Conclusions

These results further illustrate the utility of thermochemically derived bond enthalpy data in understanding organotransitionmetal 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.

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Registry No. $Cp'_{2}ZrCl_{2}$, 54039-38-2; $Cp'_{2}ZrMe_{2}$, 67108-80-9; $Cp'_{2}Zr(OH)_{2}$, 91294-93-8; $Cp'_{2}ZrPh_{2}$, 79847-76-0; $Cp'Zr(Ph)(\eta^{1}:\eta^{5}-\eta^{5})$

CH₂C₅Me₄), 105501-02-8; Cp'₂Zr(CO)₂, 61396-31-4; Cp'₂Zr(H)(NH₂), 91295-10-2; Cp'₂HfCl₂, 85959-83-7; Cp'₂HfH₂, 81956-87-8; Cp'₂HfI₂, 92786-75-9; Cp'ZrMe₃, 81476-64-4; Cp₂ZrMe₂, 12636-72-5; Cp₂ZrI₂, 1298-41-5; Cp'₂ZrH₂, 61396-34-7; Cp'₂Zr(H)Ph, 112532-20-4; Cp'₂Zr-(OH)Ph, 116436-94-3; Cp'₂ZrCH₂CH₂-o-C₆H₄, 116436-95-4; Cp'₂

 $ZrCH_2(CHEt)_2CH_2$, 116558-25-9; $Cp'_2Zr(H)(O-t-Bu)$, 116436-96-5; $Cp'_2Zr(Me)(OC_6H_5)$, 116436-97-6; Cp'_2ZrI_2 , 68209-12-1; $Cp'_2Zr-(OC_6F_5)_2$, 116436-98-7; $Cp'_2Zr(OC_6H_5)_2$, 116436-99-8; $Cp'_2Zr-(OCH_2CF_3)$, 116437-00-4; Cp'_2HfMe_2 , 116437-01-5; $Cp'_2Hf(n-Bu)_2$, 116437-02-6; $Cp'_2Hf(OC_6F_5)_2$, 116437-03-7; $Cp'HfMe_3$, 113161-86-7; $Cp'Hf(OC_6F_5)_3$, 116437-04-8; $Cp'HfCI_3$, 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

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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.,¹ and its intensely colored brown dioxygen complex was mentioned in a review by Lehn.² The dioxygen complex was first prepared in aqueous



solution, and the corresponding dioxygen formation constants were reported by Motekaitis et al.³ Potentiometric equilibrium studies, which resulted in the equilibrium constants listed in Table I, showed that the simple binuclear complex Co₂(O-BISTREN)⁴⁺ 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 Co₂(OH)(O-BISTREN)³⁺ (2) and Co₂(OH)₂(O-BISTREN)²⁺ (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^e for the O-BISTREN-Cobalt(II)-Dioxygen System

9.89	[CoL ²⁺]/[Co ²⁺][L]	11.20
9.23	$[C_{0}L^{4+1}]/[C_{0}L^{2+1}]^{2}[L]$	16.80
8.29	[CoLOH+][H+]/[CoL2+]	-9.13
7.65	$[C_{0},LOH^{3+}][H^{+}]/[C_{0},L^{4+}]$	-7.20
6.64	[Co ₂ L(OH)O ₂ ³⁺]/	1.20
6.01	$[C_{02}LOH^{3+}]P_{02}$	
	$[Co_{2}L(OH)_{2}^{2+}][H^{+}]/$	-8.80
	[Co ₂ L(OH) ³⁺]	
	9.89 9.23 8.29 7.65 6.64 6.01	9.89 $[C_0L^{2+}]/[C_0^{2+}][L]$ 9.23 $[C_0L^{4+}]/[C_0^{2+}]^2[L]$ 8.29 $[C_0LOH^+][H^+]/[C_0L^{2+}]$ 7.65 $[C_02LOH^{3+}][H^+]/[C_02L^{4+}]$ 6.64 $[C_02L(OH)Q_2^{3+}]/$ 6.01 $[C_02LOH^{3+}]P_{02}$ $[C_02L(OH)^{2+}][H^+]/$ $[C_02L(OH)^{3+}]$

 $^{a}t = 25.00 \text{ °C}; \mu = 0.100 \text{ M} (\text{KCl}). ^{b}L = \text{O-BISTREN}.$

dioxygen complex formed from 2 and 3 is the dibridged μ -hydroxo- μ -peroxo type, Co₂(OH)(O₂)(O-BISTREN)³⁺ (4), having an unexpectedly low oxygenation constant ($K_{O_2} = [4]/[2]P_{O_2} = 10^{1.2}$ atm⁻¹), compared to those of cobalt complexes of comparable polyamines such as the tetramine TREN itself.⁴ 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.⁵ It has been noted⁶ that

