prevent such interception[39d] are ill-founded, particularly where the trapping nucleophile is the solvent.[39a,d,g,i] We would stress that we by no means deny the participation of zwitterionic species in $O_2(^1\Delta_g)$ reaction pathways. We would, however, prefer to adopt an agnostic posture until definitive data are forthcoming. Current time-resolved experiments in these laboratories are concerned with the possibility of characterizing such species spectroscopically.

**Acknowledgment.** Support for this work came from SERC Grant GR/D 52169. M.C.S. thanks the University of Manchester for financial support.

**Registry No. 1**, 57-24-9; **2**, 280-57-9; **3**, 5471-63-6; **4**, 563-79-1; β-C, 7235-40-7; $O_2$, 7782-44-7; deuterium, 7782-39-0; 2-acetonaphthone, 93-08-3; protoporphyrin IX dimethyl ester, 5522-66-7.

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# Formation and Degradation of an Oxalato- and Peroxo-Bridged Dicobalt BISDIEN Dioxygen Complex. Binuclear Complexes as Hosts for the Activation of Two Coordinated Guests

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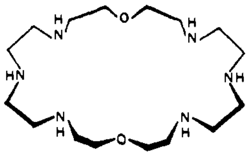
*Contribution from the Department of Chemistry, Texas A&M University, College Station, Texas 77843-3255.* *Received February 24, 1988*

**Abstract:** The rates of metal-centered degradation of the dioxygen adduct of the binuclear cobalt(II) complexes of 1,4,10,13,16,22-hexaaza-7,19-dioxacyclotetracosane (BISDIEN) have been measured, and first-order rate constants at 60 and 90 °C are reported. The binuclear cobalt(II) complex of BISDIEN, which is intrinsically unstable in solution, is strongly stabilized by coordination of oxalate ion, presumably as a bridging group between the metal centers. Thermodynamic parameters for oxalate binding to protonated forms of the free ligand and to its mono- and dicobalt complex are reported. It has now been found that the dioxygen complex of the dicobalt BISDIEN complex coordinates with and oxidizes a bridging oxalate anion, thus providing the first example of a redox reaction between two coordinated ligands within the cavity of a binuclear macrocyclic complex. Equilibrium data are reported for the formation of the triply bridged (μ-hydroxo, μ-peroxo, μ-oxalato) dicobalt BISDIEN complex, and its concentration has been determined as a function of pH. Rate constants reported for the first-order reaction of dioxygen with oxalate as coordinated entities within the binuclear macrocyclic complex indicate very strong catalysis of oxalate oxidation by molecular oxygen. The reaction proceeds readily at 45 °C, and its rate appears to be largely independent of pH.

It has been found[1] that the binucleating tendency of the macrocyclic hexamine ligand BISDIEN (1,4,10,13,16,22-hexaaza-7,19-dioxacyclotetracosane, BD, **1**) is relatively weak when compared to that of the cryptand O-BISTREN[2] (1,4,10,13,16,22,27,33-octaaza-7,19,30-trioxabicyclo[11.11.11]pentatriacontane, **2**). Because of the flexibility of its macrocyclic ring, BISDIEN forms 1:1 complexes with first-row divalent transition-metal ions in which from four to six nitrogen donors are coordinated to the metal ion. Because of its greater degree of preorganization, O-BISTREN (**2**) tends to form binuclear complexes even when the composition of the reaction solution favors 1:1 stoichiometry.[2] The tendency of BISDIEN to form binuclear complexes is greatly strengthened by combination of its metal complexes with appropriate bridging groups, such as imidazole with Cu(II) to form **3**[1,3] and dioxygen with Co(II) to form the peroxo-bridged complex **4**. The oxygenation constant of the dicobalt(II)-BISDIEN complex is nearly 3 orders of magnitude greater than that of dicobalt(II)-O-BISTREN (**5**; Table I), in spite of the larger number of basic nitrogen donors to cobalt(II) for the latter complex (log *K*'s for oxygenation of



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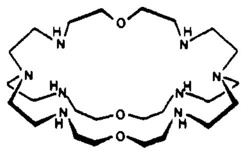

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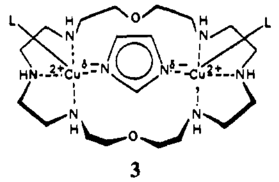

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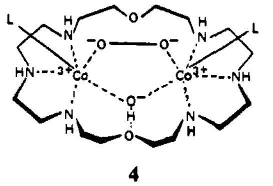

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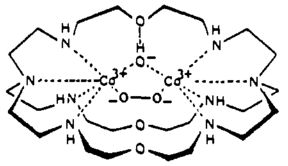
**Table I.** Equilibrium Constants for the Formation of Dioxygen Complexes of Dicobalt–BISDIEN and Dicobalt–BISTREN Complexes in Aqueous Solution

| | log *K* | |
|---|---|---|
| equilibrium quotient | BISDIEN[a] | BISTREN[b] |
| $[HL]/[L][H]$ | 9.62 | 9.99 |
| $[H_2L]/[HL][H]$ | 8.87 | 9.02 |
| $[H_3L]/[H_2L][H]$ | 8.28 | 7.98 |
| $[H_4L]/[H_3L][H]$ | 7.62 | 7.20 |
| $[H_5L]/[H_4L][H]$ | 3.79 | 6.40 |
| $[H_6L]/[H_5L][H]$ | 3.31 | 5.67 |
| $[Co_2L]/[Co]^2[L]$ | 12.4 | 16.8 |
| $[Co_2L(O_2)OH][H]/[Co_2L]P_{O_2}$[c] | −3.29 | −6.00 |
| $[Co_2L(O_2)(OH)_2][H]/[Co_2L(O_2)OH]$ | −8.25 | |
| $[Co_2L(O_2)(OH)_3][H]/[Co_2L(O_2)(OH)_2]$ | −9.36 | |

[a] 0.10 M KCl, 25.0 °C. [b] 0.10 M $NaClO_4$, 25.0 °C. [c] Units are $M \cdot atm^{-1}$.



