]/[Co <sup>2+</sup> ][L]	11.20
[H <sub>2</sub> L <sup>2+</sup> ]/[HL <sup>+</sup> ][H <sup>+</sup> ]	9.23	[Co <sub>2</sub> L <sup>4+</sup> ]/[Co <sup>2+</sup> ] <sup>2</sup> [L]	16.80
[H <sub>3</sub> L <sup>3+</sup> ]/[H <sub>2</sub> L <sup>2+</sup> ][H <sup>+</sup> ]	8.29	[CoLOH <sup>+</sup> ][H <sup>+</sup> ]/[CoL <sup>2+</sup> ]	-9.13
[H <sub>4</sub> L <sup>4+</sup> ]/[H <sub>3</sub> L <sup>3+</sup> ][H <sup>+</sup> ]	7.65	[Co <sub>2</sub> LOH <sup>3+</sup> ][H <sup>+</sup> ]/[Co <sub>2</sub> L <sup>4+</sup> ]	-7.20
[H <sub>5</sub> L <sup>5+</sup> ]/[H <sub>4</sub> L <sup>4+</sup> ][H <sup>+</sup> ]	6.64	[Co <sub>2</sub> L(OH)O <sub>2</sub> <sup>3+</sup> ]/[Co <sub>2</sub> L(OH) <sup>2+</sup> ][H <sup>+</sup> ]	1.20
[H <sub>6</sub> L <sup>6+</sup> ]/[H <sub>5</sub> L <sup>5+</sup> ][H <sup>+</sup> ]	6.01	[Co <sub>2</sub> LOH <sup>3+</sup> ] <sub>2</sub> P <sub>O<sub>2</sub></sub>	-8.80
		[Co <sub>2</sub> L(OH) <sub>2</sub> <sup>2+</sup> ][H <sup>+</sup> ]/[Co <sub>2</sub> L(OH) <sup>3+</sup> ]	

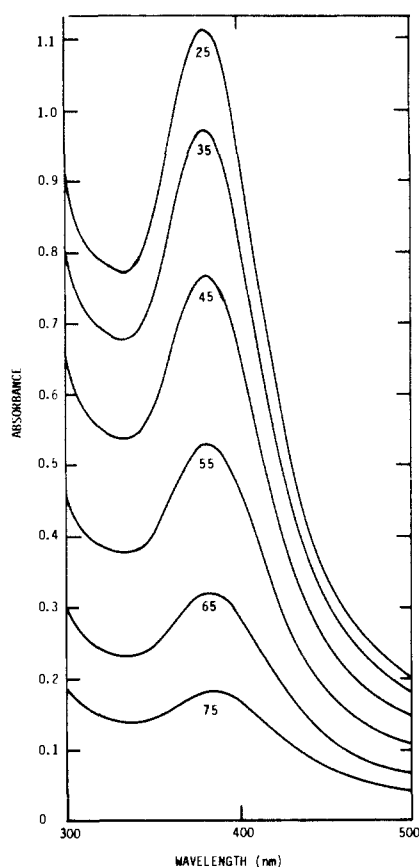
<sup>a</sup> *t* = 25.00 °C; *μ* = 0.100 M (KCl). <sup>b</sup> L = O-BISTREN.

dioxygen complex formed from 2 and 3 is the dibridged *μ*-hydroxo-*μ*-peroxy type, Co<sub>2</sub>(OH)(O<sub>2</sub>)(O-BISTREN)<sup>3+</sup> (4), having an unexpectedly low oxygenation constant (*K*<sub>O<sub>2</sub></sub> = [4]/[2]P<sub>O<sub>2</sub></sub> = 10<sup>1.2</sup> atm<sup>-1</sup>), compared to those of cobalt complexes of comparable polyamines such as the tetramine TREN itself.<sup>4</sup> The distribution curves in Figure 1 show that dioxygen complex 4 is nearly completely formed in aqueous solution, with a maximum concentration of approximately 90% at p[H] 8. At higher p[H] it dissociates and is completely replaced by the dihydroxo-bridged binuclear complex, 3. The exceptionally low stability of 4 was rationalized as the result of steric crowding of the dioxygen in the cryptate cavity.