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



Figure 1. Distribution of species vs p[H] for the system containing a 2:1 molar ratio of cobalt(II) to O-BISTREN at 25.00 °C: $\mu = 0.100$ M (NaClO₄) under oxygen saturation; $T_L = 2.00 \times 10^{-4}$ M (L = O-BIS-TREN); $P_{O_2} = 1.00$ atm.

the dioxygen carriers considered good candidates for oxygen separation and transport (which requires repeated recycling between the oxygen-free complex and its oxygen adduct) are generally those that have low oxygenation constants. Such considerations prompted a closer look at the properties of the dicobalt complexes 2 and 3 as possible oxygen carriers for oxygen separation and recovery. Surprisingly, the dioxygen complex 4 was found to have all of the properties required for successful absorption and regeneration of dioxygen. This paper describes the properties of the O-BISTREN-dicobalt-dioxygen complex and the caracteristics that make it eminently suitable for this purpose.

Experimental Section

Materials. The O-BISTREN hexahydrobromide employed was synthesized by the method described previously⁷ by modification of the procedure of Dietrich et al.⁸ Inorganic materials, CoCl₂, and the supporting electrolyte, KCl, were reagent-grade chemicals and were used without further purification.

Spectrophotometric Studies. Absorbance measurements were carried out with a Perkin-Elmer Model 553 fast scan spectrophotometer, equipped with a thermostated cell compartment attached to a refrigerated constant-temperature bath with a variable-temperature control to maintain temperatures between 0 and 100 °C. Matched cells of 1.000-cm path length were used throughout, with the reference consisting of 0.100 M KCl.

The extinction coefficient of the dioxygen complex, obtained from the absorbance at 380 nm and its concentration, was calculated from the equilibrium data for oxygenation in Table I; concentrations of the dioxygen complex as a function of p[H] are indicated by the distribution curves in Figure 1.

Equilibrium Studies. The experimental solution employed for spectrophotometric equilibrium studies was prepared from 9.90 mg (0.01013 mmol) of O-BISTREN hexahydrobromide, 0.940 mL of 0.02151 M (0.0202 mmol) CoCl₂·6H₂O, 1.00 mL of 1.00 M KCl, and 44.06 mL of H₂O. The resulting solution was slowly neutralized over a 2-h period with 0.640 mL of 0.1104 M (0.0707 mmol) NaOH. Slow neutralization was necessary in order to prevent precipitation of Co(OH)₂ during the process. The resulting dilute solution was exactly 2.00×10^{-4} M in BISTREN and 4.00×10^{-4} M in Co(II) and contained enough base to form the bridging hydroxide indicated by 2 and 4. The pH was near 8.1.

All equilibria were measured by changes in the absorbance of the 380-nm peak of the dioxygen complex. Most measurements were performed with a loose cell cap, and the solutions were considered to be in equilibrium with air. At the higher temperatures investigated, the contributions of the partial pressure of water were taken into account in determining the partial pressure of oxygen in equilibrium with the oxygen carrier in solution. The equilibrium constants involving dioxygen employed in this research are expressed in terms of the molar concentrations of dioxygen in the experimental solutions. The solubilities of dioxygen were computed from published solubilities of dioxygen in water at various temperatures in equilibrium with pure O_2 at 1.00 atm, the vapor pressure of water as a function of temperature, and the fraction of dioxygen in air. In this research hydrogen ion concentrations were employed exclusively (i.e. $p[H] = -\log [H^+]$).

Kinetics. Two types of reaction kinetics were measured: the rates of reaction of the $(\mu$ -hydroxo)dicobalt(II)-O-BISTREN complex with dioxygen at room temperature and the irreversible oxidation of the $(\mu$ -hydroxo- μ -peroxo)dicobalt-dioxygen complex at high temperatures. The former was carried out by thoroughly degassing the solution of 2 until it was practically colorless. This was followed by rapid shaking with air at time zero. The rate of dioxygen complex formation was followed by measuring the absorbance of its intense charge-transfer absorption band at 380 nm as a function of time. The amount of dioxygen contained initially in the experimental solution was computed from the ultimate absorbance of the dioxygen complex formed using the oxygenation equilibrium constant (Table I).

The kinetics of irreversible degradation of the dioxygen complex 4 was measured by monitoring the increase of absorbance near 380 nm at 95 °C. Since the increase in absorbance was not large, corrections for unreacted Co(II) were applied to the readings.