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cobalt(II) complexes usually vary linearly with the basicities ($\sum pK$'s) of the donor groups coordinated to cobalt(II)[4]). This unexpected result was ascribed to steric crowding of dioxygen in the cavity of the binuclear cobalt(II)-O-BISTREN cryptate.[2,5] Careful inspection of the formula suggested for the dioxygen complex **4**, formed from the dinuclear cobalt-BISDIEN complex, indicates that each metal ion is probably bound to a coordinated water molecule, which may be replaced by another (more basic) ligand or which may serve as the site of hydrolysis of the coordinated water (hydrogen ion dissociation) to form mono- and dihydroxo complexes, as indicated by formula **4** and the corresponding data in Table I. In view of these open coordination sites in the binuclear macrocyclic dioxygen complex, it seemed logical to investigate the properties of analogous dioxygen complexes containing coordinated bifunctional reducing bridging groups, which may react with activated dioxygen. As a first step in the study of systems containing both coordinated dioxygen and a coordinated reductant within the cavity of a macrocyclic complex, it was decided to study the coordination of the oxalate anion with the dioxygen complex **4** and determine its rate of oxidation by the coordinated dioxygen.[6] This paper describes the equilibrium and kinetics of the formation and reactions of the ($\mu$-oxalato)-dicobalt(II)-BISDIEN-dioxygen complex.

## Experimental Section

**Materials.** The sample of BISDIEN employed is the same as that used for the research previously reported on this ligand.[1] It was provided by J. M. Lehn and co-workers and synthesized by the method previously described.[7,8] The oxalic acid, potassium chloride (supporting electrolyte), and cobalt(II) nitrate were reagent-grade materials and were used without further purification. A stock solution of reagent-grade cobalt(II) nitrate was prepared in double-distilled water and was standardized by potentiometric titration with EDTA. The acid forms of the ligand were titrated with carbonate-free solutions of 0.100 M KOH, prepared with Dilut-it ampules, and standardized with potassium acid phthalate.

**Potentiometric Equilibrium Measurements.** Potentiometric studies of BISDIEN in the absence and presence of cobalt(II), dioxygen, and oxalate were carried out with a Corning Model 150 research pH meter fitted with blue-glass and calomel reference electrodes calibrated with standard HCl and KOH solutions to read $-\log [H^+]$ directly. The temperature was maintained at 25.00 ± 0.05 °C, and the ionic strength was adjusted to 0.100 M by the addition of KCl. The concentrations of the experimental solutions were approximately 0.001 M in BISDIEN and 0.0020 M in Co(II), with a slight (ca. 1%) excess of the macrocycle. The ternary systems containing BISDIEN, Co(II), and oxalate were studied at molar ratios of 1:2:1. All systems were studied under anaerobic conditions, established by a stream of purified nitrogen, and under oxygen saturation maintained by a stream of purified oxygen. Experimental runs were carried out by adding increments of standard base to a solution containing the acid (hexahydrochloride) form of the macrocycle plus other components, as appropriate, so that 50 or more equilibrium data points were obtained per run.

**Gas Chromatography.** The formation of $CO_2$ was detected with a Perkin-Elmer Model 8410 gas chromatograph (TC detector, He 20 mL/min) utilizing a 6-ft SS carbosphere packed 80/100-mesh column run at 125 °C. Typically, 50-mL sample solutions of $BDCo_2O_2Ox^{2+}$ complex at pH 7.5 were heated for 2 h at 45 °C in a septum-capped vessel of 100-mL capacity. To each vessel was introduced 0.5 mL of concentrated $H_2SO_4$ and the vessel was shaken for 15 min before the gas was sampled with a 1.0-mL Dynatech gas syringe Model PS A-2 with built-in valve. Detection time was 5.22 min for $CO_2$. Background calibration was achieved by utilizing identical methodology but leaving out the oxalate. The background $CO_2$ in the calibration run was subtracted from the sample chromatographs.

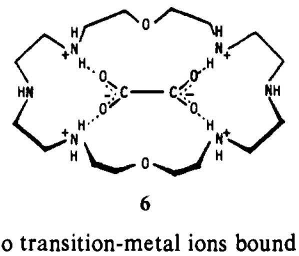
**Computations.** The proton association constants and Co(II)-binding constants of BISDIEN and O-BISTREN have been reported earlier.[1,2] For determination of oxalate binding to the binuclear (dicobalt) BISDIEN macrocycle, it was necessary to first determine the anion-binding constants of oxalate to protonated forms of BISDIEN in the absence of metal ion. This determination was carried out directly from potentiometric titrations by analyzing the differences between pH profiles of BISDIEN in the presence and absence of oxalate ions with the aid of the program BEST.[10] Protonation constants in the absence of the anion of interest were calculated with the aid of the program PKAS.[9] The equilibrium constants with metal ions at the appropriate ratios described above were also obtained with the aid of the program BEST.[10] The input for the program BEST consists of entering the millimoles of each component, the titration variables, the initial estimates of equilibrium constants of each species thought to be formed from the solution components, and the experimentally determined profiles of pH vs solution composition. The program sets up mass balance equations for all species present at each increment of base added and solves for the concentration of each species present. Magnitudes of the equilibrium constants are varied systematically in order in minimize the weighted squares of the differences between calculated and observed values of pH. The error estimates are reported as measures of the pH fit over the entire potentiometric pH profile. Considerable care was taken to not "invent" additional species for the purpose of improving the fit to the experimental data. The species introduced are those that can be justified on the basis of established principles of coordination chemistry in solution.