During the past several years there has been much interest in dioxygen carriers for the chemical separation of oxygen from air and other gaseous mixtures, and several metal chelate systems have been developed for that purpose.<sup>5</sup> It has been noted<sup>6</sup> that

(4) Martell, A. E. *Acc. Chem. Res.* 1982, 15, 155.





**Figure 2.** UV-visible absorbance spectra indicating the extent of oxygenation of  $\text{Co}_2(\text{OH})\text{L}$  (2) as a function of temperature:  $T_L = 1/2 T_{\text{Co(II)}} = 2.00 \times 10^{-4} \text{ M}$ ;  $\mu = 0.100$  (KCl). Solutions are in equilibrium with air at the temperature indicated.

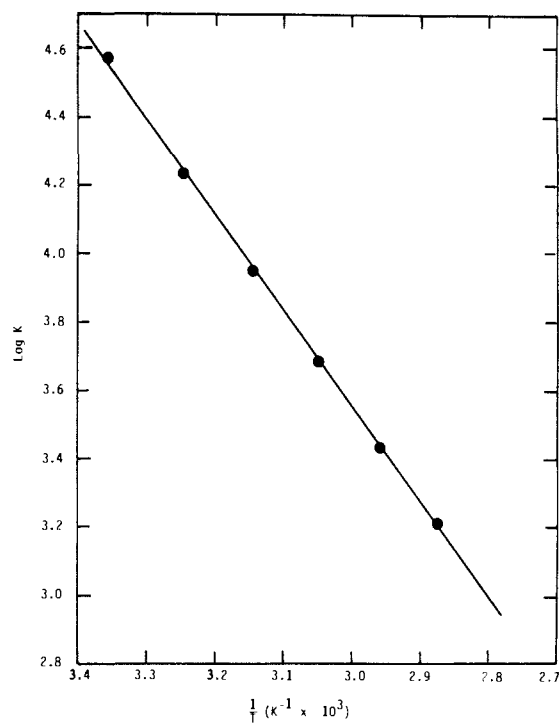
**Table II.** Oxygenation Constants of  $\text{Co}_2(\text{OH})(\text{O-BISTREN})$ ,  $K_{\text{O}_2}'$ , as a Function of Temperature

$t$ , °C	absorbance	$[\text{Co}_2(\text{OH})(\text{O}_2)\text{L}]$ , $10^4 \text{ M}$	$P_{\text{H}_2\text{O}}$ , Torr	$[\text{O}_2]$ , $10^4 \text{ M}$	$\log K';^a$ $\text{M}^{-1}$
25	1.106	1.358	23.75	2.56	4.57
35	0.962	1.181	42.2	2.17	4.23
45	0.759	0.932	71.9	1.87	3.94
55	0.515	0.645	118.0	1.56	3.68
65	0.318	0.390	187.5	1.29	3.44
75	0.178	0.218	289.1	1.02	3.22

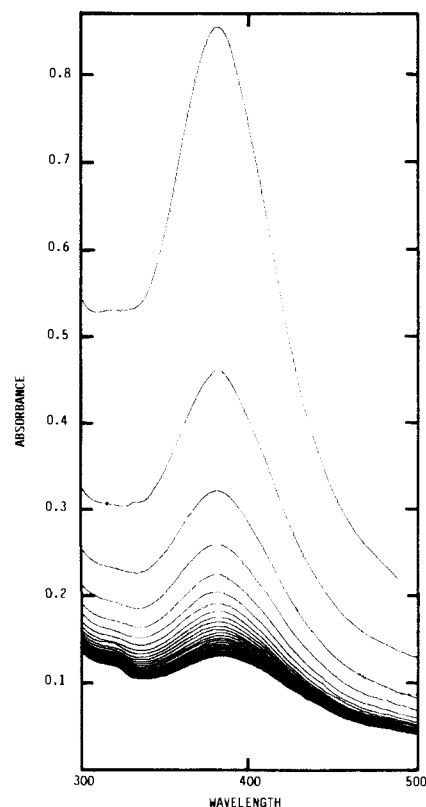
$$^a K' = [\text{Co}_2(\text{OH})\text{O}_2\text{L}] / [\text{Co}_2(\text{OH})\text{L}][\text{O}_2]$$