Results and Discussion

The species distribution diagram for the dicobalt(II)–O-BIS-TREN system under constant dioxygen concentration as a function of p[H] (Figure 1) shows that the dioxygen complex 4 starts to form at p[H] 6.2, is half formed near p[H] 7.1, is near its maximum concentration (ca. 90% of 1.0×20^{-4} M) between p[H] 7.8 and 8.8, is reduced to half this concentration at p[H] 10.0, and finally has completely disappeared from solution at p[H] 12.0 and above. The formation and disappearance of the dioxygen complex are described by the equilibrium expressions 1 and 2.

$$Co_{2}(OH)L^{3+} + O_{2} = Co_{2}(OH)O_{2}L^{3+}$$

$$2 \qquad 4 \qquad (1)$$

$$K_{O_{2}} = 10^{1.20} \text{ atm}^{-1}$$

$$Co_2(OH)L^{3+} = Co_2(OH)_2L^{2+} + H^+$$
 $K = 10^{-8.80} M$ (2)
2

Dilute solutions of 4 (ca. 2×10^{-4} M) are yellow-brown; in preliminary experiments on thermal stability, the color was observed to disappear on heating and was restored on cooling. Further study of this phenomenon showed that at low and moderately elevated temperatures this thermochromism is completely reversible, and only above 90 °C does slow irreversible deterioration occur.

Figure 2 shows the UV-visible spectra of the solution of 4 as a function of temperature, from 25 to 75 °C in 10-deg intervals. The position of the absorption maximum remains at 380 nm with virtually no shift as the temperature is increased. When the solution is cooled, the original absorbance curves are regenerated, with a small amount of hysteresis depending on the time allowed for reequilibration with atomospheric dioxygen. The absorbance at 25.0 °C and the calculated degree of dioxygen complex formation were employed to calculate the spectroscopic molar absorbance of 4 as 6110 M⁻¹ cm⁻¹.

The solutions of the dioxygen complex 4 corresponding to the spectral curves of Figure 2 were carefully equilibrated at thermostated temperatures for at least 2 h in order to assure equilibrium. The observed thermochromic behavior was quantified by calculation of the oxygenation constants at each temperature. However, in order to factor out the effect of the variation of the solubility of dioxygen on the equilibrium, the oxygenation constants, K_{O_2} , are expressed in terms of molar concentration of dioxygen rather than the partial pressure of dioxygen in equilibrium with the solution containing the dioxygen complex. Also, the partial pressure of water vapor increases considerably at the higher temperatures, thus decreasing the concentration of dioxygen in the gaseous phase, with a corresponding decrease in the molar concentration of dioxygen in solution. This effect was also taken into account in determining oxygenation constants at elevated temperatures. The oxygenation constants thus obtained, corresponding to the temperatures indicated in Figure 2, are presented in Table II.

⁽⁵⁾ See, for example: Busch, D. H.; Pez, G. In Oxygen Complexes and Oxygen Activation by Transition Metals; Martell, A. E., Sawyer, D. T., Eds.; Plenum: New York, 1988.

⁽⁶⁾ Niederhoffer, E. C.; Timmons, J. H.; Martell, A. E. Chem. Rev. 1984, 84, 137.

⁽⁷⁾ Motekaitis, R. J.; Martell, A. E.; Murase, I. Inorg. Chem. 1986, 25, 938.

⁽⁸⁾ Dietrich, B.; Hosseini, J. W.; Lehn, J. M.; Sessions, R. B. Helv. Chim. Acta 1985, 68, 289.



Figure 2. UV-visible absorbance spectra indicating the extent of oxygenation of Co₂(OH)L (2) as a function of temperature: $T_L = \frac{1}{2}T_{Co(11)}$ = 2.00 × 10⁻⁴ M; μ = 0.100 (KCl). Solutions are in equilibrium with air at the temperature indicated.

Table II. Oxygenation Constants of $Co_2(OH)(O\text{-}BISTREN)$, K_{O_2}' , as a Function of Temperature

<i>t</i> , °C	absorb- ance	[Co ₂ (OH)(O ₂)L], 10 ⁴ M	P _{H2} O, Torr	[O₂], 10⁴ M	log K',ª 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