**Table II.** log Oxalate Formation Constants with BISDIEN and Co(II)-BISDIEN Complexes (25.0 °C, $\mu$ = 0.100 M)

| quotient | *Q* values | | |
|---|---|---|---|
| | $Cu^{2+}$ | $Co^{2+}$ | other |
| $[MLHOx]/[MLH][Ox]$ | 3.33 | 4.36 | |
| $[MLH_2Ox]/[MLH_2][Ox]$ | 3.76 | 6.50 | |
| $[MLH_3Ox]/[MLH_3][Ox]$ | 5.29 | | |
| $[MLH_4Ox]/[MLH_3Ox][H]$ | 3.25 | | |
| $[M_2LOx]/[M_2L][Ox]$ | 5.79 | 9.06 | |
| $[M_2L(OH)Ox]/[M_2L(OH)][Ox]$ | 3.18 | | |
| $[H_6LOx]/[H_6L][Ox]$ | | | 4.68 |
| $[H_5LOx]/[H_5L][Ox]$ | | | 3.59 |
| $[H_4LOx]/[H_4L][Ox]$ | | | 2.06 |

## Results

The equilibrium constants (log *K* values) obtained for the binding of the oxalate anion to BISDIEN in the presence and absence of Cu(II) and Co(II) ions are presented in Table II. It is seen that, in the absence of metal ions, potentiometric data provide evidence for the binding of oxalate to only the tetra-, penta-, and hexaprotonated forms of BISDIEN. In accordance with the suggested nature of the binding of other anions to protonated forms of O-BISTREN,[2] it seems that the binding of oxalate to protonated BISDIEN must be through hydrogen bonding to the protonated, positively charged amino nitrogens of the macrocycle. Thus, the strength of binding decreases as the number of hydrogen bonds producing protonated nitrogens is decreased from the maximum value of six to four, below which oxalate binding is too weak for detection through the lowering of the p*K*'s of the amino groups. Formula **6** is a schematic representation of the nature of the hydrogen-bonding interactions that produce oxalate binding.



**6**

With one or two transition-metal ions bound to BISDIEN, it is seen that various oxalate-bound complex species are formed (Table II). For the mononuclear complexes, oxalate binding is visualized as bridging between a metal ion coordinated to a diethylenetriamine moiety and protonated amino groups at the opposite side of the macrocycle, as indicated by **7**. With two metal

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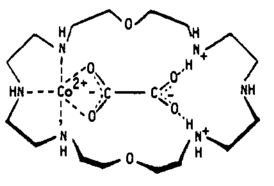

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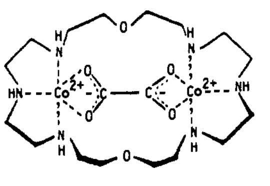

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ions coordinated by BISDIEN, oxalate is strongly bound and is thought to occupy a bridging position between the metal ions, **8**. Thus, oxalate binding in both mononuclear and binuclear BISDIEN complexes may be considered to occur in the manner previously suggested for halide ion bridging in mononuclear and binuclear Cu(II) O-BISTREN cryptates.[11,12] The strength of binding of oxalate to the mononuclear complexes is seen to increase with the number of protonated amino groups available for hydrogen bonding. In the case of the tetraprotonated monocopper(II) complex, the considerable decrease of oxalate binding strength for $MLH_4Ox$ (Table II) is significant, in view of the fact that four of the amino groups are protonated, leaving only two basic amino groups to coordinate Cu(II). In this case the oxalate anion may be coordinated to a single Cu(II) ion in a chelate fashion rather than function as a bridging group across the macrocyclic ring. Also, it is interesting that oxalate does not bridge (or rather does not bridge strongly) between Co(II) and three protonated amino groups on the opposite side of the macrocyclic ring, contrary to expectations. Explanation for this behavior, and the low oxalate affinity of the tetraprotonated mononuclear Cu(II)–BISDIEN complex, must await structural evidence for these interesting complexes.

The binding of oxalate to BISDIEN in the absence of metal ions as a function of pH is illustrated in Figure 1, which shows the complex of the hexaprotonated macrocycle to be a major species between pH 2 and 4. At higher pH the oxalato complexes of the pentaprotonated ligand and of the tetraprotonated ligand, **6**, become successively more minor solution constituents and disappear completely above pH 8. For binuclear metal ion systems the binding of oxalate is much stronger. In acid solution the oxalato complex of Co(II) is a major species (Figure 2), along with minor concentrations of the oxalato complex of the protonated ligand and of the diprotonated mononuclear complex. At pH 6, however, the metal complex species are largely converted to the oxalato-bridged binuclear complex, **8**, which becomes the only species present in solution at pH 8 and above. The strong binding of oxalate anion in the binuclear cobalt–O-BISTREN complex is indicated by failure of the complex to hydrolyze at higher pH by the addition of a bridging hydroxide anion or by displacement of bridging oxalate by one (or more) bridging hydroxide ions.