The thermodynamic parameters for the oxygenation reaction (1) were computed with the Arrhenius equation from the temperature coefficient of the values of  $\log K'$  listed in Table II. The linear plot obtained for the entire temperature range investigated is illustrated in Figure 3. The slope of the line corresponds to a  $\Delta H^\circ$  of  $-12.6 \text{ kcal/mol}$  and, at  $25^\circ \text{C}$ , a value of  $\Delta S^\circ$  of  $-30.4 \text{ eu}$ . These values reflect the strong thermal sensitivity of the reaction illustrated in Figure 2. The large negative value of  $\Delta S^\circ$  is characteristic of dioxygen complex formation, with contributions from two effects, the loss of translational entropy of the dioxygen molecule and the strengthening of the coordinate bonds to cobalt because of the increase in positive charge on the cobalt ions.

The rate of dissociation of the dioxygen complex 4 may be observed qualitatively in the spectral curves illustrated in Figure 4, which were obtained by placing a solution of the dioxygen complex 4, previously equilibrated with air at  $25^\circ \text{C}$ , into the sample compartment preheated to  $90^\circ \text{C}$ . The spectra were scanned at 1-min intervals. The result illustrated in Figure 4 shows a rapid, steady decrease in the intensity of the charge-transfer band at  $380 \text{ nm}$  as the sample warms to  $90^\circ \text{C}$ . The top curve is the initial absorbance at  $25^\circ \text{C}$ , while each of the successive lower curves represents a higher but indefinite solution temperature during the heating period. The changes in absorbance indicate



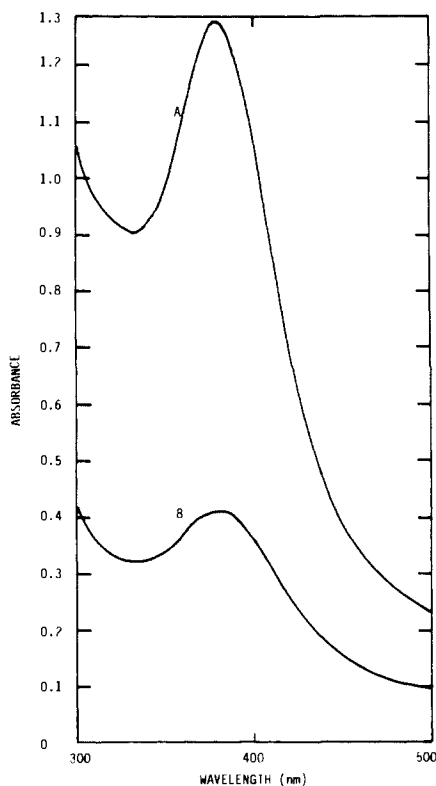
**Figure 3.** Arrhenius plot of  $\log K_{\text{O}_2}'$  (for equilibrium  $\text{Co}_2(\text{OH})\text{L}^{3+} + \text{O}_2 \rightleftharpoons \text{Co}_2(\text{OH})\text{O}_2\text{L}^{3+}$ ) vs reciprocal of the absolute temperature. The least-squares parameters are the following: slope 2798, intercept  $-4.84$ , and correlation coefficient 0.9995.