 ${}^{a}K' = [Co_{2}(OH)O_{2}L]/[Co_{2}(OH)L][O_{2}].$

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 ΔH° of -12.6 kcal/mol and, at 25 °C, a value of ΔS° of -30.4 eu. These values reflect the strong thermal sensitivity of the reaction illustrated in Figure 2. The large negative value of ΔS° 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 °C, into the sample compartment preheated to 90 °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 nm as the sample warms to 90 °C. The top curve is the initial absorbance at 25 °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 $\log K_{O_2}$ (for equilibrium $\operatorname{Co}_2(OH)L^{3+} + O_2 \approx \operatorname{Co}_2(OH)O_2L^{3+}$) 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 $Co_2(OH)O_2L$ under air saturation is heated from 25.0 to 90.9 °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 $Co_2(OH)L^{3+} + O_2 \Rightarrow Co_2(OH)O_2L^{3+}$ ([Co(II)] = 2 L = 1.0 × 10⁻⁴M, $\mu = 0.100$ (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		
Co ₂ (OH)O ₂ L ³⁺	380, 500, 620		
$Co_2(OH)L^{3+}$	368, 400, 520		
Co ₂ (OH)L ⁵⁺	390, 480, 650		

and purging with nitrogen. The upper curve of Figure 5 shows the absorption of a 1.0×10^{-4} 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 $Co_2(OH)L^{3+}$ to $Co_2(OH)L^{5+}$: $T_{O-BISTREN} = 2.00 \times 10^{-4}$; $T_{Co(11)} = 4.00 \times 10^{-4}$; $\mu = 0.100$ M (KCl); t = 95.0 °C; $P_{O_2} = 0.0349$ atm. A_{∞} is absorbance at t_{∞} , A_0 is initial absorbance, and A_t is absorbance at time t. Least-squares treatment gave a slope of 3.7×10^{-5} s⁻¹.



Figure 7. Absorbances of binuclear cobalt-O-BISTREN complexes: A, the peroxo- and hydroxo-bridged dicobalt(III)-O-BISTREN dioxygen complex, $Co_2(OH)O_2L^{3+}$ (L = Ω -BISTREN); B, the hydroxo-bridged dicobalt(II)-O-BISTREN complex, $Co_2(OH)L^{3+}$; C, the hydroxo-bridged dicobalt(III)-O-BISTREN complex, $Co_2(OH)L^{5+}$ [t = 25.0 °C; $\mu = 0.100 \text{ M} (\text{KCl})$].

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

$$Co_{2}(OH)L^{3+} + O_{2} \xrightarrow{Ao_{2}} Co_{2}(OH)O_{2}L^{3+} \xrightarrow{k} Co_{2}(OH)L^{5+} + H_{2}O_{2} (3)$$

dioxygen complex 4, and the rate constant for the degradation reaction may therefore be expressed by eq 4. The value of K_{O_2}' $k_{obs} = K_{O_2}' k[O_2]$ (4)



Figure 8. UV-visible absorbance spectra showing formation of the dicobalt-O-BISTREN-dioxygen complex 4 as a function of time. $T_{\rm L} = 1/_2 T_{\rm Co} = 2.00 \times 10^{-4}$ M; $P_{\rm O_2} = 0.21$ atm; $\mu = 0.1.00$ M (KCl); t = 25.0 °C. The absorbances increase with time and were measured at 1.00-min intervals.

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

$$k = 3.7 \times 10^{-5}/602/0.71 \times 10^{-4} = 8.6 \times 10^{-4} \,\mathrm{s}^{-1}$$
 (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 °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 °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 $\ln [4]/[O_2]$

$$\frac{\text{Co}_{2}(\text{OH})\text{L}^{3+} + \text{O}_{2} \xrightarrow{\text{NO}_{2}} \text{Co}_{2}(\text{OH})\text{O}_{2}\text{L}^{3+}}{4} \qquad (6)$$

$$\frac{\text{d}[\text{Co}_{2}(\text{OH})\text{O}_{2}\text{L}^{3+}]}{\text{d}t} = k_{\text{O}_{2}}[\text{O}_{2}][\text{Co}_{2}(\text{OH})\text{L}^{3+}]$$

vs time, a second-order line with a slope $k_{O_2}([\mathbf{4}]_0 - [O_2]_0)$ 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 M⁻¹ 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 °C. The irreversibly oxidized product $Co_2(OH)L^{5+}$ (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 °C, described above, indicates that the rate of formation of the dioxygen complex 4 at elevated temperatures (ca. 40–70 °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 occuring in cycling of oxygenation and deoxygenation in aqueous solution in the 40–70 °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.

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Registry No. Oxygen, 7782-44-7.

A Discrete Tetranuclear Complex of Niobium, Nb₄Cl₁₀(PMe₃)₆, Related to the Local Structure in CsNb₄Cl₁₁

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Abstract: By reaction of Nb₂Cl₆(THT)(THF)₂ with about a 2-fold molar ratio of Na/Hg in THF followed by addition of a moderate excess of PMe₃, the crystalline title compound is obtained. The molecule consists of two triangular Nb₃ 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 Nb₄ 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 Nb₃ 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) Å³, Z = 2.

Recent work¹ in this laboratory has shown that it is possible to prepare trinuclear Nb_3 and 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