**Dioxygen Complexes.** It has been shown[1,2] that the dicobalt–BISDIEN–dioxygen complex (**4**) is much more stable than the corresponding dioxygen complex of O-BISTREN, in spite of the fact that the latter has the larger number of basic amino groups. For Co(II) complexes of open-chain and flexible polyamines and polyamino acids, dioxygen affinity, measured by log $K_{O_2}$, varies linearly with the basicities of the coordinated donor groups of the ligands, as measured by $\sum pK$'s. The reversal of this tendency for O-BISTREN and BISDIEN was rationalized[1] on the basis of probable steric crowding of coordinated $O_2$ in the cryptate cavity.

The differences in the stabilities and the nature of the dioxygen complexes formed by the binuclear cobalt O-BISTREN cryptate and by the corresponding BISDIEN complex may be seen in the species distribution curves in Figures 3 and 4. Under an oxygen pressure of 1 atm, the hydroxo- and peroxo-bridged dicobalt O-BISTREN cryptate is the major complex in solution between pH 7 and 10, but above pH 10 the dioxygen is displaced by a second bridging hydroxide anion to form the hydroxo-bridged species ($Co_2(OH)L$ and $Co_2(OH)_2L$). In the case of BISDIEN, however, the dicobalt hydroxo- and peroxo-bridged dioxygen complexes are virtually the only complexes formed in solution. The mono-hydroxo-bridged form becomes the major species at approximately pH 6.5 and predominant up to pH 8, above which it is converted to the dihydroxo and trihydroxo forms, $Co_2O_2$(O-

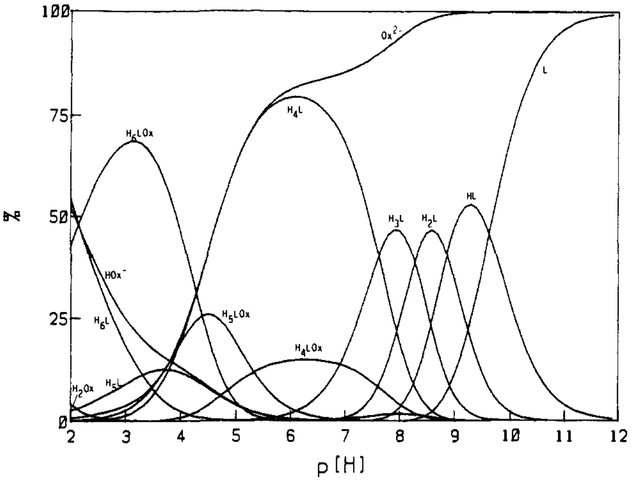

**Figure 1.** Distribution of species formed from oxalate and BISDIEN as a function of pH; [oxalate] = [BISDIEN] = 0.100 M, at 25.0 °C, $\mu$ = 0.100 M under nitrogen.

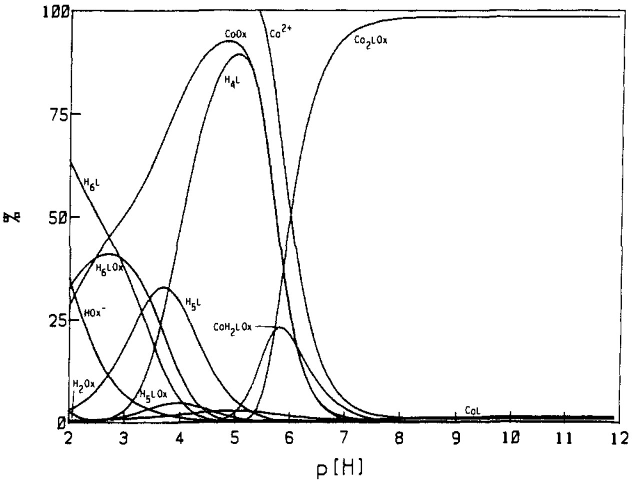

**Figure 2.** Distribution of species as a function of pH for a solution containing a 1:1:2 molar ratio of oxalic acid–BISDIEN–cobalt(II) at 25.0 °C, $\mu$ = 0.100 M under nitrogen; [BISDIEN] = 0.001 00 M.

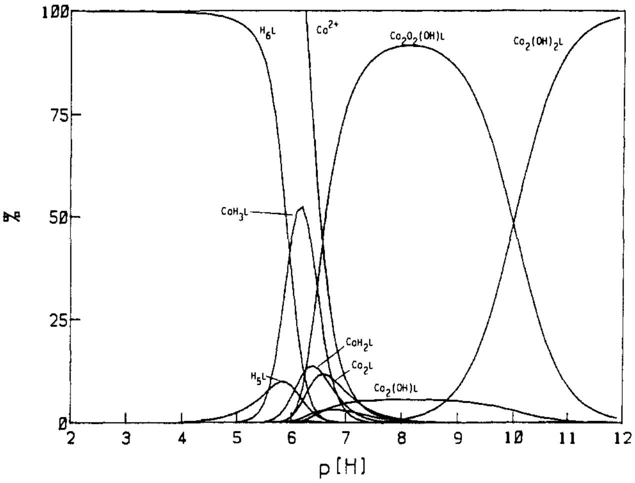

**Figure 3.** Distribution of species as a function of pH for a solution containing a 1:2 molar ratio of BISTREN–cobalt(II) at 25.0 °C, $\mu$ = 0.100 M under 1.00 atm oxygen; [BISTREN] = 0.001 00 M.

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[12] Motekaitis, R. J.; Martell, A. E.; Murase, I. *Inorg. Chem.* **1986**, *25*, 938.