**Figure 4.** Changes in UV-visible absorbances with time as a solution of  $\text{Co}_2(\text{OH})\text{O}_2\text{L}$  under air saturation is heated from  $25.0$  to  $90.9^\circ \text{C}$  in a thermostated cell maintained at the latter temperature. Curves are 1 min apart; thermal equilibrium is achieved in approximately 20 min.

that the thermostated cell requires about 20–25 min to thermally equilibrate with its surroundings. During the warming period bubbles of dioxygen were observed rising to the surface of the solution.

Reversibility of the oxygenation reaction at room temperature was demonstrated for this system by successive air equilibration



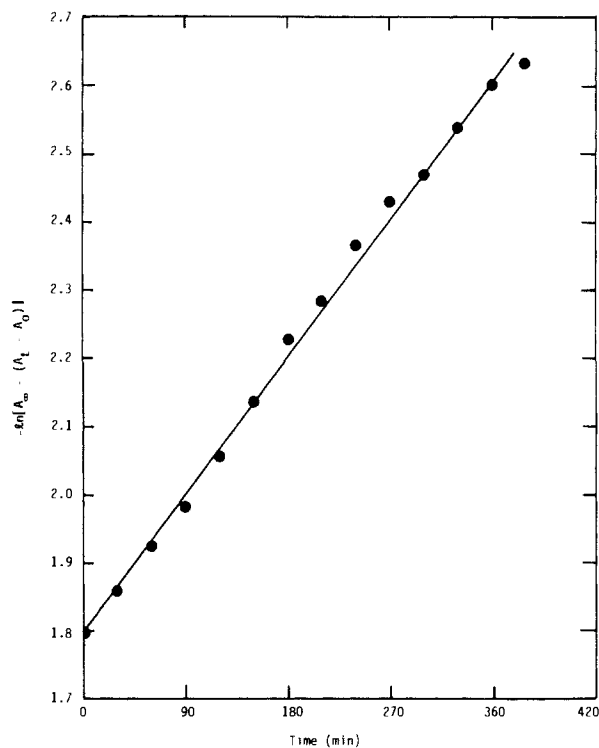
**Figure 5.** UV-visible absorbances at 25.0 °C for the equilibrium system  $\text{Co}_2(\text{OH})\text{L}^{3+} + \text{O}_2 \rightleftharpoons \text{Co}_2(\text{OH})\text{O}_2\text{L}^{3+}$  ( $[\text{Co}(\text{II})] = 2 \text{ L} = 1.0 \times 10^{-4} \text{ M}$ ,  $\mu = 0.100 \text{ (KCl)}$ ): A, under air saturation; B, after purging with nitrogen. Curve B was restored to curve A identically on resaturation with air.

**Table III.** Absorption Maxima of Binuclear O-BISTREN-Cobalt Complexes

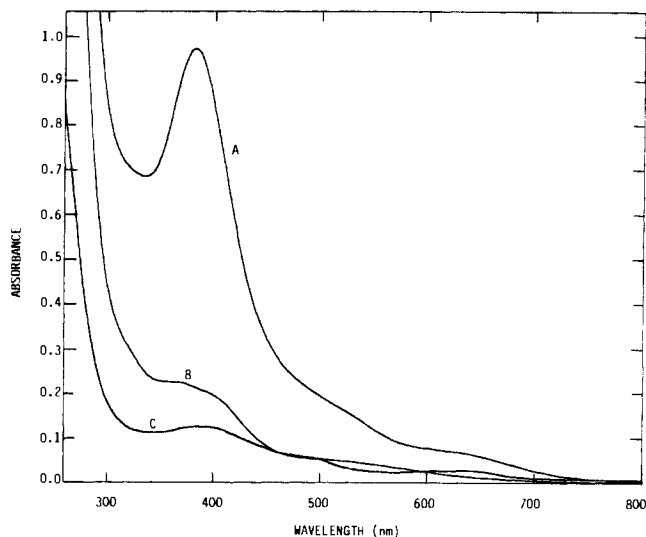
complex	absorbance maxima, nm
$\text{Co}_2(\text{OH})\text{O}_2\text{L}^{3+}$	380, 500, 620
$\text{Co}_2(\text{OH})\text{L}^{3+}$	368, 400, 520
$\text{Co}_2(\text{OH})\text{L}^{5+}$	390, 480, 650