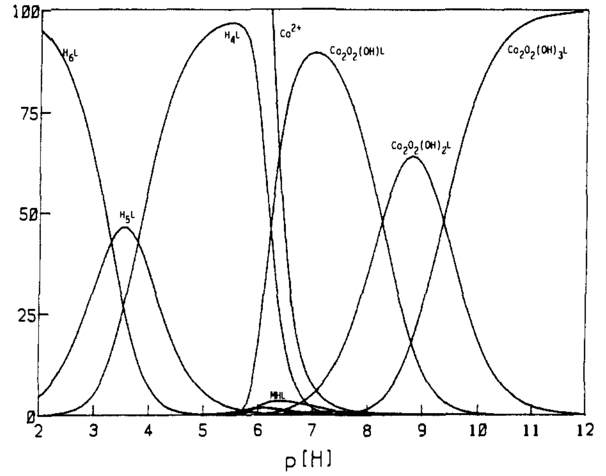


**Figure 4.** Distribution of species as a function of pH for a solution containing a 1:2 molar ratio of BISDIEN–cobalt(II) at 25.0 °C, $\mu$ = 0.100 M under 1.00 atm oxygen; [BISDIEN] = 0.001 00 M.

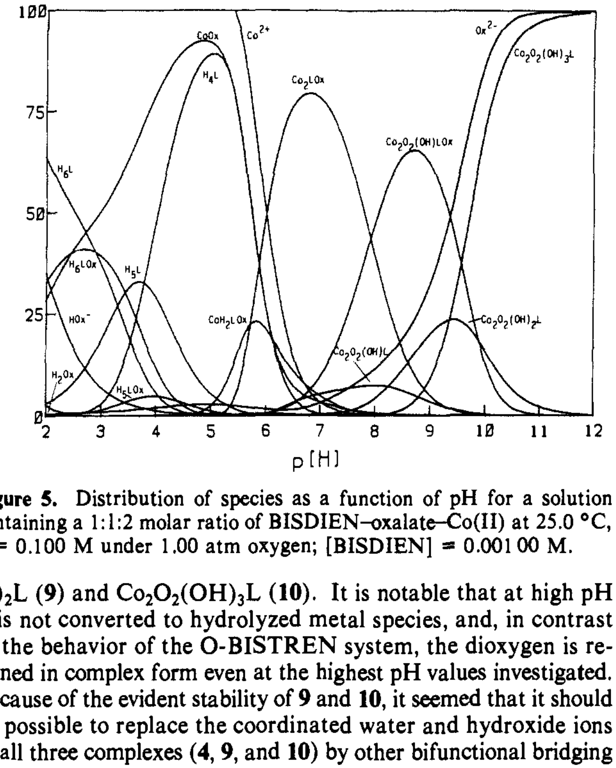


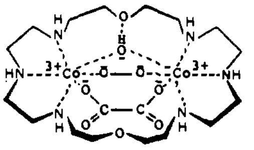
**Figure 5.** Distribution of species as a function of pH for a solution containing a 1:1:2 molar ratio of BISDIEN–oxalate–Co(II) at 25.0 °C, $\mu$ = 0.100 M under 1.00 atm oxygen; [BISDIEN] = 0.001 00 M.

$H)_2L$ (**9**) and $Co_2O_2(OH)_3L$ (**10**). It is notable that at high pH it is not converted to hydrolyzed metal species, and, in contrast to the behavior of the O-BISTREN system, the dioxygen is retained in complex form even at the highest pH values investigated. Because of the evident stability of **9** and **10**, it seemed that it should be possible to replace the coordinated water and hydroxide ions in all three complexes (**4**, **9**, and **10**) by other bifunctional bridging donor groups having suitable dimensions. It was therefore decided to investigate oxalate binding to these complexes.

**Oxalato-Bridged Dioxygen Complexes.** Potentiometric investigation of the dicobalt–BISDIEN–dioxygen complex in the presence of oxalate ion resulted in the determination of the equilibrium constant

$$[Co_2L(OH)OxO_2][H^+]/[Co_2LOx]P_{O_2} = 10^{-7.92}\ M\ atm^{-1}$$

This value, together with the appropriate equilibrium constants listed in Table II, gave the species distribution curves illustrated in Figure 5. Here, the distribution of complex species below pH 6.5 is similar to that observed in the absence of dioxygen (Figure 2). However, the mixed oxalato-, dioxygen-, and hydroxo-bridged binuclear dicobalt complex (**11**) begins to grow in between pH 6 and 7, becomes equivalent to the hydroxo-bridged dioxygen complex **4** at pH 8, and is the predominant (ca. 80%) metal complex in solution in the range pH 8–9.5. At higher pH the oxalato bridging donor group is displaced from the binuclear site by hydroxide ion, to form complexes **9** and **10**, which are the high pH forms of the dioxygen complex in the absence of oxalate ion.



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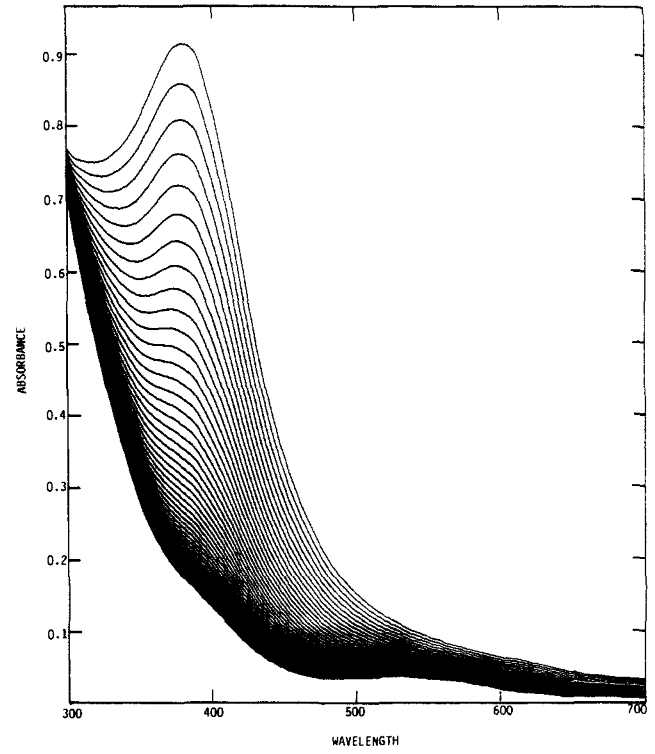


**Figure 6.** Absorption spectra illustrating the degradation of BISDIEN-dicobalt(II)–dioxygen complex at 60 °C; $\mu$ = 0.100 M KCl. $[BISDIEN]_{total} = 1.957 \times 10^{-4}$ M; pH 7.28.

**Degradation of Dioxygen Complexes.** The cobalt–BISDIEN–dioxygen complex (**4**) was found to undergo metal-centered degradation to the cobalt(III) complex of the unchanged ligand and hydrogen peroxide at a conveniently measurable rate at 60 °C. The reaction rate was followed quantitatively by the measurement of absorbance, $A$, as a function of time, whereby the intense charge-transfer band is seen (Figure 6) to be converted to the relatively weak band of the binuclear cobalt(III) complex $Co_2(OH)L^{5+}$. Plots of $-\log (A - A_\infty)$, at 380 nm vs time at 60 °C, gave a straight line showing first-order behavior, with a rate constant of $4.1 \times 10^{-5}\ s^{-1}$.

The oxalato–dioxygen complex (**11**) however, was found to undergo facile degradation at much lower temperatures, under conditions that show no measurable rate of degradation for the dioxygen complex **4**. The family of absorbance curves in Figure 7 shows two intense charge-transfer absorption bands, with maxima at 320 and 400 nm. The results of a series of absorbance vs time measurements over the range of pH in which the oxalato and peroxo bridging groups coexist are given in Table III. The data show that the 400-nm band maximum varies with pH, decreasing to 370 nm as the pH is increased from 7 to nearly 10. The 320-nm band, however, remains invariant under these conditions. The distribution curves in Figure 3 show that the dioxygen complex formed in the absence of oxalate is converted from **4** → **9** → **10** as the pH is increased from 7 to 10. The oxalato-bridged dioxygen complex (**11**), however, does not change composition as the pH is varied, although it varies considerably in concentration. Because of this observed behavior, the variable peak at 400–370 nm is assigned to the dioxygen complexes **4**, **9**, and **10**, while the invariant band at 320 nm is assigned to the oxalato-, peroxo-bridged dioxygen complex (**11**).

The stoichiometry of the redox reaction occurring between coordinated oxalate and coordinated dioxygen in the cavity of the macrocyclic complex, **11**, was established by the following ob-

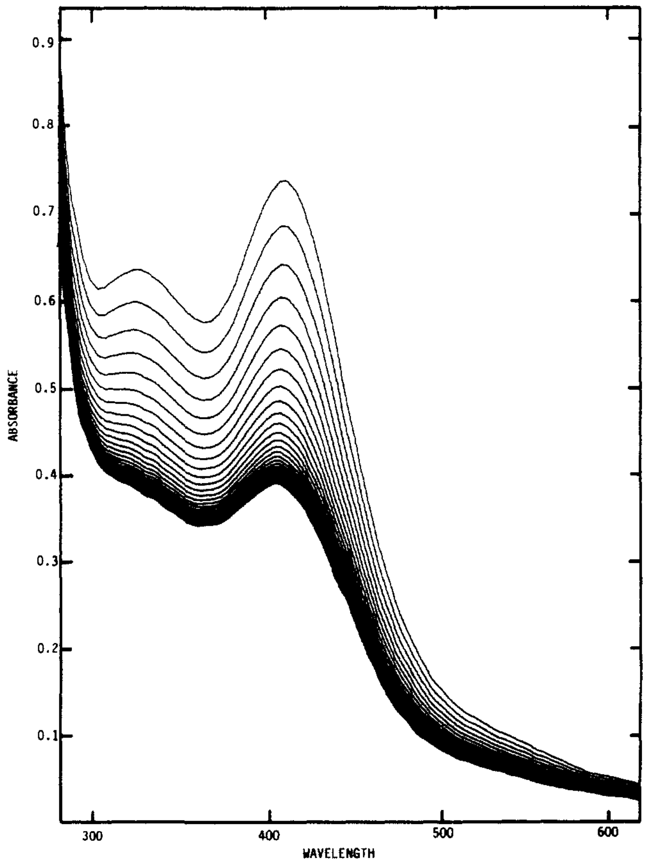


Figure 7. Absorption spectra illustrating the degradation of the (oxalato)BISDIEN–dicobalt–dioxygen complex at 45 °C; $\mu$ = 0.100 M KCl. $[\mathrm{BISDIEN}]_{\mathrm{total}} = 2.044 \times 10^{-4}$ M; pH 6.99.