and purging with nitrogen. The upper curve of Figure 5 shows the absorption of a  $1.0 \times 10^{-4} \text{ M}$  solution of the dioxygen complex formed by air saturation at 25 °C. After purified nitrogen was passed through this solution for 8 h, the absorption spectrum corresponded to the lower curve. Subsequent treatment with air restored the initial spectrum to an absorbance that was indistinguishable in magnitude from that of the original spectrum.

Irreversible degradation of the dioxygen complex **4** was observed above 90 °C. Measurement of the absorption spectrum at 95.0 °C shows slow increase of intensity at 380 nm. A solution maintained at 95.0 °C at this high temperature for an extended period of time does not absorb oxygen upon cooling, demonstrating the irreversible nature of the reaction. The first-order plot, illustrated in Figure 6, gives a rate constant of  $3.7 \times 10^{-5} \text{ s}^{-1}$ . It has already been shown (Figure 3) that the concentration of the dioxygen complex, **4**, at 95 °C is negligible and the absorbance observed initially is that of the cobalt(II) complex, **2** (at pH 8). The final absorbance corresponds to that of the binuclear monohydroxocobalt(III) complex, **5**, illustrated by curve B of Figure 7. The intensities, absorption bandwidths, and positions of absorption maxima of these complexes and of the dioxygen complex **4** differ widely. Approximate values of the band maxima are listed in Table III for these widely overlapping peaks. The characteristic differences in absorbances of the Co(II) and Co(III) complexes illustrated in Figure 7 provide additional proof that the degradation reaction occurring above at 95 °C is metal-centered oxidation of the binuclear cobalt(II) complex **2** to the corresponding cobalt(III) complex. Because of the fact that the reaction does not occur in the absence of dioxygen, the reaction must involve preequilibrium formation of the dioxygen complex **4**, which then un-

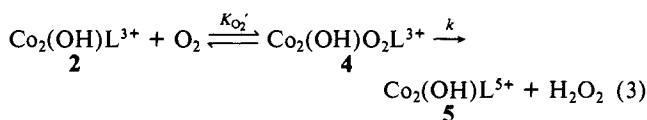


**Figure 6.** Pseudo-first-order rate plot for the irreversible oxidation reaction corresponding to the conversion of  $\text{Co}_2(\text{OH})\text{L}^{3+}$  to  $\text{Co}_2(\text{OH})\text{L}^{5+}$ :  $T_{\text{O-BISTREN}} = 2.00 \times 10^{-4}$ ;  $T_{\text{Co(II)}} = 4.00 \times 10^{-4}$ ;  $\mu = 0.100 \text{ M (KCl)}$ ;  $t = 95.0 \text{ °C}$ ;  $P_{\text{O}_2} = 0.0349 \text{ atm}$ .  $A_\infty$  is absorbance at  $t_\infty$ ,  $A_0$  is initial absorbance, and  $A_t$  is absorbance at time  $t$ . Least-squares treatment gave a slope of  $3.7 \times 10^{-5} \text{ s}^{-1}$ .



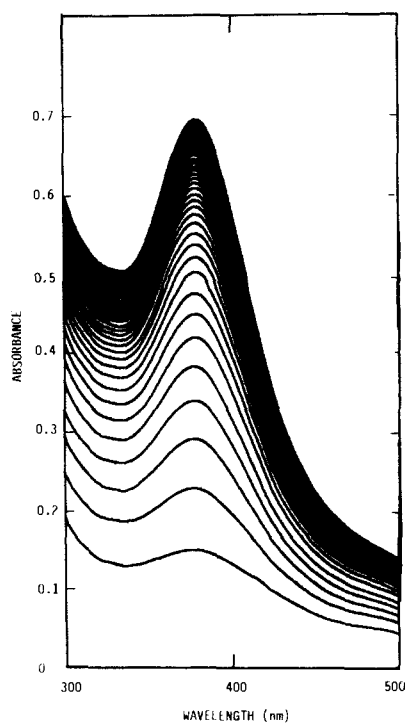
**Figure 7.** Absorbances of binuclear cobalt-O-BISTREN complexes: A, the peroxo- and hydroxo-bridged dicobalt(III)-O-BISTREN dioxygen complex,  $\text{Co}_2(\text{OH})\text{O}_2\text{L}^{3+}$  ( $\text{L} = \text{O-BISTREN}$ ); B, the hydroxo-bridged dicobalt(II)-O-BISTREN complex,  $\text{Co}_2(\text{OH})\text{L}^{3+}$ ; C, the hydroxo-bridged dicobalt(III)-O-BISTREN complex,  $\text{Co}_2(\text{OH})\text{L}^{5+}$  [ $t = 25.0 \text{ °C}$ ;  $\mu = 0.100 \text{ M (KCl)}$ ].

dergoes degradation in accordance with the reaction sequence in eq 3. The preequilibrium is rapid, forming only a trace of the



dioxygen complex **4**, and the rate constant for the degradation reaction may therefore be expressed by eq 4. The value of  $K_{\text{O}_2}'$

$$k_{\text{obs}} = K_{\text{O}_2}'k[\text{O}_2] \quad (4)$$



**Figure 8.** UV-visible absorbance spectra showing formation of the dinuclear cobalt(III)-O-BISTREN-dioxygen complex **4** as a function of time.  $T_L = 1/2 T_{Co} = 2.00 \times 10^{-4} M$ ;  $P_{O_2} = 0.21 \text{ atm}$ ;  $\mu = 0.100 M$  (KCl);  $t = 25.0 \text{ }^\circ\text{C}$ . The absorbances increase with time and were measured at 1.00-min intervals.

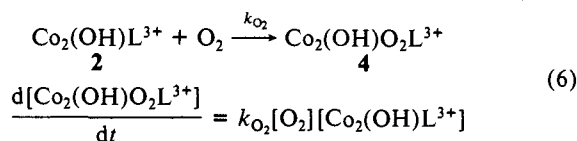
at  $95 \text{ }^\circ\text{C}$  may be obtained from the equilibrium studies described above. With the equilibrium concentration of dioxygen in contact with air at  $95 \text{ }^\circ\text{C}$ , the specific rate constant,  $k$ , for the disappearance of **2** is given by eq 5. The first-order specific rate

$$k = 3.7 \times 10^{-5} / 602 / 0.71 \times 10^{-4} = 8.6 \times 10^{-4} \text{ s}^{-1} \quad (5)$$

constant is considerably higher than the pseudo-first-order observed rate constant because of the very low equilibrium concentration of the dioxygen complex **4** at  $95 \text{ }^\circ\text{C}$ . Also, it is seen that the observed rate constant is second order, first order in the binuclear complex **2** and first order in dioxygen concentration.

The kinetics of formation of the dioxygen complex **4** at  $25 \text{ }^\circ\text{C}$  from the oxygen-free binuclear complex **2** was measured spec-

trophotometrically, and the resulting absorbance curves are illustrated in Figure 8. The rate equation for the oxygenation reaction may be expressed by eq 6. From a plot of  $\ln [4]/[O_2]$



vs time, a second-order line with a slope  $k_{O_2}([4]_0 - [O_2]_0)$  was obtained. After the differences in the initial concentrations were factored out from this expression, the rate constant  $k_{O_2}$  was found to be  $12.5 \text{ M}^{-1} \text{ s}^{-1}$ .