Table III. Rate Constants for the Degradation of the Dibridged ($\mu$-Peroxo, $\mu$-Hydroxo) Dicobalt–Dioxygen Complex and the Tribridged ($\mu$-Peroxo, $\mu$-Hydroxo, $\mu$-Oxalato) Dicobalt–Dioxygen Complex

| stoichiometry | | | | $\lambda_{\max}$ | | | |
|---|---|---|---|---|---|---|---|
| BD[a] | $Co^{2+}$ | Ox | temp, °C | peak 1 | peak 2 | initial pH | $k_{obs}$, $min^{-1}$ |
| 1 | 2 | 1 | 45 | 325 | 410 | 6.99 | 0.016 |
| 1 | 2 | 1 | 45 | 320 | 410 | 7.59 | 0.017 |
| 1 | 2 | 1 | 45 | 320 | 390 | 8.69 | 0.022 |
| 1 | 2 | 1 | 45 | 320 | 370 | 9.76 | 0.027 |
| 1 | 2 | 2 | 45 | 320 | 412 | 6.99 | 0.010 |
| 1 | 2 | 2 | 45 | 325 | 408 | 7.32 | 0.012 |
| 1 | 2 | 2 | 45 | 320 | 412 | 8.45 | 0.020 |
| 1 | 2 | 2 | 45 | 320 | 380 | 9.39 | 0.057 |
| 1 | 2 | no | 45 | | 380 | 7.28 | *b* |
| 1 | 2 | no | 60 | | 380 | 7.28 | 0.0025 |
| 1 | 2 | no | 90 | | 380 | 7.28 | 0.062 |

[a] BD = BISDIEN. [b] 2% decomposed in 2 h.

servations: (1) the final cobalt complex formed, **12**, is not capable of adding dioxygen; (2) the UV–visible absorption spectrum of the final product resembles that of the dicobalt(III) binuclear complex and closely resembles that of an authentic dinuclear cobalt(III) complex prepared in the absence of dioxygen from cobalt(III) and BISDIEN; (3) the carbon dioxide formed was quantitatively determined by strongly acidifying the reaction solution and analyzing the gas above the solution by gas chromatography.

Plots of log ($A - A_\infty$) vs time gave straight lines, indicating first-order behavior. Figure 8 shows the graphical determination of the rate constant, at pH 6.99, 45.00 °C, to give the value 2.7 $\times 10^{-4}$ $s^{-1}$. Constants obtained at other pH values for different ratios of reactants are presented in Table III, along with the rate constants obtained for the degradation of the complex 4 at various temperatures. Although the data do not provide a direct comparison of the relative rates of oxidation of oxalate within the macrocyclic complex and rates that would occur outside the host (which would be immeasurably slow), it is clear that the observed catalytic effect must involve a factor of many orders of magnitude. Perhaps a more practical comparison would be the relative rates of degradation of the dioxygen complex to irreversibly form the inert binuclear cobalt(III) complex **12** of the macrocyclic ligand and the rate of reaction of coordinated dioxygen with oxalate within the macrocyclic cavity. Here again, a direct comparison between rate constants is not possible because of the different temperatures involved. However, it seems that, taking into account the temperature differences, the ratio of the rate constant of the redox reaction of interest to the rate constant of oxidative degradation (which destroys the oxidant) is at least 2 or 3 orders of magnitude.

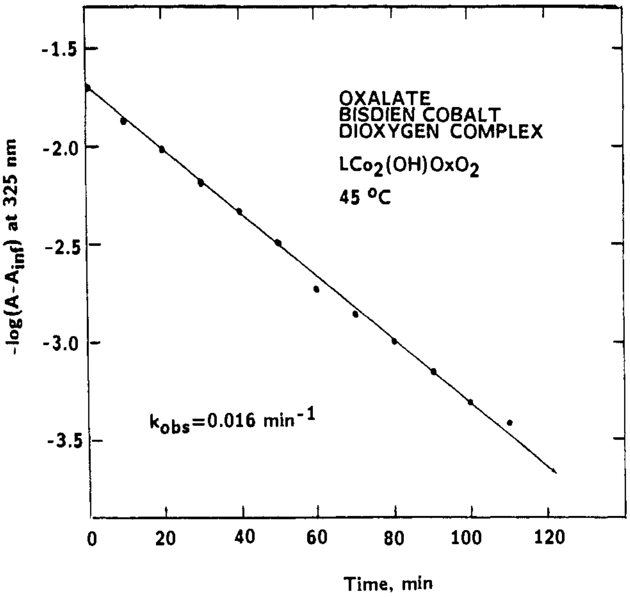
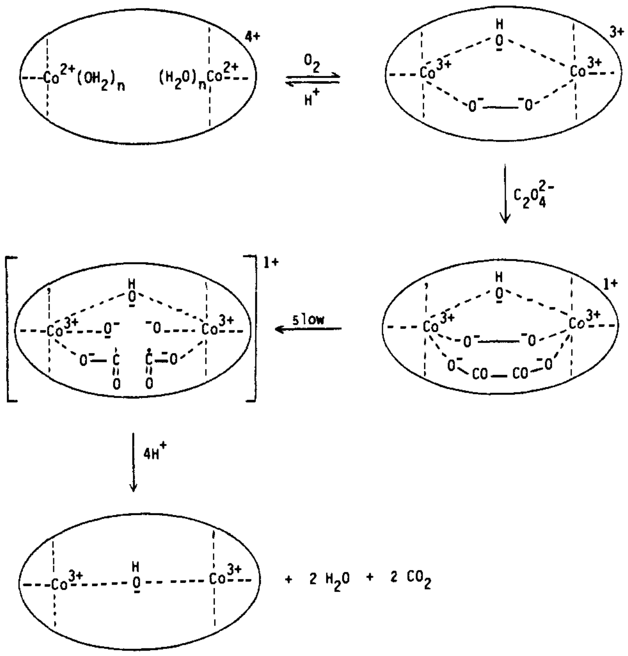
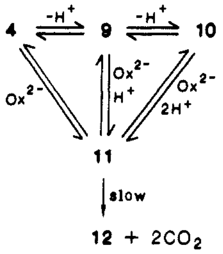


Figure 8. First-order plot for degradation of the (oxalato)BISDIEN–dicobalt–dioxygen complex at pH 6.99 and 45 °C.

Scheme I. Proposed Mechanism for Oxalate Oxidation by Dioxygen in the Cavity of the Dinuclear BISDIEN–Cobalt(II) Complex



**Reaction Mechanism.** It is noted that both charge-transfer absorption bands in Figure 7 decrease at the same rate, even though only the oxalate-containing complex is considered to be the reactive intermediate. Thus, the dioxygen complexes with and without oxalate must be involved in rapid preequilibrium but only the oxalate-containing complex undergoes the redox reaction between coordinated dioxygen and oxalate, as indicated by the following.



A more detailed picture of the reaction mechanism is illustrated in Scheme I. The proposed route for electron transfer is through the metal ions, which have low-energy orbitals capable of accepting the electrons, thus providing pathways for the electron-transfer process. Direct electron transfer from oxalate to peroxide is not considered likely because of their negative charges, leading to coulombic repulsions, which would space them far apart in the macrocyclic complex.

Further work in progress on this redox system is being directed toward obtaining structural information on the binary dioxygen-reducing substrate complex and toward the investigation of the reactions of other substrates capable of acting as bridging donors in the binuclear dicobalt-BISDIEN complex and in complexes of other binucleating macrocyclic ligands.

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# Low-Temperature Neutron Powder Diffraction Study of $CrO_2$ and the Validity of the Jahn–Teller Viewpoint

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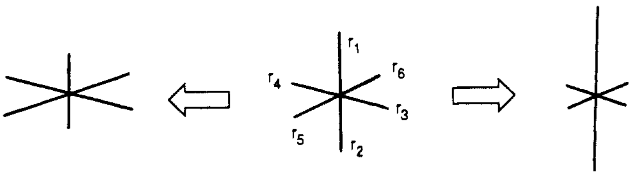
**Abstract:** The structure of $CrO_2$ has been determined at 10, 173, and 295 K by powder neutron diffraction. The structure of this material is interesting because the mode of distortion around the metal center is the reverse of that expected on the basis of local Jahn–Teller considerations. Band-structure calculations however, show that although the structure with two long and four short metal–oxygen distances is that expected for the $d^0$ configuration, where O–O repulsions control the picture, the opposite distortion is predicted for d counts leading to "$t_{2g}$" block degeneracies. We explain this result by constructing the d band dispersion curve using the angular overlap model. It is shown how through-bond coupling in the lower than octahedral local environment allows mixing between a component of each of the "$e_g$" and $t_{2g}$ orbital sets and frustrates the energetic preferences predicted for the $t_{2g}$ block alone. The factors that control the details of the geometries of the transition-metal oxides and fluorides with the rutile structure are explored.

The Jahn–Teller theorem[1] has enjoyed widespread use as a means of understanding the geometries of a variety of structures arising from a distortion of a symmetrical configuration of atoms.[2-4] According to the theorem the presence of an orbitally degenerate electronic state in a nonlinear molecule signals a geometrical instability. This may be relieved by a distortion whose symmetry species is contained within the antisymmetric direct product of the state symmetry. Such instabilities will naturally only be associated with highly symmetrical molecules. Octahedrally coordinated transition-metal complexes are particularly well-studied examples. Such orbitally degenerate states occur as the result of asymmetric occupation by electrons of degenerate orbitals.[5] The $e_g^3$ configuration of octahedral $Cu^{II}$ is a classic example. Here, the distortion route associated with the $^2E_g$ electronic state is one of $e_g$ symmetry. One component of a stretching motion of $e_g$ symmetry, which will be useful to us, is shown in **1** and **2**. These represent different phases of a motion that describes the bulk of the observed distortions in these octahedrally derived structures.



**1** **2**

Even if the levels are not exactly degenerate, a second-order Jahn–Teller effect, accessible by perturbation theory,[4,6] often suffices to allow them to mix on distortion and lead to a stabilization of the system. The geometries of many transition-metal

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(1) (a) Jahn, H. A.; Teller, E. *Proc. R. Soc. London, A* **1937**, *161*, 220. (b) Jahn, H. A., *Ibid.* **1938**, *164*, 117.

(2) See almost any modern inorganic chemistry text. For a discussion by one of the originators of these ideas, see: Orgel, L. E. *An Introduction to Transition Metal Chemistry*; Methuen: London, 1960.

(3) Gazo, J.; Bersuker, I. B.; Garaj, J.; Kabesova, M.; Kohout, J.; Langfelderova, H.; Melnik, M.; Serator, M.; Valach, V. *Coord. Chem. Rev.* **1976**, *19*, 253.

(4) Burdett, J. K. *Molecular Shapes*; Wiley: New York, 1980.

(5) Not always does such a configuration give rise to a degenerate electronic state. In cyclobutadiene the $(e_g)^2$ configuration of the square geometry gives rise to a $^1B_{2g}$ ground state. The distortion of this molecule strictly arises via a pseudo-Jahn–Teller effect through a second-order term in the expansion of the energy in a perturbation sense along the distortion coordinate.[4,6]

(6) Bartell, L. S. *J. Chem. Educ.* **1968**, *45*, 754.

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