This investigation demonstrates the rapid interconversion of the monohydroxodicobalt(II)-O-BISTREN complex (**2**) and its dioxygen complex **4**. None of the binuclear cobalt(III) cryptate formed by irreversible degradation of **4** was observed from ambient temperature up to  $75 \text{ }^\circ\text{C}$ . The irreversibly oxidized product  $\text{Co}_2(\text{OH})\text{L}^{5+}$  (**5**) formed at high temperature is not involved in this interconversion, for all practical purposes, and therefore has negligible impact on the cycling of oxygenation and deoxygenation reactions.

The rapid rate of formation of the dioxygen complex at  $25.0 \text{ }^\circ\text{C}$ , described above, indicates that the rate of formation of the dioxygen complex **4** at elevated temperatures (ca.  $40\text{--}70 \text{ }^\circ\text{C}$ ) must be quite rapid. Also, the extensive decrease in the dioxygen complex at temperatures above ambient temperature shows that the rate of dissociation of **4** must also be rapid. Therefore, the reaction rates occurring in cycling of oxygenation and deoxygenation in aqueous solution in the  $40\text{--}70 \text{ }^\circ\text{C}$  range should in no way be rate limiting, and the cycling time should be dependent only on the mechanics of bringing the reactants together and separating them. These facts, together with the lack of any measurable degradation reaction in this temperature range, make the cobalt-O-BISTREN complex an ideal reagent for dioxygen separation and transport. For this purpose, it seems to be more efficient and effective than any oxygen carrier previously reported.

Further work on this system will involve equilibrium and kinetics of oxygenation and deoxygenation of solid binuclear cobalt complexes of O-BISTREN and alkyl derivatives of O-BISTREN, as well as systems in which O-BISTREN is covalently attached to solids and polymer molecules.

**Acknowledgment.** This investigation was supported by The Robert A. Welch Foundation under research Grant A-259.

**Registry No.** Oxygen, 7782-44-7.

## A Discrete Tetranuclear Complex of Niobium, $\text{Nb}_4\text{Cl}_{10}(\text{PMe}_3)_6$ , Related to the Local Structure in $\text{CsNb}_4\text{Cl}_{11}$

F. Albert Cotton\* and Maoyu Shang

Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, Texas 77843. Received April 15, 1988

**Abstract:** By reaction of  $\text{Nb}_2\text{Cl}_6(\text{THT})(\text{THF})_2$  with about a 2-fold molar ratio of Na/Hg in THF followed by addition of a moderate excess of  $\text{PMe}_3$ , the crystalline title compound is obtained. The molecule consists of two triangular  $\text{Nb}_3$  units fused to form a centrosymmetric rhombus with outer edge lengths of 2.904 (2) and 2.934 (1) Å and an internal shortest distance of 2.987 (2) Å. There are two capping Cl atoms on opposite sides of the  $\text{Nb}_4$  plane, a bridging Cl atom on each outer edge, and a set of ten terminal ligands consisting of four Cl atoms and six phosphine molecules. There are ten electrons available for cluster bonding and we assign five Nb-Nb single bonds. The Nb-Nb distances are similar to those in  $\text{Nb}_3$  clusters having Nb-Nb bond orders of unity. The principal crystallographic data are as follows: space group  $P2_1/n$ ,  $a = 10.673$  (5) Å,  $b = 13.582$  (4) Å,  $c = 17.972$  (6) Å,  $\beta = 96.16$  (3)°,  $V = 2590$  (1) Å<sup>3</sup>,  $Z = 2$ .

Recent work<sup>1</sup> in this laboratory has shown that it is possible to prepare trinuclear  $\text{Nb}_3$  and  $\text{Ta}_3$  cluster compounds containing

equilateral triangular metal atom clusters having one capping Cl atom, three edge-bridging Cl atoms, and an assortment of Cl and